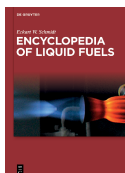


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Encyclopedia of Oxidizers

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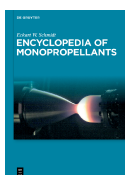


Encyclopedia of Liquid Fuels

Eckart W. Schmidt, to be published in 2022

ISBN 978-3-11-075025-6, e-ISBN (PDF) 978-3-11-075028-7,

e-ISBN (EPUB) 978-3-11-075038-6

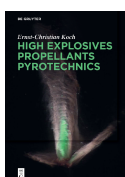


Encyclopedia of Monopropellants

Eckart W. Schmidt, to be published in 2022

ISBN 978-3-11-075127-7, e-ISBN (PDF) 978-3-11-075139-0,

e-ISBN (EPUB) 978-3-11-075147-5

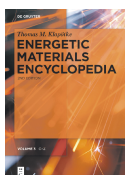


High Explosives, Propellants, Pyrotechnics

Ernst-Christian Koch, 2021

ISBN 978-3-11-066052-4, e-ISBN (PDF) 978-3-11-066056-2,

e-ISBN (EPUB) 978-3-11-066059-3

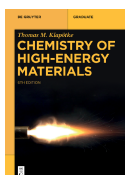


Energetic Materials Encyclopedia: Volume 3

Thomas M. Klapötke, 2021

ISBN 978-3-11-067245-9, e-ISBN (PDF) 978-3-11-067255-8,

e-ISBN (EPUB) 978-3-11-067271-8

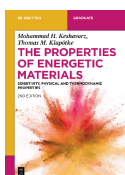


Chemistry of High-Energy Materials

Thomas M. Klapötke, to be published in 2022

ISBN 978-3-11-073949-7, e-ISBN (PDF) 978-3-11-073950-3,

e-ISBN (EPUB) 978-3-11-073610-6



The Properties of Energetic Materials

Sensitivity, Physical and Thermodynamic Properties

Mohammad Hossein Keshavarz, Thomas M. Klapötke, 2021

ISBN 978-3-11-074012-7, e-ISBN (PDF) 978-3-11-074015-8,

e-ISBN (EPUB) 978-3-11-074024-0

Eckart W. Schmidt

Encyclopedia of Oxidizers

Volume 1: Alkyl Perchlorate Esters – Fluorine

DE GRUYTER

Author

Eckart W. Schmidt
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USA

ISBN 978-3-11-075024-9

e-ISBN (PDF) 978-3-11-075029-4

e-ISBN (EPUB) 978-3-11-075039-3

Library of Congress Control Number: 2022937781

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie;
detailed bibliographic data are available on the Internet at <http://dnb.dnb.de>.

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Cover image: First 3-D printed Aerojet Rocketdyne RL-10 thrust chamber undergoing hot-fire testing
with LOX/LH2 in West Palm Beach, Florida, in 2018 (Photo courtesy of Aerojet Rocketdyne)

Typesetting: le-tex publishing services GmbH, Leipzig

Printing and binding: CPI books GmbH, Leck

www.degruyter.com

Foreword

Rocket propellants are hugely important members of the larger group of energetic materials. This continuously developing field requires knowledge and understanding of a wide-range of compounds from the highly reactive fluorine and nitrogen oxides, to organic alkylboranes and alcohols. For rocket propulsion, it is essential that accurate information on the physical and chemical properties of the chemicals involved has been determined precisely and can be relied upon. This is not only the case for known rocket propellants, but is equally essential for developing new, “greener” (less toxic) propellants for the future. The demands on rocket propellants are continuously developing and changing with time, as new needs and requirements for satellites and rockets emerge. Therefore, the *Encyclopedia of Rocket Propellants* is an essential resource for understanding current and past rocket propellants, as well as for designing those for the future. A collection of the vast physical and chemical data for past, present and modern rocket propellant systems has been missing, and it is essential that a source is available in which all reliable data has been collected together and presented in a clear and informative manner.

Amongst the many ways to categorize propellants for chemical rockets, they can be separated into two groups, namely, solid propellants or liquid propellants, with the former being subdivided into double-base or composite propellants. Liquid propellants can be subdivided into monopropellants or bipropellants, the latter of which can be again subdivided into hypergolic or nonhypergolic. Therefore, the complexity of these systems is self-evident. Hydrazine and the methylated derivatives methylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) in combination with nitric acid or dinitrogen tetroxide are currently the most widely-used hypergolic propellants, however, hydrazine and its methylated derivatives are not only toxic, but also carcinogenic in test animals, and therefore it is of considerable importance to find less-toxic and non-carcinogenic alternatives which can still form hypergolic mixtures. Properties of many candidates in this context are summarized in this book. However, many more promising alternatives need to be found for the future. Despite the harmful properties of “traditional” rocket propellants such as MMH or UDMH, or the highly corrosive WFNA and RFNA, they continue to be used, while safer and more energetic alternatives are sought for the future.

Searching for new, environmentally friendly and/or increased performance rocket propellants requires knowledge of a large and diverse number of chemical compounds, many of which are not easy to handle. Despite this, since the publication of the book *Raketentreibstoffe* (Springer) in 1968 by the same author as this

encyclopedia, no other such comprehensive and detailed book has been published on rocket propellants making the *Encyclopedia of Rocket Propellants* a seminal work for past, present and future developments in this area.

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Preface

Encyclopedia of Oxidizers

This is the first set of a series of sets in the *Encyclopedia of Rocket Propellants* summarizing the existing literature on rocket propellants, both liquid and solid rocket propellants. The first set, *Encyclopedia of Oxidizers*, contains information on both liquid and solid oxidizers. The second set to be released shortly after, *Encyclopedia of Liquid Fuels*, is a summary of literature on liquid fuels. The differentiation between liquid fuels and solid fuels was necessary because solid fuels usually are the binders for solid propellants, a topic reserved for a future, planned set in this series. The third set, *Encyclopedia of Monopropellants*, will be a very comprehensive summary of the chemistry of monopropellants. The fourth and fifth sets, planned for the coming years, will describe the performance of hypergolic and nonhypergolic bipropellant combinations, usually combinations of oxidizers and fuels. If time permits, future sets will eventually deal with various aspects of solid propellants, such as “Composite Solid Propellants” and “Double-Base Solid Propellants”, and they would also include gas generants which have found numerous industrial applications such as in airbag inflators in automobile occupant passive restraint systems. “Hybrid Propellants” may find a home in a future set in the distant future.

In spite of the increased capabilities of online search engines like Google Scholar, the current sets of books will be an indispensable tool for scientists and engineers in the rocket propulsion industry and research organizations. The hazards of working with rocket propellants need to be well understood.

Our *Encyclopedia of Rocket Propellants* book series will be the preferred reference source for future generations of rocket propellant chemists. When referring to the profession of rocket propellant chemists, this should not be done without quoting, tongue-in-cheek, the preface written by I. Asimov for J. D. Clark’s landmark book *Ignition!*:

“Now it is clear that anyone working with rocket fuels is outstandingly mad. I don’t mean garden-variety crazy or a merely raving lunatic. I mean a record-shattering exponent of far-out insanity.”

The reader will notice, though, that the correct terminology should have been “rocket propellants” and not just “rocket fuels”. The author of the current book feels that this quote from the literature adequately describes the risks involved for chemists involved with developing more energetic rocket propellants and explosives. The dividing line between powerful rocket propellants and potential explosives is very narrow and rocket propellant development is often treading on a narrow path. Nevertheless, this is one of the most exciting branches of chemistry to be involved with. It is the

chemistry of rocket propellants that has enabled the dramatic advances in space technology, with many benefits to the common consumer.

Reviewing the recent literature on rocket propellants and other energetic materials, one will notice that the increased capabilities of modern computers have enabled chemists to predict the performance of new molecules even before these compounds were ever made and tested in the laboratory. Numerous publications referenced in our books deal just with theoretical explorations of this type, and that is a difference to previous book publications on this subject.

Rocket propellants generally consist of oxidizers and fuels. The term “rocket fuels” is often misused to describe rocket propellants in general. Correct use of the term “rocket fuel” would only apply to the combustible, fuel-rich part of a propellant combination. Oxidizers for liquid rocket propellants are generally subdivided by physical properties and/or by reactivity. So we differentiate between storable and non-storable (usually cryogenic) propellants. When looking at the reactivity of hypergolic combinations, it is more often the oxidizer and not the fuel that determines if the resulting combination is self-igniting on contact or not. When listing combinations of rocket propellants, we always list the oxidizer first. This is because the properties and the activity of the oxidizer determine the nature of the combination more so than properties of the fuel would. There are fewer oxidizers than fuels in our inventory, so it is easier to organize book chapters on rocket propellant combinations first by arranging them by oxidizers and later by fuels.

A frequently used alternate term for oxidizer, mostly in biologic systems, is *oxidant*. This term is used mostly in life sciences and less frequently in the world of rocket propellants. When conducting literature searches, it may be advisable to search for both terms. A less frequently used term for propellant is *propellent*. And again, when doing literature searches, one may want to search for both variations of the spelling.

About the Format of the Several Sets in the Encyclopedia of Rocket Propellants

The manuscript for the *Encyclopedia of Rocket Propellants* has evolved through several iterations and modifications, and the terminology in designating sets, volumes, chapters, and sections has changed during this period. The most recent terminology is now referring to *Encyclopedia of Oxidizers* as a set of five volumes and similarly referring to *Encyclopedia of Liquid Fuels* as a set of five volumes. The sequence of volumes in a set and the sequence of chapters in a volume is arranged in alphabetical order, similar to a dictionary.

A critical reviewer might describe the format of the books as not much more than an annotated bibliography. The author is aware of the fact that collecting and reproducing references from the literature is not a very creative job, but to arrange these thousands of references in a systematic manner requires a good understanding of the subject matter, justifying the effort especially in the age of computers and the internet.

Fifty years ago it used to be common practice to cite literature references followed by their Chemical Abstract citation. Providing the Chemical Abstracts citation often allowed the reader to read a more detailed abstract and to decide if it is worthwhile to obtain a complete copy of the original publication. Nowadays that function has been taken over by Digital Object Identifiers (DOI) in the Internet. Nevertheless, we have continued to carry along a few Chemical Abstract citations in addition to the DOI. Some of those citations are useful because they direct users to the Chemical Abstracts Registry Number which can be used for subsequent, more specific searches in computerized data bases. Some of the books on energetic materials even contain an index of Chemical Abstract Registry Numbers.

Selection of Oxidizers

When selecting combinations of bipropellants, hypergolic or nonhypergolic, it is usually the oxidizer that determines the reactivity of the combination once oxidizer and fuel meet in the rocket engine combustion chamber. The choice of oxidizers has less of an impact on the specific impulse than the choice of fuels with their widely varying hydrogen content. The selection of oxidizers is governed by a number of considerations:

- Specific impulse
- Reactivity with the intended fuel partner (hypergolic or nonhypergolic?)
- Boiling point/critical point temperature
- Storage stability
- Density (important for compact, pressure-fed systems)
- Corrosivity (corrosive oxidizers require exotic materials for tankage and tubing)
- Toxicity
- Availability
- Cost

The same criteria apply also to the selection of fuels.

Until the beginning of the Space Age, liquid oxygen and fuming nitric acid had been used most extensively, primarily because of low cost and relatively easy handling characteristics. In the field of moderate performance, red fuming nitric acid had proved successful with proper modifications for dealing with its corrosive nature and pressure build-up problem of WFNA during storage. For high performance, liquid oxygen has been used satisfactorily, although additional engineering complications arise because of the need for refrigeration and/or insulation. Among the storable oxidizers, hydrogen peroxide and dinitrogen tetroxide have once been considered as close competitors to red fuming nitric acid. In the group of oxidizers containing fluorine, liquid fluorine has generally the highest performance. Nonmetallic fluorides have lower performance, but they are storable at room temperature. A common disadvantage of all

the compounds in this group of fluorine oxidizers stems from the fact that elemental fluorine is required for the industrial production of many of these oxidizers. The main disadvantage is the toxicity of the exhaust, hydrogen fluoride. Therefore fluorine oxidizers are now a thing of the past, and we include them here only because of historical interest. Outside the field of rocketry, fluorine and some nonmetal fluorides are still used for chemical lasers.

For solid oxidizers, ammonium perchlorate is the most widely used solid oxidizer. A detailed chapter in *Encyclopedia of Oxidizers* deals with ammonium perchlorate. Other solid oxidizers, actually used or evaluated for future use, are ammonium nitrate, ammonium dinitramide, hydrazinium salts, and hydroxylammonium salts, each represented with their own chapter.

An apology is needed to explain the incorrect display of semipolar bonds in nitro groups. Semipolar bonds are currently shown as N=O double bonds instead of semipolar bonds. Semipolar bonds should have been shown as an arrow $N \rightarrow O$. The chemical formula drawing software used here for creating chemical structures did not have an option for semipolar bonds, so for the time being these bonds were shown as double bonds instead.

Eckart W. Schmidt
Bellevue, WA, USA

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Alkyl Perchlorate Esters

It is not because alkyl perchlorate esters are very important that they ended up in this prominent location in the first chapter of the *Encyclopedia of Oxidizers*; it happened because the chapters are now arranged in alphabetical order, and the letter A, of course, comes first in the alphabet.

Many organic energetic materials do not fit into the oxidizer category because they are underoxidized. Other energetic materials are not suitable as monopropellants because they are solids. These organic solid materials may be discussed in later volumes on solid propellant additives. Solid propellant additives can be energetic materials or they can be nitrogen-rich additives that are often added as coolants to solid gas generators.

Alkyl perchlorates and alkyl difluoroamino compounds have some similarities, and both types of compounds have been considered as rocket propellants, but their notorious shock sensitivity prevented any further development.

Alcohols will form esters with many acids. If acids carry oxygen, i.e., if they are oxyacids, the resulting esters may be of interest as rocket propellants. Esters of carboxylic acids are not suitable as rocket propellant oxidizers. Some are used as plasticizers in solid propellants. The oxyacids of interest are primarily those with nitrogen or chlorine as the central atom. Alkyl nitrites and alkyl nitrates will be discussed in later chapters. Alkyl perchlorates are the subject of this chapter. While in the realm of solid propellants (more accurately, composite solid propellants) solid inorganic perchlorates occupy a dominant position, liquid organic perchlorates have not gained much (if any) importance in the realm of liquid propellants. Those who had once worked with alkyl perchlorates in the laboratory later said that they “would not want to touch them again with a ten-foot pole.”

Alkyl perchlorates are mostly of theoretical interest. The theoretical advantage of alkyl perchlorates RCIO_4 over alkyl nitrates RNO_3 is that they carry four oxygen atoms in a molecule instead of only three and the central atom, chlorine, is also an oxidizer and will combine with hydrogen to form HCl , as opposed to nitrogen in nitrates, which is only carried along as an inert ballast. For alkyl chlorates RCIO_3 the advantage is not so clear. Alkyl chlorates are less stable than alkyl perchlorates, and little is known about alkyl chlorates.

For compounds with the general formula $\text{C}_c\text{H}_h\text{Cl}_{cl}\text{O}_o$, the oxygen balance Ω is defined as

$$\Omega = \left[-32 \left(c + \frac{1}{4}h - \frac{1}{4}cl - \frac{1}{2}o \right) \right] / \text{MW} \times 100\%$$

where c , h , cl , and o represent the number of atoms of each element and MW is the molar mass of the substance. For methyl perchlorate, Ω is +14%, indicating that the

substance has more oxygen in its formula than is needed for complete combustion to CO_2 , H_2O , and HCl . It will rightfully be listed here as an oxidizer.

1 Preparation of Alkyl Perchlorates

Alkyl perchlorates (perchlorate esters, perchloric acid esters) have been prepared by the reaction of alkyl halides with anhydrous silver perchlorate [1], but they are not suitable as rocket propellants. Using a silver salt such as silver perchlorate as one of the reactants automatically makes this a very expensive proposition.

A very useful review of the synthesis and properties of covalent organic perchlorates was compiled and translated in 1988 [2]. The review provided information on the methods of synthesis and reactivities of covalent organic perchlorates and included 141 references. It was preceded by an older review [3].

In one of the first publications on the synthesis of methyl, ethyl, and propyl perchlorates, the pure substances were described as oily liquids and were said to be “extremely explosive” [4]. Surprisingly, the investigators reported a boiling point of 325 K (52°C) for methyl perchlorate and 362 K (89°C) for ethyl perchlorate, suggesting that these compounds were at least thermally stable up to that temperature. Methyl perchlorate can be purified by distillation, boiling point 323 K at 89 kPa (50°C at 670 mm Hg).

Alkyl perchlorates are miscible with ether or ethanol, but they are susceptible to hydrolysis in the presence of water and must be kept dry. Methyl perchlorate hydrolyzed faster than ethyl perchlorate and ethyl perchlorate in turn hydrolyzed faster than propyl perchlorate.

Concern about the hazards of alkyl perchlorate esters was echoed in a study that noted that many physical properties of these compounds are unknown because of their fragility [5].

Primary alkyl iodides reacted with silver perchlorate in pentane, carbon tetrachloride, or 1,1,2-trichlorotrifluoroethane to give primary and secondary perchlorates, with secondary isomers predominating [6, 7]. In benzene, only unrearranged products were obtained. An excess of alkyl iodide and, to a lesser extent, methylene chloride also inhibited isomerization. Isopropyl iodide and allyl iodide, as well as primary iodides, were converted to the corresponding perchlorates and triflates in high yield. Inhibition of rearrangement was rationalized on the basis of the reduced reactivity of complexed silver ions.

Alkyl perchlorates can form by deamination of alkylamines in the presence of perchlorate anion sources [8]. Perchlorate esters form from the interaction of electrophilic halides with alkenes in the presence of excess lithium perchlorate [9].

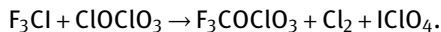
An easy preparation of secondary alkyl perchlorates that does not require the use of expensive silver perchlorate or alkyl iodides involves the addition of a secondary alcohol or unbranched olefin to a well-stirred emulsion of perchloric acid, sulfuric

acid, and an inert hydrocarbon or fluorocarbon [10]. The acid reagent can be prepared by combining 70% perchloric acid, 96% sulfuric acid, and oleum, or by dissolving lithium perchlorate in 96% sulfuric acid. The formation of isomeric secondary alkyl perchlorates was, in most cases, very rapid and virtually quantitative. The ester products were extracted into the organic layer, from which they may be isolated if desired. The composition of the isomeric mixture is dependent on the reaction conditions and can be made to highly favor one specific desired isomer.

The preparation of tetraperchlorate of methane was attempted [11]. Displacement of halogen from carbon tetrahalides was accomplished starting with either CCl_4 or CBr_4 using the halogen perchlorates ClOClO_3 and BrOClO_3 . Although the displacement process was successful, the generated carbon perchlorate intermediates could not be isolated. Instead, these species decomposed quickly to COCl_2 , CO_2 , and Cl_2O_7 . The perchlorate reactions were often uncontrolled, sometimes explosive, giving CO_2 and Cl_2O_7 . The vigorous displacement reactions that often occurred required moderation by dilution with inert fluorocarbon solvents, but the end result was the same as before. Thus, only COCl_2 , CO_2 , and Cl_2O_7 were found. Tetranitromethane was also examined as a precursor for tetraperchlorate of methane or mixed nitroperchlorate methanes. However, it was unreactive with Cl_2O_4 in the presence or absence of a solvent.

Dichlorine heptoxide is a versatile perchlorylating reagent. Reaction of Cl_2O_7 with alcohols provides a general method of synthesizing alkyl perchlorates, including electronegatively substituted samples, such as 2-fluoro-2,2-dinitroethyl perchlorate and 2,2-dinitropropyl perchlorate, which cannot be prepared by standard methods [12, 13]. Dichlorine heptoxide in carbon tetrachloride is a general reagent for converting alcohols to alkyl perchlorates. Simple primary alcohols, as well as ethylene glycol, 1,4-butanediol, 2,2,2-trifluoroethanol, 2,2-dinitropropanol, 2-fluoro-2,2-dinitroethanol, 2-(2-fluoro-2,2-dinitroethoxy)ethanol, allyl alcohol, and propargyl alcohol, gave the corresponding unrearranged perchlorates. 2-Propanol gave isopropyl perchlorate. 2-Hexanol and 3-hexanol gave mainly unrearranged perchlorates. Ketones gave *gem*-diperchlorates.

The action of chlorine perchlorate on trifluoromethyl iodide at low temperature has resulted in the formation of the simplest perfluoroalkyl perchlorate, F_3COCIO_3 [14]:



Note that in the preceding reaction scheme, iodine was printed as a Roman numeral I in order to avoid confusion with the lowercase L in the symbol for chlorine, Cl. The energy content of alkyl perchlorates can be reduced and the stability improved by making perchlorates of perfluoroalkyl groups instead of hydrogenalkyl groups. Perfluoroalkyl perchlorates can be made by the reaction of chlorine perchlorate with perfluoroalkyl halides or perhalogenated olefins [15]. The reactions of chlorine perchlorate and bromine perchlorate with numerous fluoroalkyl halides were examined. In the case of fluorocarbon iodides, these reactions were generally found to produce high yields of the fluorocarbon perchlorates CF_3ClO_4 , $\text{CF}_3\text{CF}_2\text{ClO}_4$,

$n\text{-C}_7\text{F}_{15}\text{ClO}_4$, $\text{O}_4\text{ClCF}_2\text{CF}_2\text{ClO}_4$, and $\text{ICF}_2\text{CF}_2\text{ClO}_4$. Some insight into the mechanism of formation of these compounds was obtained through the isolation of complex intermediates. Based on their vibrational spectra, these intermediates have an ionic structure. The reactions of Cl_2O_4 or BrClO_4 with perhalogenated olefins produced perhalogenated alkyl perchlorates in high yield.

Oxidative nucleophilic substitution of alkyl iodides with lithium perchlorate, such as the reaction of alkyl iodides and lithium perchlorate, proceeding in the presence of nitronium tetrafluoroborate as an oxidant, can be used to synthesize alkyl perchlorates, including those containing an adamantyl nucleus [16]. The spectral properties of alkyl perchlorates were then studied in detail for the first time.

2 Physical Properties of Alkyl Perchlorates

The physical properties of some of the higher alkyl perchlorates are listed in Table 1.

Table 1: Physical properties of alkyl perchlorates.

Compound	Formula	Boiling point (°C) at reduced pressure	Index of refraction, n_D^{25}	Density at 25 °C
<i>n</i> -Pentyl perchlorate	$\text{C}_5\text{H}_{11}\text{ClO}_4$	51.5/11 mm Hg	1.4042	—
<i>n</i> -Hexyl perchlorate	$\text{C}_6\text{H}_{13}\text{ClO}_4$	52/4.5 mm Hg	1.4146	1.11 g/cm ³
<i>n</i> -Heptyl perchlorate	$\text{C}_7\text{H}_{15}\text{ClO}_4$	49–51/2.4 mm Hg	1.5170	—
<i>n</i> -Octyl perchlorate	$\text{C}_8\text{H}_{17}\text{ClO}_4$	55–60/1.5 mm Hg	1.4192	1.07 g/cm ³

Data source: [17]

2.1 Molecular Structure of Alkyl Perchlorates

The molecular structure of methyl perchlorate is illustrated in Figure 1. Methyl perchlorate as a monopropellant or oxidizer may be compared to methyl nitrate, except that it contains more oxygen and the central halogen atom contributes to the oxygen balance, whereas nitrogen does not.

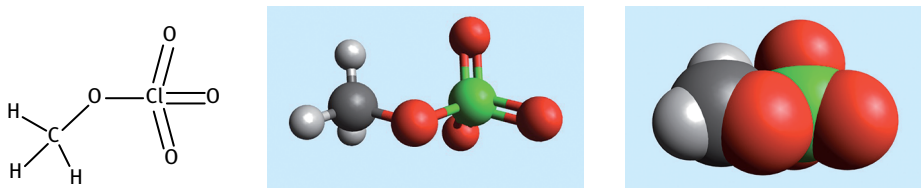


Figure 1: Molecular structure of methyl perchlorate.

Table 2: Predicted enthalpies of formation and decomposition of methyl perchlorate.

Method	ΔH_f , kJ/mol	ΔH_f , kJ/kg	ΔH_{dec} , kJ/mol	ΔH_{dec} , kJ/kg
G2	33.23	290.2	-804.9	-7030
G3	25.61	223.7	-797.3	-6964

Data source: [18]

The molecular properties, including enthalpies of formation and decomposition, of methyl chlorate and methyl perchlorate were predicted by a high-level computational study of the structure, vibrational frequencies, and enthalpies of reaction of methyl perchlorate were calculated [18]. Of interest was the amount of energy given off per unit mass when these compounds decomposed, as the specific enthalpy of decomposition is one useful measure of the utility of a high-energy material. All calculations used the G2 and G3 methods of Gaussian 03 computational chemistry software package, and the results are listed in Table 2.

Mixtures of perchloric acid with organic fuels are most likely detonable, but some people want to use them as rocket propellants [19].

3 Chemical Properties of Alkyl Perchlorates

3.1 Reactions of Alkyl Perchlorates

Alkyl perchlorates may serve as alkylating agents and are sometimes only formed as intermediates in alkylation reactions with alkanols and perchloric acid. Alkyl perchlorates that are formed as intermediates may undergo subsequent fission to carbonium and perchlorate ions [5].

Methyl perchlorate is a good methylating agent, more powerful than methyl sulfate. Much of the work on methyl perchlorate has focused on its hydrolysis or solvolysis. Methyl perchlorate solvolysis kinetics was studied in methanol, ethanol, isopropanol, *tert*-butanol, and 80% aqueous ethanol [20]. Methyl perchlorate for this study was prepared as a solution in benzene by the reaction of methyl iodide with silver perchlorate and the removal of precipitated silver iodide by filtration.

The kinetics of reactions of methyl perchlorate in hydroxylic solvents have been studied extensively [21, 22]. Such reactions may be used for the safe disposal of excess alkyl perchlorates.

3.1.1 Thermal Decomposition of Alkyl Perchlorates

All alkyl perchlorates are potentially explosive, and they are unlikely to be used as rocket propellants. The *n*-amyl perchlorate was the least stable in a group of five per-

chlorates tested. It has been possible to stabilize them by forming inclusion compounds (clathrates, endocytos) with urea, forming stable crystals analyzed by XRD [17]. The ease of formation of the urea inclusion compound was proportional to the chain length of the alkyl perchlorate. The resulting crystalline complexes had no apparent shock sensitivity in small quantities [23].

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Difluoroamino Compounds

Many organic energetic materials do not fit in the oxidizer category because they are underoxidized. Other energetic materials are not suitable as monopropellants because they are solids. These organic solid materials are discussed in another volume on solid propellant additives. Solid propellant additives can be energetic materials, or they can be nitrogen-rich additives, which are often added as coolants to solid gas generants.

Alkyl perchlorates and alkyl difluoroamino compounds have been considered as rocket propellants, but their notorious shock sensitivity prevented further development. Other energetic additives, many of those used as energetic plasticizers, do not contain oxygen, nitro, or nitrate groups at all; they contain difluoroamino —NF_2 groups instead.

When reacting with strongly reducing light alkali or earth alkaline metals, even such inert organic fluorine compounds as tetrafluoromethane or polytetrafluoroethylene can act as oxidizers. This exothermic reaction is widely used for pyrotechnic mixtures for igniters and flares.

In addition to compounds with merely relatively stable C—F bonds, other organic compounds in which the fluorine is bound to carbon via nitrogen or oxygen atoms are very energetic, often to a point where they are so sensitive that they are difficult to handle safely.

Organic nitro compounds with the —NO_2 group are known to be energetic materials. Replacing the two oxygens attached to nitrogen by two fluorine atoms, forming —NF_2 groups, leads to the formation of equally energetic or even more energetic materials. Studies have been conducted comparing the enthalpies of formation and detonation performance of polynitro compounds with those of polydifluoroamino compounds, for instance by progressively replacing one or more nitro groups in a molecule with difluoroamino groups [1, 2]. There may be some overlap in the information provided in this book on difluoroamino compounds and nitro compounds, in particular in areas where the properties of these two groups of energetic materials are compared. A complete evaluation of those mixed substituent energetic compounds is possible only by reading both sections.

Fluorine, even in the form of difluoroamino groups and diluted by the presence of nitrogen, is a very powerful oxidizer. Organic difluoroamino compounds, also called NF compounds or “domino” compounds, have a higher specific impulse than their corresponding nitro group analogs where the nitrogen carries two oxygen atoms instead of two fluorine atoms. This is partially because the exhaust products of RNF_2 combustion have a lower molecular mass than those from nitro compounds.

The simplest difluoroamino compound is difluoroamine, F_2NH , which was described in *Encyclopedia of Oxidizers*, in the chapter “Nitrogen Fluorides,” and can be used to introduce the —NF_2 group into other compounds.

Some energetic solid additives containing difluoroamino groups were intended as replacements for 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), or other nitramines, in the hope of achieving higher performance, better thermal stability, lower sensitivity, and higher density. Not all solid difluoroamino compounds meet these criteria. Other applications of liquid difluoroamino compounds are as monopropellants (see *Encyclopedia of Monopropellants*) and as energetic plasticizers (low-volatility liquids) or energetic binders in solid propellants. Additional information on applications of these NF compounds can be found in those sections. This section deals mostly with liquid difluoroamino compounds and provides information on some of the more general aspects of difluoroamino compounds that are of equal interest to all previously mentioned applications.

As far as the nomenclature is concerned, different spellings are in use: We use the word *difluoroamino* compounds, but the terms *difluoramino* or *difluoramine* can also occasionally be found in the literature. The position of the two fluorine atoms on the same nitrogen atoms is sometimes described as *geminal difluoroamino* compounds or *N,N-difluoroamino* compounds. In the propellant chemistry jargon these compounds are also called *domino compounds*.

Just as a reminder, the name difluoroamino is often abbreviated as difluoramino, omitting the “o.” At other times, the compounds are called difluoroamine instead of difluoroamino compounds. *N,N*-difluoromethylamine is also called *N,N*-difluoromethanamine.

1 Summary Literature on Organic Fluoroamino Compounds

Several summary publications on NF compounds may serve as an introduction to this heavily researched, but now mostly forgotten, chemistry; what is lacking is a systematic summary of these compounds with all physical, chemical, and safety properties in one place. Much of the literature on —NF_2 compounds had been classified at one time, but eventually it was declassified at various times and remained burdened with other distribution limitations. Considering how much money has been spent on developing —NF_2 compounds over the past 50 years, it seems that the interest in these compounds dropped abruptly, and it is a shame that nobody has since taken the time to write a complete historical summary of what was done. Dozens, perhaps hundreds, of research reports continue to collect dust on some agency's bookshelves and may never penetrate to the scientific community. The summary of the literature in this chapter of the book at hand is incomplete and would require a substantial amount of work to bring it to a state of completeness. The more simple —NF_2 compounds are often overlooked, and some publications delve immediately into the more complex —NF_2 compounds.

Many of the —NF_2 compounds listed in some of the review publications are very complex and would be difficult to prepare for actual use. Some have only been pre-

pared in milligram quantities, in part because of the hazards involved in their synthesis.

Three literature reviews summarized the chemistry revealed during the period 1955–1967 directed toward the development of energetic oxidizers for use in advanced chemical rocket propellants [3]. The source material for these reviews included over 1200 technical reports and 1150 references. An extensive chapter on organic CNF oxidizers described simple NF_2 -substituted hydrocarbons and halocarbons, NF compounds containing oxygen functional groups, and NF compounds containing N–N bonds.

A later review of organic difluoroamine derivatives published as a chapter of a book on high-energy-density materials (HEDMs) was very specific only to cyclic difluoroamino nitramines, especially *gem*-bis(difluoroamino)-substituted analogs of conventional cyclic nitramines [4].

2 Monofluoroamino Compounds

Monofluoroamino compounds are of little interest as rocket propellants compared to difluoroamino compounds. They are used as selective electrophilic fluorinating reagents in organic synthesis. Dialkyl monofluoroamino compounds of the type R_2NF are more energetic than the secondary amines from which they are derived by replacing a hydrogen on the linking nitrogen $-\text{NH}-$ group of a secondary amine with a fluorine atom. Examples include methyl *N*-fluoroamine, H_3CNHF , trifluoromethyl *N*-fluoroamine, F_3CNHF , and dimethyl *N*-fluoroamine, $(\text{H}_3\text{C})_2\text{NF}$.

Dialkyl monofluoroamino compounds can carry explosophoric groups in the alkyl groups that further enhance the energetic properties of the molecule. For instance, the kinetics of thermal decomposition of bis(2,2-dinitropropyl)-*N*-fluoroamine were studied in the liquid phase [5]. The reaction was autocatalytic in the melt. In dilute solution, the reaction rate was described by a first-order law.

Other types of monofluoro-nitrogen compounds are the fluoroimines, which carry a $>\text{C}=\text{NF}$ group instead of a $\text{C}-\text{NF}_2$ group [6]. They contain less oxidizer and are of no interest as rocket propellants.

Similar compounds are known that carry a nitro group on the nitrogen and, thus, belong in the category of nitramines. Other energetic compounds carry a fluorine atom as well as a nitro group on the same nitrogen atom from an alkylamine. The enthalpies of formation of three *N*-fluoronitramines were listed in [7], but very little is known about these compounds.

	cal/g						
663 N-FLUORO-N-BUTYLNITRAMINE	4C	9H	2O	2N	1F	0	–288
664 N-FLUORO-SEC-BUTYLNITRAMINE	4C	9H	2O	2N	1F	0	–279
665 N-FLUORO-TERT-BUTYLNITRAMINE	4C	9H	2O	2N	1F	0	–225

3 Difluoroamino Compounds

The following sections describing the properties of —NF_2 compounds are arranged first in sequence by the number of carbon atoms in the organic skeleton and after that by the number of difluoroamino groups in the molecule. Compounds that carry additional substituents (nitro groups, nitrile groups, hydroxyl groups, amino groups, cyano groups) on the carbon skeleton are listed last. The following introductory summary concentrates on difluoroamino alkanes without additional substituents on the alkyl rest. A few compounds with multiple substitution are listed in what follows as examples, but the listing is far from complete. Also, we have neglected most R—NF_2 compounds where the R group is an unsaturated alkylene group.

It is common practice to abbreviate names of difluoroamino compounds and use acronyms. This has resulted in an alphabet soup of acronyms, and occasional confusion and mix-ups were unavoidable, in particular if the same abbreviation was used for two different compounds. Some of the acronyms originated as code names during a period when the mere existence of these compounds was classified as confidential information for national security reasons and their intended use as propellants or explosives was kept secret. Some of the common abbreviations are summarized in Table 1, arranged by increasing number of carbon atoms.

Table 1: Acronyms and code names used for difluoroamino compounds.

Acronym	Formula	Gross formula	Name
Compound H	$\text{F}_2\text{C}(\text{NF}_2)_2$	$\text{C}_1\text{F}_6\text{N}_2$	bis(difluoroamino)difluoromethane
Compound R	$\text{FC}(\text{NF}_2)_3$	$\text{C}_1\text{F}_7\text{N}_3$	tris(difluoroamino)fluoromethane
Compound T or Compound Delta	$\text{C}(\text{NF}_2)_4$	$\text{C}_1\text{F}_8\text{N}_4$	tetrakis(difluoroamino)methane
DDP	$\text{H}_3\text{C—C}(\text{NF}_2)_2\text{—CN}$	$\text{C}_3\text{H}_3\text{F}_4\text{N}_3$	2,2-bis(difluoroamino)propionitrile
1,2,2-TP	$\text{H}_3\text{C—C}(\text{NF}_2)_2\text{—CH}_2\text{—NF}_2$	$\text{C}_3\text{H}_4\text{F}_6\text{N}_3$	1,2,2-tris(difluoroamino)propane
1,1-DP	$\text{H}_3\text{C—CH}_2\text{—CH}(\text{NF}_2)_2$	$\text{C}_3\text{H}_6\text{F}_4\text{N}_2$	1,1-bis(difluoroamino)propane
1,2-DP	$\text{H}_3\text{C—CH}(\text{NF}_2)\text{—CH}_2\text{—NF}_2$	$\text{C}_3\text{H}_6\text{F}_4\text{N}_2$	1,2-bis(difluoroamino)propane
1,3-DP	$\text{F}_2\text{N—CH}_2\text{—CH}_2\text{—CH}_2\text{—NF}_2$	$\text{C}_3\text{H}_6\text{F}_4\text{N}_2$	1,3-bis(difluoroamino)propane
2,2-DP	$\text{H}_3\text{CC}(\text{NF}_2)_2\text{CH}_3$	$\text{C}_3\text{H}_6\text{F}_4\text{N}_2$	2,2-bis(difluoroamino)propane
DIN	$\text{H}_3\text{C—C}(\text{CH}_3)(\text{NF}_2)\text{—CN}$	$\text{C}_4\text{H}_6\text{F}_2\text{N}_2$	2-difluoroamino-2-methylpropionitrile
2,3-DB-1	$\text{H}_3\text{C—CH}(\text{NF}_2)\text{—CH}(\text{NF}_2)\text{—CH}_3$	$\text{C}_4\text{H}_8\text{F}_4\text{N}_2$	2,3-bis(difluoroamino)butane
IBA	$(\text{H}_3\text{C})_2\text{C}(\text{NF}_2)\text{—CH}_2\text{—NF}_2$	$\text{C}_4\text{H}_8\text{F}_4\text{N}_2$	1,2-bis(difluoroamino)-2-methylpropane
TBD	$(\text{H}_3\text{C})_3\text{CNF}_2$	$\text{C}_4\text{H}_9\text{F}_2\text{N}$	<i>tert</i> -butyldifluoroamine
1-DB	$\text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{NF}_2$	$\text{C}_4\text{H}_9\text{F}_2\text{N}$	1-difluoroaminobutane
2-DB	$\text{H}_3\text{CCH}_2\text{CH}(\text{NF}_2)\text{CH}_3$	$\text{C}_4\text{H}_9\text{F}_2\text{N}$	2-difluoroaminobutane
TMEA	$(\text{H}_3\text{C})_2\text{C}(\text{NF}_2)\text{—CH}(\text{NF}_2)\text{—CH}_3$	$\text{C}_5\text{H}_{10}\text{F}_4\text{N}_2$	2,3-bis(difluoroamino)-2-methylbutane

3.1 History of Difluoroamino Compounds

Although an organic difluoroamine derivative (CF_3NF_2 byproduct formed by direct fluorination of silver cyanide) had been reported as early as 1936, the impetus for the major development of this class of compound was the recognition by the US Advanced Research Projects Agency and Department of Defense that various N–F compounds, especially organic difluoramines, might be superior rocket propellant oxidizers [8]. Among others, Project Principia was carried out over the period 1958–1965 to explore the possibilities offered by these materials. While research projects funded by this program ended in 1969, open-literature publications of their results appeared for several years afterward. Hundreds of organic difluoramines, including hundreds with the *gem*-bis(difluoroamino) linkage, $>\text{C}(\text{NF}_2)_2$, were prepared under the aegis of Project Principia and similar efforts abroad. Generally the idea was that the higher the number of difluoroamino groups per molecule, the more energetic the material would become. The $-\text{NF}_2$ groups acted much like nitro ($-\text{NO}_2$) groups do in explosives such as trinitrotoluene (TNT), and even more so. However, because the difluoroamino group has a higher density than the nitro group, the compounds had the prospect of being superior propellant oxidizers or binders in solid propellant formulations or explosives. Project Principia failed to produce difluoroamino-based rocket propellant oxidizer candidates sufficiently superior to actually replace previously used nitro compounds. Almost all difluoroamino derivatives at that time possessed inadequate stability, insensitivity, or physical properties to serve as viable replacements. Organic difluoroamine research languished for a couple of decades afterward, though results continued to be published throughout the 1970s and 1980s by a few researchers. It is unfortunate that following the abandonment of difluoroamino compound development nobody took the time to summarize all the good work that had been done. That task would be very complicated because much of the information had never been published in scientific journals and much of it is scattered throughout the patent literature. Only a few publications describe the properties of the pure ingredients by themselves. Instead, an order of magnitude more patent publications attempt to lay claim to new rocket propellants containing $-\text{NF}_2$ compounds. The main prevailing benefit of the development of difluoroamino compounds appears to be in energetic plasticizers.

For the chemistry history buff, it is interesting to note that perfluoroguanidine (PFG) and $-\text{NF}_2$ compounds played a role in a Cold War spy story when a spy in one of the hostile governments gathering intelligence on the other's progress in developing new rocket propellants was caught in the act [9].

Later work was aimed at heterocyclic analogs to RDX or HMX where some or all of the $>\text{N}-\text{NO}_2$ groups were replaced by *gem*-bis(difluoroamino) $>\text{C}(\text{NF}_2)_2$ groups.

3.2 Preparation of Difluoroamino Compounds

The synthesis and chemical reactions of organic difluoroamines and the relationships between molecular structure and explosive sensitivity were evaluated in a series of research reports [10, 11]. These reports contain useful property data (melting point [m.p.], boiling point [b.p.], index of refraction) for almost a hundred difluoroamino compounds, mostly with carbon chains in the C₆–C₈ range and with cyclohexane.

N,N-difluoromethylamine is also called methyldifluoroamine or *N,N*-difluoromethanamine. Preparing NF compounds by direct N-fluorination of amides like urea or guanidine in aqueous solution often resulted in fluorinative cleavage, but ethyl N-fluorocarbamate was obtained from ethyl carbamate.

Direct fluorination with fluorine gas, converting a –NH₂ group into a –NF₂ group, is possible in the case of aminoperfluorophenyl compounds, where the benzene ring carried one amino group and none or one other substituent (–CF₃, NO₂, –CN) but had to work in dilution and with lots of precautions [12].

The electrooxidation of NF₂H in acidic solutions results in the formation of N₂F₄ by recombination of [•]NF₂ radicals in the absence of other radical formers. In the presence of alkyl radicals, RNF₂ compounds are formed instead by radical recombination [13].

Alkyl difluoroamines can be prepared by aqueous fluorination of N-substituted alkyl sulfonamides and alkyl sulfamates [14, 15]. For example, the fluorination of sodium *N*-methylsulfamate gave methyldifluoroamine, m.p. 158 K = –115 °C, b.p. 257 K = –16 °C. The same method can be used to prepare other RNF₂ compounds, for example: EtNF₂, b.p. 288 K = 15 °C; *n*-PrNF₂, b.p. 338–340 K = 65–67 °C; *iso*-PrNF₂, b.p. 317–319 K = 44–46 °C, *n*-BuNF₂, b.p. 354–357 K = 81–84 °C; *iso*-BuNF₂, b.p. 334 K = 61 °C; *sec*-BuNF₂, b.p. 359 K = 86 °C; and *n*-pentylNF₂, b.p. 375–376 K = 102–103 °C.

3.2.1 Preparation of Geminal Bis(difluoroamino) Compounds

Geminal bis(difluoroamino) compounds were prepared by the reaction of difluoroamine, F₂NH, in the presence of a strong dehydrating acid, which does not oxidize the F₂NH, at 263–308 K (–10 to +35 °C) with aldehydes or ketones [16–18]. The first example of this reaction was the synthesis of 2,2-bis(difluoroamino)propane (DP) from acetone and difluoroamine in sulfuric acid. Yields of 2,2-DP were generally in the neighborhood of 75%, although in one reaction even a 95% yield was obtained. The example compounds listed in Table 2 were prepared.

Geminal bis(difluoroamino) derivatives of the type (F₂N)₂CR₂ can be produced by the reaction of HNF₂ with F₂NCR₂⁺ carbonium ions through the slow addition of a protonating agent (e.g., concentrated H₂SO₄ or a low concentration of oleum) to a mixture of a carbonyl compound and HNF₂ (in 1:2 or greater proportion) formed by condensing the reactants at 195 K (–78 °C) in a solvent, warming to 263 K (–10 °C), and separating the two layers in suitable solvents (CHCl₃ or CH₂Cl₂) [19]. The geminal bis(difluoroamino) compounds listed in Table 3 were prepared in this way.

Table 2: Properties of geminal bis(difluoroamino) compounds.

Compound name	Boiling point		At reduced pressure mm Hg	Melting point	
	K	°C		K	°C
2,2-bis(difluoroamino)propane	346	73	760		
1,1-bis(difluoroamino)cyclopentane ^a	308–309	35–36	20		
3,3-bis(difluoroamino)pentane	313–314	40–41	30		
1,1-bis(difluoroamino)cyclohexane	317	44	7		
1,1,4,4-tetrakis(difluoroamino)cyclohexane	—	—	—	376	103 ^b
1,1-bis(difluoroamino)propane	298	25	260		
3-methyl-2,2-bis(difluoroamino)pentane	332	59	27		
2,2,5,5-tetrakis(difluoroamino)hexane	343	70	4		
2,2,7,7-tetrakis(difluoroamino)octane	344–345	71–72	0.1	333	60

^aHas a refractive index of $n_D^{25} = 1.3887$ ^bPhase change at 353 K (80 °C)

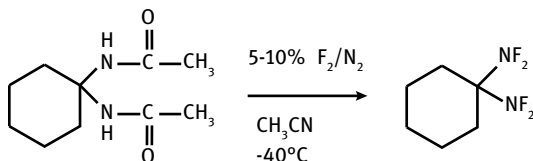
Data source: [17]

Table 3: Geminal bis(difluoroamino) compounds.

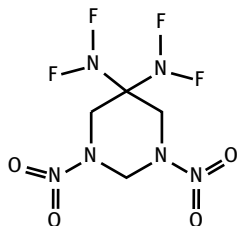
Compound	Melting point		Boiling point (at kPa)	Boiling point (at mm Hg)	Density at 20 °C g/cm ³	Refractive index, n_D^{20}
	K	°C	K	°C		
Me ₂ C(NF ₂) ₂			345–346	72–73	1.260	1.3385
EtMeC(NF ₂) ₂			370	97	1.227	1.3602
cyclo(CH ₂) ₄ C(NF ₂) ₂			348 (8)	75 (60–61)	1.299	1.3930
cyclo(CH ₂) ₅ C(NF ₂) ₂			293 (8)	20 (59)	1.284	1.4082
cyclo-(NF ₂) ₂ C(CH ₂ CH ₂) ₂ C(NF ₂) ₂	377–378	104–105				
ClCH ₂ CH ₂ CMe(NF ₂) ₂			323 (8)	50 (60)	1.382	1.4001
(O ₂ N) ₃ CCH ₂ CH ₂ CMe(NF ₂) ₂	314–315	41–42				
MeCH(NF ₂) ₂			323–324	50–51	1.309	1.3182
EtCH(NF ₂) ₂			349–350	76–77	1.246	1.3378
					(23.5°)	(23.5°)
PrCH(NF ₂) ₂			423 (7)	150 (53–54)	1.195	1.3540
[MeCH(NF ₂)] ₂ O			303.6 (9.6)	30.5 (72)	1.238	1.3516
(EtCHNF ₂) ₂ O			323 (7.7)	50 (58)	1.176	1.3742

See also [20, 21].

gem-Bis(difluoroamino) cycloalkanes can be prepared via direct fluorination of geminal bisacetamides [22]:



5,5-bis(difluoroamino)hexahydro-1,3-dinitropyrimidine, RNFX,



is an RDX analog, and HNFX, 3,3,7,7-tetrakis(difluoroamino)octahydro-1,5-dinitro-1,5-diazocine, is an HMX analog, expected to have similar or even better explosive properties [23, 24]. The acronym HNFX signifies the HMX analog of the class of NF_2 -modified cyclic nitramine explosives.

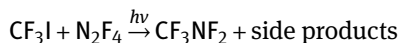
3.2.2 Preparation of Vicinal Bis(difluoroamino) Compounds

Vicinal bis(difluoroamino) compounds can be prepared by the addition of N_2F_4 to alkenes [25, 26]. This method is easier than the preparation of geminal bis(difluoroamino) compounds, which depend on the availability of difluoroamine, which is not commercially available.

3.2.3 Preparation of C_1 Difluoroamino Compounds

One of the oldest methods for the preparation of *N,N*-difluoromethylamine and *N,N*-difluoroethylamine involved the photochemical reaction of CH_3I or $\text{C}_2\text{H}_5\text{I}$ with N_2F_4 when subjected to ultraviolet excitation ($>2750 \text{ \AA}$) [27].

A photochemical process and a low-temperature fluorination procedure were used to prepare CF_3NF_2 . The latter was the better method. CF_3NF_2 can be prepared by a photochemical process, i.e.,



The photochemical method yielded many side products that required distillation and vapor phase chromatography to remove. A better method involved low-temperature

direct fluorination of KSCN in the presence of KF as a catalyst



The initial attempt at this reaction produced a quantitative yield of gaseous products consisting of CF_3NF_2 and SF_6 , which could be separated completely by two distillations.

Bis(difluoroamino)difluoromethane can be prepared by the direct fluorination of cyanuric chloride or aminoiminomethane sulfinic acid [28]. The direct fluorination of guanylurea sulfate at 263 K (-10°C) gives a mixture of several RNF_2 compounds, which is difficult to separate, and the yields are very poor. The products include bis(difluoroamino)difluoromethane, tris(difluoroamino)fluoromethane, pentafluoroguanidine, tetrafluoroformamidine, and a few others [29].

When ammonium fluoride NH_4F and formaldehyde (37% CH_2O) in aqueous solution were treated with a gaseous fluorine/nitrogen mixture at 273–275 K (0 – 2°C) for 1 h and the exit gases were condensed in two cold traps cooled to 133 K (-140°C), the condensate was mostly $\text{CH}_2(\text{NF}_2)_2$, with minor amounts of FCH_2NF_2 , CH_2F_2 , CHF_3 , and NF_3 .

Fluorine gas was passed through a glass U-tube containing potassium cyanide at room temperature, the off-gas was passed through a cold trap at liquid nitrogen temperature, and the condensate was purified by preparative gas chromatography (GC) and yielded difluoroaminotrifluoromethane, F_3CNF_2 , in 41% yield based on the amount of fluorine used [30]. The experiment was repeated at 253 K (-20°C) with similar results.

In many cases the fluorination reactions of organics result in mixtures of compounds with different degrees of fluorination. Bis(difluoroamino)difluoromethane and tris(difluoroamino)fluoromethane can be separated by selective adsorption onto crystalline zeolites as adsorbing materials [31]. A Linde 5A mol sieve will selectively adsorb bis(difluoroamino)difluoromethane while excluding the slightly larger tris(difluoroamino)fluoromethane molecule.

The polymeric reaction product of guanidine $(\text{H}_2\text{N})_2\text{C}=\text{NH}$ and urethane EtOCONH_2 in a stainless-steel boat was placed in a nickel tube, the tube was flushed with nitrogen, and a gas mixture of 8.9% fluorine in nitrogen was passed through for 3.66 h to give a yellow amorphous solid and a volatile fraction, which was condensed in a cold trap and after fractionation was found to contain $(\text{F}_2\text{N})_3\text{CF}$, b.p. = 278 K = 5°C , and density at 198 K = -75°C = $\sim 1.9\text{ g/cm}^3$, and the heat of evaporation was $\Delta H_{\text{vap}} = \sim 27\text{ kJ/mol} = \sim 6.5\text{ kcal/mol}$ [32]. The condensate also contained $(\text{F}_2\text{N})_2\text{CF}_2$ and traces of $(\text{CF}_3)_2\text{NF}$, CF_3NF_2 , and SiF_4 . The properties of $(\text{F}_2\text{N})_2\text{CF}_2$ were measured and reported as follows: b.p. = 241 K = -32°C , density at 298 K = 25°C = 1.901 g/cm^3 (under pressure), and heat of evaporation $\Delta H_{\text{vap}} = \sim 22\text{ kJ/mol} = \sim 5.3\text{ kcal/mol}$. Similarly $\text{F}_2\text{NCF}=\text{NF}$, $(\text{F}_2\text{N})_2\text{C}=\text{NF}$, $\text{F}_2\text{NCF}_2\text{NFCF}(\text{NF}_2)\text{NFCF}(\text{NF}_2)_2$, $\text{F}_2\text{NCF}_2\text{NFCF}_2\text{NFCF}(\text{NF}_2)_2$, and $\text{CF}_3\text{NFCF}(\text{NF}_2)_2$ were prepared.

The fluorination of aqueous solutions of urea was found to be a more readily controllable reaction to produce *N,N*-difluorourea, which is a useful intermediate in the production of other RNF_2 compounds [33]. The moderating effect of the solvent allowed the use of two mols of fluorine per mol of urea, and a 74% yield of *N,N*-difluorourea was isolated by ether extraction. *N,N*-Difluorourea was also prepared by the fluorination of a suspension of urea in acetonitrile. *N,N*-Difluorourea is a white solid, m.p. 314 K (41–41.5 °C), which was isolated in two crystalline forms, platelets by sublimation and needles by crystallization from halogenated solvents. *N,N*-Difluorourea must be handled with caution because it is a sensitive explosive. The amino group of *N,N*-difluorourea is unreactive, and further fluorination did not yield more highly fluorinated ureas.

PFG is a very useful reagent for the preparation of other difluoroamino compounds, including tris(difluoroamino)methane [34].

Fluorination of azidotrifluoromethane with added KF as a catalyst resulted in the formation of difluoroamino trifluoromethane in a direct, reproducible, and high-yield reaction [35]. The optimum rate of conversion with minimum degradation was obtained at 343–353 K (70–80 °C). The fluorination of CF_3N_3 to CF_3NF_2 can be catalyzed by KF [36].

Tetrakis(difluoroamino)methane can be synthesized by two different processes: One, developed by the Minnesota Mining and Manufacturing Company, involved the reaction of ammonia and PFG followed by the direct fluorination of the adduct. The other process, developed by the American Cyanamid Company, was similar and involved the reaction of isocyanic acid (HNCO) and PFG to form an adduct, followed by direct fluorination to Compound Delta.

Highly fluorinated fluoroaminomethane products, e.g., $\text{C}(\text{NF}_2)_4$, are useful as rocket fuels. Compounds such as difluoroamino(fluoroamino) fluoromethyl isocyanate, tris(difluoroamino)fluoromethane, bis(difluoroamino)fluoroaminomethyl isocyanate, tris(difluoroamino)methyl isocyanate, and tetrakis(difluoroamino)methane were synthesized [37]. For instance, biguanide was mixed with NaF, placed in a fluid-bed reactor, and fluidized and fluorinated by passing a carrier gas (4% F and 96% He) at a temperature of 343 K (70 °C) for 4 h. The product was collected and purified, containing 27% perfluoroformamidine, 18% PFG, and 8% difluorocyanamide. Difluorocyanamide $\text{F}_2\text{NC}\equiv\text{N}$ is a useful fluorinating agent.

Difluoroaminoazidomethane derivatives can be prepared by the reaction of fluoroguanidine compounds $\text{R}_2\text{C}=\text{NF}$ ($\text{R} = \text{F}, \text{NF}_2, \text{N}_3$) with hydrazoic acid and difluorine in inert halogenated solvents [38]. Compounds prepared by this method included $(\text{F}_2\text{N})_2\text{C}(\text{N}_3)\text{NHF}$, $(\text{F}_2\text{N})_3\text{CN}_3$, and $(\text{F}_2\text{N})_2\text{CFN}_3$.

In addition to difluoroamino compounds with $\text{C}-\text{NF}_2$ linkages, compounds have been prepared where the alkyl group and the $-\text{NF}_2$ group are linked by an oxygen $-\text{O}-$ bridge. Examples are H_3CONF_2 and F_3CONF_2 [39].

3.2.4 Preparation of Linear Difluoroamino Compounds

3.2.4.1 Preparation of C₂ Difluoroamino Compounds

Fluorination of 13.2 g (0.15 mol) of ethylurea in 350 mL of water (0–5 °C, 0.35 mol of fluorine, 2 h) gave 6 g (49% yield) of difluoroaminoethane identified by its infrared (IR) spectrum, which was condensed from the exit gas in a 195 K (–78 °C) trap [33].

1,2-Bis(difluoroamino)ethylnitramine $\text{F}_2\text{N}-\text{CH}_2-\text{CH}(\text{NF}_2)\text{NHNO}_2$ can be prepared by the nitration of 1,2-bis(difluoroamino)ethyl isocyanate with a 50/50 mixture of HNO_3 and H_2SO_4 [40]. The nitrated mixture must be neutralized with urea before the product can be isolated. The urea salt that formed was filtered off, the CH_2Cl_2 solution was dried with MgSO_4 and filtered, and the CH_2Cl_2 was removed under vacuum. The residue was maintained under high vacuum overnight and then distilled to give a colorless liquid, with a b.p. of 325 K (52 °C) at 0.25 mm Hg. The liquid was identified as 1,2-bis(difluoroamino)ethylnitramine by IR spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and mass spectrometry (MS).

The dry reaction of a sodium cyanamide/ MgF_2 mixture with diluted F_2/N_2 gas yielded (difluoroaminodifluoromethyl)fluorocyanamide $\text{NF}_2\text{CF}_2\text{NFCN}$, a volatile compound that could be condensed in a cold trap at 195 K [41]. The liquid boils at 291 K (18 °C). This can be dissolved in N_2O_4 and used as oxidizer for N_2H_4 .

3.2.4.2 Preparation of C₃ Difluoroamino Compounds

Fluorination of 102 g (1.0 mol) *n*-propylurea in 700 mL water (1.5 mol of fluorine, 6 h, 0–5 °C) gave 15 g (0.16 mol) 1-difluoroaminopropane, b.p. 318 K (45 °C), which was condensed from the exit gas in a 195 K (–78 °C) trap [33]. In a similar way, a solution of 70 g (0.70 mol) tetrahydro-2-pyrimidone in 650 mL water was allowed to react with fluorine at 0–5 °C for 1.5 h, giving a 6% yield of 80% pure (GC analysis) 1,3-DP after fractionated distillation, b.p. 38–50 °C (25 mm Hg).

A mixture of allyldifluoroamine, 1,2,3-tris(difluoroamino)propane, 1,2,3-tribromopropane, and 1,2-dibromo-3-(difluoroamino)-propane was obtained by treating allyl bromide with N_2F_4 at 503 K (230 °C) [42, 43]. Instead of performing this reaction in a single step and ending up with a lot of byproducts, a more selective product mix is achieved by performing the reaction in two steps [44]. In the first step, equal amounts of allyldifluoroamine and 1,2,3-tris(difluoroamino)propane were formed. Allyldifluoroamine was separated by distillation and treated for 12 h with N_2F_4 at 448 K (175 °C) and 103 kPa (15 psia) to give the desired 1,2,3-tris(difluoroamino)propane in essentially quantitative yield. 1,2,3-Tris(difluoroamino)propane had a b.p. of 400 K (127 °C) and a freezing point of 162 K (–111 °C). It could be mixed with tetranitromethane (TNM), boron powder, and a binder to give a rocket propellant with a specific impulse of 282 s.

2,3-Bis(difluoroamino)-1-propanol can be prepared by the reaction of allyl trifluoroacetate with tetrafluorohydrazine, making 2,3-bis(difluoroamino)propyl trifluoroacetate, followed by transesterification with an excess of methanol, giving 2,3-bis(difluoroamino)-1-propanol with a b.p. of 317 K at 400 Pa (44 °C at 3 mm Hg) [45].

gem-Difluoroamino compounds can be prepared by treating carbonyl compounds with F_2NH in the presence of a strong dehydrating acid that does not oxidize the F_2NH , at 263–308 K (–10 to +35 °C) [17, 46]. The reaction of acetone with F_2NH in concentrated H_2SO_4 gave 2,2-DP with a b.p. of 346 K (73 °C) at ambient pressure or 298 K at reduced pressure of 35 kPa (25 °C at 260 mm Hg).

When the amino group in allylamine is protected by being fully protonated by a strong acid such as perchloric acid, forming the allylammonium perchlorate, $H_2C=CHCH_2NH_3ClO_4$, the reaction with N_2F_4 leaves the amino group intact and instead N_2F_4 adds only to the double bond in a typical difluoroamination reaction forming the 2,3-bis(difluoroamino)propaneammonium perchlorate $F_2NCH_2CH(NF_2)CH_2NH_3ClO_4$, with a m.p. of 371–373 K (98–100 °C), and an impact sensitivity of 25 kg·cm [47]. Similarly, the energetic salt 2,3-bis(difluoroamino)propylhydrazinium(2+) perchlorate $F_2NCH_2CH(NF_2)CH_2NHNH_2 \cdot 2HClO_4$ was prepared.

3.2.4.3 Preparation of C_4 Difluoroamino Compounds

tert-Butyl difluoroamine can be prepared by dissociation of tetrafluorohydrazine into $\cdot NF_2$ free radicals and combining them with *tert*-butyl radicals via the decomposition of azoisobutane in the presence of N_2F_4 or by illumination of *tert*-butyl iodide vapor with N_2F_4 [11].

The reaction of N_2F_4 with butadiene results in the addition of only two $-NF_2$ groups in the terminal positions, forming 1,4-bis(difluoroamino)-butene-2,3, which on subsequent reaction with N_2O_5 gives 1,4-bis(difluoroamino)-2,3-bis(nitrato)butane, $F_2NCH_2CH(ONO_2)CH(ONO_2)CH_2NF_2$, a very energetic compound with a density of 1.7 g/cm³, a b.p. of 335–341 K at 13 Pa (62–68 °C at 0.1 mm Hg), and an autoignition temperature of 468 K (195 °C) [48].

A series of seven difluoroamino compounds (five aliphatic, one aromatic, and one heterocyclic) were prepared by F_2NH substitution reactions, including $F_2NCH_2N(NO_2)(CH_2)_2N(NO_2)CH_2NF_2$, $F_2NCH_2N(NO_2)CH_2N(NO_2)CH_2NF_2$, $F_2NCH_2N(NO_2)CH_2NH_2$, *p*-MeC₆H₄SO₂N(CH₂NF₂)₂, AcN(CH₂NF₂)₂, $F_2NCH_2NEtCHO$, and a piperazine derivative [49]. These compounds are potentially useful as energetic additives in solid rocket propellants.

Treatment of $(O_2N)_3CCH_2N(NO_2)CH_2CH_2OH$, $(O_2N)_3CCH_2N(NO_2)CH(CH_2OH)_2$, $(O_3N)_3CCH_2N(NO_2)C(CH_2OH)_3$, or $O_2NN[CH_2C(NO_2)CH_2OH]_2$ with $FN=C(NF_2)_2$ in MeCN in the presence of urea, followed by fluorination, gave $(O_2N)_3CCH_2N(NO_2)=CH_2CH_2OC(NF_2)_3$, $(O_2N)_3CCH_2N(NO_2)CH[CH_2OC(NF_2)_3]_2$, $(O_2N)_3CCH_2N(NO_2)C[CH_2OC(NF_2)_3]_3$, and $O_2NN[CH_2C(NO_2)_2CH_2OC(NF_2)_3]_2$, which are ethers with nitramino groups and nitroalkyl and difluoroaminoalkyl groups [50]. These compounds can be used as energetic additives in solid rocket propellants.

3.2.4.4 Preparation of C₅ Difluoroamino Compounds

Non-conjugated diolefins in the vapor or liquid phase, with one or both double bonds in the α position, react with N₂F₄ to form vicinal bis(difluoro)amines. At 313–333 K (140–160 °C), for a stoichiometric ratio of reactants and initial pressures of <1 atm, practically all the N₂F₄ is consumed in 3 h or less [51]. Liquid-phase reactions at 293–573 K (20–300 °C) and 0.2–3 MPa (2–30 atm), with or without inert diluents, are also effective. For mol ratios of N₂F₄ to diolefin of 2:1, the formation of tris- and tetrakis(difluoro)amines is favored. Lower mol ratios favor bis(difluoro)amine compound formation. Example compounds described were 1,2,4,5-tetrakis(difluoroamino)pentane, b.p. 463–465 K (190–192 °C); 3,4,5-tris(difluoroamino)-1-pentene; 1,4,5-tris(difluoroamino)-2-pentene; 4,5-bis(difluoroamino)-1-pentene, b.p. 397–398 K (124–125 °C); 3-(difluoroamino)-1,4-pentadiene; 5-(difluoroamino)-1,3-pentadiene, and 1,2,5,6-tetrakis(difluoroamino)hexane. These compounds were characterized by GC and IR and NMR spectroscopy.

3.2.4.5 Preparation of C₆ Difluoroamino Compounds

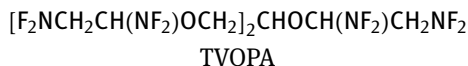
Syntheses and gas chromatographic purification of 1,1-bis(NF₂)-hexane and -heptane, 1,2-bis(NF₂)cyclohexane, 2,3-bis(NF₂)-2,3-dimethylbutane; 2,3-bis(NF₂)pentane isomers, and 1,1-, 1,2- and 2,2-bis(NF₂)phenylethane were described [52]. Elimination of HF or HNF₂ from certain organic difluoroamines yielded ketofluoroimines or trifluoroformamidines.

1,2,5,6-Tetrakis(difluoroamino)-3,4-hexanediol dinitrate can be prepared by the nitration of 1,2,4,6-tetrakis(difluoroamino)-3,4-hexanediol in CH₂Cl₂ by HNO₃ mixed with H₂SO₄ [53]. The CH₂Cl₂ layer was separated, washed, and dried and the CH₂Cl₂ removed, leaving a yellow viscous product that decomposed at 428 K (155 °C).

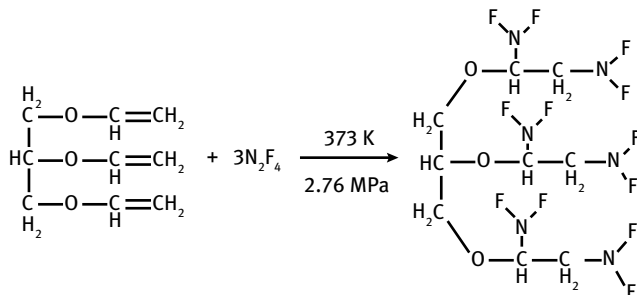
3.2.4.6 Preparation of C_{n>6} Difluoroamino Compounds

Preparation of TVOPA

One of the most energetic difluoroamino compounds is the trisvinoxypropyl adduct, an ether aldol compound, TVOPA, 1,2,3-tris[1,2-bis(difluoroamino)]ethoxy propane, C₉H₁₄F₁₂N₄O₃, Chemical Abstracts Service Registry Number (CAS RN) [53159-39-0]. The acronym TVOPA was derived from **tris vinoxy propyl adduct**. The compound was developed at Rohm and Haas and produced in pilot plant quantities large enough to demonstrate performance in 10-lb_m motors and several 100-lb_m motors before 1967.



TVOPA can be prepared by reacting tris(vinoxy)propane with tetrafluorohydrazine N_2F_4 in trifluorotrichloroethane:

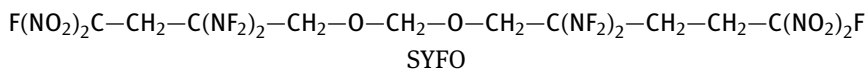


The skeleton of the TVOPA molecule is the same as that of glycerol. Where there used to be $-\text{ONO}_2$ groups in glycerol trinitrate (GTN, also called nitroglycerin NG), there are now $-\text{OCH}(\text{NF}_2)\text{CH}_2\text{NF}_2$ groups. TVOPA was intended to be used as an energetic plasticizer in double-base propellants and plastic-bonded explosives. An optimistic process scale-up study envisioned that enough TVOPA would be prepared to support an output of 136000 kg (300000 lb_m) of propellant per month, but the use of 2,3-bis(difluoroamino)propyl acrylate (NFPA) and TVOPA as propellant ingredients would add about 85% to the cost of a conventional solid propellant motor [54].

Geminal difluoroamino compounds were evaluated as a partial or complete replacement for TVOPA, tris-1,2,3-[bis(difluoroamino)-ethoxy]propane [55]. A partial or complete replacement of the vicinal-1,2-difluoroamino plasticizer of a difluoroamino-based propellant with its structural isomer or a related structural isomer, namely, a geminal-1,1-bis(difluoroamino) compound, resulted in two beneficial effects: a marked reduction in the pressure exponent and an enhancement of the burning rate of propellant.

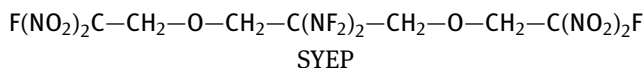
Preparation of SYEP

Some of the energetic plasticizers considered as alternatives for TVOPA contain nitro groups in addition to the difluoroamino groups on the alkyl rests. Examples of the geminal compounds are 2,2-bis(difluoroamino)-5,5-(dinitropentyl)formal or



4,10-[bis(difluoroamino)-1,13-difluoro-1,13-bis(dinitro)]-6,8-dioxatridecane
 2,2-bis(difluoroamino)-bis(5-fluoro-5,5-dinitro)pentyl formal
 bis[2,2-bis(difluoroamino)-5,5-dinitro-5-fluoropentoxyl]methane

or



2,2-bis(difluoroamino)-1,3-bis(fluorodinitroethoxy)propane
5,5-bis(difluoroamino)-1,9-bisdinitro-1,9-difluoro-3,7-dioxanonane

SYEP, CAS RN [7790-98-9], possesses more favorable properties, i.e., a lower m.p. and better processability characteristics than bis[2,2-bis(difluoroamino)-5,5-dinitro-5-fluoropentoxy]methane (SYFO), another candidate high-energy plasticizer. One of the methods for the production of SYEP is a nine-step procedure starting with trinitromethane (nitroform) as the starting material and involving difluorourea and difluorosulfamic acid as intermediates.

Another method for preparation of SYEP is the synthesis by difluoroamination of 1,3-bis(fluorodinitroethoxy)acetone [56]. This method depends on the availability of 1,3-bis(fluorodinitroethoxy)isopropanol, a key intermediate, from fluorodinitroethanol and epichlorohydrin. SYEP has been evaluated as a plasticizer in both PCDE, poly(1-cyano-2-difluoroamino)-2,3-epoxyethane, and polyethylene glycol (PEG) binder systems.

3.2.5 Preparation of Heterocyclic Difluoroamino Compounds

The addition of N_2F_4 to dioxadiene (a dioxane with two double bonds) gives a mixture of NF_2 compounds with two and four NF_2 groups attached to the dioxane ring. The mixture can be separated by reacting the unsaturated compound with an excess of N_2O_4 , forming a less volatile adduct, from which the more desirable tetrakis(difluoroamino)dioxane can be vacuum distilled after removing the excess N_2O_4 [57].

3-(Difluoroaminomethyl)-3-(difluoroamino)oxetane can be prepared by the reaction of 3-methyleneoxetane with N_2F_4 in Freon-113 [58]. The crude product can be redistilled by trap-to-trap distillation under vacuum using a warm water bath and identified by IR and NMR spectra. When treated with PF_5 , PF_5 -tetrahydrofuran, or $\text{BF}_3 \cdot \text{Et}_2\text{O}$, it polymerized. The polymer had a molecular weight of 9190 and was soluble in MeCN.

3.2.6 Preparation of Difluoroamino Compounds by Addition to Alkanes

Alkyl mono(difluoroamines) and bis(difluoroamines) can be prepared by reacting an alkane containing one to eight carbon atoms with tetrafluorohydrazine at 473–623 K (200–350 °C) [59]. For example, 10 cm³/min butane, 65 cm³/min tetrafluorohydrazine, and 32 cm³/min helium diluent gas were fed into a copper coil reactor heated to 573 K (300 °C) for 42 min. The product and excess reactants were collected in traps maintained at 193, 143, and 77 K (–80, –130, and –196 °C), and the contents of the –80 °C trap contained 21% 1-(difluoroamino)butane, 16% 2-(difluoroamino)butane, and 50%

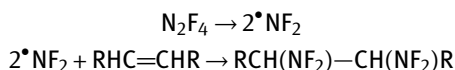
1,2-bis(difluoroamino)butane. The same method was used with other alkanes, such as propane, giving *iso*-PrNF₂, *n*-PrNF₂, and MeCH(NF₂)CH₂NF₂, or isobutene, giving Me₃CNF₂, Me₂CHCH₂NF₂, Me₂C(NF₂)CH₂NF₂, CH₃CH₂CH(NF₂)Me, and PrCH(NF₂)₂.

Alkanes can be converted to difluoroaminoalkanes by irradiation with N₂F₄, producing [•]NF₂ free radicals [60]. Selectivity ratios for photodifluoramination of *n*-butane, *n*-butyl fluoride, ethyl chloride, and ethyl difluoramine were determined by analyzing the isomeric mixture of alkyl difluoroamines produced by the irradiation of N₂F₄ with these substrates. Kinetic and stoichiometric information about the photodifluoroamination process was obtained from a study of the photolysis of N₂F₄ with the simplest alkane, methane. The irradiation of N₂F₄ with propylene and isobutylene resulted not only in the substitution of NF₂ for H but the addition of F and NF₂ to the double bond. The F was found mainly on the terminal carbon atom.

The photolysis of mixtures of nitrogen trifluoride with ketones (in the temperature range 303–486 K) leads to reactions of CH₃, CF₃, C₂H₅, *iso*-C₃H₇, and *tert*-C₄H₉ radicals with nitrogen trifluoride and the formation of difluoroaminoalkanes [61]. With the smaller radicals only the abstraction of difluoroamino radicals is important, but with *iso*-C₃H₇ and *tert*-C₄H₉ both difluoroamino and fluorine abstraction occurs.

3.2.7 Preparation of Difluoroamino Compounds by Addition to Olefins (Alkenes)

Tetrafluorohydrazine dissociates readily into two difluoroamino free radicals, which can then add to C=C double or C≡C triple bonds in what is typically a free radical mechanism. Tetrafluorohydrazine readily adds to the double bond of alkenes (olefins) to give vicinal bis(difluoroamino) derivatives in good yield [26]:



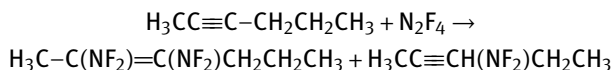
The reaction of tetrafluorohydrazine with olefins, for instance reacting with ethylene while heating for 6 h at 393–403 K (120–130 °C) gave 71.5% (CH₂)₂(NF₂)₂, b.p. 344–346 K (71°–73 °C), *d*²⁰ = 1.352 g/cm³, *n*_D²⁰ = 1.3339, and some polymer on the vessel walls [25]. Similarly (at 373 K = 100 °C) with propylene the product was F₂NCH₂C(NF₂)MeH, b.p. 353–355 K (80–82 °C), *d*²⁰ = 1.248 g/cm³, *n*_D²⁰ = 1.3481. With isobutylene Me₂C=CH₂ and N₂F₄ at 353 K (80 °C) the products were a polymer and F₂NCH₂C(NF₂)Me₂, b.p. 370 K (97 °C), *d*²⁰ = 1.202 g/cm³, *n*_D²⁰ = 1.3588.

Isoalkenes and aromatic alkenes like styrene react more readily than straight-chain alkenes. Vinylidene chloride is much more active than ethene. This reaction appears to be very general, proceeding with functional olefins such as vinyl isocyanate, vinyl-*n*-butyl ether, methyl acrylate, or divinyl carbinyl acetate and haloolefins such as trichloroethylene, 1,1-difluoroethylene, and perfluoropropylene, in addition to simple olefins such as ethylene, propylene, 1,3-butadiene, and 2-heptene. The mechanism of the addition is believed to involve a free radical chain reaction similar to that postulated for the addition of bromine and polyhalogenomethanes

to olefins. The bis(difluoroamino) compounds derived from these olefins contain the vicinal bis(difluoroamino) grouping. Most of them are distillable, air-stable liquids but some have impact sensitivities worse than that of TNT. Difluoroamino compounds prepared by the addition of N_2F_4 to $>\text{C}=\text{C}<$ compounds have been evaluated as plasticizers for nitrocellulose [62].

3.2.8 Preparation of Difluoroamino Compounds by Addition to Acetylenes (Alkynes)

Only 1 mol N_2F_4 is added to alkynes, for examples, to 2-hexyne, with the formation of a mixture of addition products and products of the substitution of the α -H atom for the NF_2 group:



gem-Bis(difluoroamino) compounds of the type $\text{R}'\text{C}(\text{NF}_2)_2\text{CH}_2\text{R}''$ can be prepared by treating NHF_2 with an acetylene of the type $\text{R}'\text{C}\equiv\text{CR}''$ in the presence of a strong acid catalyst, e.g., BF_3 , $\text{BF}_3\text{-H}_3\text{PO}_4$ complex, and SO_3 fuming H_2SO_4 [63]. When 1-hexyne was added dropwise with external cooling to a refluxing mixture of 7 g NHF_2 and 15 mL conc. H_2SO_4 at 258 to 253 K (-15 to -20°C), an upper layer separated from the H_2SO_4 . After 4 h, excess NHF_2 was removed, and a liquid product containing 2,2-bis(difluoroamino)-hexane and 3-hexyne was obtained. Under the same conditions 1,4-pentadiyne gave 2,2,4,4-tetrakis(difluoroamino)pentane.

3.3 Physical Properties of Difluoroamino Compounds

Surprisingly, it was found to be difficult to find a systematic and complete source for physical properties of difluoroamino compounds, arranged by the length and structure of the alkyl rest (methyl, ethyl, *n*-propyl, isopropyl, and so on) and by the number of difluoroamino groups in the molecule. For example, the physical properties of bis(difluoroamino) alkanes are listed in Table 4.

Table 4: Physical properties of bis(difluoroamino) alkanes.

Compound	Density, ρ , g/cm ³		Sound velocity, c mm/ μs	Coefficient of expansion 1/ $^\circ\text{C}$	Heat capacity	
	5 $^\circ\text{C}$	40 $^\circ\text{C}$			cal g ⁻¹ $^\circ\text{C}^{-1}$	cal mol ⁻¹ $^\circ\text{C}^{-1}$
1,2-DP	1.296	1.241	0.96 ± 0.02	1.26×10^{-3}	0.348 ± 0.005	51 ± 1
2,2-DP	1.287	1.245	0.89 ± 0.03	1.34×10^{-3}		~ 51
1,2-DB	1.245	1.202	1.00 ± 0.07	1.18×10^{-3}		~ 58
IBA	1.242	1.193	0.90 ± 0.05	1.15×10^{-3}		~ 58

Data source: [64]

3.3.1 Physical Properties of C₁ Difluoroamino Compounds

The physical properties of *N,N*-difluoroaminomethane compounds are listed in Table 5.

Table 5: Physical properties of *N,N*-difluoroaminomethane compounds

Compound	H ₃ CNF ₂	H ₂ C(NF ₂) ₂	HC(NF ₂) ₃	C(NF ₂) ₄	References
Gross formula	C ₁ H ₃ N ₁ F ₂	C ₁ H ₂ N ₂ F ₄	C ₁ H ₁ N ₃ F ₆	C ₁ N ₄ F ₈	
CAS RN	753-58-2	18338-50-6	121832-14-2	17125-65-4	
Molecular mass	67.0380	118.03	169.03	220.0247	[65]
Freezing point	158.3 K = −114.8 ± 0.3 °C			259.6 K = −13.5 °C	[27]
Boiling point	257.1 K = −16.0 °C	309 K (36 °C) (predicted)	341 K (68 °C) (predicted)	313 K = 40 °C	[27]
Density	1.099 ± 0.0005 g/cm ³ at 253 K	1.451 ± 0.06 g/cm ³ (predicted)	1.692 ± 0.06 g/cm ³ (predicted)	1.748 g/cm ³	[27]
Vapor pressure	see equation below				
Enthalpy of formation, liquid				−16.7 ± 11 kJ/mol = −4.0 ± 2.8 kcal/mol	[66]
Heat of vaporization	23.5 kJ/mol				[65]
Heat of vaporization	22.9 kJ/mol = 5.48 kcal/mol at NBP				[27]

Some more detailed additional physical properties of CH₃NF₂ are given in what follows [27]. The vapor pressure of CH₃NF₂ over the range 80 to 204 K = −193 to −69 °C can be expressed by

$$\log P_{10} = 5.6731 - 755.13/T - 56631/T^2$$

where *P* is the pressure in cm Hg and *T* is the temperature in kelvin. The temperature was determined accurately to within ±0.15 °C and the pressure to within ±0.005 cm Hg. The b.p. at 760 mm Hg was 257.1 K = −16.0 °C + 01 °C and the m.p. was 158.3 K = −114.8 °C ± 0.3 °C. The density at 253 K = −20 °C was 1.099 ± 0.0005 g/cm³. The latent heat of vaporization at the normal b.p. was 22.9 kJ/mol = 5.48 kcal/mol.

The IR spectra of gaseous CH₃NF₂ and CD₃NF₂ and of solid CH₃NF₂ were measured and discussed in terms of the symmetry of Point Group C_s (Figure 1 and 2) [67]. The

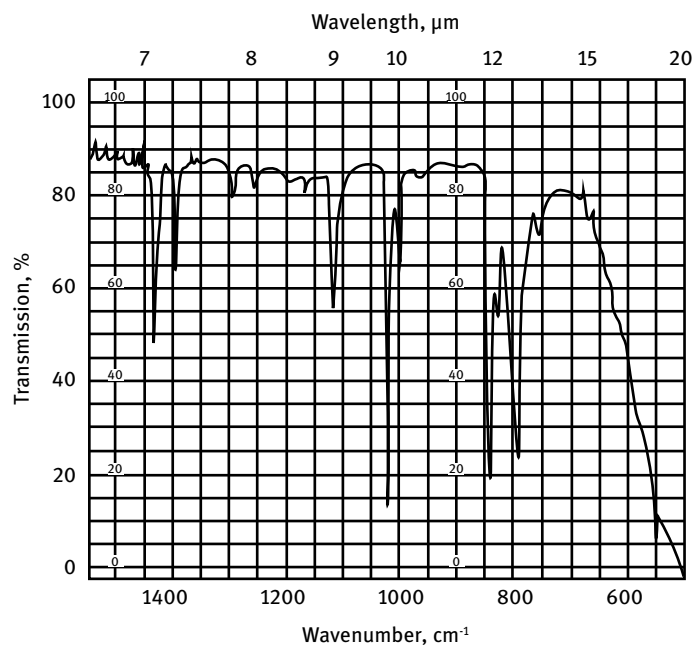


Figure 1: IR spectrum of solid *N,N*-difluoroaminomethane. (Republished and modified from [67], with permission of © 1966 American Institute of Physics; permission conveyed through Copyright Clearance Center, Inc.)

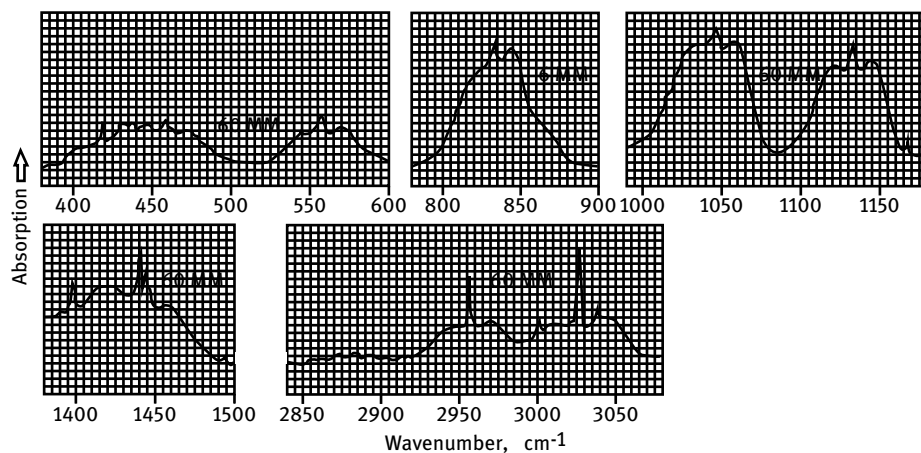


Figure 2: IR spectrum of *N,N*-difluoroaminomethane vapor. (Republished and modified from [67], with permission of © 1966 American Institute of Physics; permission conveyed through Copyright Clearance Center, Inc.)

unsymmetrical methyl vibrations, which are degenerate under the local C_{3v} symmetry of the group, were found to undergo splitting of smaller magnitude than in analogous compounds of C_s overall symmetry. The two nearly degenerate components of each of these motions appeared to be coupled through rotation. Figure 2 is a composite of five different images. The five IR spectra of CH_3NF_2 vapor in Figure 2 were measured with several sample cells of different optical path lengths, and the absorption/transmission scale of each segment is different.

Similarly, the IR spectrum of the perfluorinated compound CF_3NF_2 vapor was recorded in the region of 250 to 2000 cm^{-1} and also interpreted in terms of C_s symmetry of the molecule [68]. It was possible to identify 13 bands with fundamental vibrations.

Bis(difluoroamino)methane, $\text{H}_2\text{C}(\text{NF}_2)_2$, is the simplest geminal difluoroamino compound. The chemical name for $\text{H}_2\text{C}(\text{NF}_2)_2$ used in Chemical Abstracts (CA) is methanediamine, *N,N,N',N'*-tetrafluoro-. The predicted b.p. is 309 K (36°C) and the predicted density is $1.451 \pm 0.06\text{ g/cm}^3$, but the accuracy of those predictions is unknown.

The fourth column in the following table, Table 6, on fluorodifluoroamino-methane compounds is identical with the fourth column in the previously discussed Table 5, but the first three columns are for difluoroamino compounds where the C—H has been replaced by C—F.

To calculate the heat of formation of bis(difluoroamino)difluoromethane (Compound H), two numbers for the heat of explosion were available from the literature. Averaging these two numbers, and assuming a heat of formation ΔH_f^{298} of $-922.6\text{ kJ/mol} = -220.5\text{ kcal/mol}$ for $\text{CF}_4(\text{G})$, one obtains an enthalpy of formation ΔH_f^{298} of $-449.8\text{ kJ/mol} = -107.5 \pm 5\text{ kcal/mol}$ for $\text{F}_2\text{C}(\text{NF}_2)_2$ vapor and $-563.2\text{ kJ/mol} = -134.6 \pm 2.5\text{ kcal/mol}$ for $\text{F}_2\text{C}(\text{NF}_2)_2$ liquid. These numbers differ from those listed in Table 6.

The vapor pressure of perfluoromethylamine from the mp at 151 to 198 K (-122.1 to -75°C) follows the equation

$$\log p = 7.47 - 901.0/T$$

where p is the vapor pressure in mm Hg and T is the temperature in kelvin. The heat of vaporization is 17.2 kJ/mol (4.12 kcal/mol) and the Trouton constant is 21.0 [71].

The vapor pressure of bis(difluoroamino)difluoromethane can be expressed by the equation

$$\log p = 7.653 - 1149/T$$

where p is the vapor pressure in mm Hg and T is the temperature in kelvin [28]. The b.p. is $241 \pm 1\text{ K} = -32 \pm 1^\circ\text{C}$.

The vapor pressure of tris(difluoroamino)fluoromethane in the temperature range 190–310 K can be calculated from

$$\log p = 7.6484 - (1328.8/T)$$

Table 6: Physical properties of *N,N*-difluoroaminoperfluoromethane compounds.

Compound	F ₃ CNF ₂	F ₂ C(NF ₂) ₂	FC(NF ₂) ₃	C(NF ₂) ₄	References
Gross formula	C ₁ N ₁ F ₅	C ₁ N ₂ F ₆	C ₁ N ₃ F ₇	C ₁ N ₄ F ₈	
CAS RN	335-01-3	4394-93-8	14362-68-6	17125-65-4	
Molecular mass	121.01	154.01	187.02	220.0247	
Freezing point	141 K = −132 °C		138 K = −135 °C	259.6 K = −13.5 °C	[29]
Boiling point	198 K = −75 °C	235.9–236.6 K (−37.2– 36.5 °C)	278.7 K = 5.6 °C	313 K = 40 °C	[29]
Density		1.901 g/cm ³ at 293 K	1.56 g/cm ³	1.748 g/cm ³ ^a 1.68 g/cm ³ at 293 K	[66, 69]
Enthalpy of formation, liquid	—	−563.2 kJ/mol = −134.6 ± 2.5 kcal/mol	−220 ± 8.3 kJ/mol = −52.5 ± 2.0 kcal/mol	−16.7 ± 11 kJ/mol = −4.0 ± 2.8 kcal/mol	[66, 69]
Enthalpy of formation, liquid	—			+10.9 kJ/mol = +2.6 ± 2.8 kcal/mol	[3]
Enthalpy of formation, gas	−707 kJ/mol	−168.9 kcal/mol			[70]
Heat of vaporization	113 kJ/mol	27 kcal/mol			

^aThis number may not be very accurate.

where p is the vapor pressure in mmHg and T is the temperature in kelvin [29]. The heat of vaporization is 25.4 kJ/mol (6.08 kcal/mol). The density at 298 K = 25 °C is 1.56 g/cm³. The density as a function of temperature in the temperature range 233–353 K (−40 to 80 °C) can be calculated from

$$\rho = 1.622 - 30.020 \times 10^{-4}t - 1.701 \times 10^{-6}t^2 - 9.732 \times 10^{-8}t^3$$

where ρ is the density in g/cm³ and t is the temperature in °C. Tris(difluoroamino)fluoromethane, FC(NF₂)₃, is also known under the code name Compound R.

The enthalpy of formation of liquid tris(difluoroamino)fluoromethane is −220 ± 8.3 kJ/mol = −52.5 ± 2.0 kcal/mol. The enthalpy of formation of liquid tetrakis(difluoroamino)methane is −16.7 ± 11 kJ/mol = −4.0 ± 2.8 kcal/mol and that of tetrakis(difluoroamino)methane vapor is +10.9 ± 11 kJ/mol = +2.6 ± 2.8 kcal/mol.

Tetrakis(difluoroamino)methane, octafluoromethanetetramine, Compound Delta, C(NF₂)₄, CAS RN [17125-65-4], is an analog of tetranitromethane where all oxygens have

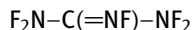
been replaced by fluorine. This compound was evaluated as a liquid oxidizer, similar to TNM, and was also mixed with TNM. Mixtures of tetrakis(difluoroamino)methane and TNM have been considered as storable oxidizers, a storable version of FLOX [1, 2].

The geometric structures of the CF_3NF_2 and $(\text{CF}_3)_2\text{NF}$ molecules were determined from electron diffraction and microwave spectroscopy data [72]. The Raman and IR spectra of both compounds were recorded in the liquid and vapor states and assigned for C_s symmetry. Normal coordinate analyses were performed using extensive transfer of force constants in the series $(\text{CF}_3)_n\text{NF}_{3-n}$. In this series the N—F bond lengths do not depend on n within the experimental error limits. The N—C bond lengths decreased and the corresponding force constants increased with increasing n . It was attempted to explain this trend on the basis of a simple bonding model.

The enthalpy of formation of trifluoromethoxy difluoroamine, F_3CONF_2 , was calculated from the heat of explosion of mixtures of hydrogen and trifluoromethoxy difluoroamine as $-791.2 \pm 3.3 \text{ kJ/mol}$ ($-189.1 \pm 0.8 \text{ kcal/mol}$) based on the NBS Technical Note 270-1 value for HF (aq.) [73].

The ^{18}F NMR spectrum of CF_3NF_2 made by fluorination of KSCN and separation from SF_6 consisted of a broad peak at ϕ 84.1 and another broad peak at -18.5 [74]. The relative area ratio of the two peaks was 3.11 : 2.0.

Another C_1 NF compound which is of interest as an intermediate for the synthesis of other NF compounds is PFG, pentafluoroguanidine, CAS RN [10051-06-6]:



PFG is a liquid with a freezing point of 113 K (-160°C), a b.p. of 271 K (-2°C), a density of 1.70 g/cm^3 (below the b.p.), and an enthalpy of formation ΔH_f^{298} of $+79 \text{ kJ/mol} = +18.9 \text{ kcal/mol}$ in the liquid state, $+101 \text{ kJ/mol} = +24.2 \text{ kcal/mol}$ in the vapor state, and a heat of evaporation of $22.2 \text{ kJ/mol} = 5.3 \text{ kcal/mol}$. The vapor pressure of PFG in the temperature range of 100–253 K can be calculated from

$$\log p = 7.322 - (1203/T)$$

where p is the vapor pressure in mm Hg and T is the temperature in kelvin. The heat of vaporization is 23 kJ/mol (5.50 kcal/mol). The IR spectrum of $(\text{NF}_2)_2\text{C}=\text{NF}$ contained bands at 6.11 (m), 7.41 (s), 7.98 (s), 8.22 (s), 8.45 (sh), 9.74 (s), 10.62 (s), and 13.60 (s) μm . It is extremely sensitive to shock and has been the cause of numerous accidents during the attempted synthesis of other difluoroamino compounds starting with PFG as the fluorinating agent.

PFG can be made by direct fluorination with nitrogen-diluted fluorine gas of guanidinium monofluoride powder in dilution with a large amount of sodium fluoride [75]. PFG boils at 272.0 K (-1.1°C) and is extremely explosive.

3.3.2 Physical Properties of C_2 Difluoroamino Compounds

The physical properties of mono-, bis-, and tris(*N,N*-difluoroamino)ethane compounds are listed in Table 7.

Table 7: Physical properties of mono-, bis-, and tris(difluoroamino)ethane compounds.

Compound	H ₃ CCH ₂ NF ₂	H ₃ CCH(NF ₂) ₂	H ₃ CC(NF ₂) ₃	F ₂ NCH ₂ CH ₂ NF ₂	References
CAS RN	758-18-9	23034-69-7	20116-54-5	15403-23-3	
Gross formula	C ₂ H ₅ N ₁ F ₂	C ₂ H ₄ N ₂ F ₄	C ₂ H ₃ N ₃ F ₆	C ₂ H ₄ N ₂ F ₄	
Molecular mass, g/mol	81.0646	132.06	183.06	132.06	
Freezing point	122.8 K = −150.3 ± 0.3 °C				[27]
Boiling point	288.0 K = 14.9° ± 0.1 °C			345 K (72 °C)	[27]
Density, g/cm ³ at 273 K	1.0165	1.309	1.577 ± 0.06 (predicted)	1.352	[27]
Vapor pressure	see equation below				
Refractive index n_D^{20}				1.3339	
Enthalpy of formation, liquid				−197 ± 17 kJ/mol = −47 ± 4 kcal/mol	[66, 69]
Enthalpy of formation, vapor				−172 ± 17 kJ/mol = −41 ± 4 kcal/mol	[66, 69]

The vapor pressure of C₂H₅NF₂ over the range 241 to 258.7 K (−32 to −14.4 °C) can be expressed by the following equation [27]:

$$\log P_{10} = 5.7005 - 856.30/T - 70345/T^2$$

where P is the pressure in cm Hg and T is the temperature in kelvin. Temperature measurements were made to ±0.1 °C, and the pressure was measured to ±0.005 cm Hg. The b.p. was at 288.0 ± 0.1 K = 14.9° ± 0.1 °C. The mp was at 122.8 ± 0.3 K = −150.3 ± 0.3 °C. The density of C₂H₅NF₂ over the range 238.3 to 258.4 K (−34.8 to −14.7 °C) can be expressed by

$$\log D_{10} = -0.41505 + 177.14/T - 16889/T^2$$

where D is the density in g/cm³ and T is the temperature in kelvin. The density at 273 K = 0 °C was 1.0165 g/cm³.

The reaction of fluorine with either trifluoroacetonitrile or pentafluoropropionitrile at 195 K (−78 °C) in the presence of activated cesium fluoride produced the corresponding perfluoroalkyl difluoramines smoothly: C₂F₅NF₂, CAS RN [354-80-3] and C₃F₇NF₂, CAS RN [423-32-5] [74].

Perfluoroethylamine, $\text{C}_2\text{F}_5\text{NF}_2$, boils at 237 K (-36°C) and solidifies to a glass near 102 K (-171°C) [71]. The vapor pressure of $\text{C}_2\text{F}_5\text{NF}_2$ in the range of 171 to 236 K (-102 to -37°C) is given by the equation

$$\log p = 7.435 - 1088/T$$

where p is the pressure in mm Hg and T is the temperature in kelvin. The heat of vaporization is 20.8 kJ/mol (4.98 kcal/mol), and the Trouton constant is 20.8. The b.p. of $(\text{CF}_2\text{NF}_2)_2$ is 268.0 to 268.6 K (-5.1 to -4.5°C).

3.3.3 Physical Properties of C_3 Difluoroamino Compounds

The physical properties of mono- and bis-(difluoroamino)propane compounds are listed in Table 8. *n*-Difluoroaminopropane, *N,N*-difluoropropylamine, $\text{H}_3\text{CCH}_2=\text{CH}_2\text{NF}_2$, is also called 1-propanamine, *N,N*-difluoro- in the CA index.

Table 8: Physical properties of difluoroaminopropane compounds.

Compound	$\text{H}_3\text{CCH}_2\text{CH}_2\text{NF}_2$	$(\text{H}_3\text{C})_2\text{CHNF}_2$	$\text{H}_3\text{CCH}(\text{NF}_2)\text{CH}_2\text{NF}_2$	$\text{F}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NF}_2$	References
Gross formula	$\text{C}_3\text{H}_7\text{N}_1\text{F}_2$	$\text{C}_3\text{H}_7\text{N}_1\text{F}_2$	$\text{C}_3\text{H}_6\text{N}_2\text{F}_4$	$\text{C}_3\text{H}_6\text{N}_2\text{F}_4$	
CAS RN	18264-07-8	18264-08-9	15403-25-5	21298-22-6	
Molecular mass	95.09	95.09	146.09	146.09	
Boiling point	338–340 K 65–67 °C	317–319 K 44–46 °C	356 K 83 °C	298–305 K 25–32 °C	
Density at 293 K	0.988 ± 0.06^a	0.984 ± 0.06^a	1.265	1.277 ± 0.06^a	
Enthalpy of formation, liquid			-213 ± 17 kJ/mol = -51.0 ± 4 kcal/mol		[66, 69]

^aPredicted

Of all the C_3 difluoroamines, the literature references the compounds isopropyldifluoroamine and 1,2-DP the most. Another C_3 difluoroamino compound of interest is tris(difluoroaminomethyl)amine, $(\text{F}_2\text{NCH}_2)_3\text{N}$, with a b.p. of 166°C and a density of 1.378 g/cm^3 at 291 K = 18°C . Perfluoropropylamine, $\text{C}_3\text{H}_7\text{NF}_2$, boils at 273 K = 0°C and solidifies at 105 K (-168°C).

The refractive indices of RNF_2 and other liquid compounds are often used to verify the purity of a substance. The refractivities of the NF_2 group and of the N–F bond in 14 liquid organic NF_2 derivatives were compared using experimental values of n_D^{20} and d^{20} as well as previously published group and bond additivity refractivity data [76]. For mono(difluoroamino) alkanes, the NF_2 refractivity was $R_{\text{NF}_2} = 4.97$ and the

refractivity of the N atom was $R_N = 3.35$. For vicinal bis(difluoroamino)- and functional mono(difluoroamino) derivatives, refractivities were $R_{NF_2} = 5.27 \pm 0.06$ and $R_N = 3.65$. The N–F bond refractivity does not depend on the structure of the R alkyl rest $RN-F = 2.14 \pm 0.02$.

3.3.4 Physical Properties of C₄ Difluoroamino Compounds

The b.p. of butyldifluoroamines is as follows: *n*-BuNF₂, b.p. = 354–357 K = 81–84 °C; *iso*-BuNF₂, b.p. = 334 K = 61 °C; *sec*-BuNF₂, b.p. = 359 K = 86 °C.

The standard enthalpy of formation of 2,2-bis(difluoroamino)butane liquid is $-211.5 \pm 5 \text{ kJ/mol} = -50.86 \pm 1.2 \text{ kcal/mol}$, and that of its 2,3 stereoisomer is $-233 \pm 5 \text{ kJ/mol} = -55.77 \pm 1.2 \text{ kcal/mol}$. The density of the latter compound is 1.212 g/cm^3 .

Tetrakis(difluoroamino)tetrahydrofuran, C₄H₄N₄F₈O, with a molecular mass of 276.09 g/mol is a liquid at room temperature. The standard enthalpy of formation of liquid tetrakis(difluoroamino)tetrahydrofuran is $-308 \pm 21 \text{ kJ/mol} = -73.5 \pm 5 \text{ kcal/mol}$ [66, 69]. The PEPCODED.DAT data file [7] lists $-266 \text{ cal/g} = -73.4 \text{ kcal/mol} = -307 \text{ kJ/mol}$. The density is 1.604 g/cm^3 . Other sources give ΔH_f^{298} of this compound as $-286 \text{ kJ/mol} = -68.3 \pm 3.2 \text{ kcal/mol}$, so there is some discrepancy among the different data sources.

1,1,3-Tris(difluoroamino)butane is a liquid at room temperature. The standard enthalpy of formation of liquid 1,1,3-tris(difluoroamino)butane is $-214 \pm 12 \text{ kJ/mol} = -57.7 \pm 3 \text{ kcal/mol}$, and the heat of combustion is $3424 \text{ kJ/mol} = 810.48 \text{ kcal/mol}$. 1,3,3-Tris(difluoroamino)butane boils at 312 K at 1.3 kPa (39 °C at 10 mm Hg). Tetrakis(difluoroamino)butane has an enthalpy of formation of $-240.5 \text{ kJ/mol} = -57.49 \text{ kcal/mol}$ and a density of 1.54 g/cm^3 .

Many energetic compounds contain both nitro or nitramide and difluoroamino groups in their molecules. An example is 1,1,3,5,5-pentanitro-1,5-bis(difluoroamino)-3-azapentane, F₂N(O₂N)₂CCH₂N(NO₂)CH₂C(NO₂)₂NF₂, C₄H₄N₈O₁₀F₄, DFAP, which can be obtained through the reaction of bis(2,2-dinitroethyl)nitramine with NF₂OSO₂F and has an extremely high density for an acyclic compound of 2.045 g/cm^3 [77]. Theoretical density functional theory (DFT) calculations were performed to study the effect of substitution of some or all of the nitro groups by nitroxy or difluoroamino groups. The predicted heat of formation ΔH_f^{298} of Compound 5 which had all $-\text{NO}_2$ replaced by $-\text{NF}_2$ was worse than that of the baseline DFAP, Compound 3. Compound 7, which had all NO₂ groups on the carbon replaced by $-\text{ONO}_2$ groups with only the nitramine NO₂ on Atom 3 remaining in place, had the lowest (worst) ΔH_f^{298} of all seven compounds studied. The heats of explosion did not parallel the heats of formation. The highest predicted heat of explosion was for Compound 4, which had all $-\text{NO}_2$ groups in the two alkyl rests replaced by $-\text{NF}_2$ groups but retained the $-\text{NO}_2$ group on the nitramine on Atom 3. The general trend was that Q increased because the ONO₂ and NO₂ groups were replaced by NF₂ groups.

3.3.5 Physical Properties of C_6 Difluoroamino Compounds

The standard heat of formation of liquid 1,2-bis(difluoroamino)4-methylpentane at 298.15 K is $-251 \text{ kJ/mol} = -60.09 \text{ kcal/mol}$, the heat of vaporization is $44 \text{ kJ/mol} = 10.51 \text{ kcal/mol}$, and the standard heat of formation of the vapor is $-207 \text{ kJ/mol} = -49.58 \text{ kcal/mol}$ [78–80]. The N–F thermochemical bond energy in this compound was $280 \text{ kJ/mol} = 67 \text{ kcal/mol}$, about the same as the N–F bond energy in NF_3 and N_2F_4 .

The standard heat of formation of the isomer liquid 2,2-bis(difluoroamino)4-methylpentane at 298.15 K is $-275 \text{ kJ/mol} = -65.61 \pm 0.45 \text{ kcal/mol}$, and its density is 1.155 g/cm^3 . The standard heat of formation of the isomer liquid 2,3-bis(difluoroamino)-4-methylpentane at 298.15 K is $-286 \text{ kJ/mol} = -68.27 \pm 0.76 \text{ kcal/mol}$, and its density is 1.150 g/cm^3 .

The b.p. of 1,1-bis(difluoroamino)cyclohexane was 318 K at 0.8 kPa (45°C at 6 mm Hg). The heat of combustion of 1,1-bis(difluoroamino)cyclohexane was $4288 \pm 2 \text{ kJ/mol} = 1024.9 \pm 0.5 \text{ kcal/mol}$ [81]. Based on this number, the enthalpy of formation was $-220 \pm 2 \text{ kJ/mol} = -52.5 \pm 0.5 \text{ kcal/mol}$, and the heat of vaporization was $10.6 \pm 0.2 \text{ kcal/mol}$. The bond energy of the N–F bond was $286 \text{ kJ/mol} = 68.4 \text{ kcal/mol}$.

A less common difluoroamino compound is di[tris(difluoroamino)propyl] ether, $\text{C}_6\text{H}_8\text{F}_{12}\text{N}_6\text{O}$ with a molecular mass of 408.178 g/mol , an enthalpy of formation of $-538 \pm 48 \text{ kJ/mol} = -128.7 \pm 10 \text{ kcal/mol}$, and a density of 1.65 g/cm^3 .

3.3.6 Physical Properties of $C_{n>6}$ Difluoroamino Compounds

The heat of combustion of liquid 1,1-bis(difluoroamino)heptane was measured, and the standard enthalpy of formation of the liquid at 298.15 K derived from this number was $-271 \text{ kJ/mol} = -64.8 \text{ kcal/mol}$, and the standard enthalpy of formation of the vapor was $-221 \text{ kJ/mol} = -52.8 \text{ kcal/mol}$ [82]. Its density was 1.18 g/cm^3 . The N–F thermochemical bond energy in this compound was $280 \text{ kJ/mol} = 67 \text{ kcal/mol}$, about the same as the N–F bond energy in NF_3 and N_2F_4 .

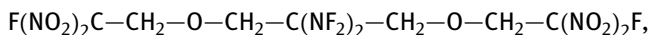
3.3.6.1 Physical Properties of TVOPA

TVOPA is a colorless liquid that freezes at $<243 \text{ K}$ ($<-30^\circ\text{C}$). The density of TVOPA is 1.54 g/cm^3 at 301 K (28°C). Other sources give a density of 1.535 g/cm^3 . The viscosity of TVOPA is 33 cPs at 303 K (30°C).

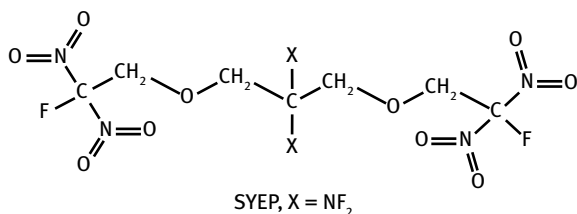
The heat of combustion of TVOPA in oxygen was determined to be $6749 \pm 15 \text{ kJ/mol}$ ($1613 \pm 3.5 \text{ kcal/mol}$) [83]. From this value and from previous data, the ΔH_f^{298} was calculated to be $-910 \pm 23 \text{ kJ/mol}$ ($-217.4 \pm 5.5 \text{ kcal/mol}$). The difference between this and other reported results may be caused by varying amounts of methylene chloride adhering to the sample. A year later, the heat of combustion of purified TVOPA in oxygen was once more measured by rotating bomb calorimetry [84]. The derived measured heat of formation of purified TVOPA was -871 kJ/mol (-208.1 kcal/mol).

3.3.6.2 Physical Properties of SYEP

2,2-bis(difluoroamino)-1,3-bis(fluorodinitroethoxy)propane, 5,5-bis(difluoroamino)-1,9-bisdinitro-1,9-difluoro-3,7-dioxanonane, SYEP, CAS RN [7790-98-9], $C_7H_8O_{10}N_6F_6$,



is a colorless liquid with a m.p. of 275 K (36 °F), a density of 1.937 g/cm³ (0.0611 lb/in.³), and an enthalpy of formation of -295.4 kJ/mol = -70.6 kcal/mol = -601 cal/g. The oral toxicity LD50 in rats was 3500 mg/kg. SYEP was intended as an energetic plasticizer but is apparently no longer in production.



SYEP possesses more favorable properties, i.e., lower mp and better processability characteristics, than bis[2,2-bis(difluoroamino)-5,5-dinitro-5-fluoropentoxy]methane (SYFO), another candidate high-energy plasticizer.

3.3.7 Mixtures with Difluoroamino Compounds

Mixtures of aliphatic difluoroamino compounds, such as 1,2-bis(difluoroamino)ethane $C_2H_4(NF_2)_2$, tris(difluoroamino)propane $C_3H_5(NF_2)_3$, tetrakis(difluoroamino)tetrahydrofuran, tetrakis(difluoroamino)butane $C_4H_6(NF_2)_4$, and pentakis(difluoroamino)pentane $C_5H_7(NF_2)_5$ with tetranitromethane have been patented as rocket propellant oxidizers [85]. The inventor failed to verify that the two liquids are miscible over the entire range of mixture ratios and will not segregate on cooling.

Mixtures of dinitrogen tetroxide (NTO) and 1,2-bis(difluoroamino)-2-methylpropane (IBA) or tris(difluoroamino)fluoromethane have been tested as storable oxidizers for pre-packaged propulsion systems [86]. The advantage of diluting the RNF_2 compound with NTO is that it greatly reduces the shock sensitivity of the undiluted RNF_2 compound.

3.3.8 Thermodynamic Properties of Difluoroamino Compounds

Thermodynamic properties such as the heats (enthalpies) of formation of difluoroamino compounds tend to be more negative than those of analogous nitro derivatives, but quantitative measures of performance (such as specific impulse of rocket propellant combustion) offer a more valid comparison of the energetics of difluoroamino derivatives. The lower molecular mass of HF compared to CO_2 as the reaction product is part of the reason for the higher specific impulse.

If fluorinated oxidizers are used in combination with metal fuel ingredients (e.g., aluminum or boron), producing more volatile, lower-molecular-weight combustion products, such as boron oxyfluoride (BOF) (rather than simple oxides like B_2O_3 produced solely by oxygenated oxidizers) also result in higher specific impulse. RNF_2 compounds also have higher densities than RNO_2 compounds. The following sections contain information on both experimental and theoretical determination of the thermodynamic properties of difluoroamino compounds, as well as those containing additional explosophoric groups in the molecule.

3.3.8.1 Experimental Determination of Thermodynamic Properties of Difluoroamino Compounds

Because many difluoroamino compounds are potentially detonable and many decompose in an uncontrolled manner, it is difficult to determine the heats of combustion and enthalpies of formation of these compounds by calorimetric methods. Some of the measured heats of combustion reported in the literature vary widely, depending on the conditions during combustion.

The heat of decomposition of CF_3NF_2 was -451.4 ± 1.5 cal/g. The enthalpy of formation $\Delta H_f^{298.15}$ (G) was determined to be -707 ± 2.5 kJ/mol (-169.0 ± 0.6 kcal/mol) by measuring its energy of decomposition to CF_4 (G), N_2 (G), and F_2 (G) in a nickel bomb and static calorimeter [87]. A gaseous mixture of C_2N_2 and NF_3 was used to trigger the reaction. The experimental $\Delta H_f^{298.15}$ was compared with that calculated from additive bond energies, which gave -724.7 kJ/mol (-173.2 kcal/mol) (uncorrected).

The heat of formation of tetrakis(difluoroamino)methane (Compound Delta) was determined by the heat of explosion measurements to be $+10.9 \pm 11.7$ kJ/mol ($+2.6 \pm 2.8$ kcal/mol), as in [88]. This result correlated well with previous work on $FC(NF_2)_3$ and $F_2C(NF_2)_2$. An estimate of -686 kJ/mol (-164 kcal/mol) was derived for $CF_3(NF_2)(G)$. A heat of combustion of 1,2,3-tris[1,2-bis(difluoroamino)ethoxy]propane (TVOPA) in oxygen showed a strong trend to low values with increasing residual solvent. By extrapolation to zero solvent, a heat of formation of -910 ± 15 kJ/mol (-217.4 ± 3.5 kcal/mol) was derived for TVOPA. The heat of combustion of poly[1,2-bis(difluoroamino)epoxy propane] (P-BEP) in oxygen was determined by rotating bomb calorimetry. Prolonged stripping of the sample under vacuum resulted in satisfactorily low residual solvent. The heat of combustion in oxygen was 15.814 kJ/g (3.629 kcal/g). If one assumes a molecular mass of exactly 100 g/mol and the empirical composition $C_{2.238} H_{3.240} O_{0.898} N_{1.094} F_{2.114}$, the derived heat of formation would be -200 ± 3 kJ/mol (-47.8 ± 0.7 kcal/mol).

The heats of formation of 1,2,3-tris[1,2-bis(difluoroaminoethoxy)]propane, TVOPA, and CF_3ONF_2 (G) were determined by combustion in oxygen in a rotating bomb calorimeter and found to be -870.7 ± 12.1 and -791.2 ± 3.3 kJ/mol (-208.1 ± 2.9 and -189.1 ± 0.8 kcal/mol), respectively [89]. Prior to determining the heat of reaction, solvent had to be removed from TVOPA and CF_3ONF_2 had to be purified. Undiluted TVOPA detonated under combustion bomb conditions and had to be

diluted. Other sources list the heat of formation of TVOPA as -867 ± 12.4 kJ/mol (-207.19 ± 2.96 kcal/mol) [66, 69].

Table 9 gives the measured enthalpies of reaction (heat of explosion) of three gaseous difluoroaminomethanes and PFG and the enthalpies of formation derived therefrom [70].

Table 9: Heat of explosion and enthalpies of formation of three gaseous difluoroaminomethanes and perfluoroguanidine.

Compound name	Gross formula	Alternate compound name	ΔE_{expl}	ΔH_{expl}	ΔH_f
			kcal/mol		
Bis(difluoroamino)-difluoromethane	CF_6N_2	Hexafluoromethanediamine	-115.5	-114.3	-108.7
Tris(difluoroamino)-fluoromethane	CF_7N_3	Heptafluoromethanetriamine	-177.0	-175.3	-47.7
Tetrakis(difluoroamino)-methane	CF_8N_4	Octafluoromethanetetraamine	-225.9	-223.5	+0.5
Perfluoroguanidine	CF_5N_3	Pentafluoroguanidine	-247.2	-246.0	+23.0

Data source: [70]

From calorimetric measurements of the energies of explosion, the enthalpies of formation of some fully fluorinated amines in the gas state were derived as listed in Table 10, and the eventual deviations of these values from those calculated from additive standard bond-energy terms were discussed [70].

Table 10: Enthalpies of formation of difluoroamino compounds in gas phase.

Compound	Enthalpy of formation	
	kJ/mol	kcal/mol
$\text{F}_2\text{C}(\text{NF}_2)_2$	-455	-108.7
$\text{FC}(\text{NF}_2)_3$	-199.6	-47.7
$\text{C}(\text{NF}_2)_4$	+2.1	+0.5
$\text{FN}=\text{C}(\text{NF}_2)_2$	+96	+23.0
$(\text{F}_2\text{N})_2\text{CFNFCF}(\text{NF}_2)_2$	-353	-84.4

Data source: [70]

The PEPCODED.DAT data file of [7] contained enthalpy of formation data and a few density data for several difluoroamino compounds. These data were converted to SI units and are summarized in Table 11. Some of the compounds had more than one entry, and it was not possible to determine which were the more correct data, so we listed them all. See also [90].

Table 11: Enthalpies of formation and densities of difluoroamino compounds.

Compound name	CHNOF	Mol. mass g/mol	Enthalpy of formation, ΔH_f^{298}			Density g/cm ³
			cal/g	kcal/mol	kJ/mol	
<i>unsym</i> -Difluorourea (UDFU)	C1H2N2O1F2	96.0364	−705	−67.71	−283.3	
Perfluoroguanidine (PFG) (gas)	C1N3F5	149.0231	+162	+24.14	+101.0	
Perfluoroguanidine (PFG) (liq)	C1N3F5	149.0231	+127	+18.93	+79.2	
Bis(difluoroamino)difluoromethane	C1N2F6	154.0148	−698	−107.50	−449.8	
Tris(difluoroamino)fluoromethane	C1N3F7	187.0199	−248	−46.38	−194.1	
Tris(difluoroamino)fluoromethane	C1N3F7	187.0199	−281	−52.55	−219.9	1.558
Tetrakis(difluoroamino)methane	C1N4F8	220.025	+18	+3.96	+16.6	1.747
1,2-Bis(difluoroamino)propane	C3H6N2F4	146.0874	−294	−42.95	−179.7	
1,2-Bis(difluoroamino)propane	C3H6N2F4	146.0874	−349	−50.98	−213.3	
Tris(difluoroamino)propane	C3H5N3F6	197.083	−411	−81.00	−338.9	1.539
2,3-Bis(difluoroamino)butane	C4H8N2F4	160.1142	−353	−56.52	−236.5	1.210
2,3-Bis(difluoroamino)butane	C4H8N2F4	160.1142	−348	−55.72	−233.1	1.212
2,2-Bis(difluoroamino)butane	C4H8N2F4	160.1142	−318	−50.92	−213.0	
2,3-Bis(difluoroamino)butane	C4H8N2F4	160.1142	−348	−55.72	−233.1	
Tris(difluoroamino)butane	C4H7N3F6	211.1098	−273	−57.63	−241.1	1.199
Tetrakis(difluoroamino)tetrahydro-furan	C4H4N4O1F8	276.089	−266	−73.44	−307.3	1.603
Bis(difluoroamino)methylpentane	C6H12N2F4	188.1678	−309	−58.14	−243.3	
Bis(difluoroamino)methylpentane	C6H12N2F4	188.1678	−363	−68.30	−285.8	1.149
2,2-Bis(difluoroamino)octane	C8H16N2F4	216.2214	−347	−75.03	−313.9	1.099
TVOPA	C9H14N6O3F12	482.2288	−385	−185.66	−776.8	
TVOPA	C9H14N6O3F12	482.2288	−430	−207.36	−867.6	1.533
Difluoroamine	H1N1F2	53.0114	−600	−31.81	−133.1	

Data source: [7]. Sorted by number of carbon atoms and number of fluorine atoms.

3.3.8.2 Theoretical Computation of Thermodynamic Properties of Difluoroamino Compounds

The thermodynamic properties of simple difluoroaminoalkanes can be predicted based on quantum-mechanical calculations. An attempt was made to calculate the entropies, heats of formation, and bond dissociation energies of alkyl difluoroamines and fluorides for which experimental or published calculated data were lacking [91]. The estimated enthalpies of formation and entropies of alkyl difluoroamines and fluorides, and bond dissociation energies for R–NF₂ and R–F molecules (R = Me, Et, *iso*-Pr, *tert*-Bu, and trifluoromethyl) were published, but the foreign publication was not accessible to the author.

The enthalpies of formation of a series of polyatomic molecules containing –NF₂ and/or –NO₂ groups were computed using the isodesmic procedure of Pople et al. at the self-consistent field (SCF) level [92, 93]. An excellent correlation between the predicted enthalpies of formation and the corresponding available experimental (calori-

metric) data was achieved. It was found that $-\text{NO}_2$ and $-\text{NF}_2$ groups had significant and comparable destabilizing effects on hydrocarbon compounds.

The well-known simple Benson method predicts the enthalpies of formation of gaseous compounds by adding contributions from individual bonds. Expanding on this method, a similar additive method was developed for estimating the gaseous enthalpies of formation of energetic molecules containing NO_2 and/or NF_2 groups, and its accuracy was checked against measured values taken from previously published sources [94].

Polynitrocubanes have already been described in *Encyclopedia of Oxidizers*, in the chapter “Higher Nitroaliphatic Compounds,” as promising high-energy-density materials (HEDMs).

In analogy, polydifluoroaminocubanes and polydifluoroaminoadamantanes were expected to have high density and high explosive power.

The enthalpies of formation for a series of polydifluoroaminocubanes were calculated using DFT, Hartree-Fock, and MP2 methods, as well as semi-empirical methods [95]. The cubane skeleton was not broken in the process of designing isodesmic reactions, i.e., the cubane skeleton was chosen for a reference compound. The contribution of difluoroamino group to the heat of formation deviated from group additivity rules. The semi-empirical MO (Modified Neglect of Diatomic Overlap = MNDO, Austin Model 1 = AM1, and PM3) methods did not produce accurate and reliable results for the enthalpies of formation. It was found that the enthalpies of formation decreased dramatically initially and then gradually with each difluoroamino group attached to the cubane skeleton. The distance between difluoroamino groups influenced the values of enthalpies of formation. The NF_2 group can rotate freely around the C–N bond. Similar observations were made when calculating the predicted enthalpies of formation of polydifluoroaminoadamantanes with increasing numbers of $-\text{NF}_2$ groups attached to the cage skeleton [96].

A theoretical study of the effect of progressive replacement of $-\text{NO}_2$ groups in 1,1,1,3,5,5,5-heptanitro-3-azapentane by $-\text{NF}_2$ groups or $-\text{O}-\text{NO}_2$ groups showed that (depending on the computational method and level used) the predicted enthalpy of formation decreased incrementally from $+98 < \Delta H < +104$ kJ/mol for 1,1,1,3,5,5,5-heptanitro-3-azapentane to $-150 < \Delta H < -160$ kJ/mol for 1,1,1,3,5,5,5-hepta(difluoroamino)-3-azapentane [97].

3.3.9 Molecular Structure of Difluoroamino Compounds

3.3.9.1 Molecular Structure of Linear Difluoroamino Compounds

The molecular structures of difluoroamino compounds are often compared to those of the corresponding nitro compounds that contain oxygen in the place of the fluorines.

In designing energetic molecules, it can be advantageous to include some difluoroamino ($-\text{NF}_2$) groups along with the usual nitro ($-\text{NO}_2$) groups [98]. Although the $-\text{NF}_2$ groups can have the desirable effects of increasing the density, there may also

be a decrease in the amount of energy released during decomposition. The overall result is likely to be improved energetic performance. Although C–NF₂ and N–NF₂ bonds are slightly stronger than C–NO₂ and N–NO₂ bonds, the lack of stability of difluoramines is known to be a challenge to propellant chemists. Molecules of the type R_aR_bN–NF₂ may have a tendency to lose F[–]. However, this can be prevented by making R_a and R_b sufficiently electron-attracting and by structuring the molecule so that there are no hydrogens on carbons bearing –NF₂ groups. It is also advisable to not have –NO₂ and –NF₂ groups on the same carbon atom, since this leads to a destabilizing weakening of both the C–NO₂ and C–NF₂ bonds.

The structure of methyldifluoroamine, CH₃NF₂, was determined by gas-phase electron diffraction augmented by rotational constants from microwave spectroscopy and by results from molecular orbital calculations [99]. The structural results were consistent with C_s symmetry for a molecule with staggered bonds. The experimental bond distances and bond angles with estimated 2σ uncertainties were C–H = 1.104/1.124(5) Å (average value), N–F = 1.406/1.408(2) Å, C–N = 1.467/1.469(6) Å, ∠ C–N–F = 104.1(2)°, ∠ F–N–F = 101.7(2)°, ∠ N–C–H_{anti} = 109.9(11)°, ∠ N–C–H_{gauche} = 106.5(10)°, ∠ H_{gauche}C–H_{gauche} = 110.6(28)°; the subscripts indicate orientation with respect to the lone nitrogen pair. The bond lengths and bond angles of a family of fluoroamino compounds, including two methyl fluoro amines as determined from microwave spectra and electron diffraction, are summarized in Table 12.

Table 12: Bond lengths and bond angles of fluoroamino compounds.

Compound	Unit	H ₂ NF	HNF ₂	NF ₃			MeNF ₂		Me ₂ NF
Method:			MW	MW	MW		MW	ED/MW	MW
r(X–N)	Å	1.0225(3)	1.026(2)				1.467(6)	1.449(5)	1.462(7)
r(N–F)	Å	1.4329(3)	1.400(2)	1.365(2)	1.371		1.406(2)	1.413(5)	1.447(6)
∠ X–N–F	°	101.08(7)	99.8(2)				104.1(2)	104.6(3)	103.6(5)
∠ F–N–F	°	—	102.9(2)	102.4(1)	102.2		101.7(2)	101.0(3)	—

Data source: [99]

See also [100]. This document contains a data set of geometric parameters for *N,N*-difluoromethanamine (methyldifluoroamine).

3.3.9.2 Molecular Structure of Cyclic Difluoroamino Compounds

The structures of cyclic compounds containing geminal-difluoroamino groups were examined by XRD [101]. As an example of the structure of molecules containing geminal-difluoroamine groups, the crystal parameters of 1,1,4,4-tetrakis(difluoroamino)cyclohexane are listed here: monoclinic, *P*₂1/*n*, *a* = 6.277(1) Å,

$b = 10.502(2) \text{ \AA}$, $c = 7.910(1) \text{ \AA}$, $\beta = 99.50(1)^\circ$. The pyramidal difluoroamino group sometimes displays extensive torsional disorder in crystals, but in some structures, the geminal $-\text{NF}_2$ groups are primarily ordered owing to interactions with their steric environments. There are increases in the thermal parameters of the fluorine atoms indicating libration in some cases, where there are fewer steric demands in the NF_2 environment. The conformation adopted by each NF_2 group can be explained in terms of minimization of non-bonded $\text{F}\cdots\text{H}$ and $\text{F}\cdots\text{F}$ contacts. All NF_2 groups are non-planar and show unusual metrical parameters compared to amines containing no fluorine substituents. The interior $\text{F}-\text{N}-\text{F}$ and $\text{C}-\text{N}-\text{F}$ angles are very small, indicating a high degree of pyramidalization.

The IR spectrum of perfluoro-1,3,5-triazacyclohexane $(\text{CF}_2\text{NF})_3$ in the region $300\text{--}3000 \text{ cm}^{-1}$ was interpreted in terms of a structure with C_{3v} symmetry (the ring in chair form) in which the N-fluorines are equatorial [102].

DFT calculations were performed to predict the enthalpies of formation for three eight-membered ring compounds and four six-membered ring compounds via designed isodesmic reactions [103]. In the isodesmic reactions designed for the computation of enthalpies of formation, $(\text{CH}_3\text{CH}_2)_2\text{NNO}_2$ and piperidine were chosen as reference compounds. The enthalpies of formation for $-\text{NO}_2$ substituted derivations were larger than those of $-\text{NF}_2$ substituent groups. Thermal stabilities were evaluated by looking at bond dissociation energies. As a whole, the homolysis of $\text{C}-\text{NF}_2$ or $\text{C}-\text{NO}_2$ bonds is the main step for bond dissociation of these compounds. The detonation properties of seven compounds were evaluated using the Kamlet-Jacobs equation based on the calculated densities and enthalpies of formation. It was found that properties of 3,3,7,7-tetrakis(difluoroamino)octahydro-1,5-dinitro-1,5-diazocine (HNFX) and 3,3,5,5-tetrakis(difluoroamino)-1-nitro piperidine, with a predicted density of ca. 2.0 g/cm^3 , a detonation velocity of approximately 9.9 km/s , and a detonation pressure of 47 GPa are larger than those of HMX. The detonation data of 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane and 3,3-bis(difluoroamino)-7,7-dinitro-1-nitro piperidine showed that they would meet the requirements for HEDMs. See also [104]

3.4 Chemical Properties of Difluoroamino Compounds

3.4.1 Reactions of Difluoroamino Compounds

tert-Butyl-*N,N*-difluoroamine reacted rapidly with *n*-butyllithium, and the product was *n*-octane, with traces of azo-*tert*-butane [105]. A similar reaction of triphenylmethyl-*N,N*-difluoroamine with *n*-butyllithium gave biphenyl. In a reaction of *tert*-butyl-*N,N*-difluoroamine with concentrated nitric acid, the amine might be protonated but then decomposed into NO_2 and CO_2 .

Tris(difluoroamino)fluoromethane resists hydrolytic attack by dilute aqueous alkaline or acidic media at room temperature [29].

Hypergolic ignition of liquid difluoroamino compounds of the general structure $RR^1R^2CNF_2$, for instance 1,2-IBA, can be accomplished by contact with Lewis acids such as $AlCl_3$, $SbCl_5$, $TiCl_4$, or $GaCl_3$ [106]. Hypergolic ignition at sea level pressure occurred in 10–15 ms; at 0.69, 2.4, or 4.1 MPa (100, 350, or 600 psi) the ignition was instantaneous.

Generally difluoroamino compounds react with dehydrofluorinating agents (Et_3N , pyridine, KOH) that remove HF from molecules. Heating difluoroamino compounds like $R_2C(NF_2)CH_2NF_2$ with excess amines gave nitriles $R_2C(NF_2)CN$, with the amine forming its HF salt [107]. In all instances where HF was lost, the primary act was elimination of a proton from one of the C atoms bound to the NF_2 group. Diazomethane is a dehydrofluorinating agent where the carbanion intermediate is rapidly stabilized by elimination of F^- . Compounds with $-NF_2$ groups may be regarded as forms of amphoteric substances. The following compounds were examined (Table 13).

Table 13: Physical properties of difluoroamino compounds.

Compound	Melting point		Boiling point		Density	Refractive index
	K	°C	K	°C		
$MeCH(NF_2)CH_2NF_2$			355	82	1.265	1.3452
$Me_2C(NF_2)CH_2NF_2$			370	97	1.202	1.3598
<i>iso</i> - $PrCMe(NF_2)CH_2NF_2$			321 K at 2.67 kPa	48 °C at 20 mm Hg	1.178	1.3906
$Me_2C(NF_2)CMe_2NF_2$	365	92				

1,2-DP can be prepared in 98% yield by heating a 1:1 mixture of $MeCH=CH_2$ and N_2F_4 for 30 min at 408 K and can then be used for a study of dehydrofluorination reactions. Arrhenius factors in the dehydrofluorination of chemically activated 1,2-DP were calculated, giving a pre-exponential factor of $10^{13.1} s^{-1}$ and an activation energy of 159 kJ/mol (38 kcal/mol) [108]. *tert*-Butyldifluoroamine can form *N*-isopropylidene-*N*-fluoro-*N*-methylammonium ions [109].

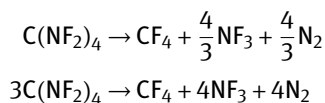
3.4.2 Thermal Stability and Decomposition of Difluoroamino Compounds

3.4.2.1 Thermal Stability and Decomposition of Linear Difluoroamino Compounds

Thermal sensitivity was measured for a variety of C_3 – C_8 bis(difluoroamino) compounds. Vicinally and geminally substituted NF_2 compounds could be categorized into separate classes [110]. For example, 1,2,4,5-tetrakis(difluoroamino)pentane initiated 180 °C higher than the corresponding 2,2,4,4-isomer. Geminal NF_2 compounds with the substituents on an end carbon appear to fall in a different sensitivity class than compounds with the NF_2 groups on an internal carbon. Plotting the log of the ignition delay time versus $1/T$ allowed the derivation of activation energies. The most

sensitive compounds were the fluorinated biguanides and tris(difluoroamino)methyl ethers. A PFG explosion took place after a hypodermic needle tubing had been filled with the sample. A sample of $F_2NC(=NF)-NF-C(=NF)NF_2$, exploded while the container was being opened. Whether this sensitivity is the result of impurities or is inherent in the structure is not known.

The decomposition of 2-tris(difluoroamino)methoxyethylammonium perchlorate, an ionic solid salt, code name INFO-635P, in various forms was studied under widely different conditions ranging from aqueous and non-aqueous solutions and aqueous acid to the pure solid state [111]. Decomposition of the α -form of INFO-635P was rapid at room temperature and took place as a unimolecular reaction. The free amine from which the perchlorate salt was derived was unstable, and detonation of the salt in the solid state occurred almost immediately as soon as anhydrous ammonia gas was admitted. The tris- group of INFO-635P in acid decomposed at 373 K (100 °C) by homolytic rupture into free radicals, and the final products were analyzed by GC, IR, and NMR. In general, the gaseous product distribution from solid-phase decomposition was similar to that in acid solution. In the same report, the kinetics of decomposition of tetrakis(difluoroamino)methane (Compound Delta) in the gas phase was found to be very complex. The stoichiometry of the complete decomposition of Compound Delta apparently followed the equation



At the high end of the temperature range studied, 413–463 K (140–190 °C), the dominant reaction was homogeneous gas phase and first order in Compound Delta. A second competing mechanism became more dominant at the intermediate temperatures, where no distinct first-order rate was observed. The decomposition reaction at these lower temperatures was homogeneous, and possibly a reaction of 3/2 order.

Tris(difluoroamino)fluoromethane appeared to be thermally stable at temperatures below 473 K (200 °C). Differential thermal analysis in a sealed Monel cup revealed a slow exotherm beginning at 523 K (250 °C) with inflections at about 543 and 551 K (270 and 278 °C) [29]. The decomposition products were mainly carbon tetrafluoride, nitrogen trifluoride, and nitrogen.

A 193-page summary of the sensitivity and stability of NF compounds included some thermal stability data on 389 compounds assembled from 292 references, but unfortunately it did not include a summary of fundamental physical properties, which would have been available from the same sources [112].

The decomposition of 2,3-bis(*N,N*-difluoroamino)butane leads to a loss of two HF and the formation of 2,3-bis(*N*-fluoroimino)butane [113]. The decomposition of alkyl difluoroamino compounds at very low pressures (10^{-3} mm Hg) and high temperatures (1273 K = 1000 °C) was examined with only minor contributions from wall-catalyzed

decomposition and from chain processes. The initial step is the scission of the C—N bond. In the case of compounds containing two —NF₂ groups, migration of fluorine from nitrogen to carbon in the initially formed difluoroamino alkyl free radical takes place to a large extent. The heat release during decomposition is on the order of 160 kJ/mol (40 kcal/mol).

Alkyldifluoroamino compounds undergo rapid base-catalyzed dehydrofluorination leading to *N*-fluoroketimines, aldimines, or nitriles. The kinetics of dehydrofluorination of several mono-, bis-, and tris(*N,N*-difluoroamino) alkanes were measured in 3:7 diglyme-water dilution at 323 and 348 K (50° and 75 °C) [114]. The rates of these imine-forming reactions were relatively insensitive to the inductive and conjugative effects of substituents in the alkyl group. The stereoselectivity of the dehydrofluorination seems to reflect the steric requirements of the alkyl group. The elimination appears to be a concerted process in which the degree of N—F bond breaking is not only quite extensive but also nearly equal to the degree of C—H bond breaking in the transition state.

The pyrolyses of 1,2- and 2,2-DP were carried out at 923 and 1023 K (650 and 750 °C), respectively, and at 0.13 to 1.3 Pa (10⁻³ to 10⁻² mm Hg) [115]. The major reaction of 1,2 isomer was stepwise loss of both NF₂ groups to yield propylene, this process being the reverse of the addition of N₂F₄ to olefins. The 2,2 isomer decomposed completely by initial C—N scission, followed by both **(1)** migration of fluorine from nitrogen to carbon with subsequent fragmentation, yielding both the *syn* and *anti* isomers of CH₃C(=NF)F, and **(2)** loss of fluorine to yield (CH₃)₂C=NF. 1,1-DP, pyrolyzed at 923 K (650 °C), underwent C—N scission followed by fluorine migration to yield both the *syn* and *anti* isomers of HC(NF)F.

The thermal decomposition of ethyl difluoroamine C₂H₅NF₂ at 573–735 K (300–462 °C) was measured using static and flow methods [116]. The principal organic products were ethylene and acetonitrile. The reaction appeared to follow a molecular rather than a chain mechanism. The reaction was first order according to the rate expression

$$k = 10^{11} \exp(-38000/RT) \text{ s}^{-1}$$

The homogeneous thermal decomposition of gaseous tris(difluoroamino)fluoromethane FC(NF₂)₃ in the temperature range 498–523 K (225–250 °C) resulted in the formation of N₂, CF₄, and NF₃ in 1:1:1 molar ratio upon completion of the reaction [117]. The time-resolved growth and decay profile of difluoroaminotrifluoromethane and bis(difluoroamino)difluoromethane indicated that these compounds are intermediates. At an initial pressure of 13.33 kPa (100 mm Hg), the first-order rate constant would fit the Arrhenius equation

$$k = 1.36 \times 10^{15} \exp(-45800/RT) \text{ s}^{-1}$$

The gas-phase thermal decomposition kinetics of tris(difluoroamino)methyl chloride, (NF₂)₃C—Cl, tris(difluoroamino)methylamine, (NF₂)₃C—NH₂, tris(difluoroamino)-

methyl methyl ether, and $(\text{NF}_2)_3\text{C}-\text{O}-\text{CH}_3$ were measured in static reactors over the temperature range 457–503 K (184–230 °C) [118]. The reactions in each case were first order with activation energies of 151, 124, and 151 kJ/mol (36.1, 29.6, and 36.2 kcal/mol), respectively. A correlation was found between the order of stability and electronegativity of the group attached to the trisdifluoroamino functionality. The rate-determining step may be the homolysis of the C–N bond, similar to what happens in nitro compounds.

The abundance of positive ions in the mass spectra of three DPs (1,2-DP, 2,2-DP, and 2,3-DP) was measured to give an indication of the weakest links in the molecules [119]. The most abundant ions observed were the methylene fluoroimmonium ion $(\text{H}_2\text{C}=\text{NF})^+$ from the 1,2-DP and 1,3-DP and hydrocarbon-type ions from the 2,2-DP. The identities of the ions were verified by exact mass measurements. Mechanisms were postulated to account for the observed fragmentation patterns. Some of the observed ionization products originate via rearrangement reactions, possibly having a ring-like intermediate configuration. The ions seen in greatest abundance were those that proceeded through the minimal path for the overall ionic reaction process. Appearance potentials were measured for the more abundant ions formed from the three isomeric DPs studied.

The kinetics of thermal decomposition in the liquid state of 15 difluoroamino compounds with NF_2 groups at primary, secondary, and tertiary carbon atoms were investigated [120]. Activation energies (E_{act}) for all of these compounds were in the range 100–120 kJ/mol. The reaction rate did not depend on the electronic effects of the α -substituents and decreased only in the case of steric shielding of the NF_2 group. Based on the results obtained, a mechanism for liquid-phase decomposition was suggested that involved heterolysis of the N–F bonds.

The compounds $\text{RC}(\text{NO}_2)_2\text{NF}_2$ differed little from their nitro analogs, $\text{RC}(\text{NO}_2)_3$, in stability. They decomposed in the gas and liquid phases at identical rates and the decomposition was controlled by cleavage of a C– NO_2 bond [121]. For $\text{R} = \text{NO}_2$, F, and Me, the Arrhenius parameters E_{a} (kJ/mol) and $\log(A/\text{s})$ were as follows: 161.3 and 16.00; 180.2 and 16.20; 168.4 and 16.00, respectively. The facts that these decomposition reactions obeyed first-order kinetics and the rate constants did not depend on p_0 , S/V , or inhibitors and that the rates of decomposition in the gas and liquid states were similar implied that the decomposition was a homolytic monomolecular reaction. The magnitude of the pre-exponential factors agreed with a mechanism that involved dissociation of the molecule into two large moieties, i.e., cleavage of a C– NO_2 or C– NF_2 bond.

It has been shown that the decomposition of $\text{C}(\text{NF}_2)_4$, $\text{FC}(\text{NF}_2)_3$, and $\text{F}_2\text{C}(\text{NF}_2)_2$ starts with the cleavage of the C–N bond. The composition of gaseous products of 1,2- and 2,2-DP thermal decomposition also indicated that C–N bond cleavage took place first. Three types of difluoroamines were included in a study on NF_2 compound thermal decomposition: *gem*-bis(difluoroamino) compounds, compounds with solitary NF_2 groups, and α -polynitro(difluoroamino)alkanes with the aim of

determining the influence of molecular structure and substance aggregate state on decomposition parameters [122]. Reaction kinetics was studied under static conditions by a manometric method. The initial sample pressure p_0 varied from 20 to 150 Torr, and the S/V ratio of the vessel changed from 0.6 to 20 cm⁻¹. The decomposition of PhCH(NF₂)₂ vapors at $p_0 > 20$ Torr and S/V > 0.6 cm⁻¹ occurred on the surface and followed a different mechanism. The liquid-phase decomposition of some compounds proceeded with self-acceleration. The degree of the latter depended on the pressure of gaseous products (venting or non-venting) and decreased with increasing temperature. A comparison of difluoroamines and polynitroalkanes showed that the bond dissociation energy D(C–N) in difluoroamines was 12–16 kJ/mol higher than that in similarly structured nitroalkanes. The decomposition of α -(difluoroamino)polynitroalkanes occurred via cleavage of the C–NO₂ bond rather than the C–NF₂ bond. The kinetic parameters of thermal decomposition of α -(difluoroamino)polynitroalkanes and their nitro analogs are listed in Table 14.

Table 14: Kinetic parameters of thermal decomposition of α -(difluoroamino)polynitroalkanes and their nitro analogs.

Compound	State	Temperature		E_{act} kJ/mol	log(A/s)	k s ⁻¹ at 100 °C
		K	°C			
F ₂ NC(NO ₂) ₃	Gas	383–448	110–175	161.3	16.00	2.7×10^{-7}
F ₂ NC(NO ₂) ₃	Liquid	353–363	80– 90	162.1	16.40	5.2×10^{-7}
FC(NO ₂) ₂ NF ₂	Gas	443–493	170–220	180.2	16.20	1.0×10^{-9}
MeC(NO ₂) ₂ NF ₂	Gas	443–473	170–190	168.4	16.00	2.7×10^{-8}
MeC(NO ₂) ₂ NF ₂	Liquid	393–413	120–140	168.4	16.00	2.7×10^{-8}
C(NO ₂) ₄	Gas	—	—	160.0	16.30	8.1×10^{-7}
C(NO ₂) ₄	Liquid	353–383	80–110	156.7	15.50	3.8×10^{-7}
FC(NO ₂) ₃	Gas	451–509	178–236	175.6	15.40	6.9×10^{-10}
MeC(NO ₂) ₃	Gas	433–493	160–210	181.0	17.11	6.2×10^{-9}
MeC(NO ₂) ₃	Liquid	373–413	100–140	178.5	16.93	9.1×10^{-9}

Data source: [122]

DFT calculations have shown that the elimination of HF from H₃C–NF₂ is thermodynamically favored, $\Delta G(298.15 \text{ K}) = -121 \text{ kJ/mol}$ (-29 kcal/mol), but has a relatively high activation barrier, $\Delta G = 159 \text{ kJ/mol}$ (38 kcal/mol) [123]. The N–F dissociation energy, $\Delta E \text{ N–F}$, was found to be 289 kJ/mol (69 kcal/mol). The introduction of a nitro group, giving H₂C(NO₂)NF₂, produced only small changes in these values: $\Delta G(298.15 \text{ K}) = -117 \text{ kJ/mol}$ (-28 kcal/mol); barrier of $\Delta G = 151 \text{ kJ/mol}$ (36 kcal/mol); $\Delta E \text{ N–F} = 276 \text{ kJ/mol}$ (66 kcal/mol). Replacement of all alpha hydrogens by methyl groups increased the N–F dissociation energies slightly ($< 8.4 \text{ kJ/mol} = < 2 \text{ kcal/mol}$). These substituent effects can be interpreted in terms of geminal interactions.

The thermal stability of TVOPA in the Differential Thermal Analysis (DTA) showed an exothermic peak at 538 K (265 °C). For comparison, GTN (NG) showed an exothermic peak at 469 K (196 °C). Other sources reported a start of decomposition at 374 K (111 °C) and a major exotherm at 547 K (274 °C).

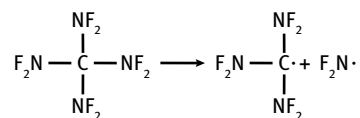
The stability and compatibility of the plasticizers TVOPA, 1,2,3-tris[1,2-bis(difluoroamino)]ethoxy propane, and P-722, 2,3-bis(difluoroamino)propyl-2,2-dinitropropyl carbonate were investigated and compared [124]. A study of their stability and compatibility with the oxidizers hydroxylammonium perchlorate (HAP) and ammonium perchlorate (AP), the fuel AlH_3 , and an ethyl acrylate-acrylic acid copolymer showed that neat P-722 did not yield appreciable quantities of gaseous decomposition products at ambient temperature or 313 K (40 °C) for test durations up to 340 d. At 328 K (55 °C), only small quantities of gases were formed over the same time period. Samples stored at 343 K (70 °C) for approximately 1 year (340 d) yielded a total gas volume of about 36 mL/g of P-722; the gases were primarily CO , CO_2 , and N_2O with small amounts of H_2 and N_2 . Little gas evolution was observed from TVOPA after 310 d at 343 K (70 °C). Mixtures of P-722 and AP showed very small quantities of gaseous products at all four temperatures after 326 d. The same result was observed for P-722/HAP mixtures at 298 and 313 K (25 and 40 °C) over the same time interval. At 328 K (55 °C), the P-722/HAP mixtures evolved a total volume of gaseous products equal to 37 mL/g. In general, TVOPA and P-722 exhibited comparable stabilities after 300 d at 298, 313, or 328 K (25, 40, or 55 °C). At 343 K (70 °C), TVOPA appeared to be slightly more stable than P-722. Both materials had adequate thermal stability for use in a propellant system. Compatibilities with the oxidizers HAP and AP are very similar. At 298, 313, or 328 K (25, 40, or 55 °C), P-722 appeared to be slightly more compatible with the two oxidizers than TVOPA, while at 343 K (70 °C) TVOPA was better.

The gas-phase thermal decomposition of tetrakis(difluoroamino)methane, $\text{C}(\text{NF}_2)_4$, tris(difluoroamino)fluoromethane, $\text{FC}(\text{NF}_2)_3$, and bis(difluoroamino)difluoromethane, $\text{F}_2\text{C}(\text{NF}_2)_2$, in an inert carrier gas was investigated over the temperature range 463–733 K (190–460 °C) in stirred flow, tubular flow, and static reactors [125]. The reactions are first-order, non-chain processes with C–N bond rupture as the rate-determining step in each case. The rate constants are given by the following Arrhenius expressions:

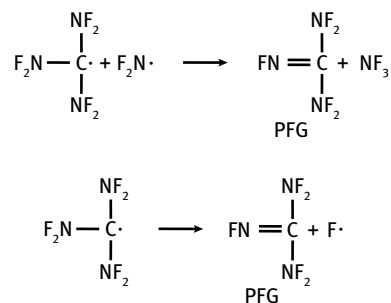
$$\begin{array}{ll} \text{C}(\text{NF}_2)_4 & k = 10^{16.14} \exp(-40400/RT) \text{s}^{-1} \\ \text{FC}(\text{NF}_2)_3 & k = 10^{16.45} \exp(-48300/RT) \text{s}^{-1} \\ \text{F}_2\text{C}(\text{NF}_2)_2 & k = 10^{15.75} \exp(-53600/RT) \text{s}^{-1} \end{array}$$

The compound with the lowest activation energy was the thermally least stable. The rate parameters obtained were quite analogous to the polynitro compounds, again suggesting that the rate-determining step involves the simple cleavage of a C–N bond.

A study of the kinetics of thermal decomposition of difluoroamino compounds was conducted with the goal of obtaining leads to methods of reducing their detonation sensitivity [126]. The investigation of the pyrolysis of tetrakis(difluoroamino)-methane (Compound T or Compound Delta) was extended up to 800 K (528 °C). For this purpose, a tubular 2.4-mL-volume reactor was constructed from 1/8-in. copper tubing. This small reactor allowed for very short residence times (7 to 190 ms) and, therefore, much higher temperatures. At higher temperatures, the initial products were almost exclusively PFG, NF_3 , and N_2F_4 . It was definitively established that PFG is a direct intermediate in the decomposition of Compound T. The pyrolysis of Compound T occurs via the cleavage of a C—N bond:



followed by the first or both of the following processes:



The pyrolysis of PFG was then studied in the same reactor. The thermal stabilities of Compounds T, R, and H studied over the temperature range of 463 to 733 K (190 to 460 °C) were found to decrease markedly in the order $\text{H} > \text{R} > \text{T}$. This is precisely the order of increasing detonation sensitivity for this series of compounds.

The thermal decomposition of

INFO-635P	2-Tris (difluoroamino) methoxy ethylammonium perchlorate
PBEP	Poly [1,2-bis(difluoroamino)-2,3-epoxy propane]
PFABD	Poly [1,4-bis[tris(difluoroamino) methoxy butene oxide-2,3]

was investigated by a mass spectral thermal analysis (MTA) method using a time-of-flight mass spectrometer [127, 128]. In this method, microgram quantities of the materials were deposited on a small platinum ribbon that was heated ohmically by battery current or by condenser discharge. Using battery current, a linear heating rate was obtained that could be varied from 10 to 1000 °C/s (dynamic heating). With the

condenser discharge, the sample temperature was brought instantaneously (10 ms) to a predetermined temperature that was maintained for 50 ms (isothermal heating). The decomposition of these compounds was accelerated by impurities, and subsequent work served to determine which, if any, of the purification procedures produced desirable gains in propellant thermal stability and shelf life [129].

3.4.2.2 Thermal Stability and Decomposition of Cyclic Difluoroamino Compounds

The decomposition reactions of $-\text{NF}_2$ compounds discussed thus far were for open-chain compounds. The following compounds contain a ring to which F atoms or $-\text{NF}_2$ groups have been attached.

Ammonium, 1,5-diamino-4-methyl-tetrazolium, and 4-amino-1-methyl-triazolium salts of 5-difluoroaminodifluoromethyl-tetrazolate were prepared by metathesis reactions of silver 5-difluoroaminodifluoromethyl-tetrazolate and the corresponding iodides [130]. All salts were thermally stable to $\sim 423\text{ K}$ ($\sim 150^\circ\text{C}$). The ammonium salt had a density of 1.88 g/cm^3 . The standard heat of formation of ammonium 5-difluoroaminodifluoromethyl-tetrazolate was calculated to be -53.13 kcal/mol using the CBS-4 method. 1,5-Diamino-4-methyl-tetrazolium 5-difluoroaminodifluoromethyl-tetrazolate had a density of 1.69 g/cm^3 and an enthalpy of formation of $+52.56\text{ kJ/mol}$.

The following alicyclic and heterocyclic difluoroamino and nitro compounds may not necessarily be suitable as rocket propellants, but they have served as model compounds to study the effect of molecular structure on thermal stability.

The decomposition rates and product distributions of a number of nitro- and difluoroamino-substituted six-membered rings were compared: nitrocyclohexane (I); 1,1-dinitro-cyclohexane (II); 1,1,4,4-tetranitrocyclohexane (III); 1,1,4,4-tetrakis(difluoroamino)cyclohexane (IV); 1,4-dinitropiperazine (V); 1,4,4-trinitropiperidine (VI); and 4,4-bis(difluoroamino)-1-nitropiperidine (VII). The following order was suggested for decreasing susceptibility to decomposition: $\text{N}-\text{NO}_2 > \text{C}-(\text{NO}_2)_2 > \text{C}-(\text{NF}_2)_2$ [131]. The difference in bond energies among the compounds was small. Geminal bis(difluoroamino) compounds appeared to be somewhat more stable than the corresponding *gem*-dinitro compounds, although they released more heat during decomposition. The decomposition of *gem*-bis(difluoroamino) and *gem*-dinitro compounds exhibited some similarities. Both experienced loss of one geminal NX_2 group followed by the rearrangement of the remaining NX_2 . Where X was oxygen, loss of the initial nitro by homolysis was favored; rearrangement of the remaining nitro followed by the homolysis of NO resulted in a C—O bond. Where X was fluorine, the initial difluoroamino may have been lost as HNF_2 . The remaining difluoroamino reacted by losing fluorine, leaving CNF, or losing HNF, resulting in C—F.

The decomposition of 1,1,4,4-tetrakis(difluoroamino)cyclohexane and 3,3,7,7-tetrakis(difluoroamino)octahydro-1,5-dinitro-1,5-diazocine (HNFX) under the conditions of electron ionization mass spectrometry appeared to parallel the thermal decomposition of nitramines where $\text{N}-\text{NO}_2$ cleavage is often the first step [132].

3.4.3 Strand Burning of Difluoroamino Compounds

Very little is known about the strand burning rates of difluoroamino compounds. They appear to be so sensitive that in many instances a plain burning quickly transitions to a detonation. Strand burning of difluoroamino compounds will be discussed again in *Encyclopedia of Monopropellants*.

Normally, the addition of metal salts increases the linear burning rates of monopropellants, but here the opposite appears to be the case. FeCl_3 (preferred), ZnCl_2 , SnCl_2 , and $\text{Pb}(\text{OAc})_2$ were proposed to reduce the high burning rate and danger of explosions attendant upon use of difluoroamino compounds as propellants and, at the same time, increase injection port critical quench diameters to facilitate injection of fuel into rocket motor combustion chambers without flashbacks [133]. Thus, 1 mass-% of FeCl_3 was added to 1,2-IBA, stirred for 1 min at ambient temperature, and excess FeCl_3 was removed by filtration. In 0.5-mm-diameter burning tubes at 0.69 MPa (100 psi), the desensitized mixture thus prepared burned at 0.6 cm/s, while the pure difluoroamino compound burned at 1.3 cm/s. At 6.2 MPa (900 psi), the pure material always detonated, while the FeCl_3 -containing solution burned progressively (no burning rate given).

3.4.4 Analysis of Difluoroamino Compounds

Fluorination of PFG or guanylurea results in the formation of a medley of difluoroamino compounds that are difficult to separate, unless one uses preparative liquid column chromatography, which avoids the accumulation of detonable fractions that might otherwise form during preparative GC or fractionated condensation [134].

Linde 5A molecular sieves will selectively adsorb bis(difluoroamino)difluoromethane while quantitatively excluding the slightly larger tris(difluoroamino)fluoromethane [31].

3.5 Safety Properties of Difluoroamino Compounds

3.5.1 Explosion Sensitivity of Difluoroamino Compounds

Difluoroamino compounds can be divided roughly into three classes based on their sensitivity: (1) relatively insensitive compounds, substituted with a low ratio of NF_2 groups to carbon; (2) compounds with substitution at a ratio of up to one NF_2 group per carbon, possessing high energy, and exhibiting sensitivity characteristics that are about the same as those of nitroglycerin or HMX; and (3) ultrasensitive compounds, of very high energy, which are more sensitive than nitroglycerin and HMX and are difficult to desensitize [135]. In the first class are long-chain alkanes, mono- and bis-substituted with NF_2 groups (exceptions are the geminally substituted compounds). In the second class are bis(difluoroamino) compounds such as the DPs, tris(difluoroamino)alkane compounds at a ratio of one NF_2 to one methylene

group and substituted in the 1,2,3-, 1,1,2- or 2,2 positions, and compounds with more than three NF_2 groups. The third class consists primarily of tris(difluoroamino) compounds. The sensitivity characteristics of the various classes of NF compounds can be correlated with the number and position of the NF_2 groups on the carbon chain, and some types of substitution are particularly sensitive to certain methods of energy input, e.g., to spark initiation or to friction. The general sensitivity of a compound is established by the NF_2 substitution and is usually not intensified by the effect of other oxidizing groups such as nitro or nitrate. Vicinal substituted compounds at a ratio of about two NF_2 groups to three carbon atoms are in the nitroglycerin sensitivity range. Geminal NF_2 groups impart more sensitivity to a compound than do vicinal groups, particularly when the geminal group is terminal, as in the 1,1 position. Desensitization of geminal compounds by increasing the carbon content is ineffective. Generally, energetic geminal compounds are in the nitroglycerin sensitivity range and appear to be especially susceptible to spark and shock initiation. Separation of NF_2 groups by one or more CH_2 groups appears to make the compounds less sensitive, but the magnitude of improvement is not large.

3.5.1.1 Explosion Limits of Difluoroamino Compounds

The explosion limits of difluoroamino compound vapors in sturdy vessels made from various construction materials and in dilution with inert gases were determined as a function of the mode of initiation, total pressure, partial pressure, and composition [136]. The explosion products were analyzed, and an attempt was made to explain the chain of reactions that led to their formation. A long series of progress reports documented this work, which lasted several years from 1963 to 1969. It is unclear what compound was used for most of the tests; 1,2-DP was initially supposed to be used, and it was examined exhaustively for its explosion limits. Presumably it was intended to be used as a monopropellant.

Vapors of bis(difluoroamino)propanes (DP) $\text{C}_3\text{H}_6(\text{NF}_2)_2$ and bis(difluoroamino)butanes (DB) $\text{C}_4\text{H}_7(\text{NF}_2)_2$ were exploded either thermally by raising the temperature or by injecting a small amount of fluorine. For the thermally induced explosion the experiments yielded explosion limits as functions of pressure p , temperature T , and vessel diameter d . Three DP isomers and three bis(difluoroamino)butane isomers were selected for this study. These compounds were sufficiently volatile at room temperature (25°C) for admission of the vapors to a reaction vessel at 4.0 to 5.3 kPa (30 to 40 mm Hg) for DP and 1,2-IBA (IBA), and at 2.7 to 4 kPa (20 to 30 mm Hg) for 1,2-DB and 2,3-DB. For the fluorine-induced explosion the experiments yielded explosion limits in terms of critical fluorine concentrations $F_{2\text{crit}}$. The data showed that the reaction is of the branched-chain type and that at the explosion limits the relation Rate of Chain Branching = Rate of Chain Breaking is applicable. Using this relation in conjunction with chemical analysis of the reaction products and auxiliary data from photochemical experiments, a series of reaction mechanisms was proposed. Abstraction of the first hydrogen gave a free radical $\cdot\text{C}_3\text{H}_5(\text{NF}_2)_2$. The decomposition of the free radical

$\cdot\text{C}_3\text{H}_5(\text{NF}_2)_2$ to yield $\text{NF} + \text{F}$ rather than NF_2 was interpreted in terms of a sequential activation of the F-atoms in the two NF_2 groups of the radical R. Each group loses one F atom in reactions with neighboring H atoms to form HF, so that the formation of the molecules HCN and C_2H_2 in the final break-up releases one radical NF and one F atom. This principle also applies to the ternary reaction $\text{F} + \text{DP} + \text{F}_2$, except that one NF_2 group is preserved because the F_2 molecule furnishes an F atom to serve as reaction partner to one of the H atoms in the carbon chain.

The go/no go results were graphed in terms of the product of pressure and vessel diameter versus reciprocal absolute temperature. The boundary between explosion and no explosion was a fairly sharp line curving upward. The activation energy for the unimolecular decomposition reaction of 1,2-DP was $\sim 105 \text{ kJ/mol}$ ($\sim 25 \text{ kcal/mol}$).

The existence of a critical fluorine concentration above which a DP-F_2 mixture explodes spontaneously even at low temperature was noted in attempts at preparing a 1,2-DP/ F_2 mixture at room temperature. For this purpose fluorine was gradually added in small increments to 1,2-DP vapor. No detectable reaction took place between F_2 and 1,2-DP vapor if the partial pressure of F_2 was less than about 200 Pa (1.5 mm Hg), whereas an increase of the F_2 pressure to 200 Pa (1.5 mm Hg) or more produced explosive reaction characterized by a clicking sound, a luminous flash, and a sharp pressure rise.

Initial pyrolysis data of gaseous 1,2-DP at 523–543 K (250–270 °C) appeared to obey half-order kinetics and were surface dependent [137]. Additional measurements of pyrolysis rates of 1,2-DP in the 300–350 °C range reinforced earlier evidence that the reaction was surface dependent [138]. Induction times could be correlated to explosion limit pressures.

Critical pressure limits for explosion at 633–663 K (360–390 °C) for pure 1,2-DP determined in a 1090-cm^3 bulb were found to be lower by a factor of about 3 than the values found in a 216-cm^3 bulb [139]. Helium dilution did not affect the limit at all, while nitric oxide addition lowered it sharply.

The explosion limits of 1,2-DP were compared to those of equimolar mixtures of propylene and tetrafluorohydrazine (reactants used in the preparation of 1,2-DP) [140]. Analyses of the gaseous products of the explosion of 1,2-DP showed nitrogen, hydrogen, carbon monoxide, hydrogen cyanide, acetylene, and silicon tetrafluoride to be among the products, but acetylene was not present among the products below the explosion limit [141].

Manometric measurements of the thermal decomposition of 2,2-DP in Pyrex vessels of differing surface-area-to-volume ratios in the temperature range 549–573 K (276–300 °C) indicated that the reaction is a homogeneous first-order reaction with an activation energy of about 159 kJ/mol (38 kcal/mol) [142]. Equimolar nitric oxide-2,2-DP mixtures exploded less readily than pure 2,2-DP.

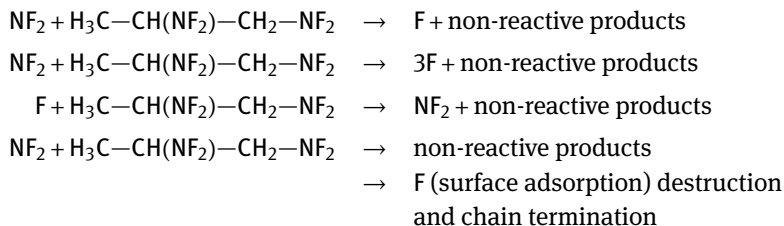
The products of the explosive and non-explosive thermal decompositions of IBA were analyzed for HCN and C_2H_2 and products not condensable in liquid nitrogen [143]. The HCN yields for explosion were approximately 1 mol per mol IBA consumed;

for non-explosive decomposition the yields were much lower. An analytical method utilizing IR spectroscopy to determine the rate of thermal decomposition of 2,2-DP indicated that the reaction was homogeneous and first-order and had an activation energy of about 188 kJ/mol (45 kcal/mol). Butane homologs differed from the propane homologs by their high sensitivity to traces of fluorine, and it is therefore very probable that the occurrence of an accidental, premature reaction involved the generation of traces of fluorine by catalytic decomposition of IBA or DB at the vessel surface.

Drop weight sensitivity of 1,2-DP and IBA correlated very well with sensitivity, as indicated by thermal explosion limit measurements [144]. The thermal decomposition of 2,2-DB followed a first-order rate corresponding to

$$k = 10^{15.7} \exp(-46,500/RT) \text{ s}^{-1}$$

Data on the explosion limit of 1,2-DP were inconsistent with the concept of thermal explosion and required interpretation in terms of a branched-chain mechanism [145]. The chemical and kinetic evidence suggested a mechanism of the form



The initiation mechanism in drop weight tests can be interpreted in terms of heat transfer from adiabatically compressed gas bubbles in the sample volume to the explosive liquid. Data from the initiation of IBA using various gases in the sample volume can be correlated in terms of the temperature rise of the gas-liquid interface due to the impact of the drop weight.

Explosion limits of 1,2-DP and 2,2-DP were measured at pressures up to 26.7 kPa (200 mm Hg) by rapid immersion of a flask containing a measured liquid volume in a heated salt bath [146].

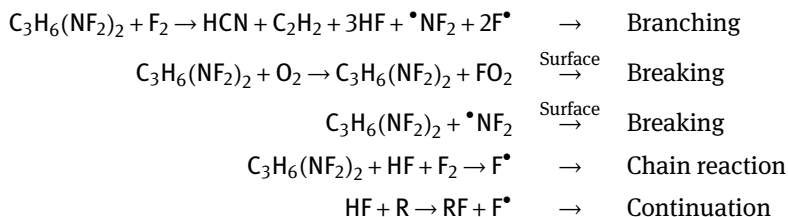
Explosion limits for 1,3-DP indicated that the chain branching step involved a unimolecular decomposition of the chain carrier $\text{F}_2\text{N}-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-\text{NF}_2$ [147]. In the absence of a low temperature limit, chain branching occurred in the gas phase and chain termination occurred at the surface only. Kinetic data indicated that 1,2-DP decomposed heterogeneously while 2,2-DP decomposed homogeneously [148]. For explosive conditions the volume ratio of 1,2-DP decomposition products was $\text{N}_2:\text{C}_2\text{H}_2:\text{HCN} = 2.5:1:1$ [149].

The key problem in the branched-chain explosion of difluoroamino propanes is the mechanism of deactivation of F atoms. This may occur either subsequently to the reaction $\text{F} + \text{DP} = \text{HF} + \text{R}$ by decomposition of the free radical R to yield inert NF_2 instead of $\text{NF} + \text{F}$, or competitively by the reaction $\text{F} + \text{DP} = \text{C}_3\text{H}_6\text{F}(\text{NF}_2) + \text{NF}_2$ while R in

the presence of F_2 at low temperature reacts to yield $RF + F$ and at high temperature decomposes to yield $NF + F$. Photochemical experiments with Cl_2 and F_2 at subcritical concentrations have confirmed the latter theory, pointing to a common branched-chain mechanism for the various DP isomers [150]. Comparison of the kinetic data for 1,3-DP with 1,2- and 2,2-DP showed that a primary carbon atom was much less susceptible to reaction $F + DP = C_3H_6F(NF_2) + NF_2$ than a secondary carbon atom.

The fluorine-induced explosions of C_4 difluoroamino compounds $(CH_3)_2C(NF_2)-CH_2(NF_2)$, $F_2N-CH_2-CH(NF_2)-CH_2-CH_3$, $CH_3-CH(NF_2)-CH(NF_2)-CH_3$ (code names IBA, 1,2-DB, and 2,3-DB, respectively) and the C_5 homolog $(CH_3)_2C(NF_2)-CH(NF_2)-CH_3$ (code name M-2,3-DB) were studied by admitting measured amounts of F_2 to the vapors of these compounds in a 200-cm³ Pyrex bulb at pressures of 1.07 kPa (8 mm Hg) or less [151]. Whereas very small amounts of F_2 were required to produce explosions with IBA, larger amounts of F_2 were required to produce explosions with 1,2-DB and 2,3-DB, and substantial amounts of F_2 were required to produce an observable luminous flash with M-2,3-DB. Samples of IBA and 1,3-DP were decomposed to completion with F_2 , and the decomposition products were analyzed by MS.

From the explosions of vapors of the three isomeric DPs, 1,2-DP, 1,3-DP, and 2,2-DP, and bis(difluoroamino)butanes in spherical glass vessels, either by heating or by addition of difluorine at 273–373 K (0–100°C), and from photochemical experiments and thermochemical and kinetic consideration of the data, the mechanisms of the reactions of DPs and bis(difluoroamino)butanes with difluorine were examined [152]. The vapor-phase reaction of DPs with F_2 below 100°C involved chain branching and breaking by reaction with $F^\bullet$ and $O^\bullet$ to form O_2F and then inert products. Differences among the 1,2, 1,3, and 2,2 isomers of DP were documented. Collisions between bis(difluoroamino)butanes and F_2 led to chain breakage by complex reactions, depending on the isomer structure. Data on the vapor-phase reaction of propyl isomers $C_3H_6(NF_2)_2$ with F_2 below 373 K (100°C) conform to the chain mechanism



with R being the free radical $\bullet C_3H_6(NF_2)_2$. These equations are not stoichiometrically balanced.

Over a period of several years, Stanford Research Institute (SRI International) has conducted an exhaustive series of investigations on the sensitivity fundamentals of difluoroamino compounds, as well as in comparison with nitro compounds. Much of the work was directed at determining the ability of energetic compounds to undergo low-

velocity detonations (LVDs). This has resulted in a flood of quarterly, semi-annual, and annual progress reports; only a few selected ones have been reviewed for this chapter on difluoroamino compounds, and the reader will need to dig through a stack of additional reports if more detailed information is needed. A 193-page summary of the sensitivity and stability of NF compounds included sensitivity data on 389 compounds, including Compound R, Compound T (= Compound Delta), and many others [112]. The information on sensitivity obtained during previous RNF_2 synthesis research programs had been primarily incidental (accidental) and uncorrelated, gathered by laboratories working independently of each other and each using different empirical tests, often modified from their “standardized” forms. Other sensitivity testing has been reported by laboratories engaged in development programs. Consequently, a large volume of sensitivity information is scattered throughout the technical literature. Data from sensitivity tests conducted on 400 NF compounds between 1960 and mid 1966 were compiled by SRI. The scope of the compilation included testing information from impact, friction, static, shock, and compression tests and from thermal stability measurements. The objective was to establish relationships between sensitivity, structure, and thermal decomposition mechanisms and kinetics. The physical properties of these compounds should have been documented at the same time, but that was not done.

The LVD wave propagation characteristics of 1,2-, 1,3-, 1,1-, and 2,2-DP, 1,2-bis(difluoroamino)2-methylpropane, 2,3-bis(difluoroamino)butane, 1,2,2-tris(difluoroamino)propane, and 2,3,3-tris(difluoroamino)butane were examined [153]. This was supposed to give a better understanding of the effect of vicinal and geminal difluoroamino groups on the stability of the molecules. See also [154, 155].

3.5.2 Drop Weight Impact Sensitivity of Difluoroamino Compounds

The drop weight impact sensitivities of several difluoroamino alkyl compounds are listed in Table 15. In some cases, the impact sensitivity of RDX as determined on the same apparatus was listed for comparison. These data came from different laboratories and may reflect the use of different machines, as indicated by the different units used. The least sensitive compound in this collection was *tert*-butyldifluoroamine; the most sensitive compound was PFG.

Completely fluorinated guanidine (PFG) is an extremely sensitive molecule and has contributed to several accidental explosions in the laboratory and pilot plants. Explosions can be initiated easily by shock, spark, or impact. Other guanidine derivatives have similar severe sensitivity characteristics.

An evaluation of $\text{C}(\text{NF}_2)_4$ (Compound T or Compound Δ) as a higher-performance replacement for $\text{FC}(\text{NF}_2)_3$ (Compound R) in formulated oxidizer mixtures was terminated because of the extremely unfavorable results obtained from shock sensitivity and detonation propagation experiments on mixtures containing Compound T [126]. Mixtures of Compound T with ClF_5 , N_2F_4 , and $\text{C}(\text{NO}_2)_4$ fared no better, but their vapor

Table 15: Drop weight impact sensitivities of difluoroamino alkyl compounds.

Compound formula	50% drop weight impact sensitivity
$(\text{H}_3\text{C})_3\text{CNF}_2$	39 kg in.; RDX = 10 kg in.
$\text{CH}_2(\text{NF}_2)_2$	0.1 kg cm
$\text{F}_2\text{NCH}_2\text{CH}_2\text{NF}_2$	11 kg in.; RDX = 20 kg in.
$\text{CH}_3\text{C}(\text{NF}_2)_2\text{CH}_3$	2.8 kg in.; RDX = 10 kg in.
$\text{CH}_3\text{CH}(\text{NF}_2)\text{CH}_2\text{NF}_2$	14 kg in.; RDX = 20 kg in.
$\text{F}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NF}_2$	>170 cm/2 kg
$\text{F}_2\text{NCH}_2\text{C}(\text{CH}_3)(\text{NF}_2)\text{CH}_3$	5.7 kg cm
$[\text{H}_3\text{CCH}(\text{NF}_2)]_2$	32 kg in
$\text{H}_3\text{CC}(\text{NF}_2)_2\text{CH}_2\text{CH}_3$	4.0 kg in.
$\text{F}_2\text{NCH}_2\text{CH}(\text{NF}_2)_2$	1–5 kg in.
$\text{F}_2\text{NCH}_2\text{CH}(\text{NF}_2)_2\text{CH}_2\text{NF}_2$	7–18 kg cm
$\text{C}(\text{NF}_2)_4$	42 kg cm
$\text{FN}=\text{C}(\text{NF}_2)_2$	0.1 kg cm (!!!)

Data source: [112]

pressures were measured, and the theoretical performance with B_5H_9 and MMH was calculated anyway.

The drop weight impact sensitivity of $\text{C}_9\text{H}_{14}\text{F}_{12}\text{N}_4\text{O}_3$, $[\text{F}_2\text{NCH}_2\text{CH}(\text{NF}_2)\text{OCH}_2-]_2\text{CHOCH}(\text{NF}_2)\text{CH}_2\text{NF}_2$, and TVOPA liquid was measured in a Bureau of Mines machine [112]. Its impact sensitivity was greater than that of RDX and comparable to that of glycerol trinitrate (GTN), also called nitroglycerin (NG). Impact sensitivities of difluoroamino compounds in comparison with that of other energetic materials determined with the Picatinny drop weight tester are shown in Table 16.

Table 16: Drop weight impact sensitivities of difluoroamino compounds in comparison with other energetic materials.

Compound	Acronym	Calculated 50% point	
		cm	in.
Trimethylolethane trinitrate	TMETN	56	22.2
Glycerol trinitrate/ethylene glycol mix	GTN (NG)/EG (60/40)	30	11.7
Glycerol trinitrate	GTN (NG)	27	10.7
Triethylene glycol dinitrate	TEGDN	>96	>38
1,2,3-Tris[1,2-bis(difluoroamino)]ethoxy propane	TVOPA (Batch 500)	39	15.5
1,2,3-Tris[1,2-bis(difluoroamino)]ethoxy propane	TVOPA (Batch 573B)	28	10.9
2,3-Bis(difluoroamino)propyl acrylate	NFPA	>96	>38

Data source: [156]

Note: Acronyms are identified in Table 18

3.5.2.1 Drop Weight Impact Sensitivity of Difluoroamino Compound Mixtures

Difluoroamino compounds derived from the reaction of tetrafluorohydrazine with alkenes with up to eight carbon atoms can be mixed with nitric acid to reduce their impact sensitivity [157]. A preferred example was HNO_3 at 0.5–0.6 times the stoichiometrically required amount of oxidizer mixed with IBA made from isobutylene and N_2F_4 . The IBA thus obtained had a vapor pressure of 12 mm Hg at 0 °C, 26 mm Hg at 15 °C, and 49 mm Hg at 28 °C. The atmospheric pressure b.p. was predicted to be 99 °C. These mixtures have reduced shock sensitivity compared to pure difluoroamino compounds. The drop weight sensitivity of pure IBA was $E_{50} = 6.9 \text{ kg}\cdot\text{cm}$, which is more sensitive than GTN, but the E50 mixture was 50 kg·cm. The lower homolog 1,2-bis(difluoroamino)propane had a vapor pressure of 21 mm Hg at 0 °C.

3.5.3 Friction Sensitivity of Difluoroamino Compounds

The friction sensitivity of TVOPA was positive at a 0.37 relative friction number at 750 rpm and negative at 2700 rpm but positive at 2800 rpm.

3.5.4 Card Gap Sensitivity of Difluoroamino Compounds

The card gap sensitivity of difluoroamino compounds (and that of many other energetic compounds) depends on the strength of confinement. In a series of tests, keeping the charge diameter constant, the effect of the ratio of wall thickness to charge diameter on the number of cards required to obtain the first negative test was measured.

The SRI Sensitivity Fundamentals program has existed for a very long time. During one period of this program, the card gap sensitivity of 1,2-DP and IBA had been measured [154]. 1,2-DP was so sensitive in the card gap test that it required a large number of Plexiglas cards before the shock wave was sufficiently attenuated and the first negative test was obtained. Therefore, additional LVD tests were conducted with IBA instead. In a 1.27-cm diameter, 10.2-cm-long charge of IBA with a wall thickness:diameter ratio of 0.2, the card gap value for all negative initiation was 18.5–21 cm Plexiglas. For 1,2-DP under the same condition it was 66–122 cm. For comparison, the card gap of ethyl nitrate was 3.1–3.8 cm. This means that the difluoroamino compounds were much more sensitive than the alkyl nitrate.

In another card gap test, the 50% point of TVOPA was at a stack of cards 27 mm (1.05 in.) thick. For comparison, the card gap sensitivity of GTN was 23 mm (0.9 in.).

In a series of tests to study LVD, 1,2-DP was tested in lead and steel tubes in comparison with ethyl nitrate and a nitromethane (NM)/TNM mixture. The results differed depending on whether a witness plate was at the end of the sample or not. The results are shown in Table 17.

Because only a limited amount of difluoroamino compounds was available to test card gap sensitivity, the standard card gap test (3.6 cm ID $\times$ 15.2 cm length acceptor with a 9.5-mm-thick witness plate geometry) had to be scaled down to an acceptor geometry of 0.9-cm diameter $\times$ 6.3-cm length in a Schedule 40 water pipe [156]. A small-

Table 17: LVD gap sensitivities of 1,2-DP in comparison with ethyl nitrate and a NM/TNM mixture.

Compound	Confinement, steel tubes		LVD gap sensitivity, cm of Plexiglas	
	ID, cm	Wall thickness, cm	Witness plate	No witness plate
1,2-DP	12.7	0.63	>91–<126	<61 (camera)
Ethyl nitrate	12.7	0.23	>2.54–<5.4	>3.8–<5.1 (probe)
NM/TNM (18.7/81.3 mass-%)	12.7	0.63	>8.9–<10.2	11.0 (probe)

Data source: [158]

scale test was used in which only the acceptor and witness plate were reduced in size and the donor and barrier remained the same. The premise was that, with a given gap and explosive train, the card gap value would not be strongly dependent upon the acceptor diameter. The acceptor configuration was that of a sample contained in a 6.3-cm (2.5-in.) length of nominal 0.9-cm (3/8-in.) ID Schedule 40 steel water pipe; the witness plate was a 7.6 × 7.6-cm (3 × 3-in.) sheet of 3.2-mm (1/8-in.) thick mild steel. A series of substances was tested in each configuration and a comparison was made. The two tests correlated well, and the small-scale test gave card gap values 2–2.5 mm

Table 18: Small-scale card gap sensitivity values of difluoroamino compounds in comparison with other energetic materials.

Compound	Acronym	Formula	Gap width	
			mm	in.
Trimethylolethane trinitrate	TMETN	$(\text{O}_2\text{NOCH}_2)_3\text{CCH}_3$	7.6	0.30
Glycerol trinitrate/ethylene glycol mix	NG/EG (3/1)		13	0.51
Glycerol trinitrate	GTN (NG)	$\text{O}_2\text{NOCH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{ONO}_2$	23	0.91
1,2,3-Tris[1,2-bis(difluoroamino)]ethoxy propane	TVOPA	$[\text{F}_2\text{NCH}_2\text{CH}(\text{NF}_2)\text{OCH}_2]_2\text{CHOCH}(\text{NF}_2)\text{CH}_2\text{NF}_2$	27	1.05
1,2,2,5,9,9,10-Octakis(difluoroamino)-4,7-dioxadecane	OPE	$(\text{F}_2\text{NCH}_2\text{CHNF}_2\text{CHNF}_2\text{OCHNF}_2)_2$	26	1.03
1,2,3,5,6,7-Hexakis(difluoroamino)-4-oxaheptane	HPE	$(\text{F}_2\text{NCH}_2\text{CHNF}_2\text{CHNF}_2)_2\text{O}$	30	1.19
2,3-Bis(difluoroamino)-propyl acrylate	NFPA (monomer)	$\text{H}_2\text{C}=\text{CHCOOCH}_2\text{CHNF}_2\text{CH}_2\text{NF}_2$	31	1.21

Data source: [156]

(0.08 to 0.10 in.) higher, on average, than the large-scale test. Table 18 gives small-scale card gap sensitivity values for TVOPA, NFPA, and several other energetic liquids. It is assumed that the gap listed is the gap where the sample failed to detonate (negative test) and not the gap at the last positive test.

The failure diameter of TVOPA and NFPA in a Schedule 40 steel pipe with $L/D > 4$ was <0.48 in. In the DTA, the exotherm of TVOPA maxed out at 538 K (265 °C), compared to 469 K (196 °C) for GTN (NG).

3.5.5 Adiabatic Compression Sensitivity of Difluoroamino Compounds

Several difluoroamino compounds were tested for adiabatic compression sensitivity in a U-tube apparatus in comparison with ethyl nitrate and isopropyl nitrate [126]. The 50% probability for positive results in these sensitivity tests of Compound R under its own vapor in the gas bubble showed that the driving pressure ratio for 50% positive results was 4.3. High-speed photographic coverage of Compound R, ethyl nitrate, and *n*-propyl nitrate in which glass U-tubes instead of metal tubes were used showed both the liquid and vapor phase of Compound R participating in the explosion. This contrasted with the ethyl nitrate and *n*-propyl nitrate photographs where it could be seen that the explosion occurred only in the vapor phase. These observations were supported by the damage sustained by the stainless-steel U-tubes during the standard tests. During tests with Compounds R and T and mixtures containing these materials, 5 to 8 cm (2 to 3 in.) of tubing were completely fragmented in positive tests. During positive tests with ethyl nitrate, only a small portion of the tubing next to the crimp was ruptured. Additional tests were conducted where the Compound R in the gas/vapor bubble prior to the test was diluted with dry air, and the boundary in a graph of dilution vs. pressure ratio could be drawn on a graph.

Six tests were conducted on Compound T under its own vapor in the gas bubble and the driving pressure ratio to cause 50% positive results was 4.4. These results contradicted earlier reports that Compound T was more sensitive than Compound R. Both Compounds R and T are very sensitive materials. The Wenograd test indicated that Compound T was significantly more sensitive than Compound R. However, the U-tube test did not show this difference. Additional tests were conducted for mixtures of Compound R or T with TNM, N_2O_4 , or N_2F_4 . Mixtures containing up to 23 to 30% Compound R or T in N_2O_4 appeared to be safe to handle on the basis of U-tube tests.

3.5.6 Electrostatic Discharge Sensitivity of Difluoroamino Compounds

In the electrostatic discharge (ESD) test, TVOPA was negative at 1 J, but positive at 2 J.

3.6 Explosive Performance of Difluoroamino Compounds

3.6.1 Detonation Velocity of Difluoroamino Compounds

LVDs propagate at velocities only slightly supersonic with respect to the unreacted liquid and may be very easily initiated in some liquids. A hypothesis based on shock wave interactions and Mach reflections was proposed to explain the initiation and propagation of LVD in the card gap test, but certain anomalous effects were noted with difluoroamino compounds [158]. Theories proposed for LVD require that the container wall sound speed be greater than that of the liquid explosive. This prediction was tested using lead tubes with 1,2-difluoroaminopropane, a liquid known to sustain normal- and low-velocity detonations. Because of the low sound velocity, it was expected that weak initiating shocks would not yield LVD in lead, though identical shocks would in steel. Unexpectedly, there was definite evidence of LVD propagation even in lead pipes [159].

Detonation shock temperatures for liquid TNT, NM, $F_2NCH_2CH(NF_2)CH_3$ (= 1,2-DP), $H_3CC(NF_2)_2CH_3$ (= 2,2-DP), $F_2NCH_2CH(NF_2)CH_2CH_3$, and $F_2NCH_2C(CH_3)_2NF_2$ were calculated as functions of pre-shock temperature ($278 < T < 313$ K) and shock pressure (0–200 kbar) using a constant heat capacity (C_v) model and a $C_v = f(T)$ model [160]. For NM and the alkyl difluoroamino liquids, there was very little diversion for various pre-shock temperatures. For the alkyl difluoroamino liquids, there was little difference between isomers and homologs. The higher C_v of the bis(difluoroamino)butanes was almost exactly offset by their lower initial density.

The detonation velocities of 1,4-bis(difluoroamino)butane, CAS RN [16096-78-9], 1,3-bis(difluoroamino)butene-2,3, $F_2NCH_2CH=C(CH_3)NF_2$, CAS RN [29369-65-1], 1,2,3,4-tetrakis(difluoroamino)pentane, $F_2NCH_2CH(NF_2)CH(NF_2)CH(NF_2)CH_3$, CAS RN [15270-10-7], and their mixtures with TNT were measured and compared to their analogs with nitro groups instead of difluoroamino groups [161, 162]. The relative ranking of the three compounds within each group was the same.

3.6.2 Critical Diameter of Difluoroamino Compound Detonations

Detonation studies on the isomers 1,2-DP and 2,2-DP including shock sensitivity of the liquid phase, adiabatic self-heating of the liquid phase, and the mechanism and kinetics of thermal decomposition of the liquid phase established that both 1,2- and 2,2-DP detonate at velocities of 5–7 mm/ms and have failure diameters of less than 10 mm [163]. The thermal decomposition of 1,2-DP/nitrobenzene solution over the range 449–460 K (176–187°C) was found to be autocatalytic.

During one period of the SRI Sensitivity Fundamentals program, the critical diameter for propagation of detonation in 1,2-DP and 2,2-DP was measured in a wedge test [154]. The failure diameter of 2,2-DP was 4 mm, whereas the failure diameter of 1,2-DP was 1.6 mm. This is an unusually small critical diameter.

Failure diameters and shock reaction times were determined for all four DP isomers and some of the bis(difluoroamino)butanes, including two homologs. The failure diameter during a detonation is indicated by a drop from the Chapman-Jouguet (C-J) velocity (6 mm/ μ s) to about one-third this value. The difference between the failure diameters of the vicinal (for 1,2-DP: 1.6 mm) and geminal (for 2,2-DP: 4.0 mm) difluoroamino compounds presented a striking example of the dependence of a transient detonation characteristic on isomeric structure [164]. The reaction times for the difluoroaminobutanes were indistinguishable from those of the homologous propanes, but the failure diameters were several times larger (IBA and 2,3-DB; 9.5 mm).

Compounds R and T were capable of propagating an explosion in very-small-diameter charges [126]. The velocity of the propagation was unexpected, being considerably lower than the sonic velocity, but much higher than traditional deflagration propagation rates. These “explosions” did have sufficient energy, however, to fragment very strong tubing, the wall thickness of the capillary tubing being one-half of the ID. A 3-foot length of stainless-steel hypodermic tubing (0.007-in. ID and 0.014-in. OD) was loaded with liquid Compound T and the ends were sealed with clamps made from a 1/4-in. bolt and two tubing sleeves. The length of tubing was placed inside a polyethylene bag and then struck lightly near one end with a small hammer. The entire length of tubing was fragmented. The average explosion propagation velocity was 187 m/s. This value indicated that propagation by means of a CJ shock wave was not involved in these explosions. A much higher velocity would be expected for a CJ detonation and self-supporting shock wave. A possible explanation is a chain reaction of initiations at local “hot spots” caused by adiabatic compression of small gas bubbles in the liquid, causing LVDs.

3.6.3 Initiation of Difluoroamino Compound Detonations

Reaction times for shock initiation were measured for liquid explosives using a high-speed smear camera and a modified gap test. In all cases the reaction times decreased as the initiating shock pressure increased in the range 70 to 130 kbar and as the pre-shock temperature was raised in the range 278–313 K (5–40 °C). For constant shock pressure, the reaction time of 1,2-DP was significantly less than that of 2,2-DP [165]. Similarly, the reaction time of 1,2-bis(difluoroamino)butane was significantly less than that of 2,2-bis(difluoroamino)butane. It was proposed that vicinal compounds decompose faster than geminal compounds because vicinal compounds can undergo a low-activation-energy, exothermic elimination of HF.

3.7 Toxicity of Difluoroamino Compounds

Organic NF_2 compounds were tested for acute oral and/or inhalation toxicity in rats [166]. As a class the difluoroamines were toxic enough to warrant special handling, especially with respect to vapor inhalation. No meaningful pathological data could be collected. The acute oral toxicities of the difluoroamine compounds correlated roughly with that of fluoride ion. There was no systematic difference in toxicity between the vicinal and geminal bis(difluoroamino) compounds. See also [167].

The acute toxic properties of 2,3-bis(difluoroamino)propyl acrylate (NFPA), 1,2,3-tris[1,2-bis(difluoroamino)]ethoxy propane (TVOPA), tris(difluoroamino)fluoromethane (Compound R), and pentafluoroguanidine (PFG) were evaluated in rats and mice by the inhalation, i.p., and intragastric routes of administration [168–170]. The i.p. LD50s in rats were 25, 215, 140, and 155 mg/kg for NFPA, TVOPA, Compound R, and PFG, respectively. There was little interspecies difference in toxicity.

Further studies of TVOPA toxicity in rats, dogs, and monkeys emphasized *in vivo* and *in vitro* degradation of the compound and its action at the cellular level [171, 172]. A very low rate of TVOPA hydrolysis in aqueous solutions was determined in earlier experiments. The assumption that degradation in biological media would not differ significantly from *in vitro* buffered media was incorrect. TVOPA or early organic degradation products have direct toxic action. Inorganic degradation products influence the delayed effects of TVOPA, but are not responsible for death at high doses.

One of the penalties for developing more energetic propellants and explosives using fluoro- and difluoroamino-group-containing binders and plasticizers is the toxicity not only of the propellant itself, but also the toxicity of HF in the exhaust. An attempt was made to reduce the amount of HF in exhaust by adding calcium disilicide (CaSi_2) to the propellant formulation [173].

3.8 Applications of Difluoroamino Compounds

Difluoroamino compounds were considered mostly for energetic binders and energetic plasticizers in solid propellants. Attempts to use them as liquid monopropellants were less successful. Many patent applications have been filed in connection with the use of liquid alkyl difluoroamino compounds as rocket propellants. However, the only practical use found for them was as plasticizers for solid propellants, as described in the chapters on TVOPA and SYEP. Listed here are only a few examples for the use of alkyl difluoroamino compounds in monopropellants. Additional proposed applications as monopropellants are described in *Encyclopedia of Monopropellants*, but none of them has ever flown.

Alkyl difluoroamino compounds are soluble in White Fuming Nitric Acid (WFNA) or Red Fuming Nitric Acid (RFNA). These mixtures are safer to handle than the undiluted difluoroamino compounds and have higher specific impulses as monopropel-

lants than underoxidized alkyl difluoroamino compounds. High-energy, stable, insensitive liquid monopropellants can be formulated that are composed of alkyl difluoroamino compounds and fuming nitric acid. These propellants provide specific impulses $>280 \text{ lb}_f \text{ s/lb}_m$ at $P_c = 6.8 \text{ MPa} = 1000 \text{ psia}$, low sensitivity to impact and adiabatic compression, and good thermal stability [174]. For example, a sample of DP was added to 100% HNO_3 (WFNA). Immediate solution occurred with no chemical reaction indicated by heat release or gas evolution. Examination of the IR spectrum of this solution showed that DP was present substantially unchanged. Upon standing for many days at room temperature, no change in the composition could be detected. The drop weight sensitivity (Olin Mathieson Drop Weight Tester) of this composition was 30–40 kg-cm. This indicates a remarkably low sensitivity for a monopropellant of this energy content. A compression sensitivity value of 21 kg-cm/mL was obtained for this mixture (JANAF Test Method No. 5). This value is compared with values of 6.7 for PrNO_3 and 10.4 for MeNO_2 , both low-energy monopropellants considered to be insensitive. The thermal stability or “self-heat” temperature of this mixture, determined per JANAF Test Method No. 6, with a heating rate of $2.8^\circ\text{C}/\text{min} = 5^\circ\text{F}/\text{min}$, was $411 \text{ K} = 130^\circ\text{C} = 280^\circ\text{F}$.

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Dinitramide Oxidizers

1 Ammonium Dinitramide (= Dinitramide) and Ammonium Nitroformate

1.1 Introduction

This chapter deals mostly with ammonium dinitramide (ADN) and other dinitramide salts, but a smaller section on ammonium nitroformate has been added at the end. If this section on ammonium nitroformate had not been included here, it would have been placed in the chapter “Hydrazinium Salts.”

Replacing hydrogen in ammonia with electron-absorbing groups ($-\text{NO}_2$, $-\text{NO}$, $-\text{C}\equiv\text{N}$) draws electrons away from the remaining $\text{N}-\text{H}$ bonds and makes them easier to split, making the molecule more acidic. This progression can be seen when comparing the pK values of nitramine and dinitramine. Of the two, dinitramide – $\text{HN}(\text{NO}_2)_2$, dinitramidic acid, dinitraminic acid, nitronitramide, CAS RN [114045-20-4] – is the more acidic and forms salts with a wide range of metals and bases. A similar progression of increasing acidity has been observed when replacing one, two, or three hydrogen atoms in methane with a nitro group (see *Encyclopedia of Oxidizers*, chapter “Nitromethanes”).

Dinitramidic acid is a very strong mineral acid, having a pK_a value of -5.6 and being thermally labile. It forms stable salts with almost all bases, ammonia, metals, tertiary amines, melamine, cubane tetraamine, dinitro azetidine, and more. The dinitramide salts are more stable than the parent acid and the related covalently bound N,N -dinitro derivatives such as alkyl dinitramines. The higher stability of ionic dinitramide salts is due to the fact that the overall negative charge is distributed by resonance over the entire molecule, thereby imparting a higher $\text{N}-\text{N}$ bond order (Section 3.10.1).

Figure 1 shows the structural formula of ADN.

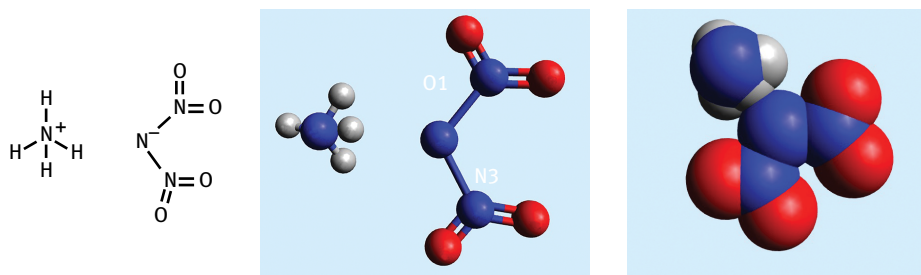


Figure 1: Structural formula of ammonium dinitramide.

1.2 Nomenclature

The parent acid of ADN, $\text{HN}(\text{NO}_2)_2$, CAS RN [114045-20-4], is variably called dinitramine, dinitramide, dinitramidic acid, dinitraminic acid, *N*-nitronitramide, or dinitroamide, but the correct name, a good tongue twister (used by *Chemical Abstracts* and the International Union of Pure and Applied Chemistry [IUPAC]), is 1,1,3,3-tetraoxo-1,2,3-triazapropene.

Because many salt names of oxyacids end with “-ate,” salts formed from dinitramide should be called dinitramidates, but this nomenclature is not widely accepted. Most researchers prefer to call the salts dinitramides. In French, ADN is called *dinitroamidure d’ammonium*.

It has been argued [1] that the name “amide” should be reserved for $-\text{NH}_2$ derivatives in which only one hydrogen atom on the NH_3 is substituted by a functional group, e.g., acetamide H_3CCONH_2 . The compounds with two hydrogen atoms substituted by functional groups are called imides, e.g., $(\text{H}_3\text{CCO})_2\text{NH}$, acetimide. Hence, a more appropriate name for salts with the $(\text{O}_2\text{N})_2\text{N}^-$ anion would be dinitrimide salts.

1.3 Summary Publications on Ammonium Dinitramide

Many publications on ADN as a rocket propellant emphasize the environmentally friendly composition of the exhaust products, which are less toxic, less corrosive, and less damaging to the ozone layer than the exhaust from propellants based on ammonium perchlorate (AP) [2].

The very best summary on the production, physical properties, chemistry, and applications of energetic dinitramides published to date is a book written by Ang and Santhosh [3]. This book is a very thorough summary of all information published up to that time and contains a detailed list of references (including complete titles of the publications referenced, which makes the list of references more useful, similar to the format used in our book).

There are several good survey and summary publications on the application of ADN as a rocket propellant, including [4]. Propellants based on ADN are more environmentally friendly compared to solid propellants based on AP. There are, however, some drawbacks: ADN is relatively shock sensitive, and it is also sensitive to light and moisture. The Langlet, Wingborg, and Oestmark 1997 paper [4] also presents a comparison of the specific impulse of composite propellants based on ADN and other oxidizers such as ammonium nitrate (AN), AP, hexanitrohexaazaisowurtzitane (CL-20), and hydrazinium nitroformate (HNF), with hydroxyl terminated polybutadiene (HTPB) as a binder. The friction sensitivity of ADN is much lower than that of 1,3,5-trinitrotriazine (RDX). The impact sensitivity of ADN is of the same magnitude as that of RDX but varies a great deal with the shape of the particles, e.g., prilled ADN is nearly twice as insensitive as RDX.

ADN and HNF are two new oxidizers that compete for applications both in solid propellants and in monopropellants. It depends on the application one has in mind before one can decide which of the two would make a better rocket propellant. For solid propellants, ADN has the advantage of higher oxygen content, but it has the disadvantages of hygroscopicity and worse sensitivity [5]. In this study, the sensitivity, density, and thermal stability of ADN and HNF were measured and compared. The results showed that the thermal stability is of major concern for both ADN and HNF. ADN has very unusual thermal stability behavior, being less stable at 333 K (60 °C) than at 343 or 353 K (70 or 80 °C). This paradox is very difficult to explain. To increase the thermal stability, a stabilizer will probably be needed for both ADN and HNF. From the impact sensitivity testing, it was found that both ADN and HNF should be considered to be sensitive materials. HNF does not meet the United Nations criteria with respect to friction sensitivity, and thus it cannot be transported without making special arrangements, such as shipping it covered with excess water.

See also [6–8]. Some survey papers are quite general and do not provide many hard facts, but others are a good introduction to the topic of ADN and related dinitramide salts as oxidizers for rocket propellants and explosives.

An excellent overview of the synthetic routes and properties of ADN and other dinitramide salts, with 56 references, is the summary by Venkatachalam, Santhosh, and Ninan [9].

Another excellent summary of applications of ADN is the publication by Vandel, Lobanova, and Loginova, [10] with 79 valuable literature references. Several sections in this chapter of the book at hand draw on information taken from that publication. Originally suggested as oxidants for rocket propellants and explosives, dinitramide compounds have significantly expanded their application areas, and this occurred not only in military but also in non-military applications.

The researchers at the Swedish organizations who have been leading the commercial ADN development continue to publish very good summaries on applications of ADN in monopropellants and in solid propellants [11–15].

1.4 History of the Discovery of Ammonium Dinitramide

The precursor to dinitramine (dinitramide, dinitramidic acid), nitramine (nitramide, nitroamide) H_2NNO_2 is very unstable and is not suitable as a rocket propellant. Its salts are more stable, depending on the stability of the cation.

There are many descriptions in the literature for preparation of nitramine under conditions very similar to those leading to dinitramides. It seems that if the former chemists had only varied their operating conditions and had had better methods for molecular structure analysis, ADN and its parent acid might have been discovered decades earlier.

ADN was first discovered on 18 May 1971 at the N. D. Zelinsky Institute of Organic Chemistry in Russia [1, 16, 17], but it was kept a closely guarded secret until its independent rediscovery in the United States by Bottaro and coworkers in 1989 [18]. Part of the earlier Russian work on dinitramide was not published until the early 1990s. During the period 1971–1975, more than one hundred different dinitramidic acid salts were prepared and characterized in Russia in secret.

In the early 1980s, the U.S. Office of Naval Research began a search for improved energetic materials. This program led to studies on the development of cubane-based explosives, fuels, and oxidizers. In 1988, while developing an improved route to dinitramines for application on cubanes, SRI International synthesized the dinitramide molecule, the parent of ADN, and prepared cesium dinitramide by a β -elimination reaction starting with 1-(*N,N*-dinitramino)-2-trimethylsilane and catalyzed by cesium fluoride [19]. In true line with instructions from IUPAC, dinitraminic acid was called 1,1,3,3-tetraoxo-1,2,3-triazapropene [20], or dinitramide for short. Several methods for making dinitramide salts were later patented, and these were the first patents for ADN production filed in the United States [21, 22]. In the United States, at one time SRI owned the composition-of-matter patent for all dinitramide salts. SRI granted licenses to the right to synthesize ADN to other entities and was seeking a commercial partner for further development.

Following publication of the patents in 1991, rumors began circulating that the USSR had already used ADN in some of their missile systems. These rumors were confirmed in 1993 when Z. Pak of the Lyubertsy Soyuz Science and Production Association presented a paper at an American Institute of Aeronautics and Astronautics (AIAA) meeting describing some of their work [2]. The development work in the former Soviet Union was later described in a 1995 newspaper article [23]. ADN is recognized as a potential revolutionary replacement for AP in missile systems [24]. The use of ADN can give propellants with high specific impulse, and ADN is environmentally benign and degradable. Once spilled, the dinitramide anion is not as persistent as the perchlorate anion.

All developments in the Soviet Union were of a secretive nature, and, presumably, only a small part of the work on ADN was declassified after dinitramide salts were synthesized by U.S. researchers in 1990. The indubitable attractiveness of the ammonium (ADN), potassium (KDN), and other dinitramide salts as components in various defense applications gives reason to believe that, even as of 2009, the available information (both domestic and foreign) was only the “visible part of an iceberg” [10].

As far as availability of ADN is concerned, the lead in ADN production and application development in Sweden has continued for many years and resulted in some spectacular successes, such as the first firing of a non-hydrazine/non-hydrogen peroxide monopropellant thruster in a satellite in Earth orbit. Several U.S. government agencies, including the Energetics Manufacturing Technology Center at Indian Head, Maryland, have taken steps to achieve a broader ADN manufacturing base

in the United States by sponsoring government contracts and procuring sample quantities, but the U.S. market for ADN is very limited, and profit-motivated industry was slow to respond. The goal was to develop the technology to eventually reduce the manufacturing cost of ADN from between \$3000/lb and \$5000/lb for laboratory scale quantities to less than \$100/lb for pilot scale production quantities [25]. When the National Aeronautics and Space Administration's Glenn Research Center announced in 2008 that they would start procuring ADN from Sweden, a critical discussion erupted on the internet about the lagging U.S. industry being unable to supply this important chemical from domestic sources.

ADN is available in commercial quantities from Eurenco Bofors in Sweden. Many foreign countries have started their own ADN production efforts and are competing with Sweden and the United States [26]; that includes prilling and after-treatment processes to reduce hygroscopicity.

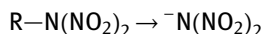
2 Production of Ammonium Dinitramide

There are many different methods for preparation of dinitramide salts, starting with either inorganic or organic chemical ingredients as feedstock. Most of the methods described here end up with ADN, but some create the free dinitramidic acid as an unstable intermediate in a nitration reaction, from where it is easy to prepare any salt desired by neutralizing it with the appropriate base in a subsequent neutralization reaction.

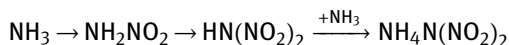
Several very good summaries of the various methods (starting with either inorganic or organic reactants) for production of ADN and similar dinitramides have been published. The most authentic is the one by Lukyanov and Tartakovsky, two of the original discoverers of dinitramidic acid [1]. This publication includes a firsthand account of the work that led to the discovery of dinitramidic acid and efforts to synthesize and characterize a host of dinitramidic acid salts with a variety of bases. It also includes a very detailed summary of the more than twenty synthesis routes leading to dinitramidic acid, including some of the more circuitous routes that are no longer used. Many of the earlier synthesis routes used organic dinitramide intermediates that were then split under alkaline conditions. Now that they are readily available in industrial quantities, ammonium, potassium, or cesium dinitramides can be used in the synthesis of many organic dinitramide compounds.

The methods of preparation of dinitramides can be classified into four groups:

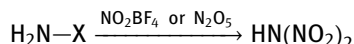
1. The first group is the formation of alkyl *N,N*-dinitro derivatives $R-N(NO_2)_2$ and subsequently the cleavage of the $R-N$ bond, leading to the dinitramide anion:



2. The second method of synthesis is based on inorganic synthetic routes involving direct nitration of NH_3 or NH_2NO_2 using either NO_2BF_4 or N_2O_5 , followed by reaction with a base:

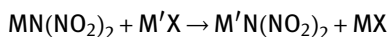


3. The third method involves nitration of deactivated amines such as $\text{NH}_2\text{SO}_3\text{H}$, NH_2NO_2 , NH_2CONH_2 , or $\text{NH}_2\text{COOCH}_3$ using strong nitrating agents such as NO_2BF_4 or N_2O_5 to give dinitramidic acid:



where X can be $-\text{SO}_3\text{H}$, $-\text{NO}_2$, $-\text{CONH}_2$, or $-\text{COOR}$. The most commonly used method is the nitration of sulfamic acid.

4. The fourth method consists of metathetical reactions of the already synthesized dinitramide salts with respective metal salts:



where X can be $-\text{OH}$, Cl , or $-\text{HSO}_4$, and M and M' are metal or amine base cations.

An excellent overview of the synthetic routes leading to ADN published by Venkatachalam, Santhosh, and Ninan in 2004 [9] gives an overview of the yields one can expect from the various methods for preparation of ADN, depending on which reactants one starts (Table 1):

Table 1: Yield of ADN preparation depending on type of starting reactants.

Rxn. No.	Starting material	Nitrating agent	Reaction temperature		Yield %	References
			K	°C		
1	$\text{Me}_3\text{Si}(\text{CH}_2)_2\text{NCO}$	$\text{NO}_2\text{BF}_4/\text{HNO}_3$	<273	<0	25	[20]
2a	NH_2NO_2	NO_2BF_4	253	-20	60	[27]
2b	NH_2NO_2	N_2O_5	253	-20	<1	[27]
2c	NH_2NO_2	$\text{NO}_2\text{HS}_2\text{O}_7$	233	-40	53	[28]
3	$\text{NH}_2\text{COONH}_2$	NO_2BF_4	273	0	15	[21]
4a	NH_3	NO_2BF_4	195	-78	25	[29]
4b	NH_3	N_2O_5	195	-78	15	[29]
4c	NH_3	$\text{NO}_2\text{HS}_2\text{O}_7$	195	-78	15	[29]
5	$\text{NH}_2\text{CONHNO}_2$	NO_2BF_4	233	-40	20	[30, 31]
6a	$\text{NH}_2\text{COOC}_2\text{H}_5$	N_2O_5	225	-48	70	[32]
6b	$\text{NH}_2\text{COOC}_2\text{H}_5$	NO_2BF_4	213	-60	60	[33]
7	$\text{HN}(\text{CH}_2\text{CH}_2\text{COOEt})_2$	NO_2BF_4	<273	<0	31	[34]
8	$\text{HN}(\text{CH}_2\text{CH}_2\text{CN})_2$	NO_2BF_4	263	-10	60	[35]
9	$\text{NH}_2\text{SO}_3\text{NH}_4$	$\text{HNO}_3/\text{H}_2\text{SO}_4$	228	-45	60	[36]

A summary published by Wang et al. [37] lists ten different methods for preparation of dinitraminic acid and its salts, including the following:

1. reaction of β -substituted *N*-alkyl-*N,N*-dinitroamide salts;
2. cation exchange of dinitramide salts;
3. reaction of ADN with a strong base (eliminating ammonia by sparging);
4. reaction of $\text{XN}(\text{NO}_2)_2$ with ammonia;
5. reaction of urethanes with carbonic acid anhydrides and anhydrous HNO_3 , then a base to yield *N*-(alkoxycarbonyl)-*N*-nitroamide salts, followed by reaction with a nitronium compound;
6. reaction of nitramides with a nitrating agent to form dinitramides;
7. reaction of an aliphatic isocyanate with NO_2BF_4 and HNO_3 to form *N,N*-dinitramines, which can be further reacted with a base to form dinitramides;
8. reaction of ammonium carbamate with a nitrating agent;
9. reaction of ammonia with nitronium compounds;
10. reaction of 2-(trimethylsilylethyl)-*N,N*-dinitramines with CsF to form cesium dinitramide [20].

Among the ten methods listed above, only methods 5, 6, and 10 have high yields. The yields of the other methods are less than 30%.

ADN is still difficult to make in large quantities, and scaling up the operation to a kilogram output level is already a substantial achievement and requires operating at low temperatures [38]. Regardless of which production process is used, one must have effective methods for isolation and removal of by-products to obtain a good yield of a pure main product [39].

2.1 Production of Ammonium Dinitramide from Inorganic Starting Materials

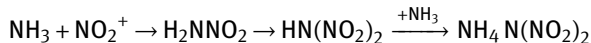
2.1.1 Different Types of Nitrating Agents

Different types of nitrating agents can be used for the preparation of ADN [40]. Instead of trying to isolate the product as the very soluble ADN, it is easier to isolate the dinitramide salt in the form of the poorly soluble guanidinium dinitramide, which precipitates, is filtered, and can later be converted to ADN [41].

2.1.2 Starting with Ammonia

There are many different methods to synthesize ammonium dinitramide $\text{NH}_4\text{N}(\text{NO}_2)_2$, ADN. Most syntheses proceed over several intermediate steps, but only the reactions of ammonia with dinitrogen pentoxide or with nitronium tetrafluoroborate lead to ADN directly in one step. The most direct method of synthesis is based on an inorganic synthetic route involving the direct nitration of NH_3 or NH_2NO_2 at 253 K (-20°C) using

either NO_2BF_4 or N_2O_5 , followed by reaction with ammonia as shown below [21]. This patent describes two different methods, one starting with ammonia:



The other method described in [21] is a β elimination reaction of 2-trimethylsilylethyl-N,N-dinitramine $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_2\text{N}(\text{NO}_2)_2$ with an ammonium salt catalyzed by cesium fluoride. Other nitrating agents instead of NO_2BF_4 that may be reacted with nitramine include $(\text{NO}_2^+)_2$ ($\text{S}_2\text{O}_7^{2-}$), NO_2AlCl_4 , N_2O_5 , $\text{N}_2\text{O}_2\text{F}$, NO_2PF_6 , NO_2AsF_6 , NO_2SbF_6 , acetyl nitrate, trifluoroacetyl-nitrate, trifluoroacetyl nitrate in combination with catalytic BF_3 , acetone cyanohydrin nitrate in combination with catalytic BF_3 , and any one of these in combination with white fuming nitric acid.

Another direct nitration of ammonia operates at lower temperatures, 253 to 153 K (-20 to -120°C) [29]. The preferable temperature range is from 233 K (-40°C) to about 193 K (-80°C). The nitrating agents are nitronium salts or covalently bound compounds containing the $-\text{NO}_2$ group. Suitable nitronium compounds are those with BF_4^- , NO_3^- , HS_2O_7^- , AlCl_4^- , F^- , PF_6^- , ClS_2O_6^- , F_2PO_2^- , AsF_6^- , SbF_6^- , FS_2O_6^- , ClO_4^- , $\text{S}_2\text{O}_7^{2-}$, SiF_6^{2-} , or SO_3F^- as the anions. For this procedure, the nitronium-containing compound is first dissolved in an aprotic liquid such as diethyl ether, methylene chloride, chloroform, carbon tetrachloride, methyl ether, a halocarbon, acetonitrile, ethyl acetate, or sulfolane. The process can be conducted as a batch process, and at the end of the reaction period, the reaction mass is allowed to warm up to room temperature while a basic condition is maintained by keeping it under an ammonia atmosphere. The nitronium compound should be free of nitrosonium compounds, NO or NO_2 , which interfere with the formation of dinitramide. The reaction must be carried out under anhydrous conditions.

The ammonia can be dissolved up front in an aprotic liquid to form a solution that is then mixed with a nitronium-containing compound solution to form ADN, or it can be bubbled through the solution of the nitronium compound. It is important that the reaction temperature not be lower than 153 K (-120°C) because the formation of the covalently bonded and less stable nitramide may be more favored at a temperature lower than about 153 K (-120°C). In one variation of the process, the gaseous ammonia reactant is fed into the reactor at a rate sufficient to maintain the desired low temperature of the reaction mixture. The ammonia feed rate may vary from about 0.1 L/min to about 3 L/min per liter of the aprotic liquid/nitronium-containing compound solution. The total amount of ammonia used in the reaction must be sufficient to provide an excess of ammonia above the stoichiometric requirements at the end of the reaction (at least 4 mol ammonia for 2 nitronium ions).

Preferably, the gaseous ammonia reactant is introduced into the reactor below the surface of the liquid and allowed to bubble through the liquid, or it is added above the liquid and allowed to condense or be absorbed into the reaction mixture. The liquid is stirred during the ammonia addition to further facilitate dissolving of the ammonia and achieve intimate contact between the reactants. The ammonia may also be added

from above as liquid ammonia. When the ammonia is added to the reaction mixture as a gas, it must be precooled to just above 240 K (-33°C), its condensation point. The reaction may be carried out as a batch process or on a continuous basis with batch or continuous extraction of portions of the reaction mass. After 1–8 h, the reaction mixture is maintained under basic conditions by adjusting the total quantity of ammonia; the stirring is continued, and the temperature of the reaction mass is allowed to rise slowly up to room temperature. The flow of ammonia into the reactor during this heating period may be adjusted to keep the overall reaction mixture basic, as well as to maintain a blanket of ammonia gas over the reaction mixture.

The disadvantage of the above ADN production methods is that they require nitronium tetrafluoroborate (CAS RN 13826-86-3) as the nitrating agent, which is available commercially but can be quite expensive. Commercial $\text{NO}_2^+\text{BF}_4^-$ often contains varying amounts of NO^+BF_4^- . Removal of the nitronium ion NO^+ from $\text{NO}_2^+\text{BF}_4^-$ is difficult. Therefore, pure nitronium tetrafluoroborate should be prepared directly from urea-treated purified HNO_3 . There are several examples of how to prepare NO_2BF_4 immediately prior to ADN synthesis. Nitronium tetrafluoroborate may be formed by the slow addition of BF_3 to a solution of HF and ethyl nitrate in methylene chloride or nitromethane. In one example, nitronium tetrafluoroborate (free of nitronium ion), was prepared by the slow addition of 100 g (1.5 mol, excess) of BF_3 to a solution of 8.8 g (0.44 mol) of HF and 40 g (0.44 mol) of ethyl nitrate in 300 mL of dry nitromethane kept at 263–268 K (10 – 15°C) by adjusting the rate of BF_3 addition. After formation of the nitronium salt was complete, it was allowed to settle, and the nitromethane was decanted. The salt was washed twice with 400 mL of a 1 : 1 mixture of CH_2Cl_2 and CH_3NO_2 , and then once with 400 mL of CH_2Cl_2 , and was finally suspended in 400 mL of CH_2Cl_2 .

For making ADN, the CH_2Cl_2 liquid containing NO_2BF_4 salt was stirred and cooled to 195 K (-78°C), and 35 g (2.059 mol, excess) of anhydrous NH_3 was bubbled into the slurry over a 2-h period. The reaction mass was stirred for 12 h, during which time it was allowed to warm to room temperature. The product solids were allowed to settle, and the CH_2Cl_2 was decanted. The remaining solids were then washed with 400 mL of CH_2Cl_2 , and the mixture was then evaporated under vacuum to dryness. Next, 150 mL of acetone was added, the solids digested for 1 h, and then 150 mL of ethyl acetate was added to decrease the solubility of NH_4BF_4 and NH_4NO_3 , which were separated from the solution. The filtrate was concentrated to dryness to give 9 g of a pale brown solid that, when recrystallized from 70 g of *n*-butanol, gave 5.5 g of ADN, with a yield of 21 % of theory.

A more economical nitrating agent is “nitronium nitrate” (= dinitrogen pentoxide, N_2O_5). It can be formed by passing ozone through a stirred solution of N_2O_4 in CH_2Cl_2 , for instance by dissolving 12.3 g of N_2O_4 (0.13 mol) in 300 mL of dry CH_2Cl_2 and cooling the solution to 195 K (-78°C). In this example, an ozone stream was passed through the solution, while stirring, until the solution was dark blue, resulting in the formation of a solid precipitate of nitronium nitrate. Oxygen was then bubbled through the solution to remove excess O_3 . To the nitronium nitrate-containing liquid was added 6 g

(0.35 mol) of anhydrous NH_3 over a 30-min period, while the mixture was maintained at 195 K (-78°C) with stirring. Stirring was continued for 2 h at 195 K (-78°C), and then the reaction was allowed to warm to room temperature. The CH_2Cl_2 was evaporated, and the remaining solids were washed with 100 mL of CH_2Cl_2 . The ADN salt product was extracted twice with 50 mL of acetone. The acetone extracts were concentrated to dryness to yield 1.77 g of a light yellow solid, which was recrystallized from *n*-butanol to give 1.16 g of ADN with a 15% yield. Changing the operating temperature to 243 or 233 K (-30 or -40°C) gave ADN yields of only 5%.

Another nitrating agent is nitronium hydrogen pyrosulfate, which can be made by mixing SO_3 and anhydrous HNO_3 in dry CH_2Cl_2 at room temperature. In one example, 40 g (0.5 mol) of SO_3 was slowly added to 15.5 g (0.25 mol) HNO_3 in 400 mL of dry CH_2Cl_2 while stirring, and the mixture was allowed to reflux to conduct away the heat of reaction. After the exotherm, the resulting nitronium salt was stirred for 2 h at room temperature, during which time it changed from a gelatinous state to a crystalline material. The slurry was cooled to 195 K (-78°C), and 30 g of anhydrous ammonia was introduced over 2 h. The mixture was stirred for 12 h while it was allowed to warm to room temperature. Excess NH_3 was blown out with argon; 100 mL of isopropanol was added, in which the ADN is soluble; and this mixture was stirred for 1 h and then was allowed to settle and was decanted. The extraction solvent was stripped off and concentrated to yield about 5 g of solids, which, when recrystallized from *n*-butanol, gave 2.8 g of ADN, with a 20% yield.

Reactions of ammonia with the lower nitrogen oxides (state of oxidation of nitrogen lower than +5, as in N_2O_5) have been investigated extensively for over one hundred years, but the aspect of potential formation of nitramine as an intermediate has been considered for only a few years.

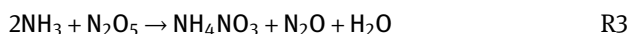
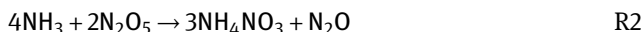
2.1.2.1 Mechanism of ADN Formation from Ammonia and Dinitrogen Pentoxide

The reaction of dinitrogen pentoxide with ammonia leads to the formation of AN, nitramide (NH_2NO_2), and ADN. The yields for the latter two are 30 and 13%, respectively. The mechanism of this ADN synthesis was described as a double nitration of NH_3 via the intermediate nitramide and dinitramidic acid [42–44]. Three types of reactions between NH_3 and N_2O_5 seem to be possible to form AN in different molar amounts, whereas the formation of ADN is possible only by one of the three reactions. Due to the catalytic decomposition of the intermediates, H_2O and N_2O are formed as further reaction products and can be identified by infrared (IR) spectroscopy. In addition to the well-known reaction of NH_3 with N_2O_5 , forming ADN, nitramide, and its decomposition products, a third reaction was discovered: the reaction of NH_3 with N_2O_5 , forming AN and N_2O with the same stoichiometry as is observed for ADN synthesis. This reaction was not previously reported in the literature. The operating conditions (sequence of adding the reactants) and temperature were varied systematically, and the ADN yield and the ratio of (unwanted) AN formation to N_2O_5 were measured. The results in Table 2 show that the best ADN yield is obtained by adding N_2O_5 to NH_3 dissolved in chloroform at 261 K (-12°C).

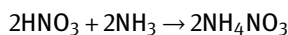
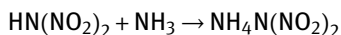
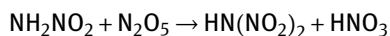
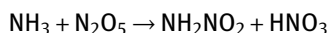
Table 2: Yields of ADN under different reaction conditions and with different molar ratios of AN to N_2O_5 .

No.	Conditions of reaction	Yield of ADN, mol	Mol ratio $n(\text{AN})/n(\text{N}_2\text{O}_5)$
1	NH_3 gas added to N_2O_5	0	1.47
2	Liquid NH_3 added to N_2O_5	0.1	1.34
3	N_2O_5 added to liquid NH_3	0.01	1.00
4	N_2O_5 added to dissolved NH_3 (+7 °C)	0.08	1.32
5	N_2O_5 added to dissolved NH_3 (+20 °C)	0.07	1.18
6	N_2O_5 added to dissolved NH_3 at -22 °C	0.14	1.27
7	N_2O_5 added to dissolved NH_3 (-12 °C)	0.19	1.31

Three types of reactions between NH_3 and N_2O_5 are possible to form AN in different molar amounts, whereas the formation of ADN is possible only by one of the reactions. These results can be explained by the three following chemical equations, R1 to R3:



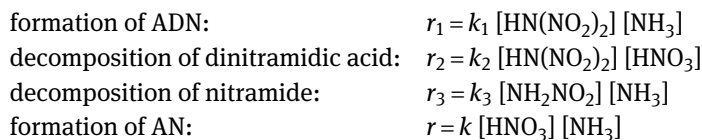
Reaction R2 without any ADN formation is dominant if NH_3 gas is added to the N_2O_5 solution. If NH_3 is added as a liquid, only a small amount of the reactants form ADN due to the reaction R1, but R2 is still the main reaction. In the reverse case, namely the addition of a N_2O_5 solution to liquid NH_3 , R3 is the dominating reaction. By analyzing the gaseous products and the amount of AN formed, the relative contribution of each of these three reactions was identified. The AN and ADN can be separated because AN is not soluble in ethyl acetate. By summarizing the known reactions of NH_3 with N_2O_5 and those of the intermediate products in a reaction scheme, a kinetic model was established for the selectivity of ADN formation and for its dependence on the reaction conditions. Kinetic modeling of the overall reaction scheme led to an equation for the differential selectivity for the formation of ADN. The accuracy of the equation could be confirmed by comparison to experimental measurements. The sequence of events is thus:



First-order reaction rate constants for five partial reactions are expressed and combined to form the model:

first nitration step: $r_0 = k_0 [\text{NH}_3] [\text{N}_2\text{O}_5]$

second nitration step: $r_{0'} = k_{0'} [\text{NH}_2\text{NO}_2] [\text{N}_2\text{O}_5]$



where the species in brackets indicate the molar concentrations of the reactants and products. The decomposition of dinitramidic acid is an autocatalytic reaction accelerated by the presence of nitric acid. Therefore, an excess of ammonia neutralizing the nitric acid is necessary for the formation of ADN.

2.1.3 Formation of Nitramine as an Intermediate and By-Product

There are several publications dating to the 1960s by chemists who came very close to discovering dinitramidic acid and its salts. Although nitramine (nitroamine, nitramide) is not considered a rocket propellant, its formation as an intermediate and unwanted by-product of ADN production deserves some discussion in this book. Nitramine was known long before dinitramidic acid and its salts. It is surprising that chemists working with nitramine in the 1960s did not recognize the potential of forming dinitramidic acid under conditions not much different from those used for making nitramine. They reacted ammonia with nitronium compounds at very low temperatures, but they reported only the formation of nitramide and never recognized the potential formation of dinitramide under very similar conditions. Chemists in the old days lacked the analytical instrumentation to identify dinitramide as a by-product. It has been theorized that by keeping the temperature above 193 K (−80 °C), the unstable nitramide will react with additional nitrating agent to form the desired dinitramide, which is more stable than the mononitramide. The decomposition of nitroamine (nitramine) has been studied in concentrated aqueous perchloric acid, sulfuric acid, and hydrochloric acid over a range of temperatures [45]. In all cases there is a linear correlation between $\log k_1$ and the Hammett acidity function H_0 , with a slope of about 0.35. These results have been interpreted in terms of a rate-determining nucleophilic attack of water upon the protonated nitroamine to give hydroxylamine and nitrous acid, which then react to give dinitrogen oxide. Only after the intermediacy of nitramine in the production of ADN became known did chemists start to take another look at this compound. Nitroamine vapor phase decomposition may also play a role in the decomposition of ADN during its end use in rocket propellants [46].

Nitramide was synthesized for the first time by Thiele and Lachmann in 1894. It is surprising how long it has taken from then until the discovery of dinitramidic acid and its salts. The reaction of ammonia with nitronium salts or N_2O_5 at 77 K (−196 °C) to form nitramide was reported in the early literature [47]. Small (200–300 mg) portions of N_2O_5 cooled to 77 K (−196 °C) were introduced into partially crystallized ammonia under dry nitrogen. The operation lasted 15–30 min. The nitramide was recovered by

extraction of the product with ether and precipitated with petroleum ether or isopentane. Quantities of up to 5 g of nitramide were obtained with yields of 25–30%, based on N_2O_5 . A complete literature review of nitramide chemistry included a few of the reactions (overlooked by early nitramide researchers) leading to dinitraminic acid [48].

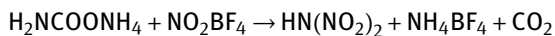
The reaction of HNO_3 with $\text{H}_2\text{NSO}_3\text{Na}$ with a contact time of 10–60 min and a temperature of 238 K (-35°C) gave nitramine with a 70% yield [49]. Best results were obtained by neutralization with NaHCO_3 solution.

The reaction between nitryl salts, including NO_2BF_4 , NO_2ClO_4 , NO_2FSO_3 , $\text{NO}_2\text{Cl}_2\text{SO}_3$, or N_2O_5 , and liquid NH_3 at low temperature (77 K; -196°C) gave nitramine [50, 51]. The product was extracted and determined potentiometrically. The ionization of the nitryl salt into an anion and NO_2^+ decreases in the order $\text{NO}_2\text{NO}_3 > \text{NO}_2\text{BF}_4 > \text{NO}_2\text{ClO}_4 > \text{NO}_2\text{FSO}_3 > (\text{NO}_2)_2\text{S}_2\text{O}_7 > \text{NO}_2\text{S}_2\text{O}_6\text{Cl} > \text{NO}_2\text{Cl}$. The decrease is related to the more or less ionic structure of the nitryl salts and has an influence on the nitramine yield and the product mix.

Only after the intermediacy of nitramine in the production and decomposition of ADN became apparent did chemists go back to take another look at this compound, including efforts to interpret its molecular structure, types of bonding, and mechanisms of decomposition [52]. Nitramine decomposes readily in acidic solutions in the presence of catalysts [53].

2.1.4 Starting with Ammonium Carbamate

As an alternative to ammonia, one cheap starting material is ammonium carbamate, which after reaction with NO_2BF_4 forms the dinitramidic acid [27]:



This reaction is best carried out in acetonitrile as the solvent and at moderately low temperature (233–243 K; -40 to -30°C). The theoretical yield is 15%.

The following method does not use special nitrating agents such as NO_2BF_4 or N_2O_5 , but instead uses common nitrating acid, a mixture of anhydrous nitric acid and sulfuric acid, which should make it even more economical than the previously described methods.

In the previously described syntheses of the dinitramidic acid, use was made of very strong oxidizing systems of the type N_2O_5 or NO_2BF_4 . These are relatively expensive and very moisture sensitive and are not suitable for large-scale industrial preparation of ADN. One advantage of the following method is that dinitramidic acid can be prepared by nitration with a common nitrating acid, such as nitric acid/sulfuric acid, or a corresponding inexpensive nitration system [36]. According to this patent, dinitramidic acid can be prepared by nitration of a compound selected from the group consisting of NH_2NO_2 , $\text{NH}_2\text{COONH}_4$, $\text{NH}_2\text{SO}_3\text{H}$, $\text{NH}(\text{SO}_3\text{H})_2$, $\text{N}(\text{SO}_3\text{H})_3$, or reaction products of ammonia and sulfur trioxide with a nitrating acid mixture selected from the group consisting of nitric acid/sulfuric acid ($\text{HNO}_3/\text{H}_2\text{SO}_4$), nitric

acid/oleum ($\text{HNO}_3/\text{H}_2\text{SO}_4/\text{SO}_3$), nitric acid/sulfur trioxide, nitric acid/perchloric acid, nitric acid/phosphoric acid, nitric acid/diphosphorus pentoxide, nitric acid/acetic acid, nitric acid/acetic anhydride, nitric acid/trifluoroacetic acid, or nitric acid/trifluoroacetic anhydride, at a temperature of 248 K (-25°C) or below to form dinitraminic acid. No aprotic solvent for the nitrating agent is required when nitrating with the nitrating acids, which facilitates the subsequent processing.

Dinitramidic acid, once formed, is then neutralized with a base to form the corresponding dinitramide salt. The base can be ammonia, KOH, hydrazine, hydroxylamine, or an alkylamino.

The concentration of dinitramidic acid in the reacting mixture is constantly monitored, and the base is added only when the $\text{HN}(\text{NO}_2)_2$ concentration has reached an optimal level. The continuous analysis of the reacting mixture can be performed by ultraviolet (UV) spectroscopy.

2.1.5 Starting with Sulfamic Acid

Starting with aminosulfonic acid (sulfamic acid) as starting material, ADN was obtained by the process of neutralization, nitration, ammonolysis, and purification [54]. The purity of the product was characterized by IR, UV, and elemental analysis. The effect of nitration reaction temperature and duration on the yield were investigated, and the operating conditions were optimized. ADN was separated and purified by the adsorption on charcoal, and relative conditions were studied, such as the weight of the charcoal, the speed of extraction, the terminal point of washing, and the method of desorption. The purity of ADN was improved to 99.8% ADN without recrystallization and with a yield of 50%.

Dinitramide, the energetic anion in, for instance, guanylurea dinitramide (GuDN), KDN, and ADN, is produced at Eurenco Bofors using the sulfamate method patented by the Swedish Defence Research Agency (FOI). The synthetic route involves fuming nitric and sulfuric acid. In the FOI process, the sulfamate nitration was terminated by water quenching, and then the reaction solution was neutralized with potassium hydroxide. A pure but weak potassium dinitramide solution was produced by adsorption separation on columns. The dilute KDN solution was concentrated prior to ion exchange to produce ADN, which was finally crystallized from ethanol solution. The whole process generated large amounts of waste. Terminating the sulfamate nitration using minute amounts of water and separating the dinitramide from the strong spent acid using guanylurea or its hydrolysis precursor dicyandiamide to obtain relatively insoluble crystalline GuDN made a great improvement in process economics and ecologic impact [55]. This improvement in the sulfamate method also made it possible to recover and possibly reuse the spent acid as high concentration acids, which was not practically possible by the old method. Because of this changeover, waste generation could be reduced by up to 75%.

2.1.6 Starting with Ammonium Sulfamate

For starting products, it is best to use salts that contain a cation of the same type as the cation of the neutralizing agent that is later used for neutralizing the formed dinitramidic acid to dinitramide salt. Particularly preferred are ammonium and potassium salts of the initial substances (e.g., ammonium sulfamate $\text{H}_2\text{NSO}_3\text{NH}_4$ or potassium sulfamate $\text{H}_2\text{NSO}_3\text{K}$), and the neutralization after the nitrating is carried out with NH_3 and KOH , respectively, which provides a direct path to ADN and KDN, respectively.

Dinitramidic acid is not stable in an acidic environment, and the dinitramidic acid content of the reaction mixture rises to a maximum and then decays. The yield deteriorates if the reaction is not interrupted at the correct time. The acid content is checked repeatedly as the reaction proceeds by samples being taken, diluted, and examined by UV spectroscopy. The dinitramidic acid has a maximum UV absorbance at 285 nm. The reaction is interrupted by the reaction mixture being diluted with water during intense cooling, for instance by pouring it into an ice bath. When the neutralization approaches its terminal point, the solution obtains a characteristic green-yellow color.

Another technique of separating KDN from a reaction mixture neutralized with KOH is to vacuum-concentrate the mixture to a dry powder and extract the powder with acetone. Subsequently, 2-propanol is added to the acetone solution, and the extract is evaporated. First, acetone dissipates, and KDN, having low solubility in 2-propanol, precipitates and can be separated from the solution.

For preparing ADN in small quantities, ammonium sulfamate was added in small portions to a mixture containing 98% sulfuric acid and white fuming nitric acid (WFNA) at 238 to 228 K (-35 to -45°C) in a three-necked round-bottom flask with stirring [56]. The mol ratio of sulfuric acid to nitric acid was varied from 0 to 4, and the yield of ADN formation was measured. The initial yield of ADN increased with increase of the sulfuric acid content in the acid mixture and started to decrease again as the reaction time was extended (Figure 2).

The variation of product yield with change in reaction time and total acid concentration was measured to optimize the process. When the ratio $\text{H}_2\text{SO}_4 : \text{HNO}_3$ was 2 : 1, the optimum yield of 45% was obtained in 20 min. If the reaction time was extended to 30 min, the yield dropped to 35%. It is difficult to explain the shape of the curve obtained with a 1 : 1 ratio. With $\text{H}_2\text{SO}_4 : \text{HNO}_3$ ratios of 1 : 1 and 2 : 1, the reaction mixture became very viscous at temperatures below 243 K (-30°C). The Santhosh et al. publication [57] and Santhosh's PhD dissertation [58] also contain clean UV- and IR-spectra and differential scanning calorimetry (DSC) thermograms of ADN produced using this method. The Santhosh PhD dissertation [58] is a genuinely valuable work with discussion of some of the most pertinent aspects related to the synthesis and characterization of several dinitramide salts. The chemistry, mechanism and kinetics of the formation of dinitramide salts by nitration of deactivated amines were investigated in detail. The effects of the sulfuric acid to nitric acid ratio, reaction duration, trace amounts of water, and temperature on the dinitramidic acid yield were measured and

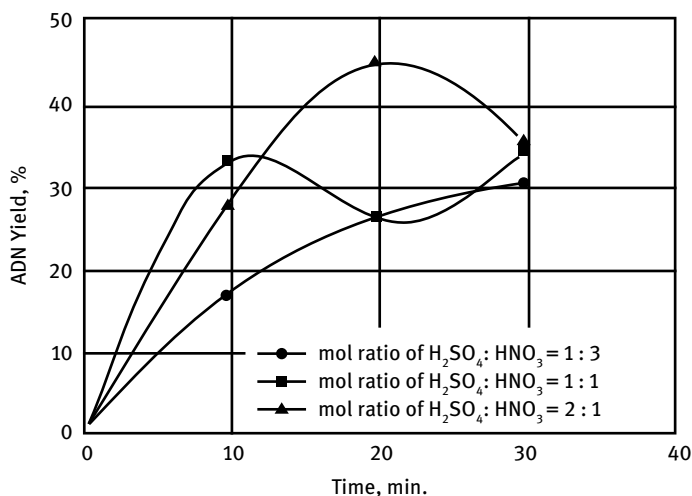


Figure 2: Ammonium dinitramide yield as a function of time for different sulfuric acid to nitric acid ratios. (Reproduced and modified from Santhosh et al. [57]; licensed under Creative Commons License: CC Attribution-Noncommercial-No Derivative Works 2.5.)

optimized. When experiments were carried out using a stoichiometric sulfuric acid to nitric acid mol ratio of 2, a maximum yield of 45% was obtained in 20 min. The acid mixture, however, is very viscous at 233 K (-40°C), hence fast addition of the ammonium sulfamate reactant at a controlled rate becomes very difficult. The evaluation of the thermal and spectral properties along with the adsorption and thermal decomposition characteristics of the dinitramide salts were part of this valuable thesis.

Preparation of dinitraminic acid and its salts by nitration of ammonium sulfamate with fuming nitric acid as a nitrating agent using solid acid catalysts selected from the group consisting of a montmorillonite clay catalyst, metal ion-exchanged K10 montmorillonite clay catalysts, or surface-supported catalysts is supposed to reduce the amount of waste acid generated [59, 60]. The dinitraminic acid is then used for the preparation of ADN by neutralization with ammonia followed by separation of ADN.

Recommended operating conditions for synthesis of ADN from ammonium sulfamate are a nitric acid to ammonium sulfamate molar ratio of 9, a nitric acid to sulfuric acid molar ratio of 6.67, operating temperature of 233 K (-40°C), and reaction time of 45–65 min. [61]. The promised ADN yield is 55% in theory.

The reaction kinetics for the preparation of ADN by the nitration of ammonium sulfamate using mixed acid, followed by hydrolysis, neutralization with ammonia (gas), and extraction using a solvent were studied in order to optimize the yield of ADN [62]. The nitration of ammonium sulfamate was carried out at a temperature of 233 K ($-40 \pm 1^\circ\text{C}$). The yield of ADN is dependent on the formation of dinitramidic acid, an intermediate product formed during the hydrolysis step, and its stability is predom-

inantly dependent on the level of acidity and temperature of the reaction medium. Since the nitration of ammonium sulfamate is sensitive to temperature, the rate of reaction was studied at fixed temperatures with variation of time, keeping all of the other parameters, such as vessel volume, agitator speed, feed rate, etc., constant. In order to find the effect of temperature on the reaction rate and yield, experiments were conducted at other temperatures such as 243 and 223 K (-30 and -50 °C). It was found that the optimum temperature of nitration was 233 K (-40 ± 1 °C) (Figure 3) and that the rate of reaction followed a pseudo second-order process with a rate constant of $0.01113 \text{ min}^{-1}(\text{mol/L})^{-1}$. The reaction time evaluated for 55–60% conversion was about 70–80 min at 233 K (-40 °C).

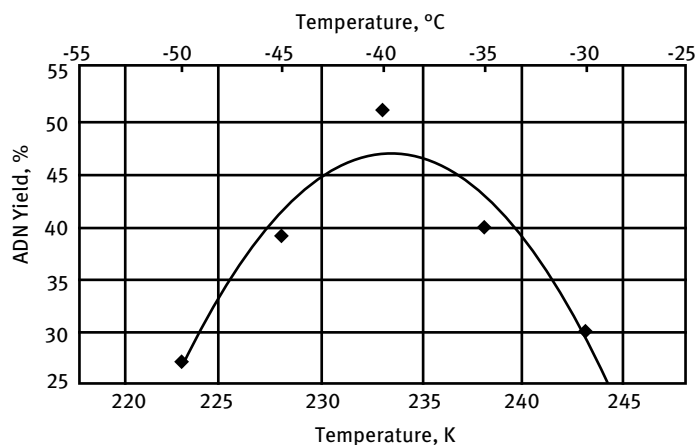


Figure 3: Effect of temperature on the yield of ADN. (Reproduced and modified from Mandal et al. [62]; Cent. Eur. J. Energ. Mater.; licensed under <https://creativecommons.org/licenses/by-nc-nd/4.0/>.)

During the synthesis of ADN, N-nitration is required to form the $\text{N}(\text{NO}_2)_2$ group, in conjunction with the decomposition of sulfamate. Calorimetric studies to assess thermal variations during the nitration of both K and NH_4 sulfamates, applying a number of different nitration agents ($\text{HNO}_3/\text{H}_2\text{SO}_4$, $\text{HNO}_3/\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$, HNO_3/AcOH , and HNO_3 alone), determined that the heat of decomposition of sulfamates in $\text{HNO}_3/\text{H}_2\text{SO}_4$ at 273 K (0 °C) was greater than at 293 K (20 °C), although a similar trend was not observed in HNO_3/AcOH or HNO_3 by itself [63, 64]. The heats of decomposition in HNO_3/AcOH and in HNO_3 were greater than in $\text{HNO}_3/\text{H}_2\text{SO}_4$ because of how the nitration reagent affects the relative contributions of different pathways to the decomposition process. The heat of decomposition in $\text{HNO}_3/\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ was less than that in $\text{HNO}_3/\text{H}_2\text{SO}_4$ because the addition of water inhibits both nitration and decomposition by HNO_3 . Under such conditions, however, a second exothermic peak was observed because of the hydrolysis of potassium sulfamate.

2.1.7 Starting with Potassium Sulfamate

The following is an example for nitration of potassium sulfamate [65]: 45 mL of WFNA and 16 mL of sulfuric acid (95%) were mixed and stirred and then cooled to about 243 K (−30 °C) with a mixture of dry ice and dichloroethane. The potassium salt of sulfamic acid was then added in small portions of 0.5–1 g during very powerful agitation. The viscosity increased significantly as the reaction proceeded when KHSO_4 precipitated. The amount of dinitramidic acid formed was checked by taking off 1 mL of the solution, diluting it to 1000 mL, and examining it by means of a UV spectrometer at 285 nm. The reaction was interrupted to obtain an optimum yield of the acid. At this point, an additional 17 g of potassium sulfamate was added, and the reaction was interrupted after about 20 min. The reaction mixture was poured into a bath containing 150 g of crushed ice and 150 mL of water, and the neutralization with cold KOH solution was immediately initiated during the cooling in the ice bath. When the neutralization approached its terminal point, the solution obtained a characteristic green-yellow color. The neutralization was then continued until the solution was weakly basic. The reaction mixture was evaporated in a rotavapor under vacuum to a completely dry powder. The dry powder was extracted with 10 mL of acetone; 100 mL of 2-propanol was added to the acetone solution, and the mixture was evaporated to dryness. Acetone dissipated first, and potassium dinitramide, having a low solubility in 2-propanol, precipitated. The crystals were filtered off and dried in a hot cabinet at 343 K (70 °C). The yield was 10.7 g KDN, which was 60% of theoretical yield. ADN can be made in the same way by starting out with $\text{H}_2\text{NSO}_3\text{NH}_4$ and neutralizing with NH_4OH . An alternate nitrating agent would be WFNA containing 28% by weight of pure SO_3 . KDN was recovered in yields between 50 and 70%.

Nitration of potassium sulfamate was carried out using a mixture of sulfuric and nitric acid at 243 K (−30 °C) using a sulfuric acid to nitric acid mol ratio of 1:3.5. Comparing the product yield by using ammonium sulfamate instead of potassium sulfamate, it was found that both the yield and purity of the product were better starting with potassium sulfamate [65].

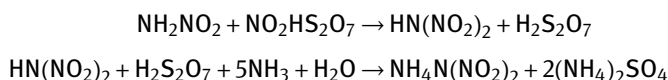
Potassium sulfamate is one of the key precursors for ADN synthesis. Potassium sulfamate as a starting material was prepared in a lab scale from sulfamic acid solution with pH control by the addition of potassium hydroxide solution. The final pH of the solution was 7.5. Crystallization was induced by adding ethanol, methanol, acetone, and isopropanol and their mixtures [66]. Potassium sulfamate was then nitrated with nitric acid and neutralized with potassium hydroxide to make potassium dinitramide. Potassium dinitramide was converted to ADN. The effects of the quality of potassium sulfamate on the ADN yield and purity were evaluated by IR and UV analysis, X-ray diffraction (XRD), and DSC–thermogravimetric analysis (TGA). Potassium sulfamate made with acetone and/or a mixture of acetone and isopropanol, which was ground to 20 μm , showed the highest yield, which was more than 48%. The ADN purity obtained from the small-batch potassium sulfamate was better than that obtained from a commercial product. Crystallinity, porosity, and pore size of the lab-prepared

potassium sulfamate were compared with those of a commercial potassium sulfamate sample.

Crystallinity, porosity, and pore size are critical for potassium sulfamate to participate in the nitration reaction with rapid dissolution at low temperature because the reaction is reversible and the products can be destroyed in a strong acid; the reaction must be completed as quickly as possible. Five different solvents were evaluated for the synthesis of potassium sulfamate ($\text{H}_2\text{NSO}_3\text{K}$) to obtain different crystal properties [67]. The nitration of potassium sulfamate with WFNA was carried out at 238 K (-35°C). The nitration reaction with the gradual addition of potassium sulfamate powder was performed with very strong agitation to minimize extraction of by-products such as KHSO_4 . The neutralization with potassium hydroxide solution is exothermic and requires cooling. The metathetical reaction of KDN with ammonium sulfate was carried out in aqueous solutions. The solutions were concentrated, potassium sulfate was precipitated by the addition of acetone, and the ADN was extracted with ethyl acetate. The yield and purity of ADN depend on the quality of potassium sulfamate. Of the five potassium sulfamate samples, the maximum ADN yield (57.3%) was achieved using potassium sulfamate that had been obtained by precipitation by the addition of acetone. This ADN had a purity of 99.2%. Commercial potassium sulfamate did not give anywhere near such good results.

2.1.8 Starting with Nitramide

Nitramide (nitramine) is unstable and is not available commercially. It would have to be prepared by a separate process immediately prior to the synthesis of ADN. Nitration of nitramide leads to dinitraminic acid, which can be neutralized to form the ADN salt. ADN was prepared according to the method described by Bottaro et al. [27].



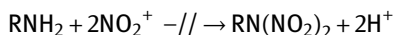
Separation of ADN from the reaction mix is difficult. To separate ADN from the reaction mixture obtained in the reaction between $\text{NO}_2\text{HS}_2\text{O}_7$ and nitramine in acetonitrile at 233 K and subsequent neutralization with aqueous ammonia, the following procedure was applied [28], consisting of separation of the unwanted solid that precipitated during the reaction, evaporation of the acetonitrile solution filtrate, extraction of the obtained solid with isopropanol, and evaporation of the isopropanol solution. Recrystallization from boiling ethyl acetate resulted in crude ADN with adhering ethyl acetate solvent. The purity of the products was examined using IR, TGA, differential thermal analysis (DTA), and elementary analysis. At best, the product contained 89% ADN with occluded ethyl acetate.

Initial attempts to nitrate nitramine H_2NNO_2 with a mixture of nitric acid and acetanhydride or dinitrogen pentoxide were unsuccessful. Treating nitramide with

a mixture of trifluoroacetic anhydride and nitric acid gave only very low yields of dinitramide. Thus, nitryl tetrafluoroborate, nitryl fluorosulfonate, nitryl hydrogen pyrosulfate, and nitryl pyrosulfate were tested as nitrating agents [68]. The best results were achieved with nitryl tetrafluoroborate and nitryl fluorosulfonate in acetonitrile at 253–273 K (–20 to 0 °C), which nitrated nitramine in only 5 min in very good yields. Extending the reaction time did not improve the yields. In methylene chloride or ethyl acetate as solvents instead of acetonitrile, the yield was substantially reduced. In hexane it was zero.

2.2 Production of Ammonium Dinitramide from Organic Starting Materials

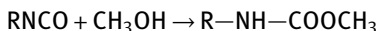
An organic chemistry route prepares a doubly nitrated organic amine (alkyl-dinitramine) first followed by hydrolysis of the R–N bond and liberation of the dinitramide anion. Direct dinitration of primary amines is not always possible.



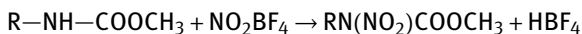
Most often, one of the hydrogen atoms on the amino group is protected by an inert group (inert to oxidation), which is later hydrolyzed to make space for the second nitro group. One should be concerned about safety when mixing any organic chemical with strong oxidizers such as dinitrogen pentoxide or nitronium salts. The reaction may turn into a hypergolic ignition. Many of the intermediates are potentially explosive.

2.2.1 Starting with Isocyanates.

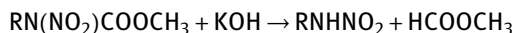
In practice, synthesis started with aliphatic isocyanate reacting with methanol to form an alkylamino acid ester



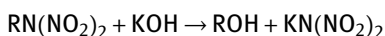
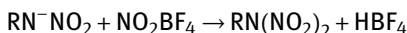
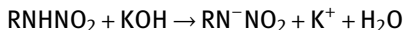
could be nitrated in the first stage



hydrolyzed to the alkylmononitramine

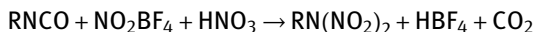


converted to a salt, and nitrated in the second stage to form an alkyl-*N,N*-dinitramide [69].



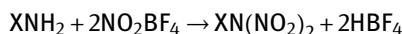
KOH is shown as an example, but other strong bases can be used as well. This multistep route can be performed as a one-step reaction by reacting the aliphatic iso-

cyanate with stoichiometric quantities of NO_2BF_4 and HNO_3 in acetonitrile as the solvent. A facile conversion of aliphatic isocyanates to *N,N*-dinitramines is the treatment of isocyanates with a mixture of nitronium fluoroborate and nitric acid in acetonitrile, giving fair yields and simplifying the existing synthesis [18, 21].

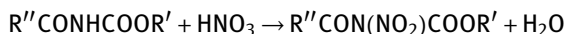
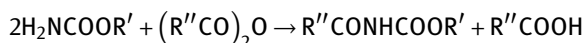


The yield in this reaction was only 1–35% of theory, depending on the type of alkyl group in the isocyanate. The best yield (35%) was obtained with *n*-butyl isocyanate. The second-best yield (30%) was obtained with methyl isocyanate.

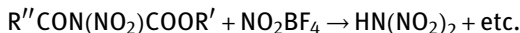
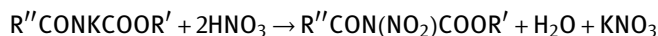
Another method for production of alkyl dinitramides is also an organic synthetic route. The amine in this case is derivatized with a group X such as in urea or bound to an electron-draining group such as $-\text{COOH}$ or $-\text{COOCH}_3$. This requires a stronger nitrating agent such as NO_2BF_4 or N_2O_5 .



Another method for producing ADN is to first prepare an *N*-(alkoxycarbonyl)-*N*-nitroamide compound. The *N*-(alkoxycarbonyl)-*N*-nitroamide may be formed by first mixing the corresponding alkyl carbamate with an anhydride of an alkyl carboxyl organic acid and then adding nitric acid to the reaction mixture [33, 70].



or



If a salt of the *N*-(alkoxycarbonyl)-*N*-nitroamide is to be formed first, a base (e.g., KOH) is added until the pH reaches about 7–10.

2.2.2 Starting with Urethanes

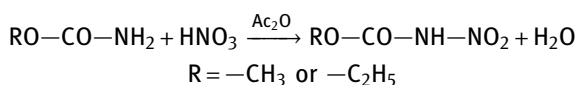
The reaction of *N,N*-dinitro urethanes, *N,N*-dinitrobenzamide, or *N,N*-dinitro-*p*-toluenesulfonamide with ammonia produced ADN in a yield of 44–85% [71].

For preparing KDN, 50 mL of acetonitrile was introduced into a 250-mL three-necked round-bottom flask equipped with an argon inlet, thermometer, stir bar, and gas outlet [72]. The flask and its contents were cooled to 235 K (–38 °C) in a liquid nitrogen/acetonitrile bath. To the cooled contents was then added 4.7 g (0.035 mol) of nitronium tetrafluoroborate. As soon as the temperature had re-equilibrated, 3.0 g (0.018 mol) of dipotassium nitrourethane was added in small portions such that the temperature did not exceed 238 K (–35 °C). The resulting suspension was stirred while allowing the temperature to rise to 254 K (–19 °C) until no further gas evolution was detected by visual inspection. The contents were then recooled to a temperature of

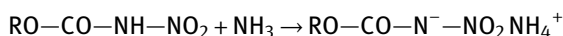
about 235 K (−38 °C), and a solution of 5.9 g (0.106 mol) KOH in 50 mL of ethanol was slowly added while monitoring the temperature such that it did not rise above 253 K (−20 °C). The contents of the reaction flask were then passed through a pad of silica gel on a glass frit, washed with several portions of ethyl acetate, and the combined filtrate was evaporated in vacuo. The resulting pale yellow solid, having a melting point of 381 K (108 °C), was pure potassium dinitramide (260 mg) as determined by ion chromatography.

2.2.3 Starting with Alkyl Carbamates

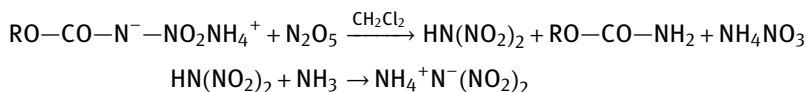
Ethyl or methyl carbamate can be nitrated using $\text{Ac}_2\text{O}/\text{HNO}_3$ to the corresponding mononitro compound [32].



followed by treatment with ammonia under anhydrous conditions to produce the ammonium salt of ethyl or methyl *N*-nitrocarbamate

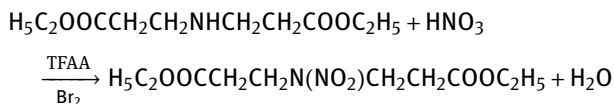


which was further nitrated using nitronium salts or N_2O_5 and then treated with ammonia to give ADN, thus regenerating the starting compound $\text{RO}-\text{CO}-\text{NH}_2$ in the final step:

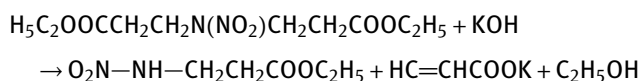


The first step of nitration was performed at <281 K (<8 °C), while the second step of nitration was performed in CH_2Cl_2 at 225 K (−48 °C) using N_2O_5 , and an overall yield of 70–76% was obtained, which is quite good.

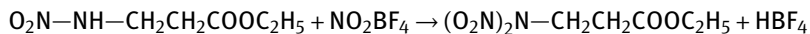
In a method used by Chung and Sim [34, 35], nitration of the diethyl-4-azaheptanedioate using HNO_3 -trifluoroacetic anhydride (TFAA) gave *N*-nitro-4-azaheptanedioate



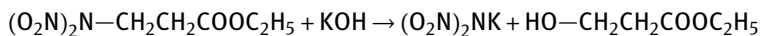
which was then base-treated in a retro-Michael reaction to give ethyl 3-nitraminopropanoate



The nitramino compound was treated with NO_2BF_4 at below 281 K (+8 °C) to give a dinitramino compound

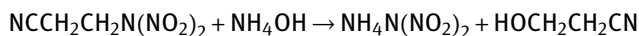
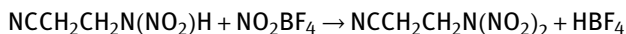
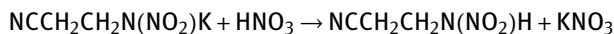
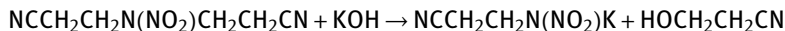
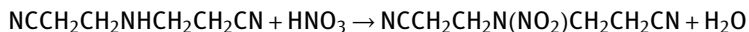


and subsequently reacted with base to give dinitramide salts. The yield was 30% of theory.



Lukyanov et al. [73] developed a similar method for the synthesis of dinitramide salts in direct and retro-Michael-type reactions. $\text{HN}(\text{NO}_2)_2$ adds readily to $\text{CH}_2=\text{CHCOR}$ (**I**; $\text{R} = \text{H}, \text{Me}, \text{Ph}$) to give 53–85.5% $\text{RCOCH}_2\text{CH}_2\text{N}(\text{NO}_2)_2$ (**II**; same R), but did not react with $\text{CH}_2=\text{CHCN}$ or methyl acrylate **I** ($\text{R} = \text{OMe}$). Compound **II** ($\text{R} = \text{MeO}$) was prepared in four steps from $\text{MeO}_2\text{CCH}_2\text{CH}_2\text{NH}_2\cdot\text{HCl}$. Treating **II** ($\text{R} = \text{H}, \text{Me}, \text{Ph}, \text{MeO}$) with bases gave dinitramide salts in a 66–83% yield.

Instead of the ethyl ester of 4-azaheptanedioic acid, one can use the nitrile of the same acid. Such a method for preparation of ADN by nitration of bis(2-cyanoethyl)amine by nitric acid in acetanhydride, followed by decyanoethylation of 3-*N,N*-dinitraminopropanitrile by a strong base and further nitration with NO_2BF_4 , is shown below [35]. 3-*N*-Nitro-bis(2-cyanoethyl)amine could also be obtained by the oxidation of the corresponding *N*-nitroso compound:

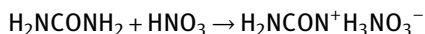


The reaction was carried out at 381 K (108 °C). The yield was 60% of theory.

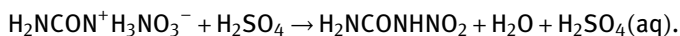
Ammonium *N*-nitro carbamate ethyl ester was synthesized from ethyl carbamate in $\text{HNO}_3/\text{H}_2\text{SO}_4$, and then, using N_2O_5 as the nitrating agent, ADN was prepared in a 70% yield [74]. It was recrystallized to yield a white hygroscopic powder with a melting point of 363 to 365 K (90 to 92 °C). Its structure was identified by elemental analysis, IR spectrum, and UV spectroscopy. The main factors such as reaction medium, reactant ratio, and reaction temperature were optimized.

2.2.4 Starting with Urea

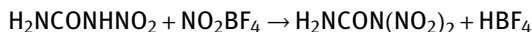
Hatano et al. [30, 31, 75] invented a clean and safe method for the formation of ADN starting with the preparation of urea nitrate from urea and dilute nitric acid:



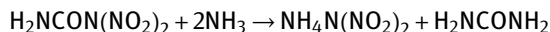
As the next step, nitrourea was made by reacting urea nitrate with sulfuric acid:



Dinitrourea (DNU) was made by reaction of nitrourea with a nitrating agent:



Neutralizing the formed DNU with ammonia gave ADN (and urea, which can be recycled):



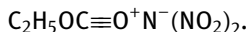
The reaction was carried out at 233 K (−40 °C) in acetonitrile as a solvent. The yield of this method varied between 5 and 20% depending on the reaction temperature and reaction time. The yield in the last step of the preparation was ~15% based on nitrourea consumed. See also [76].

2.2.5 Starting with Urethane

A similar method for preparation of potassium dinitramide from urethane and acetyl nitrate proceeded as follows (although the resulting KDN product leaves a lot to be desired with respect to purity) [72]. In a jacketed 500-mL four-necked round-bottom flask equipped with a thermometer, top stirrer, and drying tube, 22.3 g (0.25 mol) of ethyl carbamate (also called urethane) was dissolved in 25 mL of dichloromethane (AR grade). The flask and its contents were immediately cooled to 263 K (−10 °C) with a refrigeration unit. To the cooled contents was then added an acetyl nitrate solution (prepared from 94.5 mL = 102 g = 1 mol of acetic anhydride and 35 mL = 51.8 g = 0.74 mol of 90% nitric acid), not allowing the temperature to exceed 298 K (25 °C). The addition took roughly 1 h, and after an additional hour at 263 K (−10 °C), the reaction was monitored by gas chromatography for the disappearance of urethane and subsequently the consumption of nitrourethane. When the reaction was judged to be complete, a strong solution of KOH in ethanol was added between 268 and 278 K (−5 and +5 °C). Enough of the base solution was added so that the pH was 8.18 (potentiometric). Following this addition, the reaction was stirred for 30 min and then filtered to remove the solids that had precipitated. The filter cake was washed with several portions of ethyl acetate, the filtrate and washings were combined, and the solvents were removed *in vacuo*. The yellow residue contained much acetic acid and acetic anhydride, which were removed by evaporation in a vacuum at ambient temperature at about 1 mm Hg. The resultant pasty solid was recrystallized several times from isopropanol to remove much of the potassium acetate and then from acetonitrile, yielding 4 g of potassium dinitramide, still contaminated with much potassium acetate. This sample was determined to be ~13% potassium dinitramide by ion chromatography.

An intermediate product prior to hydrolysis is *N,N*-dinitrourethane, $\text{C}_2\text{H}_5\text{OC}(=\text{O})\text{N}(\text{NO}_2)_2$, a precursor to ADN. In an effort to improve ADN yield,

its molecular structure was computed at the *ab initio* HF/6-31G level [77]. No structural evidence was found that *N,N*-dinitrourethane exists in the ionic form



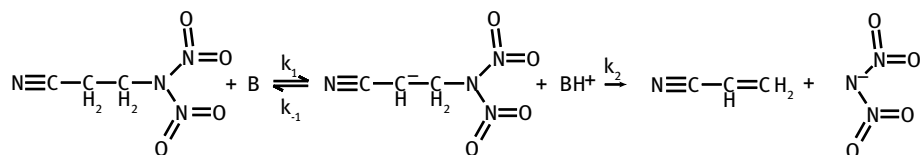
The reaction of *N,N*-dinitrourethane with NH_3 passed through a transition state that is consistent with a concerted substitution in which $\text{N}^-(\text{NO}_2)_2$ is the leaving group.

2.2.6 Starting with Nitriles

In the synthesis of dinitramide from organic dinitramines of the type $\text{X}-\text{CH}_2-\text{CH}_2-\text{N}(\text{NO}_2)_2$, one will want to select alkyl rests where X consists of electron-withdrawing groups activating the α hydrogen atoms to nucleophilic attack, thus facilitating the creation of an anionic center in the β position to the dinitramine moiety [78]. The basic concepts have been tested in model reactions of β -substituted derivatives of *N*-alkyl-*N*-nitrotoluene sulfonamides with bases and were confirmed by the decyanoethylation of *N,N*-dinitro- β -aminopropionitrile.

Another method was developed to synthesize ADN from 3-aminopropionitrile [79]. The condensation and second nitration were identified as the critical steps of ADN synthesis.

Similarly, a method of ADN preparation from acrylonitrile or 2,2-dicyanoethylamine was developed, and the optimum reaction conditions were determined [80]. According to spectrophotometric data, decomposition of 2-(*N,N*-dinitroamino)propionitrile in aqueous buffer solutions (pH 9.5–11.5) at 290–318 K (17–45 °C) quantitatively yields dinitramide anion [81].



The process follows the general base catalysis pattern in terms of the E1cb mechanism, with deprotonation of the substrate as the rate-determining step. The reaction conforms to the Brønsted equation with a coefficient *b* close to unity.

2.3 Separation of Dinitramide Salts from Reaction Product Mixture

There are several ways the desired dinitramide salts can be separated from the mixture of unreacted reagents, products, and by-products. The cost of the separation process may determine the overall economy of ADN production. These separation methods can be used for dinitramidic acid and dinitramide salt solutions obtained from a variety of different processes, regardless of whether they started with inorganic or organic reactants.

2.3.1 Separation by Extraction

The dinitramide salt product may be extracted and separated from the by-product by solvent extraction. Typical solvents that may be used for solvent extraction include acetone, isopropanol, *t*-butanol, ethyl acetate, and tetrahydrofuran. The dinitramide salt can also be extracted by solutions of ammonia in chlorinated hydrocarbons such as $\text{CH}_3\text{Cl}_2\text{CHCl}_3$ and CCl_4 , as well as a mixture of ethyl acetate and *n*-butanol.

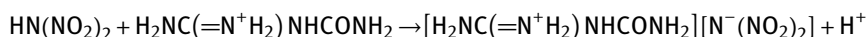
The solution containing the dinitramide salt product can then be evaporated to dryness in a rotavapor under vacuum.

The dried raw product residue may then be purified by redissolving and recrystallizing. For example, when *n*-butanol is used as the solvent, from about 5 mL to about 15 mL of *n*-butanol per gram of residue is used to dissolve the residue with heating to about 333–353 K (60–80 °C), after which the solution is cooled to about 258 K (–15 °C) and chloroform is added to precipitate the dinitramide salts as white crystals.

A useful method to separate impurities from the ADN product and to determine its purity is extraction with methyl isobutyl ketone [82]. The results showed that methyl isobutyl ketone is not only an effective solvent to separate the AN impurities but is also a good medium to chemically titrate the ADN. Both precision and accuracy of the purity analysis are good; the coefficient of variation is not more than 0.19%, and the relative deviation of the results to be determined with two methods is not more than 0.25%.

2.3.2 Separation by Precipitation

One separation method is to isolate the dinitramide in the form of a sparingly soluble salt that precipitates and can be separated by filtration and later converted to other dinitramide salts. The least soluble salt best suitable for this purpose seems to be guanylurea dinitramide (GUDN).



This method was patented [83, 84]. The addition of guanylurea gives a precipitate of GUDN. The precipitate is easily separated and can be used as starting material for preparation of other dinitramide salts, such as KDN and ADN. The guanylurea ion can be formed in situ in the process by cyanoguanidine that reacts and hydrolyzes within the reaction mixture.

Cyanoguanidine is not soluble and has to be added as a slurry. The remaining spent acid can be reprocessed for recovery of acid for preparation of a new nitrating acid mixture. This method allows the amount of waste to be reduced significantly, and partially spent acid can be recovered for preparing new nitrating acid. The main difference between the invention described in patent WO2005070823 and prior art is that the reaction mixture is not neutralized after a certain reaction time, but instead a cation is added, which forms an insoluble salt with the dinitramide anion that precipitates in the acidic reaction mixture.

In one example, a batch of 12 kg ammonium sulfamate was nitrated in a batch reactor with nitrating acid consisting of white fuming HNO_3 and 100% H_2SO_4 . The weight ratio of $\text{HNO}_3/\text{H}_2\text{SO}_4$ was 7 : 3, and the weight ratio of substrate/nitrating acid was about 1 : 5. The temperature was kept between 313 and 248 K (+40 and -25°C) during nitration, which lasted about 30 min. Then the reaction mixture was poured into a mixture of 6 kg cyanoguanidine in about 60 L of water. The aqueous mixture had a temperature of 288 K (15°C) and at this temperature was a slurry of partially dissolved and partially suspended cyanoguanidine. When the reaction mixture was mixed with the slurry, the temperature quickly rose to about 343 K (70°C), and after a short while a precipitate began to form. The mixture was cooled to 298 K (25°C), after which the precipitate of GUDN was filtered off and washed with water.

Part of the recovered GUDN was used for preparation of potassium dinitramide (KDN). A solution containing about 30 mass-% water, 60% ethanol, and 10% KOH was heated to about 323 K (50°C), and GUDN was dissolved in this solution during continued heating. After about 15 min, the solution contained 30 mass-% of dissolved GUDN, and cooling of the solution was started. KDN began to crystallize, and the mixture was further cooled to 288–293 K ($15\text{--}20^\circ\text{C}$), after which the crystallized KDN was filtered off and washed with ethanol. The mother liquor from crystallization contained guanylurea and was kept for recovery and later use in the process for precipitation of the dinitramide ion in nitration.

In a variation of this experiment, the experiment was repeated, with the difference that the reaction mixture from nitration was poured into an aqueous solution of guanylurea nitrate. The solution contained 15 mass-% of guanylurea nitrate and was cooled to about 285 K (12°C). The temperature rose when the reaction mixture was poured into the solution and the mixture was cooled to 298 K (25°C). Precipitation of GUDN started immediately, and the precipitate was filtered off and washed with water.

2.3.3 Separation by Adsorption

Conventional methods for separation of ADN from reactant mixtures and by-products involved precipitation, drying, extraction, and recrystallization from different solvents. This is a time-consuming and costly process. Adsorption techniques promise a more effective method of separation at a relatively lower cost in comparison to solvent extraction procedures for many materials, but the most economical method is precipitation. By using adsorption one will end up with ADN in a very dilute solution and getting rid of all water is very costly. ADN can be adsorbed on a variety of adsorbents such as molecular sieves, activated alumina, silica gel, and activated charcoal. The adsorbed ADN is then eluted with a suitable eluting solvent.

A different method (different from other patent applications) for separating the dinitramide salts is the passing of an aqueous solution of a mixture of salts formed in the neutralization through a column filled with an adsorbing agent, which selectively adsorbs the dinitramide salt [36]. The adsorbing agent can be activated carbon [85],

powdered activated charcoal (PAC) or granular activated charcoal (GAC) [58], silica gel, or zeolites. The adsorption of ADN from aqueous solutions on GAC follows monolayer adsorption because the data fit in a Langmuir isotherm. The dinitramide salt can be eluted from the adsorbing agent with hot water and/or a polar organic solvent such as acetone, acetonitrile, 2-propanol, or other lower alcohols.

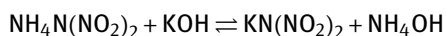
Contamination by a large number of inorganic salt by-products is inevitable in the synthesis of ADN by the mixed-acid method. ADN can be effectively separated and purified by adsorption with activated charcoal [86]. Different kinds of activated charcoal, adsorption solvent, and desorption solvent, as well as concentration and method of adsorption were tested, and the optimum operating conditions were determined. Pure ADN with greater than 99.5% assay was prepared by this method.

2.4 Purification of Ammonium Dinitramide

ADN that has been prepared by a variety of methods can be purified by a combination of recrystallization and adsorption. Several purification processes for precipitated ADN particles have been evaluated, including repetition extraction, activated carbon adsorption, and low-temperature extraction [87, 88]. The purifying methods helped improve the chemical purity as analyzed by Fourier-transform infrared (FTIR) spectroscopy and UV-visible spectroscopy in addition to ion chromatography (IC) analyses. Among the purification processes, adsorption was found to be the best method, resulting in a final purity of 99.8% based on analysis by IC.

2.4.1 Cation Conversion Among Dinitramide Salts

Once one dinitramide salt is obtained, and the dinitramide salt of a different base is desired, the cation can be exchanged by metathetical reactions, e.g.



In the case of the reaction above, ammonia can be removed by sparging, and the equilibrium will be shifted to the right.

Dinitramide salts have good solubility in several organic solvents. Selective extraction will allow the separation of dinitramide salts from reaction mixtures and purification of the salts by recrystallization.

ADN can be prepared from KDN by mixing an aqueous solution of KDN with an aqueous solution of $(\text{NH}_4)_2\text{SO}_4$, whereby a white precipitate of K_2SO_4 is formed. 2-propanol is added to the mixture, and the K_2SO_4 precipitate is separated. The decanted solution is evaporated until ADN precipitates. If necessary, the product from the evaporation can be redissolved in 2-propanol and poured into a non-polar solvent, e.g., petroleum ether, whereby a purified grade of ADN precipitates and can be separated [36]. ADN can also be prepared from KDN by mixing KDN and $(\text{NH}_4)_2\text{SO}_4$

in 2-propanol and heating the mixture, and optionally reflux-boiling the mixture until the ammonium sulfate has dissolved. The solution is then cooled, whereby K_2SO_4 precipitates and can be separated. The remaining solution is concentrated by evaporation, and the concentrate is poured into a non-polar solvent, e.g., petroleum ether. A pure form of ADN precipitates and can be separated.

Another method to convert one dinitramide salt into another is by ion exchange on an ion exchange resin.

There are several patents in the literature describing the preparation of various dinitramide salts of less common bases, starting with either ADN or KDN. Of particular interest are the dinitramide salts of guanidine, aminoguanidine, triaminoguanidine, guanylurea, and other nitrogen-rich bases that can be used as ingredients in gas generators for airbag inflation (see *Encyclopedia of Liquid Fuels*, chapter “Amides”).

A simple method for converting ADN or KDN into guanidinium dinitramide or GUDN by metathetical reaction is described in [89]. This is done by mixing a concentrated aqueous solution of ADN with a concentrated aqueous solution of an organic ammonium salt whose anion is either OH^- or CO_3^{2-} , which is capable of taking up a proton from the ammonium ion of ADN and forming an ammonium salt. Ammonia (and possibly carbon dioxide) is driven off from the solution, as well as a certain amount of water to maintain a concentrated solution. The organic dinitramide salt is then precipitated by cooling the solution and is recrystallized if needed.

2.5 Morphology and Particle Shapes of Ammonium Dinitramide

The as-produced ADN is in crystalline form, and the particle size and shape depend on the rate of cooldown during crystallization. This may not be the optimum particle size and shape for incorporating ADN in solid propellants. ADN normally grows in long, flat blades from a variety of organic solvents. However, these shapes have a large length/diameter ratio and do not allow a dense, cohesive packing in a composite solid propellant. Friction between the flat crystals does not allow the powder to be poured out of containers as a free-flowing powder. Alterations of crystal shape can be achieved by changing the conditions of crystallization from either a melt or a solution. This can be done by changing the temperature, rate of cooling, pressure, solvent, or supersaturation and seed crystals. Recrystallization is necessary to improve the physical properties of ADN, its burning characteristics, and its chemical purity.

2.5.1 Recrystallization of Ammonium Dinitramide Without Additives

The simplest approach would be to recrystallize the salt and change the solvent and the rate of cooling in order to achieve ADN crystals with a more favorable aspect ratio. In one such investigation, 1-propanol and 1-octanol were used as candidate solvents [90]. Cooling crystallization experiments were carried out under different

process conditions using 1-propanol and 1-octanol as solvents to see how they influenced the crystal morphology [91]. Supersaturation during the process was determined, and the crystal shapes and the thermal behavior were characterized. The experimental work was supplemented by computer simulations examining the vacuum morphologies. The relevant growth-faces were identified by comparing the calculated morphologies to the crystals collected from the crystallization dish. Force-field methods were used to determine the influence of the polarity of the solvent and the interaction energies of the solvents with the ammonium ion, the dinitramide ion, and the crystal faces. The crystal growth behavior was described step by step while taking the molecular structure of the crystal faces into account. From the natural cooling experiments, 1-propanol turned out to be the most promising solvent for obtaining crystals with a low aspect ratio. The crystallization of ADN from 1-octanol resulted in differently shaped crystals depending on the level of supersaturation during the process. At low supersaturations, plate-shaped crystals with a compact base area were obtained. A key parameter during particle formation by crystallization is the supersaturation as the driving force for kinetic processes like nucleation and growth. Therefore, its control is indispensable for monitoring and optimizing ongoing crystallization processes to achieve reproducibility and product quality. Before a supersaturation-controlled crystallization process can be run, a suitable method for the inline real-time measurement of the concentration has to be evaluated for the material system. High supersaturations lead to rod-shaped crystals but with a rough surface [92, 93]. Plate-shaped crystals resulted from all crystallization experiments with 1-propanol as solvent. Different cooling rates did not change the morphology, and that was recrystallized from three different alcohols was thoroughly characterized by scanning electron microscope (SEM) imagery, XRD, DSC, and TGA [90].

Repeated recrystallization of ADN may actually increase its AN content instead of purifying the material. ADN received from Eurenco Bofors in Sweden with a purity >99% contained the following impurities: K^+ , guanidinium⁺, NO_3^- , H_2O , Si. Instead of recrystallization, the users decided on *in situ* filtering of the finished product (FLP-106) to remove insoluble contaminants that might clog the rocket injectors.

The influence of solvents on ADN crystal shapes and morphology was investigated using a combined experimental and molecular dynamics simulation approach [94]. Scanning electron microscopy showed that ADN recrystallized from acetone, propanol, dimethyl sulfoxide, or ethanol exhibited a lamellar structure, in contrast to the polyhedron structure obtained with isopropanol/NaF. XRD scans revealed that ADN crystals are mainly composed of six crystal faces (010, 011, 110, 100, 121, 031), and acetone, propanol, dimethyl sulfoxide, and ethanol resulted in crystals in which growth was preferentially at face (100). Molecular dynamics computations indicated that the accessible surfaces and lattice energy vary with the crystal faces. The interaction energy between solutions and crystal faces was dependent on both crystal faces and solution components, as was the attachment energy. Based on XRD data, a larger relative standard deviation of the growth rate

of the crystal faces resulted in a lamellar structure, while a smaller relative standard deviation gave more homogeneous growth rates that resulted in polyhedron crystals.

The solubilities of ADN in *n*-butanol, isopropanol, and mixtures of water and isopropanol (volume ratios of 1:10 and 1:6) were measured by a dynamic method, and the solubility data were fitted by the Apelblat equation and λh equation, respectively [95]. The effects of stirring speed and cooling rate on the metastable zone width of ADN in *n*-butanol and isopropanol and the effects of different supersaturation on the induction period were investigated. The results showed that the Apelblat equation and the λh equation can describe the solubility of ADN accurately. The width of the crystalline metastable zone narrows with a decrease of the cooling rate and an increase of the stirring speed. The crystallization induction period shortens with an increase of supersaturation. Using the self-consistent Nyvlt equation and three-dimensional (3D) nucleation theory, combined with the metastable zone width and induction period data, the nucleation order m was calculated to be about 4, and the solid-liquid interfacial tensions of ADN in *n*-butanol and isopropanol were 0.235 and 0.191 mJ/m² for homogeneous nucleation, and 0.070 and 0.067 mJ/m² for heterogeneous nucleation, respectively.

A solvent/antisolvent method can be used for recrystallizing ADN and changing the morphology of the rapidly precipitated crystals [96].

2.5.2 Recrystallization of Ammonium Dinitramide with Additives

Another promising approach is to recrystallize the material from a solution in the presence of surfactants or additives. Better yet, instead of recrystallizing (unless it is done for purification), one can apply the additives when ADN is first made and the precipitates from the reaction mix. Some additives act as contaminants, inhibiting growth through specific surfaces of a crystal, thereby changing the crystal habit and its morphology. Such additives can also stabilize polymorphs or can inhibit nucleation of polymorphs. The crystal habit modifiers must be effective in small amounts, which minimizes the risk of contaminating the crystals, modifying other critical properties of the ADN crystals.

Attempts have been made to modify the habit of crystalline ADN from blades to short prisms by controlling its growth behavior in isobutanol or methyl acetate using tailor-made additives [97]. A series of long-chain alkyl diamines, amino acids, and aromatic diamines were tested as additives. The strategy was unsuccessful, but in the process, a new compound, butanediammonium dinitramide (BDDN), was isolated and characterized. BDDN has a similar space group to ADN, and its habit is sensitive to growth conditions, crystallizing in short prisms and two types of blades. For these reasons, the growth behavior, surface, and packing structure of BDDN were analyzed in the hope that these might give some clues to ADN habit modification. It was also observed that ADN can have a “twinned prism” habit. These crystals possess a much lower aspect ratio than the blades and exhibit an unusual threefold twinning. To com-

plement the study, a texture analysis study of ADN spherulites (small spheres made up of millimeter-to-micron-sized ADN crystallites) was made. Using XRD and mathematical analysis, it was determined that the crystallites in spherulites do not adopt any obvious preferred orientation.

A French patent contains a long list of calcium or magnesium salts of carboxylic acids as modifiers for ADN crystallization [98–100]. Among others, a mixture of calcium nitrate and finely divided calcium carbonate is said to improve the crystal shape. Crystals prepared in this manner were also less hygroscopic than normal ADN. As solvents, mixtures of ethanol and methanol were used. Calcium and magnesium salts that are soluble in ethanol and methanol were recommended as growth modifiers. The anions of the salts did not disturb the crystal growth of ADN. Different temperature profiles (linear, stepped profiles) were tested. The aspect ratio of crystals could be reduced from 10 (crude ADN) to 1.5–5. The modified crystals were used in an energetic formulation containing ADN, hexogen, aluminum, and a binder material. The processability of the formulation was improved by reducing the viscosity from 1020 Pa · s (crude ADN) to 560 Pa · s (improved crystals).

Crystallization by spontaneous nucleation and crystal growth can be used to purify ADN, starting from a saturated solution and with cooling in the presence of a protic solvent with a viscosity of $\eta = 250$ cPs, especially 450–550 cPs [101]. A preferred solvent is a mixture of glycerol and 1,4-butanediol. The resulting crystals have a median diameter of $\sim 100 \mu\text{m}$.

2.5.3 Prilling of Ammonium Dinitramide

Prilling (converting irregularly shaped crystals to spherical particles or beads) can be done by spraying molten ADN into a suspension with an inert liquid or allowing it to free-fall in a tall prilling tower in dry air.

In a prilling tower, needle-shaped ADN powder is melted, and it cools when falling through the tower against an updraft of cold air. This enables production of ADN prills of good quality. However, the particle size cannot be altered. There are concerns about the safety of the process because of the high temperature in the prill tower.

ADN, as manufactured, is difficult to formulate since it forms crystals of excessive length, making it process poorly in propellant formulations, raising their viscosity and making them difficult to cast. The cooling of molten droplets to form tiny spheres may be used to manufacture the ADN in a more suitable form for processing, but prilling involves melting the ADN and then stirring or spraying. Stabilizers are not needed as long as ADN is not kept in the molten state for prolonged time. Stabilizers are not typically used when prilling is done quickly. Particulate oxidizer requirements have led to the demand for spherical particles with defined particle sizes for composite solid propellants. We want to create mixtures of liquid polymer binder systems with a high solids content of particulate energetic materials (oxidizers and energetic additives). Spherical particles generally can be formed via the dispersion of a liquid phase,

which then becomes droplets, in a continuous phase. Because the spherical shape and the particle size are important particle properties, it is, in the case of both AN and ADN, more convenient to work with melts than with solutions. Very uniform packing and good solids loading densities are achieved with spherical particles prepared by melting ADN and dripping the melt into a cooled and rapidly stirred bath of an inert fluid in which ADN is not soluble (“prilling in suspension”). The melt droplets solidify in a spherical shape (prilled shape). The ADN prills are reported to possess higher thermal stability and are less sensitive than the crystalline ADN resulting from the synthesis and the use of bimodal mixtures of ADN. Prills of varying particle sizes in a propellant composition are expected to offer a higher solids loading and a high theoretical maximum density. Figure 4 shows a comparison of as-crystallized and prilled ADN particles.

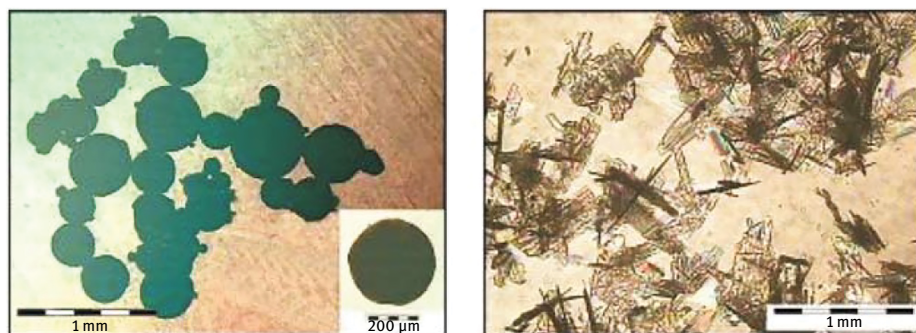


Figure 4: Comparison of prilled and as-crystallized ADN. (Reprinted from [102], by permission from © 2008 Springer Nature; permission conveyed through Copyright Clearance Center Inc.)

The particle shape and particle size of as-synthesized ADN are not uniform, and particles tend to agglomerate. In order to have a reproducible burning rate, it is necessary to modify the particle shape of the initial material to form particles with a defined ratio of surface/volume and a predetermined mean particle size and particle size distribution. It is best to form spherical particles. Spheres can be shaped in a two-phase system. In this case, the molten ADN is dispersed in a continuous phase, which is not miscible with ADN [103]. The surface tension and interfacial tension cause the molten droplets to assume a spherical shape. The solidification of the molten droplets to spherical prills takes place during the cooldown to a temperature below the melting point of ADN. With proper choice of suitable oil bath fluids and spray nozzles and optimization of the process parameters, spherical ADN particles with mean particle sizes ranging from 5 to 800 μm can be manufactured reproducibly.

Other publications give mean particle sizes ranging from 10 to 600 μm [104, 105]. The prilling process consists of two stages: In the first stage, molten ADN is dispersed in a continuous phase in which ADN is insoluble. The droplet size produced can

be controlled by varying the amount of agitation. The influence of the different process parameters, such as dispersion rate, dispersion power, emulsification time, influence of emulsifying agents, and the rheological behavior of the continuous phase, has been studied to optimize the process. In the second stage of the process, crystallization of the emulsified ADN droplets to spherical, solid particles is obtained by quickly reducing the temperature of the system. This process gives spherical ADN particles with mean sizes ranging from 10 to 600 μm . The ADN concentration in the stirred hot-oil bath was varied from 5 to 25 mass-%. Fumed silicon dioxide was used as a protective colloid to promote emulsification. After crystallization and filtration, the particles were washed and dried. The product quality of the crystallized ADN was determined using various analysis techniques, including DSC, IR spectroscopy, IC, and laser light diffraction spectrometry.

The Fraunhofer Institute of Chemical Technology (ICT) in Germany has studied several prilling processes and characterized the spherical particles, as well as made comparisons to prilled AN. Melt spraying is preferred because molten AN and ADN droplets usually nearly keep their shape and size while solidifying, whereas droplets of a solution always have to dispose the solvent to become solid particles. These oxidizer melts can be dispersed in a gaseous or liquid phase. Depending on the crystallization kinetics (nucleation and crystal growth) of the molten droplets, two possible processes can occur: In the case of AN, the recrystallization is fast enough to enable a spray crystallization process by using a prilling tower. ADN, unfortunately, has inhibited and delayed crystallization properties. This makes it necessary to give the molten droplets more time and encouragement to nucleate to complete their phase transformation into solid particles. Therefore, a liquid-liquid emulsion crystallization process was adapted at ICT to the special properties of ADN [106–111].

This process can be modified such that additives (stabilizers, combustion modifiers, and/or energy carriers) are trapped deliberately in the solidifying ADN droplets, giving them more favorable burn characteristics in a solid propellant [112].

Very small droplets in the size range of 40 μm are formed if the melt/oil mixture is agitated with ultrasonic agitation [113]. However, one must consider that ultrasound may also induce decomposition of ADN [114]. The viscosity of the non-polar fluid dispersion bath can be adjusted to obtain the desired particle size. Another method would be to spray the molten salt into a prilling tower and let it solidify during free fall. Doing this in an evacuated tower or operating at lower pressure will reduce the porosity of the solidified prills. Packing densities better than hexagonal dense packing of spheres are possible with multimodal particle size distribution of ADN.

While porosity of the prills may be undesirable for solid propellants, it may be acceptable for prills that are intended to be filled with organic oils and used as explosives [115]. One can also coat the particles with HTPB monomer and plasticizers in preparation for their being embedded in a matrix of polymerized HTPB [116]. The desired aspect ratio of ADN crystals may be achieved by adding surfactants to the solution from which the ADN crystallizes. The melt method of prilling ADN using HTPB/

dioctyl adipate/dioctyl sebacate as the liquid medium has been optimized to produce good-quality spherical ADN particles. The parameters studied and optimized include stirring speed, viscosity and components of the liquid medium, effect of additives, and the design of stirrers and reactors. Water is the possible cause of particle agglomeration (highly undesirable). Particles in the size range of 25–250 μm could be obtained by adjustment of the liquid medium and stirring speed.

Prilling by spraying droplets of molten salts into a stirred pool of an inert, cool liquid in which the droplets can assume a spherical shape before they solidify can be applied to a wide range of energetic materials, including ADN and AN [117, 118].

The particle size of prilled ADN is determined by the surface tension of the molten ADN as it sprays out into the stirred fluid bath, and the droplets are suspended in the fluid until they solidify. The surface tension and the wetting angles of molten ADN were measured in order to select proper equipment (nozzles, agitator paddles, heaters) and materials of construction in contact with ADN [119]. It is difficult to get the dispersion of molten ADN droplets to solidify before the droplets stick together and re-agglomerate. Because the melt has a tendency to supercool, seed crystals may be required to induce solidification.

Up to the year 2000, the production of spherical ADN particles (so-called ADN prills) at ICT was a batch process, using the emulsion crystallization technique. The next step was to develop a continuously working ADN-prilling process. The advantages of a continuous process for ADN are the following:

- less thermal stress, as the ADN remains in the heating zone only for a very short time
- a safer process because there is less ADN in the heating zone
- the possibility to scale up the process

It was shown that it is possible to generate spherical and particles with an adequate particle size distribution by combining the micro reaction technique and the ADN emulsion crystallization process [106, 120, 121].

To obtain ADN particles in a spherical form, decane is used as an antisolvent (continuous phase of the emulsion). A surfactant is also necessary to lower the surface tension, in this case the interfacial tension, and to obtain smaller particle size. An anticaking agent is needed to reduce unwanted agglomeration. A suspension of these solids is fed to a heating zone microreactor, where it emerges as a liquid-liquid emulsion that is fed to the stirred cooling tank, from which ADN prills crystallize on cooling [122]. Among the parameters to be optimized are the flow rate, reactor diameter, and reactor temperature. Reactor temperatures below 393 K (120 °C) may lead to clogging, while reactor temperatures above 398 K (125 °C) may cause premature ADN decomposition and explosions.

Shortly after ADN first became commercially available, the U.S. Navy at Naval Air Weapons Station China Lake in California conducted an evaluation of samples procured from two different domestic sources [123]. Most of the ADN samples were

very pure, containing only 0.05–0.55% AN. Occasionally, a trace of ammonium nitrourethane (one of the starting reactants for making ADN) was detected. One of the samples contained 0.55% nitrate ion and 0.52% ammonium nitrourethane. For preparing small (2–3 g) batches of prilled ADN, the temperature of the melt had to be carefully controlled and kept below 383 K (110 °C), and the time spent at this temperature was limited to 15 min. This very much limits the size of a batch process. The addition of 0.3% hexamethylenetetramine (“hexamine”) stabilized the ADN. A vacuum thermal stability test of the product (4 h at 371 K [98 °C]) showed substantial improvement of ADN stability because of the addition of hexamine when compared to unstabilized ADN. If the temperature was allowed to exceed 393 K (120 °C), the material started gassing, and the prills became porous.

Thiokol developed a prilling process involving the addition of additives before prilling to overcome potential shortcomings of ADN when compared to AP [124]. In this process, solid granular ADN is introduced into the top of a melting column and is allowed to melt to form pre-prills while passing through a hot zone in the prilling column. The pre-prills are allowed to “spheridize” in the presence of an upwardly flowing inert, immiscible fluid, which partially counteracts the gravity of the ADN in the prilling column. The flow rate is selected so as not to carry the ADN out of the top of the prilling column. The rate of “spheridization” can be accelerated by providing additional cooling to the cooling zone in the prilling column where the spherular granules leave the apparatus [125–128].

ADN that was produced by Bofors in Sweden was evaluated at Naval Air Weapons Station China Lake [129]. This ADN was composed of either plate-like or needle-like crystals and was of an excellent chemical purity (as analyzed by IC). The IC analysis showed it to be at least 99% pure, with 0.13% nitrate and 0.03% sulfate and no detectable nitrite. The Chemical Systems Division of United Technologies had converted some of the Swedish ADN into prills by a process that involved molten ADN and immiscible mineral oil emulsion technology. This patented process [130, 131] minimizes the time during which the ADN is in the molten state by feeding the coarse ADN at a controlled continuous rate into a heating chamber, melting the ADN, and immediately spraying the melted ADN continuously into a non-solvent cooling fluid maintained at a temperature below the temperature of solidification of the ADN. The cooling fluid bath is agitated to promote the formation of droplets of controlled size, which solidify in the cooling fluid to produce substantially spherical ADN in a narrow particle size distribution.

The quality of prilled ADN depends on the immiscible liquid organic fluid, dispersant, surface active agents, and stabilizers, and on the methods of selecting these auxiliary agents. Hygroscopicity, particle size distribution, impact sensitivity, friction sensitivity, and surface structure of prilled ADN were studied. Results showed that prilled ADN has lower hygroscopicity and sensitivity than flake or needle ADN. Prilled ADN with particle sizes from 5 to 800 μm can be produced in this way [132, 133]. Crystal shapes of many solid propellant oxidizers need to be changed to decrease sensitiv-

ity, improve mechanical properties, and obtain optimum performance from oxidizers such as ADN and HNF [134].

The emulsion crystallization process involves the melting of ADN in paraffin oil maintained above the melting temperature of ADN. The hot paraffin oil along with the molten ADN was mechanically stirred using a propeller stirrer (M) at 400–500 rpm to get uniform spherical droplets of ADN, followed by cooling of the paraffin oil to room temperature and isolation of spherical grains by washing with a solvent. In a typical experiment, 20 g of dried ADN was slowly introduced into hot paraffin oil maintained at 365–366 K (92–93 °C) in a jacketed reactor, along with 0.1% of fumed silica (Cab-O-Sil) as a protective colloid to prevent particle-particle adhesion [58, 135, 136]. This process enables production of spherical grains of ADN with a mean particle size of 100–500 μm .

Processing ADN into solid propellant mixes has been a significant challenge because it emerges from the basic manufacturing process as hard, angular crystals that do not lend themselves to being mixed into high-solid-loading solid propellants. Even after grinding, the smaller, but still hard, crystalline material has sharp edges and does not process very well. That is one reason why prilling efforts continued at several organizations even long after this material had been discovered.

The ADN used in Sweden was procured from Eurenco Bofors in Sweden, which has been producing dinitramides on a pilot plant scale since 1996. The particle shape of ADN as received from Eurenco is needle shaped and thus not suitable for solid propellant formulation. At FOI in Sweden, a method to produce spherical ADN particles was therefore developed [11, 12]. The prills are produced by spraying molten ADN through a nozzle. In the nozzle, the molten ADN is atomized to form droplets, which then solidify to the desired prills seen in Figure 5 and 6.

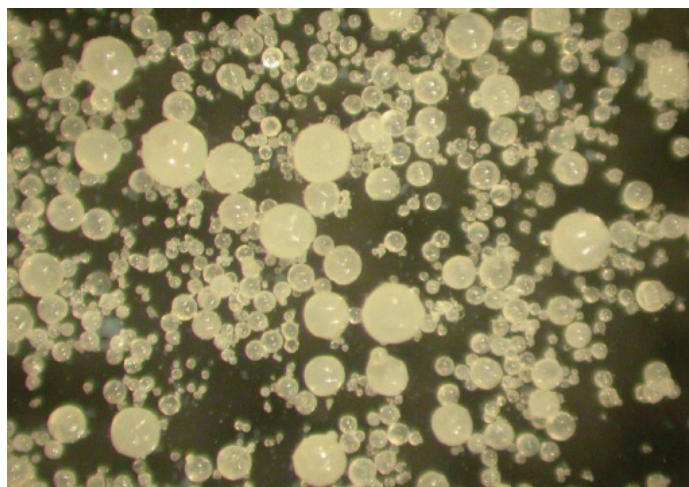


Figure 5: Prilled ADN. (Photo courtesy of FOI Sweden, reprinted with permission.)

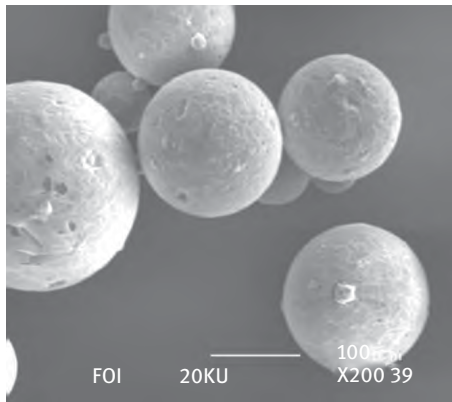


Figure 6: Scanning electron microscope image of prilled ADN. (Photo courtesy of FOI Sweden, reprinted with permission.)

The particle size can be controlled to some extent by varying the spray nozzle size and pressure. Typical particle size distributions for the fine and coarse prills produced are given in Table 3 and illustrated in Figure 7 from [14].

Table 3: Typical particle size distributions of prilled ADN.

Grade	d10 (µm)	d50 (µm)	d90 (µm)
Fine	30	60	120
Coarse	30	200	400

Data source: Wingborg et al. [11]

As a result of the heating and prilling, the nitrate contamination in ADN increased from 0.03 to 0.08 mass-%, which is undesirable and lowers the melting point from 366.3 to 365.6 K (93.2 to 92.5 °C). Particle density drops from 1.81 to 1.79 g/cm³, but tap density is improved from 0.86 to 1.11 g/cm³.

Johansson et al. produced spherical ADN particles using a spray prilling process [137]. The ADN was first melted and then atomized by spraying it through a nozzle by the use of pressurized nitrogen into a cold bath of liquid nitrogen. The relative humidity in the working chamber had to be kept very low. The particle size can be varied by using nozzles with different diameters. The particle size distribution obtained with two different nozzles is shown in Figure 8.

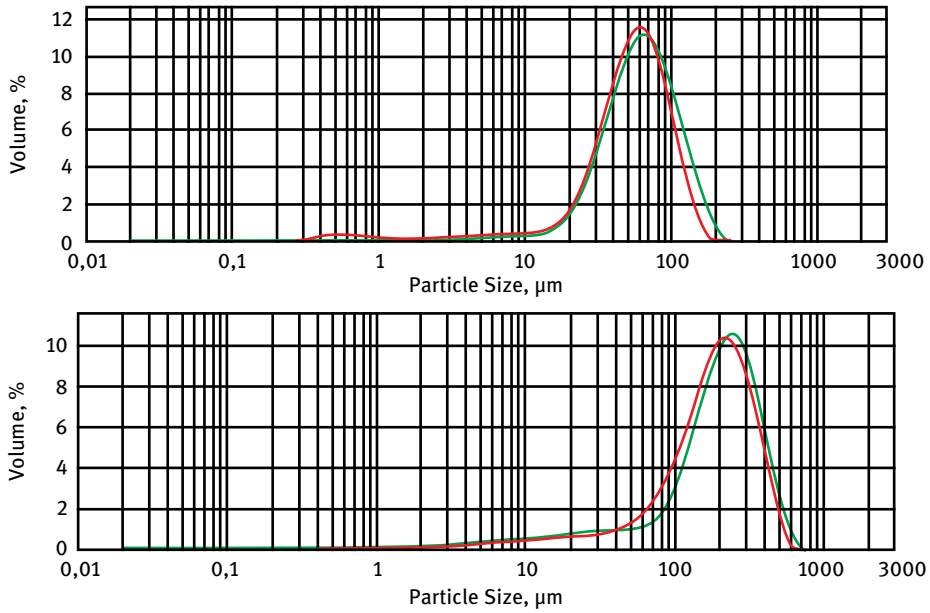


Figure 7: Particle size distribution of fine (upper graph) and coarse (lower graph) ADN prills. Two measurements on each grade. (Reproduced and modified from [14]. Creative Commons Attribution-NonCommercial 4.0 International, CC BY-NC 4.0)

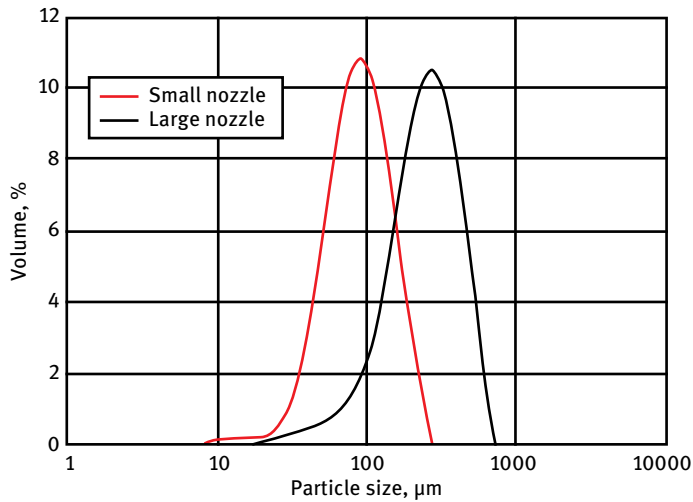


Figure 8: Particle size distribution of ADN prills obtained with nozzles of two different sizes. (Reproduced/Printed/Used and modified from [137] with permission obtained from FOI Sweden 9-Jun-2020)

The density of spray-prilled ADN spherules was in good agreement with its theoretical value (1.818 g/cm^3). This showed that the spray-prilled ADN particles were homogeneous, without any voids. The spray process may actually increase the purity of ADN by removing volatile impurities. Some initial results indicated that freshly spray-prilled ADN may not be completely morphologically stable. After storage for some days, it seems that the surface structure of spray-prilled ADN becomes more irregular. This behavior was more pronounced when the prills were stored at higher humidity. See also reference [138].

ADN that is intended for melt casting (also in mixtures with aluminum powder) can be stabilized by the addition of 1% MgO [139].

Other stabilizing additives can be co-dispersed with the molten ADN and will be embedded in the prilled spherules [112, 140]. This method enables the homogeneous distribution of additives in ADN particles with minimal adverse thermal effects.

The application of ADN in solid propellant formulations requires spherical particles of at least two different particle sizes, typically a coarse particle-size fraction in the range of 200–250 μm and a medium particle-size fraction in the range of 30–60 μm . In addition, a fine fraction of about 5 μm would be desirable for multimodal particle-size distribution. Several process variables of the emulsion crystallization process for ADN, the so-called ADN-prilling process, were modified to achieve these particle-size distributions [141]. By varying process fluids, additives, stirring energy, and recrystallization behavior, it was possible to generate medium-sized ADN prills with a mean particle size of 50 μm and coarse ADN prills of approximately 200 μm in technical-scale batches.

The possible particle size range for producing ADN prills could be expanded down to 35 μm and up to 320 μm [142]. Demonstrated particle size ranges for reproducible kilogram-scale production batches were as follows:

- medium-fine ADN prills: 50–60 μm
- coarse ADN prills: 150–250 μm

These ADN prills will be tested in bimodal oxidizer particle size propellant formulations. Important parameters to investigate are the casting viscosity and mechanical stability of the formulations. Another investigation is the dependency of the burn rate on the particle size of ADN prills. The large ADN prills generated by targeted seeding showed an inner layer structure.

The ADN-prilling process by emulsion crystallization can be scaled up to the multiple-kilogram production level [143].

The particle size, the outer shape, and the surface area of ADN prills are the most important particle properties of ADN prills formed by the emulsion crystallization process. If necessary, the surface may be additionally refined by particle-coating technologies. Besides the external appearance, the internal characteristics of particles are of considerable importance. Defects, pores, or impurities have unfavorable effects on the particle's properties, e.g., increased sensitivity, whereas the crystal structure of

particulate energetic materials may affect the mechanical properties of the particles. It was found that the crystal formations inside the and prills have a layered structure or at least a preferential direction [144, 145]. This phenomenon was investigated using XRD, microscopy, and measuring of the mechanical strength of the particles.

ADN prills are producible in the particle-size range of 40–200 μm . If necessary, the ADN prills can be refined by fluidized bed technology, such as by creating coating layers with improved bonding behavior to solid propellant binder systems. This leads to comparatively better mechanical properties of propellants made with thusly coated ADN prills than with uncoated ADN prills. The crystal structure was investigated using XRD, and the thermal stability was determined by vacuum stability tests and mass-loss measurements [146].

Spherical ADN particles (ADN prills) can be produced continuously in microfluidic droplet generators that promise improved size and dispersity control of the prills and open new possibilities to explore the influence of additives on the properties of ADN [147]. This process can minimize the thermal decomposition of ADN during the prilling process by heating up only small amounts that are used immediately for the process. Microfluidic droplet generators using parallelized microchannels offer the potential of scaling up the process.

Prilled ADN can be made by an emulsion crystallization process that allows the operator to control the morphology of the product [148].

2.5.4 Grinding of Ammonium Dinitramide Particles

In attempting higher burning rates, it is common practice to work with smaller and smaller oxidizer particle sizes. Grinding can achieve smaller particle sizes than prilling from the melt. With the high friction sensitivity of ADN, it is not a good idea to comminute ADN by grinding, unless it is done in a suspension with an inert solvent. Ultrafine, potentially explosive particles can be produced by a bead-milling technology. Micro-scaled ADN was obtained by milling of a non-aqueous ADN/decane suspension with a diving basket mill, filled with ceramic beads. Particles with a mean size of 2.06 μm could be successfully produced in technical-scale batches [149].

2.6 Coatings for Ammonium Dinitramide Particles

Several coating methods have been developed and tested for ADN to reduce its sensitivity to moisture and improve the wettability by binders in solid propellants. Without any anti-caking agent, the prilled ADN cakes after a short time of storage, even in dry conditions. Sometimes the coating process is combined with the incorporation of other additives into the ADN particles.

An improved coating method coats the ADN prills first with wax and then with an amine resin [150]. Coating of ADN favorably reduced its friction and electrostatic

discharge (ESD) sensitivity. Prilled ADN was coated with polymeric materials, and the extent of moisture absorption at different relative humidities was measured [58]. Ethyl cellulose (EC) and poly(methyl methacrylate) (PMMA) dissolved in methylene chloride were used as coating materials. The coated ADN granules were then evaluated for their moisture pickup at relative humidities of 62 and 74%. Varying amounts of coating material (0.5–2%) showed a decrease in the moisture uptake of ADN. For ADN coated with 2% EC, the moisture uptake at 60 min was 4.43%. The moisture absorption profile of ADN coated with PMMA showed a similar trend as that observed for ADN coated with EC. At 60 min at 74% relative humidity, the moisture uptake was 7.6% for uncoated and 4.03% for ADN coated with 2% PMMA. ADN samples coated with PMMA showed lower moisture uptake than those coated with EC.

A combination of additives and coatings can improve the thermal stability and safety property of the oxidizer and the solid propellants made therefrom [151]. The particles are suspended in a fluidized bed, and the coating solution is sprayed on and must dry quickly before the particles agglomerate and stick together [152]. Particles with a mean size of 120 μm can be coated separately and with uniformly thin layers. Supercritical solvents can be used for coating and microencapsulation of energetic materials such as ADN. With this method, drops or fine particles of a solution of the coating agent in a supercritical fluid are sprayed onto <100- μm particles of the substrate in a fluidized bed [153, 154].

A potential drawback of ADN is the lack of compatibility with common curing agents used in most binder systems. This incompatibility can be overcome by coating the ADN particles. At ICT, a fluidized bed technology was used for the processing of hygroscopic and explosive granular materials [155, 156]. Different polymeric coating materials have been tested to find one suitable for application in a fluidized bed. The properties of the coated ADN particles were characterized by microscopy, particle-size distribution, specific surface area, and crushing strength of individual particles. ADN prills can be coated without agglomeration and with uniformly thin layers. The mechanical strength of particles was improved by the coating. The compatibility of coated and uncoated ADN prills and isocyanate containing binder systems was investigated by microcalorimetric measurements and vacuum stability tests [157]. It was shown that the compatibility could be improved by coating the ADN prills with polyacrylates, HTPB, or glycidyl azide polymer (GAP).

The fluidized bed technology allows production of composite particles consisting of layers of different energetic materials. Three different examples of layered energetic composite particles were demonstrated [158]:

1. ADN prills (spherical ADN particles) were coated with thin layers of GAP, which increased the compatibility with isocyanate-containing binder systems and the mechanical stability.
2. Spherical AN particles could be coated with UV-curing polymers, which led to mechanically stable core-shell structures.

3. Composites of mostly HMX (approximately 90 mass-%) and small amounts of FOX-7 or FOX-12 resulted in reduced friction sensitivity of the whole composites.

Prilled ADN was coated with polyurethane (PU) to reduce its hygroscopicity [159]. The surface appearance and hygroscopicity of ADN after coating were analyzed by SEM and gravimetry. When coated ADN was exposed in air for 30 d with relative humidity less than 60%, the weight gain of coated ADN was only 0.136% and did not increase with extension of the exposure time. Differential thermal analysis and mechanical sensitivity tests showed that PU had little effect on the melting point, decomposition peak temperature, or enthalpy of coated ADN, but the friction and impact sensitivity of ADN increased. The drop height for the impact sensitivity 50% point decreased from 30.5 to 27.8 cm.

ADN in its generic form has long needle-shaped crystals, which hinders higher solids-loading in formulating solid propellants. It is preferred to change its crystal morphology into octagonal shapes and at the same time encapsulate it with a hydrophobic polymer. ADN was mixed with toluene, graphene, citryl ammonium butyl, Cab-o-sil, and a coating polymer (polystyrene or HTPB) and treated with ultrasound to obtain semi-spherical ADN-coated particles [160]. The method offers a reduction in operating temperature in that it eliminates ADN melting in the shape-altering and prilling process used by others. The ADN processed by this method had a similar particle size and thermal stability compared to ADN made by a conventional ADN melt-prilling method. The ultrasound-treated coated ADN particles showed significant reduction in moisture absorption, from 68 to 16% at 65% relative humidity.

ADN is difficult to use in solid propellants due to its high surface polarity and strong hygroscopicity. An improved grade of ADN was prepared by coating spherical ADN particles using ultrasonic and *in situ* coating technology [161]. The properties of coated ADN prills were characterized by SEM–energy-dispersive X-ray spectroscopy (EDS), XRD, DSC-TGA, IR spectroscopy, impact sensitivity, friction sensitivity, the dryer balance method, and the creation of propellant mixes. Results showed that the sphericity of the coated ADN prills was less than 1.5, and the crystal form remained unchanged. The peak temperature of thermal decomposition was increased by 11 °C, the onset temperature of thermal weight-loss temperature was delayed by 15 °C, and the impact sensitivity was increased by 3.6 J. Under a condition of 30 °C and relative humidity of 75%, the saturated hygroscopicity of coated ADN prills decreased from 55% to less than 2.5%. Under a condition of 59% relative humidity, the saturated hygroscopicity of coated ADN prills was further reduced to 1.2%. Compared with an earlier HTPB propellant containing raw ADN, the porosity of the propellant containing coated ADN prills was significantly reduced. See also [162, 163].

3 Physical Properties of Ammonium Dinitramide

ADN, ammonium dinitramide, azanium dinitroazanide, $\text{NH}_4\text{N}(\text{NO}_2)_2$, $\text{N}_4\text{H}_4\text{O}_4$, CAS RN [140456-78-6], $M = 124.0569$ g/mol. Although discovered only a few decades ago, the physical properties of ADN have been thoroughly measured. Although some of the oxygen in this molecule is tied up for burning the hydrogen from the ammonium ion to form water, ADN has a high oxygen balance, +25.79%.

3.1 Melting Point and Phase Diagrams of Ammonium Dinitramide

3.1.1 Melting Point of Ammonium Dinitramide

The melting point of ADN prills as determined by DSC is 365.04 K (91.89 °C), which is slightly lower than that of recrystallized ADN, which melts at 365.6 K (92.44 °C) [102]. Other reports indicate that the ammonium salt of dinitramidic acid melts at 365 K (92 °C) and starts to decompose at 403–408 K (130–135 °C). Table 4 gives a summary of reported melting-point data for ADN.

Table 4: Melting point of ammonium dinitramide.

Sample condition	Melting point		DSC heating rate	DSC heat of melting	References
	K	°C	°C/min	J/g	
Prilled	365.04	91.89			[102]
Recrystallized	365.59	92.44			[102]
SRI-12	361	88			[164]
Recrystallized	365.6	92.5			[2]
Crystals	365 ± 1	92 ± 1	5	138 ± 3	[165]
Prilled	363 ± 1	90 ± 1	5	126 ± 1	[165]
Crystals	367	94*	20	—	[166]
Crystals	364.6	91.5	0.5	134	[167]
Crystals	363.8	90.7	10	124	[168]
Crystals	366.6	93.5 ^a	10	—	[169]
Crystals	365	92	5	—	[170]

^aPeak temperature of DSC endotherm

In addition to measuring the melting point of ADN, it has been attempted to predict the melting point of ADN and other nitramines based on theoretical molecular orbital calculations [171]. This can be applied to calculating the melting point of complex molecular and ionic solids and nanoparticles. Various approaches for simulating melting and computing the thermodynamic melting point were identified along with some force-field calculations that have been used in simulations of the melting of molecular and ionic solids, and the different structural, energetic, and dynamical quantities used to characterize the melting transition were described.

The surface tension of molten ADN determines the droplet size during prilling of ADN. Surface energy and crystallization phenomena of ADN were characterized during recrystallization from the melt [172]. The surface tension of molten ADN at 370 K (97 °C) was measured to be 89 mN/m. The wetting angles between molten ADN and different solid surfaces (polytetrafluoroethylene, glass, steel, and aluminum) were also determined. The wettability depends on the surface tension of molten ADN, the free surface energy of the solid surfaces, and the interfacial tension between the solid and liquid. Observations of the recrystallization behavior of molten ADN showed that nucleation does not occur readily, even at rapid cooling rates of 70 K/min. Crystallization can be initiated by insemination with seed crystals.

3.1.2 Phase Diagram of Ammonium Dinitramide

The pressure/temperature reaction-phase diagram for ADN was determined using a high-temperature-high-pressure diamond anvil cell with optical polarizing light microscopy, FTIR spectroscopy, laser Raman spectroscopy, and energy-dispersive XRD, and was also compared to RDX, HNIW, and *p*-nitroaniline [173, 174]. The starting material for all experiments was the α polymorph of ADN. Some results suggested a new monoclinic phase above 2.0 GPa. The phase diagram was determined between ambient pressure and 10.0 GPa over the entire temperature range from 198 K (−75 °C) to the decomposition temperature near 393 K (120 °C) (Figure 9). The diagram delineates the melting curve for α -ADN.

ADN exhibits a reversible phase transition in α -ADN forming a new high-pressure monoclinic polymorph, β -ADN. The monoclinic α phase is stable up to about 2.0 GPa between 198 and 393 K (−75 and +120 °C). The high-pressure β phase, which is also

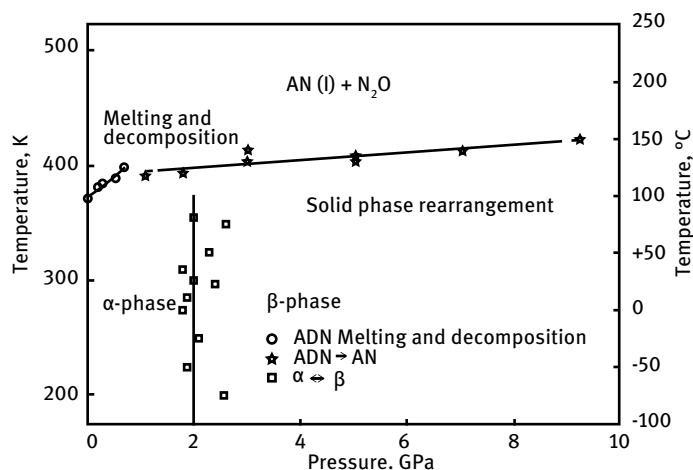


Figure 9: High-pressure phase diagram for ADN. (Reprinted and modified from [174], with permission from © 1996 American Chemical Society; permission conveyed through RightsLink.)

monoclinic, is stable above 2.1 GPa between 198 and 393 K (−75 and +120 °C). The β phase cannot be retrieved to ambient conditions but reverts to the α phase as the pressure is lowered to below about 2.0 GPa. The $\alpha \leftrightarrow \beta$ transition is reversible and can be approached from both the α and β phases, but the spread in the data points is large. The $\alpha \leftrightarrow \beta$ transition pressure is estimated to be 2.0 ± 0.2 GPa. At high pressures and above 393 K (120 °C), a solid-phase rearrangement and decomposition occur to form AN and N_2O .

3.1.3 Binary Phase Diagrams of Ammonium Dinitramide Solutions

The phase diagram of the ADN/water system is very similar to that of the AN/water system. Figure 10 shows the binary phase diagram with melting point versus a mass fraction scale, and Figure 11 shows the same data with a mol fraction scale [175]. Note that changing the abscissa scale changes the shape of the curve from concave to convex. The eutectic is at 16.9 mol percent (58.3 mass-%) ADN with a melting point of 258 K (−15 °C). These data are very similar to those for AN.

Another phase diagram is shown in Figure 12 from reference [176]. From the phase diagram, the eutectic composition mass fraction was found to be $w_{\text{ADN}} = 0.58$, which corresponds to a mol fraction (x_{ADN}) equal to 0.167. For comparison, the eutectic composition reported by others for the AN/water system is $w_{\text{AN}} = 0.428$ and $x_{\text{AN}} = 0.144$, with a melting point in the range of 256.4 to 256.3 K (−16.7 to −16.8 °C).

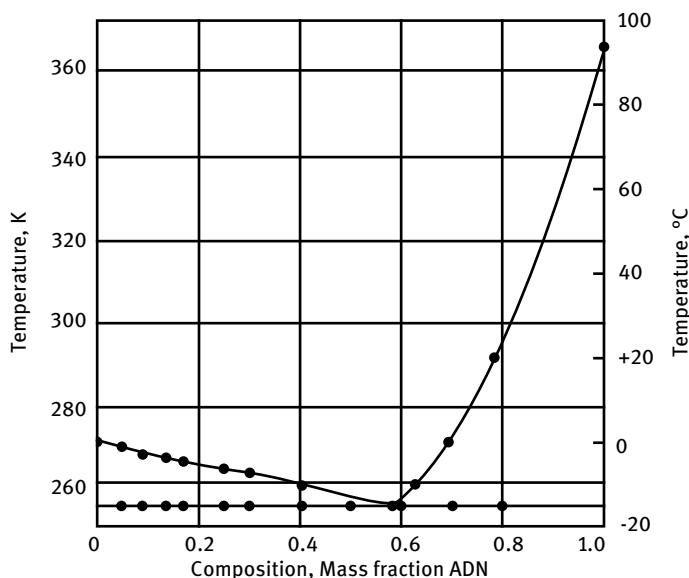


Figure 10: Phase diagram of the ADN/water system, mass fraction abscissa. (Reproduced and modified from Kappenstein, Batonneau, Perianu and Wingborg [175] with permission from Dr. Charles Kappenstein.)

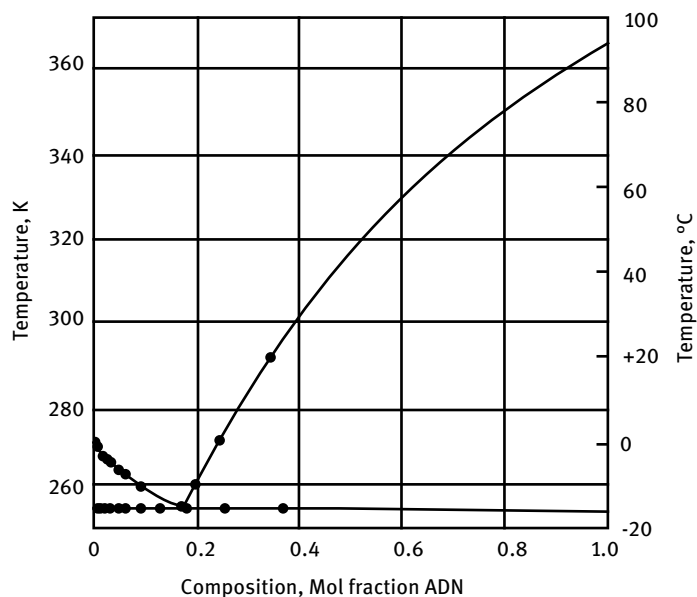


Figure 11: Phase diagram of the ADN/water system, mol fraction abscissa. (Reproduced and modified from Kappenstein, Batonneau, Perianu and Wingborg [175] with permission from Dr. Charles Kappenstein.)

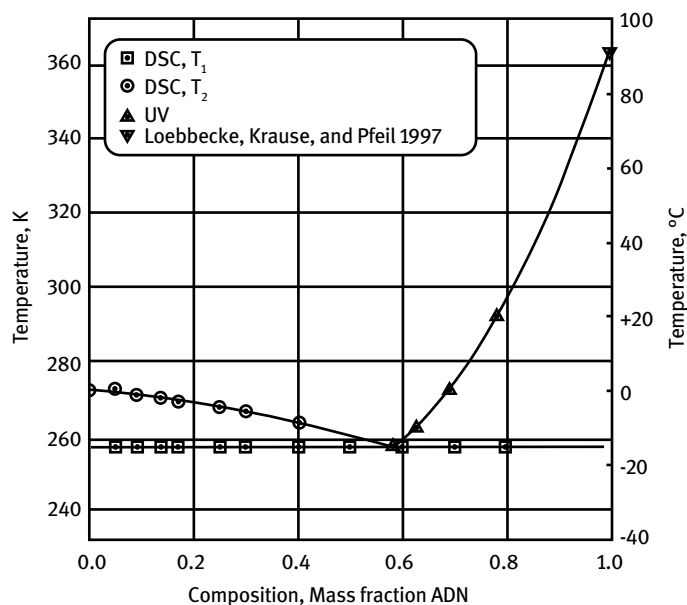


Figure 12: Solid-liquid phase diagram of the ADN/water system. (Reprinted and modified from [176], with permission from © 2006 American Chemical Society; permission conveyed through RightsLink.)

3.2 Solubility of Ammonium Dinitramide in Solvents

ADN is quite soluble in a number of polar solvents and only sparingly soluble in non-polar solvents. The solubility of ADN in water at different temperatures is summarized in Table 5.

Table 5: Solubility of ADN in water at different temperatures.

Temperature		Solubility
K	°C	Mass-%
258	-15.0	58.3 ± 0.2
263	-10.0	62.7 ± 0.2
273	0.0	69.3 ± 0.1
298	20.0	78.1 ± 0.1

Data source: [176]

Measurements below 258 K (-15 °C) were prevented because of incipient freezing of the aqueous ADN solution. The measurement procedure was double-checked by measuring the solubility of AN in water at 293 K, and it was found to be 65.6 mass-%, which is

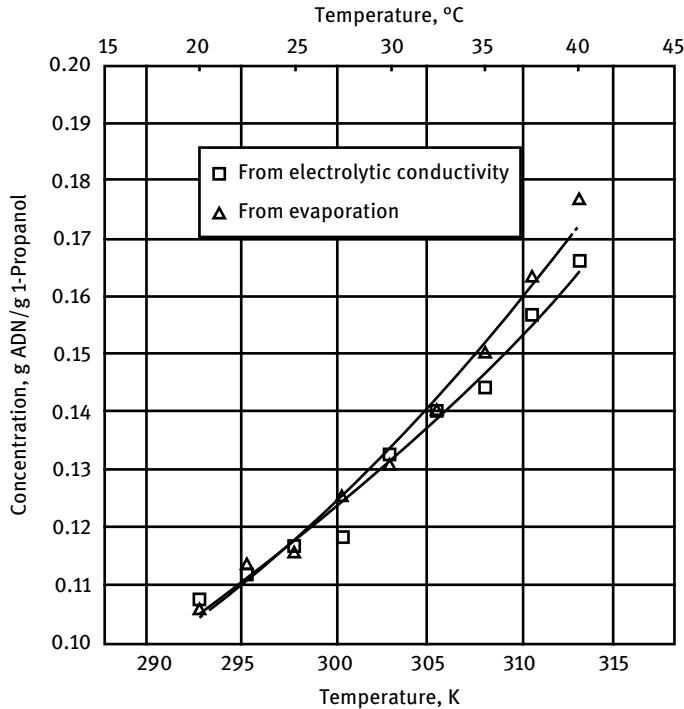


Figure 13: Solubility of ADN in 1-propanol. (Reprinted and modified from [90] with permission granted by ICT.)

in good agreement with data in the literature (65.5%). The solubility of ADN in water is considerably higher than that of AN.

Solid oxidizers like ADN are readily soluble in hydrogen peroxide, and such solutions have been evaluated as liquid oxidizers, which have a lower freezing point and higher density than plain hydrogen peroxide. Many of these solutions do not have sharp freezing points but instead have glass transition points as the sample temperature decreases. The ignition delays of ADN/HTP solutions with an ionic liquid fuel, 1-allyl-3-methylimidazolium dicyanamide, were measured [177].

Numerous non-aqueous solvents have been evaluated to facilitate the separation of freshly produced ADN from reactants and by-products [178]; 357 g ADN dissolves in 100 g water at room temperature to make a saturated solution.

A patent describes a monopropellant consisting of at least 65% ADN in ammonia with at most 5% water, freezing at 233 K (−40 °C) [179]. Physical properties of this solution are shown in *Encyclopedia of Monopropellants*.

The solubility of ADN in 1-propanol and 1-octanol was measured as part of a search for solvents from which ADN can be recrystallized to obtain crystals with more favorable length/diameter ratios [90]. From the natural cooling experiments, 1-propanol turned out to be the most promising solvent to obtain crystals with a low aspect ratio. The ADN recrystallized from three different alcohols was characterized by SEM imagery, XRD, DSC, and TGA. The solubility of ADN in 1-propanol is shown in Figure 13. Similar data are available for ADN in 1-octanol. The solubility of ADN in various solvents is summarized in Table 6.

Table 6: Solubility of ADN in organic and inorganic solvents.

Solvent	Solubility g/100 g solvent	Temperature K	Solubility Mass-%	References
1-Propanol	0.117	298		[90]
Water	357	293	78.1	[176]
Methanol	86.9	293	46.5	[14]
Butyl acetate	0.18	293	1.8E-03	[14]
<i>n</i> -heptane	0.005	293	0	[14]
Dichloromethane	0.003	293	0	[14]
Ethyl acetate		305	2.0	[58]
2-Propanol		305	14	[58]
2-Propanol		283	7	[58]
2-Propanol		273	4.9	[58]
Acetonitrile		305	26.5	[58]
Acetonitrile		283	14.6	[58]
Acetonitrile		273	10.8	[58]
Acetone		305	47.6	[58]
Acetone		283	33	[58]
Acetone		273	30	[58]
Methanol		305	90.3	[58]
Water		305	423.5	[58]

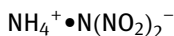
ADN is soluble in *N*-methyl pyrrolidone, [180] and its heat of solution was measured. The obtained enthalpies can be regarded as the enthalpies at infinite dilution because of the very low molalities used in this experiment. The differential enthalpies ΔH_{sol} were -22.26 , -21.85 , -22.84 , and -23.11 kJ/mol for ADN in NMP at 298, 303, 308, and 313 K, respectively. The molality had little effect on the values of the molar enthalpy at each temperature.

3.3 Hygroscopicity of Ammonium Dinitramide

The hygroscopic properties of dinitramide salts vary widely. The ammonium salt of dinitramidic acid is very hygroscopic (more so than AN), while quaternary alkylammonium, aminoguanidinium, and acetamidinium salts are less hygroscopic.

Computations can explain the affinity between ADN and water leading to unwanted hygroscopicity, but they do not offer any methods to circumvent this problem in propellants.

DFT and a dispersion-corrected DFT have been used to investigate the hygroscopicity of ADN [181]. Calculation results showed that the gaseous ADN has a strong hydrogen bond. But the ionic pair structure



is stabilized upon the addition of water molecules. Natural bond orbital calculations suggest that the intra-molecular and inter-molecular orbital interactions make the system stabilized as a whole. An energy decomposition analysis revealed that the interactions between ADN and H_2O are dominated by electrostatic and orbital interactions. The formation reactions become more spontaneous with the increasing number of water molecules, but they can be weakened by increasing temperatures from 200 to 400 K. A more realistic cluster model of the interactions between ADN and H_2O was described using a molecular dynamics method.

The hygroscopicity of spherical ADN and its changes of morphology in the process were analyzed using a dynamic hygroscopic analytical method and SEM [182, 183]. The hygroscopic process can be divided into three stages: gentle moisture absorption, dramatically enhanced moisture absorption, and deliquescence. The first and second stages involve the interaction of water vapor and the surface of solid ADN, while the third stage is the interaction of water vapor and the ADN liquid membrane surface. The hygroscopic process of the first stage is a multi-molecular layer adsorption between water vapor and ADN, which adsorbs in accordance with the Brunner–Emmett–Teller theory model, and the force between water vapor and ADN plays a leading role in the hygroscopicities of ADN. The hygroscopic mechanism of the second stage can be explained by a capillary condensation theory. See also [184, 185].

The critical relative humidity for ADN is 55.2% at 25 °C [176]. This means that the relative humidity must be less than 55.2% to prevent ADN from absorbing moisture

from the atmosphere during processing. ADN is more hygroscopic than AN, and the hygroscopicity of crystalline ADN is more severe than that of AP. This property seriously affects its use when ADN is considered as a drop-in replacement for AP. This different hygroscopicity is possibly associated with their different crystal structures.

The hygroscopicity of ADN was studied at various controlled relative humidity levels [123]. It would be ideal to handle it only in a desert climate where it always stays very dry (0.02% H_2O). ADN samples were equilibrated in controlled humidity chambers with 38 and 58% relative humidity. In the 58% relative humidity chamber, their water content was 0.4% after 24 h and 1.76% after 95 h. In the 38% relative humidity chamber, the weight gain fluctuated between 0.06 and 0.08% for 94 to 1104 h. The moistened samples lost most of their water again after being stored at ambient desert conditions, and the water content dropped back down to 0.07% after 2 weeks. Similar tests were performed with two particle sizes of ADN at two different ambient relative humidity levels. The moisture absorption curves are shown in Figure 14 and 15. It is unusual that the equilibrium condition is achieved rapidly for the ADN samples at 62% relative humidity (160–180 h) but is slow at 74% relative humidity (320–370 h).

Comparing the hygroscopicity of crystalline ADN and AP, it is noted that the unwanted hygroscopicity of crystalline ADN is more severe than that of AP, and it seriously affects its use [186]. An equilibrium moisture content of ADN could not be achieved even after 1200 min when the relative humidity values were 65 or 80% (Figure 16).

The water content of ADN slightly decreased at 45% relative humidity because its critical relative humidity is 55.2%. The conditions at relative humidity 52% are completely similar to those at relative humidity 45%; therefore, the two lines overlap. At both 65 and 80% relative humidity, the water content in ADN was higher than

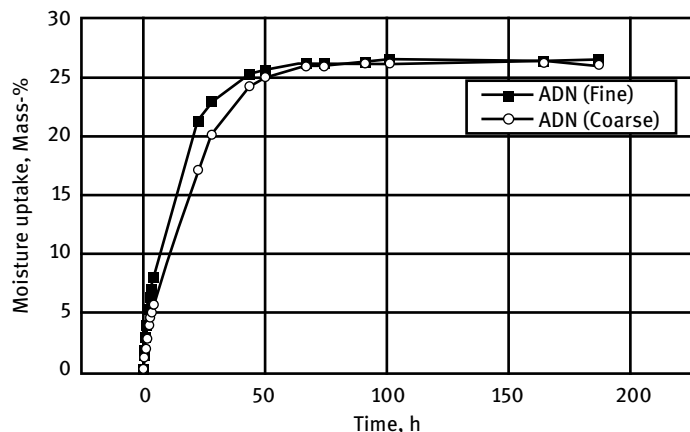


Figure 14: Moisture uptake of ADN at 62% relative humidity (Reprinted and modified from [58] with permission granted by Dr. Santhosh 8-Feb-2021.)

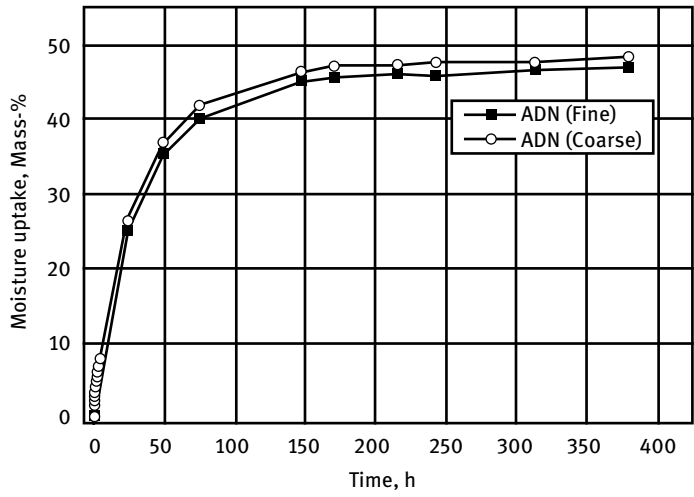


Figure 15: Moisture uptake of ADN at 74% relative humidity (Reprinted and modified from [58] with permission granted by Dr. Santhosh 8-Feb-2021.)

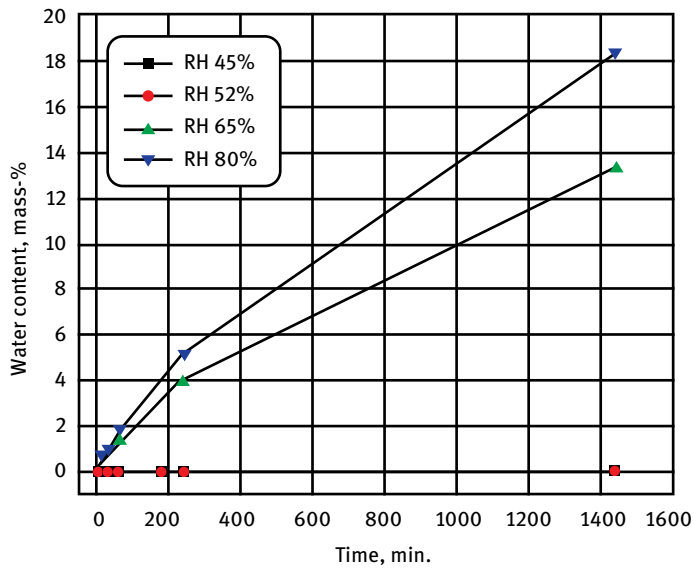


Figure 16: Water absorption by ADN. (Reprinted and modified from [186], with permission from © 2010 American Chemical Society, permission conveyed through RightsLink.)

0.4 mass-% in less than 20 min. In 60 min at 65 and 80% relative humidity, the water content reached about 1.4 and 1.8%, respectively.

3.4 Phase Diagrams of Ammonium Dinitramide Mixtures

3.4.1 Ternary Phase Diagrams of Ammonium Dinitramide Solutions

Ternary systems containing ADN and water and a third ingredient could be ternary mixtures containing two oxidizers or systems containing one oxidizer, a fuel, and a solvent. The third ingredient could have a salting-out effect (as in the case of adding ethanol or methanol) or a salting-in effect (only a few additives improve the solubility of ADN).

The solubility of ADN in water, methanol, and water/methanol mixtures was measured and compared to that of AN and HNF. ADN is more soluble in either solvent than either of the other two oxidizers (Table 7).

Table 7: Solubility of different oxidizers in water/methanol mixtures at 293 K (20 °C).

Oxidizer	Water/methanol (mass-%)		
	100/0	50/50	0/100
ADN	78.1 (0.07)	71.4 (0.15)	46.5 (0.14)
AN	65.6 (0.33)	47.5 (0.42)	14.6 (0.06)
HNF	52.9	No data	18.2

Solubility in mass-% solute (g solute in 100 g solution);
standard deviations in parentheses

Data source: [187]

The data from Table 7 are illustrated in Figure 17.

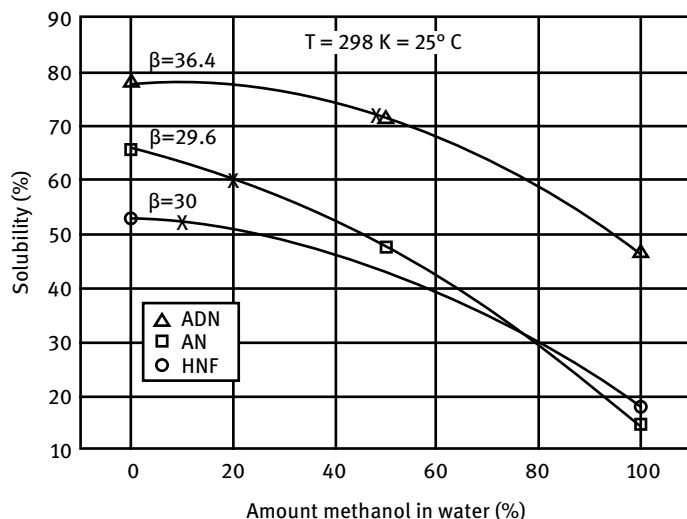


Figure 17: Solubility of ADN in water/methanol mixtures at 293 K (20 °C) in comparison to that of AN and HNF. (Reproduced and modified from [187].)

Additional solubility data for ADN in methanol/water mixtures were obtained at 273 K (0 °C) (Table 8).

Table 8: Solubility of ADN in water/methanol mixtures at 273 K (0 °C).

Water/methanol (mass-%)			
100/0	70/30	60/40	50/50
69.3 (0.10)	63.5 (0.30)	60.6 (0.25)	57.0 (0.04)

Solubility in mass-% solute (g solute in 100 g solution);
standard deviations in parentheses

Data source: [187]

The ternary diagram of ADN/methanol/water mixtures was constructed from published data [187] and is shown in Figure 18. Additional data were entered for AN, hydroxylammonium nitrate (HAN), and HNF, which makes the diagram a bit confusing.

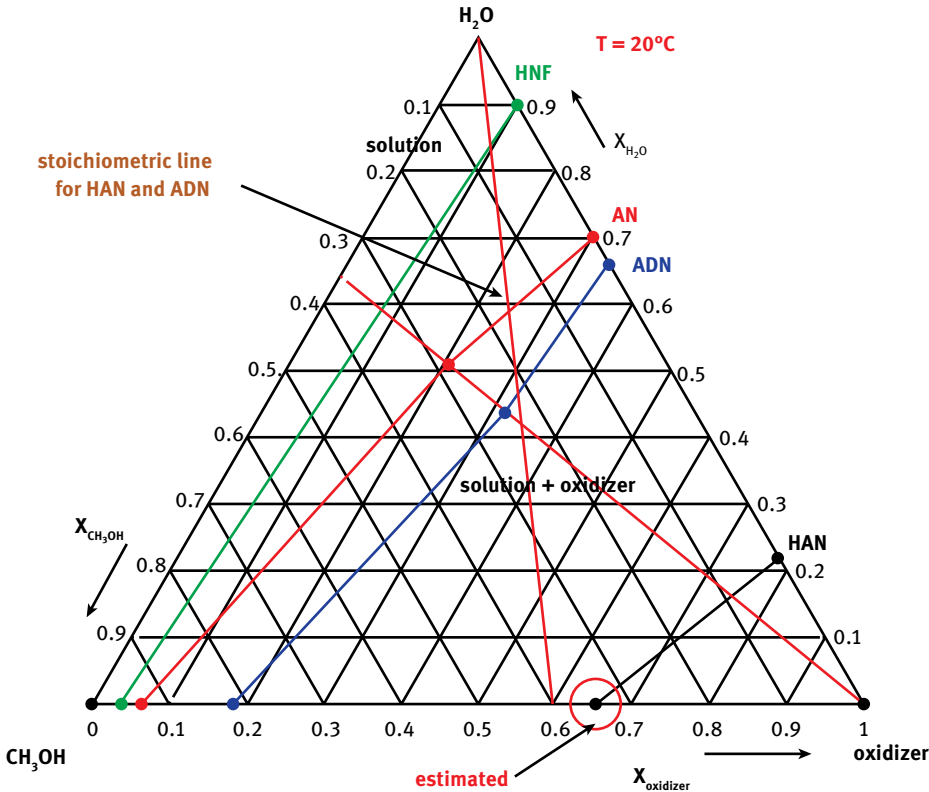


Figure 18: Ternary phase diagram of oxidizer solutions with methanol. (Reproduced and modified from Kappenstein, Batonneau, Perianu and Wingborg [175] with permission from Dr. Charles Kappenstein.)

There are four phase boundary lines emanating from the right side of the triangle and running toward the fuel corner (left corner). The compositions above those lines are liquid, and the compositions below the lines contain undissolved oxidizer. The line for ADN is shown in blue. In addition to the colored phase boundary lines, a red line dropping from the water corner (top corner) of the diagram marks the stoichiometric ratio of oxidizer : fuel (OMOX line). If one wants to select an optimum high-performance ternary propellant composition, one would want to select a composition close to the OMOX line and above the phase boundary.

A composition that meets these criteria would be 72% ADN, 13.4% methanol, and 14.6% water. The theoretical specific vacuum impulse of such a monopropellant would be 2698 N s kg^{-1} (275 s) ($p_c = 2 \text{ MPa}$, $A_e/A_t = 50$), compared to 2300 N s kg^{-1} (234 s) for hydrazine.

3.4.2 Binary Phase Diagrams of Ammonium Dinitramide Mixtures

Mixtures of ADN with other dinitramide salts or other ammonium salts can give solid solutions and oxidizers with improved sensitivity or performance properties.

ADN melts between 365 and 368 K (92 and 95 °C), depending on the amount of AN impurity present. The melting point can be as low as 328 K (55 °C) at the ADN/AN (70/30 mol percent) eutectic point. The melting of an ADN/AN mixture containing 5% AN starts at 328 K (55 °C), and temperature-resolved XRD shows transitions in the crystal structure [188]. AN expands the ADN lattice by forming a solid solution that favors the formation of a eutectic melt.

Mixtures of ADN with some hydrogen bond donor compounds result in the formation of ionic liquids that have been evaluated as monopropellants [189]. For instance, acetamide that melts at 355.5 K (82.4 °C) forms a eutectic with a melting point of 280 K (7 °C), for a melting point of ADN depression of $\Delta T = 86$ °C. Similarly, oxalic acid, which melts at 463 K (190 °C), forms a eutectic melting at 323 K (50 °C) for a depression of $\Delta T = 43$ °C. Urea, which melts at 406 K (133 °C), forms a eutectic melting at 325 K (52 °C) for a depression of $\Delta T = 41$ °C. It was found that the amount of melting point depression depends on the hydrogen bond donor's molecular volume.

Binary eutectic mixtures of ADN with methylammonium nitrate and ternary mixtures of ADN with urea and methylammonium nitrate are ionic liquids at room temperature and were evaluated as energetic ionic liquid propellants [190, 191]. The theoretical specific impulse of such mixtures is potentially higher than that of SHP163 or LMP103 (see *Encyclopedia of Monopropellants*, chapter “Ammonium Dinitramide-Based Monopropellants”). These ionic liquids were characterized by DTA, TGA–mass spectroscopy, and IR and mass spectrometric analysis of their thermal decomposition products. In the DTA, the first exotherm started at 423 K (150 °C).

The addition of ADN to AN is a means of eliminating the troublesome IV → II phase transition (see *Encyclopedia of Oxidizers*, chapter “Nitrate Oxidizers”).

A detailed study of the ADN/AN binary system was based on both experimental and computational methods. Binary ADN/AN phase diagram calculation were performed using a basic model based on ideal ionic liquid and pure non-miscible solid phases and were compared to the experimental phase diagram determined by DSC analyses of 24 prepared compositions [192]. The ADN/AN phase diagram illustrated in Figure 19 is based on the $T_{\max}$ peak temperatures of the DSC experiments and contains a combination of experimental and computed data. Results from computations and experiments are not in perfect agreement. The locations of the calculated and measured eutectic points are about 0.17 mol-fraction units apart. The measured eutectic has a melting point of 330 K (57 °C) and occurs at an ADN mol fraction of 0.6.

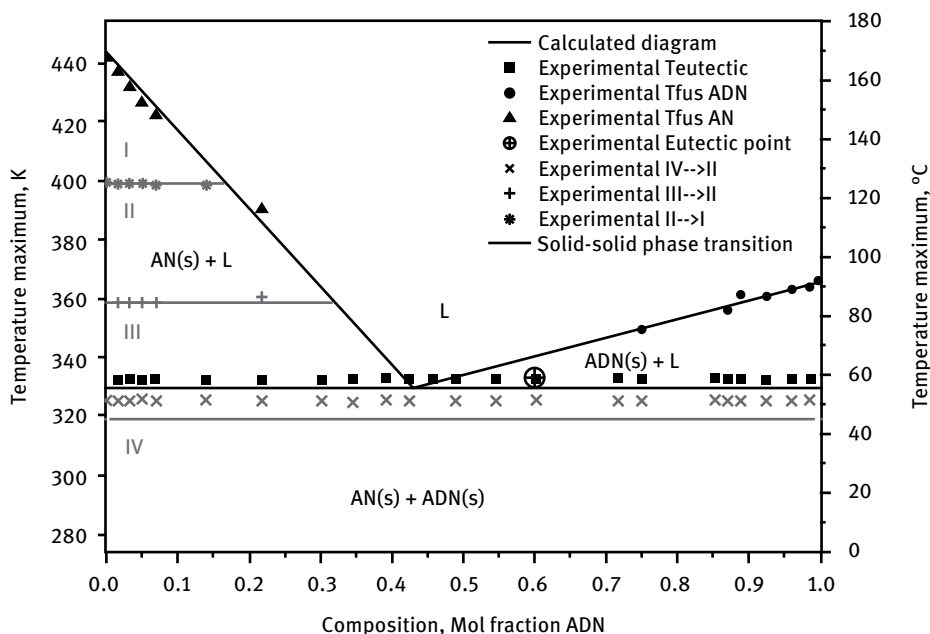


Figure 19: Experimental and calculated ADN/AN binary phase diagram. (Reproduced and modified from [192] with permission granted by Dr. Xavier Secordel 26-May-2020.)

3.5 Density of Ammonium Dinitramide

The density of solid crystalline ADN is 1.81 g/cm^3 . That is higher than the density of AN and lower than the density of AP. HAN and HNF have higher densities than ADN. The density of molten ADN at 100°C is 1.560 g/cm^3 [193]. A summary of literature data on the density of ADN is given in Table 9. Additional XRD density data are in the crystallographic properties table (Table 14).

Table 9: Density of ammonium dinitramide.

Density g/cm ³	Temperature K	Method	References
1.801		X-ray	[164]
1.808		Volumetric	[193]
1.824 ± 0.009		Pycnometric	[137]
1.831		X-ray	[194]
1.831	223	X-ray	[195]
1.8184	293	X-ray	[169]
1.872	90	X-ray	[196]
1.807	295	Synchrotron	[90]

Based on pycnometric measurements, the density of spray-prilled ADN was 1.824 ± 0.009 g/cm³ (average of six measurements) [137].

The coefficient of thermal expansion of ADN was measured using temperature-resolved XRD [188]. Density versus temperature data from different sources have been plotted in Figure 20 and give a linear relationship.

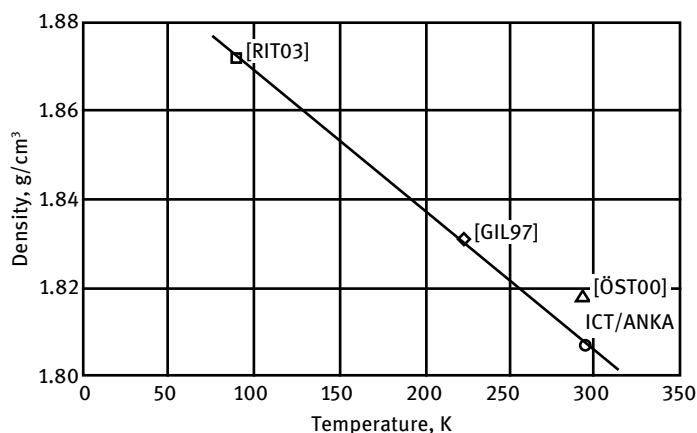


Figure 20: Density of ADN. (Reprinted and modified from [90] with permission granted by ICT 12-Mar-2021.)

By extrapolating the liquid density in Figure 21 (in Section 3.5.1.1) to higher temperature, the liquid density of ADN at 373 K (100 °C) was estimated to be 1.61 g/cm³. This is 11% lower than the density of solid ADN at ambient conditions. Thus, pure molten ADN at 373 K (100 °C) will, on crystallization and cooling to ambient temperature, shrink by 11% [176].

3.5.1.1 Density of Ammonium Dinitramide Solutions

If the density of ADN solutions is plotted against the mass fraction, the curve is slightly concave. Figure 21 shows the density of aqueous ADN solutions at 298 K in comparison to densities of two other oxidizers [175]. The AN data were measured at a temperature higher than room temperature (323 K) because AN is less soluble in water than the other two oxidizers.

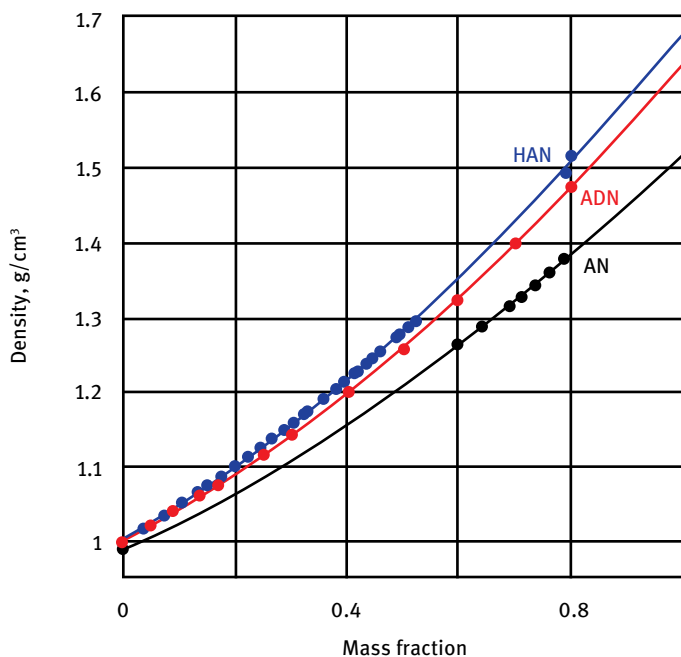


Figure 21: Density of aqueous ADN solutions in comparison to other oxidizers. (Reproduced and modified from Kappenstein, Batonneau, Perianu and Wingborg [175] with permission from Dr. Charles Kappenstein.)

The molar volumina of ADN and other oxidizers was measured so that the theoretical density of oxidizer/fuel/water mixtures in monopropellants could be calculated assuming additive behavior of the molar volumina in mixtures. As a start, the reciprocal density (i.e., the specific volume) was plotted versus the mol fraction of oxidizer as shown in Figure 22.

The curves in Figure 22 are straight lines, such that their shape can be expressed by a simple linear function

$$V_m = V_{m\text{H}_2\text{O}} \times X_{\text{H}_2\text{O}} + V_{m\text{ADN}} \times X_{\text{ADN}}$$

$$V_m = V_{m\text{H}_2\text{O}} + (V_{m\text{ADN}} - V_{m\text{H}_2\text{O}}) \times X_{\text{ADN}}$$

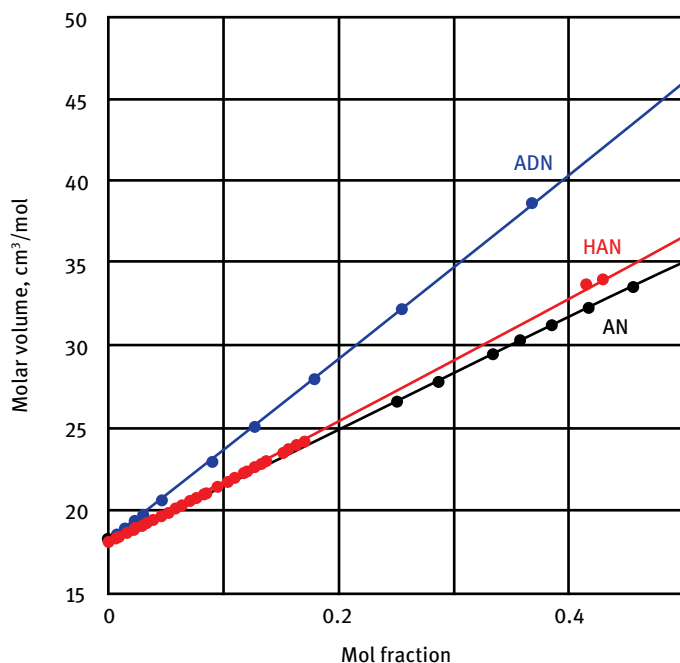


Figure 22: Molar volume of ADN solutions versus mol fraction of ADN in comparison to other oxidizers. (Reproduced and modified from Kappenstein, Batonneau, Perianu and Wingborg [175] with permission from Dr. Charles Kappenstein.)

The molar volumina of the salts are derived from the intercept of the lines. The results are summarized in Table 10.

Table 10: Extrapolated molar volume and density of pure ionic liquid oxidizers.

Compound name	Formula	Molar volume, mL/mol	Density of pure ionic liquid (no solvent), g/cm ³
Ammonium nitrate	NH ₄ NO ₃	52.00 (15)*	1.539 (5)*
Ammonium dinitramide	NH ₄ N(NO ₂) ₂	74.06 (13)	1.675 (3)
Hydroxylammonium nitrate	NH ₃ OH NO ₃	55.45 (19)	1.732 (6)

*Numbers in parentheses designate the standard deviation of the last digits.

Data source: [175]

A similar set of density and molar volume measurements was reported 2 years later (Wingborg [176]). The density of ADN solutions in comparison to the density of AN solutions in water at 298 K is shown in Figure 23.

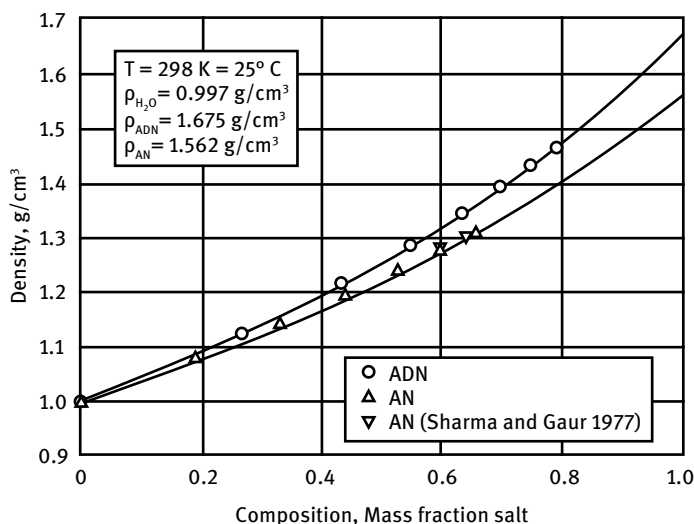


Figure 23: Density of ADN and AN solutions in water at 298 K. (Reprinted and modified from [176], with permission from © 2006 American Chemical Society; permission conveyed through RightsLink.)

The molar volumes of ADN and AN in aqueous solutions obtained from a linear regression analysis are tabulated in Table 11.

Table 11: Molar volumes of ADN and AN in aqueous solutions at 298 K (25°C).

	ADN	AN
Linear correlation coefficient r^2	0.99995	0.99975
Molar volumes for water, V_w , cm^3/mol	17.98 ± 0.03	17.98 ± 0.04
Molar volumes for salts, V_s , cm^3/mol	74.08 ± 0.17	51.23 ± 0.24
Density of the salts in the liquid state, ρ_s , g/cm^3	1.675 ± 0.004	1.562 ± 0.007

Data source: [176]

3.6 Vapor Pressure and Sublimation of Ammonium Dinitramide

Sublimation of undecomposed ADN is a prime step in the decomposition and burning of ADN. The mechanism for sublimation of ADN has been investigated quantum mechanically with generalized gradient approximation plane-wave DFT calculations [197]. The calculated total sublimation enthalpy for $\text{ADN}(\text{S}) \rightarrow \text{NH}_3(\text{G}) + \text{HN}(\text{NO}_2)_2(\text{G})$, 188 kJ/mol (44.9 kcal/mol), was in good agreement with the value of 176 kJ/mol (42.1 kcal/mol) predicted for the one-step sublimation process and the value of 184 kJ/mol (44.0 kcal/mol) using experimental thermochemical data.

3.7 Viscosity and Surface Tension of Ammonium Dinitramide Solutions

The surface tension of propellants is important for the design of injection orifices and passive propellant management devices in propellant tanks operating in zero gravity.

The surface tension and the wetting angles of molten ADN were measured in order to select proper equipment (nozzles, agitator paddles) and materials of construction in contact with ADN [119]. The surface tension of molten ADN at 370 K (97°C) is relatively high due to the molecular structure of ADN and the ion–ion interactions in the melt. The surface tension of molten ADN is 89 mN m^{-1} , and the surface tension of an 80 mass-% solution of HAN in water is 88 mN m^{-1} [198].

3.8 Thermal Conductivity and Thermal Diffusivity of Ammonium Dinitramide

The heat capacity, thermal conductivity, and thermal diffusivity of a range of other oxidizers, binders, and rocket propellants were determined and compared with data in the literature [199]. The thermal diffusivity α of ADN for the range from 20 to 65°C can be described by the linear equation

$$\alpha = 1.89 \times 10^{-3} - 1.74 \times 10^{-6}t$$

where α is the thermal diffusivity in cm^2/s and t is the temperature in °C. Likewise, the thermal conductivity λ of ADN for the range from 293 to 338 K (20 to 65°C) can be described by the linear equation

$$\lambda = 1.08 \times 10^{-3} - 5.78 \times 10^{-7}t$$

where λ is the thermal conductivity in $\text{cal cm}^{-1} \text{s}^{-1} \text{°C}^{-1}$ and t is the temperature in °C. Similar data are contained in the same publication for a wide range of oxidizers, binders, and solid propellants.

3.9 Thermophysical Properties of Ammonium Dinitramide

3.9.1 Heat Capacity of Ammonium Dinitramide

The heat capacity (C_p , solid) of ADN is $1.8 \pm 0.2 \text{ J g}^{-1} \text{°C}^{-1}$ [193]. The heat capacity of ADN in the range 293–338 K (20–65°C) can be described by the following linear equation [199]:

$$c_p = 0.308 + 3.61 \times 10^{-4}t$$

where c_p is the heat capacity in $\text{cal g}^{-1} \text{°C}^{-1}$ and t is the temperature in °C.

3.9.2 Heat of Fusion of Ammonium Dinitramide

The heat of fusion of ADN was estimated to be $17.4 \text{ kJ/mol} = 140.14 \text{ J/g}$. The entropy of fusion was estimated to be $47.8 \text{ J K}^{-1} \text{ mol}^{-1}$ [198].

Experimental heat of fusion measured during melt-casting of large charges of ADN was $130 \pm 5 \text{ J/g}$ [193]. Other sources give the heat of fusion as 140 J/g [200] or 142 J/g [14]. Based on DSC measurements, several other samples had a heat of fusion of $146.0 \pm 0.21 \text{ J/g}$ (unprilled ADN) and $92.4 \pm 0.2 \text{ J/g}$ (prilled) [137]. Table 12 gives the heat of fusion of ADN in comparison to those of AN and AP.

Table 12: Heat of fusion and melting points of AN, ADN, and AP.

	ΔH_{fus}		T_{fus}	
	kJ/mol	kcal/mol	K	°C
AN	6.11	1.46	442.7	169.6
ADN	17.62	4.21	366.0	92.9
AP	29.30	7.00	513.1	240

Data source: [192]

3.9.3 Heat of Solution of Ammonium Dinitramide

When ADN is dissolved in water, the temperature of the mixture decreases substantially. This means that the heat of solution is positive and that the enthalpy of the solution increases by absorbing heat from the environment.

Enthalpies of formation and solution of ADN along with other salts of nitric and dinitramidic acids with organic amines were determined by combustion and solution calorimetry methods [201]. The enthalpy of solution of ADN in water at high dilutions was measured as $36.44 \pm 0.04 \text{ kJ/mol}$ ($8.71 \pm 0.01 \text{ kcal/mol}$).

The ADN heat of solution was measured using a solution/mixing calorimeter based on a dewar vessel equipped with a magnetic stirrer and a precision thermometer [202, 203]. The amount of water in the vessel was 100 g, and the sample weight was 1 g. The ADN heat of solution was found to be $+35.7 \text{ kJ/mol}$. For more concentrated solutions like those in monopropellants, the ADN heat of solution is only $+24 \text{ kJ/mol}$.

3.9.4 Enthalpy of Formation of Ammonium Dinitramide

Enthalpy of formation data for ADN reported in the literature vary considerably, most likely because of the poor quality of ADN (contamination by AN) used by some of the early investigators. Table 13 gives a historical summary of the numbers reported by different sources.

The enthalpy of formation of ADN was determined from experimental data of the enthalpy of dissolution of this salt [206]. The enthalpy of formation of the dinitramide

Table 13: Enthalpy of formation data for ADN.

Enthalpy of formation, ΔH_{298}^f				Remarks	References
kJ/mol	kJ/kg	kcal/mol	kcal/kg		
-149.8	-1207	-35.8	-288.6	Measured	[164]
-133.0	-1072	-31.79	-256.3		[2]
-150.6	-1214	-36.0	-290		[105]
-135.0	-1088	-32.26	-260		[193]
-151.3	-1220	-36.2	-291.6		[204]
-137	-1104	-32.74	-263.9		[205]
-134.6 ± 0.46	-1085	32.16 ± 0.11	-259.2	Measured from heat of combustion	[206]
-134.6 ± 0.46	-1085	-32.16 ± 0.11	-259.2		[201]
		-35.4			
-151.5	-1221	-36.2	-291.8	Calculated	[207]
-148	-1193	-35.37	-285	Calculated	[14]
-135.6	-1085	-32.41	-261.2		[203]

$M = 124.0569 \text{ g/mol}; 8.0608 \text{ mol/kg}$

anion was calculated from four groups of independent data on burning and dissolution of nitraminic acid salts and salts with identical cations. Using combustion and dissolution calorimetry, the enthalpies of formation and dissolution of the salts of hydrazinium, guanidinium, aminoguanidinium, and triaminoguanidinium of nitric and dinitraminic acids were obtained and compared to literature data. Based on using the known enthalpy of formation of the nitrate ion, the enthalpies of formation of the cations in the infinitely diluted aqueous solutions were then calculated. The enthalpy of dissolution of ADN is $36.4 \pm 0.04 \text{ kJ/mol}$ ($8.71 \pm 0.01 \text{ kcal/mol}$). Using combustion calorimetry, the energy of combustion of ADN for a sample with purity greater than 99.9% was measured, and the best value for its enthalpy of formation was then $134.5 \pm 0.5 \text{ kJ/mol}$ ($32.16 \pm 0.11 \text{ kcal/mol}$).

Enthalpies of formation of cations (ammonium, hydrazinium, and a series of guanidinium ions) by themselves in infinitely diluted aqueous solutions were calculated using the known enthalpy of formation of the nitrate ion ($-206.8 \text{ kJ/mol} = -49.44 \text{ kcal/mol}$) [201]. The enthalpy of formation of the dinitramidic acid anion could then be determined based on the enthalpy of formation and solution of the acid salts. The enthalpy of formation of the dinitramidic acid anion averaged to $35.1 \pm 0.5 \text{ kJ/mol}$ ($8.40 \pm 0.13 \text{ kcal/mol}$). From these data, the enthalpy of formation of ADN was calculated as $-134.5 \pm 0.6 \text{ kJ/mol}$ ($-32.14 \pm 0.14 \text{ kcal/mol}$). This compares well with the enthalpy of formation of ADN that was measured for a sample with purity greater than 99.9% and turned out to be $-134.7 \pm 0.8 \text{ kJ/mol}$ ($-32.20 \pm 0.19 \text{ kcal/mol}$) based on the energy of combustion of ADN in a constant-volume calorimetric bomb. Combining calculated and measured enthalpies of formation of ADN leads

to a recommended weighted value of $-134.6 \pm 0.46 \text{ kJ/mol}$ ($-32.16 \pm 0.11 \text{ kcal/mol}$) for the enthalpy of formation of ADN. As of 2014, this seems to be the most reliable number found in the literature so far. This number is consistent with the enthalpies of formation of sodium, potassium, and cesium salts of dinitramidic acid that were determined as part of the same study.

A linear relationship seems to exist between the enthalpies of formation of nitrates and dinitramide salts having the same cation, as illustrated in Figure 24. Thus, if the enthalpy of formation for a nitrate salt (XN) is known, the enthalpy of formation of its corresponding dinitramide salt (XDN) can be estimated according to the equation

$$\Delta H_f(\text{XDN}) = \Delta H_f(\text{XN}) + 230n \left(\frac{\text{kJ}}{\text{mol}} \right)$$

where n is the number of anions per cation. Using the established data for the enthalpy of formation for AN (-365.6 kJ/mol), the enthalpy of formation for ADN was estimated to be -135.6 kJ/mol , which is in good agreement with the experimental value (-134.6 kJ/mol). The dissociation energy for ADN to dissociate into its ions is $255 \pm 12.5 \text{ kJ/mol}$, reference [105].

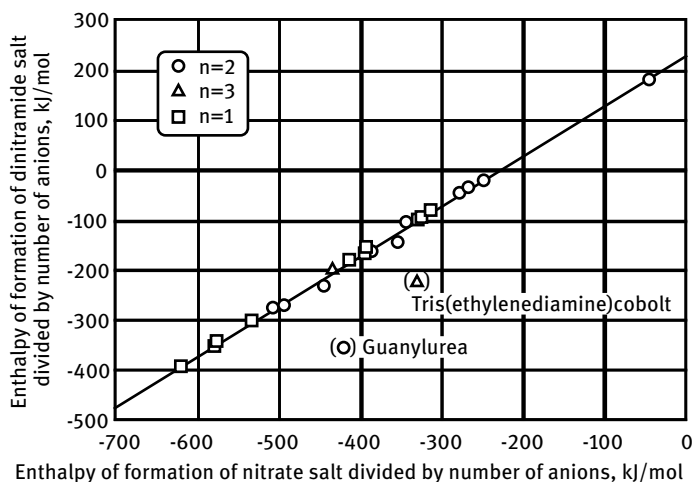


Figure 24: Enthalpy of formation of XDN/XN pairs divided by the number of anions per cation. Salts in parentheses were excluded in the linear regression analysis. (Reproduced and modified from [13].)

3.10 Molecular Properties of Ammonium Dinitramide

The high stability of the dinitramide anion is attributed to the resonance delocalization of the net negative charge over the molecular system, which strengthens those N—NO₂ bonds that are most susceptible to rupture. Three of the resonance forms are shown in Figure 25, which illustrates the conjugation between the nitro groups and the central nitrogen.

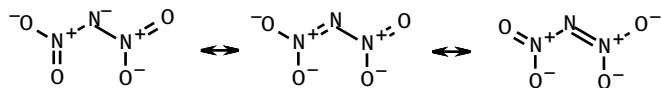


Figure 25: Three resonance structures of the dinitramide anion. (Reproduced and modified from [164].)

Actually, there are eight possible resonance forms of the dinitramide ion (Figure 26).

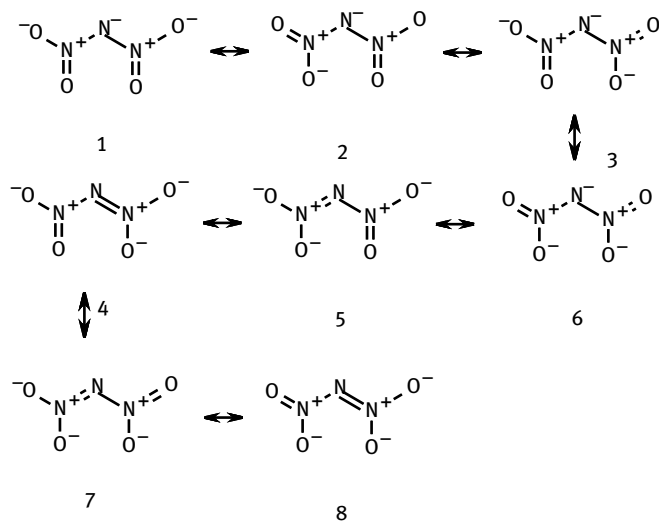
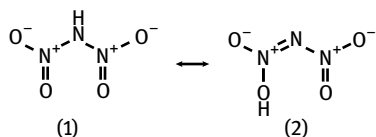


Figure 26: Eight resonance structures of the dinitramide anion. (Reproduced and modified from [208].)

Resonance forms 1 through 3 would most likely make major contributions to the statistical distribution. Forms 6 through 8 are less likely because they contain negative charges on two adjacent oxygen atoms, which would render the molecule less stable [208].

There are two possible locations of the hydrogen in dinitramidic acid: one on the central nitrogen (1), or on one of the oxygens (2). While there is only one stable nitro form, there are several stable conformers of the aci form (2).



Theoretical ab initio calculations for the free anion indicated that structure (1) with an equal negative charge distribution between the nitro groups is the more stable form, lying 9.4 kcal/mol lower in energy than structure (2) [209]. They determined the gas-phase acidities of isomers (1) and (2) as 1305 ± 8 and 1266 ± 8 kJ/mol (312.0 ± 2 and 302.6 ± 2 kcal/mol), respectively. For the free acid $\text{HN}(\text{NO}_2)_2$, Michels and Montgomery reported ΔH_0^f (0 K), a range from 119 to 124 kJ/mol (28.4–29.7 kcal/mol). In aqueous solutions, however, the initial anion structure distorts as a result of the low-energy barrier to rotation around the N–N bond.

The bond angles and bond distances in the dinitramide ion are shown in Figure 27.

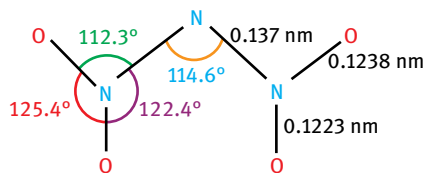


Figure 27: Bond angles and bond distances in dinitramide ion.

The dinitramide ion is very flexible, with twisting around each of the N—N axes, and it can assume different shapes depending on the environment it is in. It will have different shapes in solution or in a solid state. And even in the solid state, its shape depends on the cations it is paired with.

Vibrational and electronic spectra of dinitramide and its salts $M^+N(NO_2)_2$ ($M = K, Na, Li, NH_4, Hg, Fe$), were studied under different conditions (aggregate states, solvents, and temperature) [210, 211]. The spectra were interpreted from experimental and theoretical data using the normal coordinate analysis method, leading to conclusions about the structure of the $HN(NO_2)_2$ molecule and its ion. It is surprising that the UV spectra of dinitramidic acid can differ dramatically depending on the preparation of the chemical, the solvent it is in, and the acidity of the solution (Figure 28).

IR and UV spectroscopic studies of the free dinitraminic acid showed that in the covalent state it can exist in two different forms. In one of these forms, (1), the proton is bound to the central nitrogen atom, $\text{HN}(\text{NO}_2)_2$. In the other form, (3), the proton is equally bound to two oxygen atoms of both nitro groups ([212]; Figure 29).

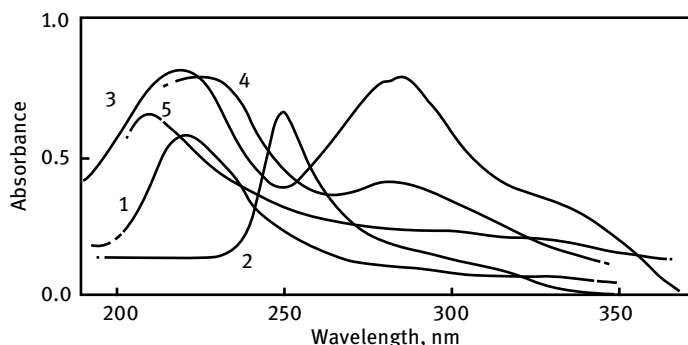


Figure 28: UV spectra of dinitramidic acid and its potassium salt. (Reprinted and modified from [212], with permission of © 1994 Springer Nature; permission conveyed through Copyright Clearance Center Inc.) Legend: (1) DNA in ether; (2) KDN extracted with dichloroethane from 65% H_2SO_4 ; (3) KDN in H_2O ; (4) KDN in 65% H_2SO_4 ; (5) KDN in 98% H_2SO_4

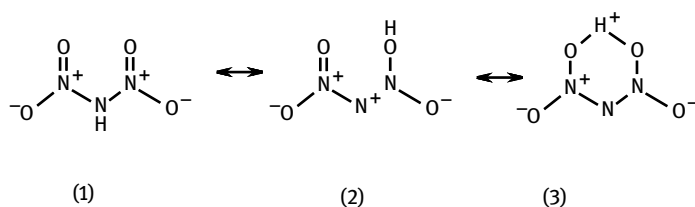


Figure 29: Rotation and stabilization in the dinitramide ion in the presence of a cation. (Reproduced and modified from [211] with permission of © 2001 Elsevier; permission conveyed through Copyright Clearance Center Inc.)

3.10.1 Molecular Structure of Ammonium Dinitramide

ADN is known to exist in two polymorphic forms: α -ADN and β -ADN. For $p < 2.02 \text{ GPa}$ ($2 \times 10^4 \text{ atm}$), α -ADN with a stable monoclinic prism crystal structure is observed, and β -ADN exists only at higher pressures ($p > 2.02 \text{ GPa} = 2 \times 10^4 \text{ atm}$) [174, 213].

3.10.1.1 Crystal Structure of Ammonium Dinitramide from X-Ray Diffraction

ADN forms monoclinic crystals with the space group designation $P2_1/c$. It possesses a twofold screw axis parallel to the b -axis, with a c -glide plane perpendicular to the screw axis [196]. The lattice parameters are $a = 6.908 \text{ \AA}$, $b = 11.895 \text{ \AA}$, $c = 5.638 \text{ \AA}$, and $\beta = 100.278^\circ$. One dinitramide anion and one ammonium cation comprise the asymmetric subunit cell, a unique subset of atoms from which all the other components of the unit cell can be assembled. The bonds between N1 at the apex and the nitrogens N2 and N3 of the two terminal nitro groups form an 113.8° angle. The two nitro groups are rotated

out of the N2—N1—N3 plane, one by 27.9°, the other by 22.8°. This rotation may be due to repulsive forces between the negatively charged oxygen atoms. This observation is also confirmed by measurement of the IR and Raman spectra of dinitramide salts. The calculated energy differences between twisted structures and those with either coplanar or perpendicular —NO₂ groups are very small, and the rotational barriers are less than 12.5 kJ/mol (3 kcal/mol). As a result of these small energy differences, the torsional angles observed in the crystal structures of different N(NO₂)₂[−] salts can vary by as much as 30° because of crystal packing effects and interactions with counterions. Table 14 gives a comparison of crystallographic data for ADN reported by different authors.

Table 14: Comparison of crystallographic data for ADN.

Author(s)	Gidaspov et al.	Gilardi et al.	Oestmark et al.	Ritchie et al.	Fuhr	Zhu et al.
Year	1995	1997	2000	2003	2008	2008
Reference	[194]	[195]	[169]	[196]	[93]	[214]
Temperature, K	—	223	293	90	295	
Radiation	—	Mo K α	Mo K α	Mo K α	Synchrotron	Calculated
<i>a</i> , Å	6.84	6.914(1)	5.6228	6.933(1)	6.908	6.98
<i>b</i> , Å	11.90	11.787(3)	11.8750	11.603(1)	11.895	12.121
<i>c</i> , Å	5.61	5.614(1)	6.8954	5.567(1)	5.638	5.416
β , °	99.8	100.40(2)	100.17	100.58	100.278	99.15
XRD density, g/cm ³	1.831	1.831	1.8184	1.872	1.807	

The charge distribution may have some effect on the extent of hydrogen bonding seen in ADN that helps to stabilize the molecule. Each of the four hydrogens of the ammonium cation participates in hydrogen bonding, but only three of the oxygen atoms participate in this scheme. A fairly thorough review of the crystal structure of ADN is given in reference [97] as part of an effort to modify the crystal habit of ADN crystals.

The XRD of several dinitramide salts with organic, inorganic, and metal cations revealed that these dinitramide salts exist in different conformations depending on the cation present [195]. In addition to ADN, the crystal structures of the lithium, potassium, and cesium salts of dinitramidic acid were analyzed using XRD. The theoretical and structural studies of the dinitramide anion showed that it is quite flexible and adopts different conformations depending on its environment. Ideal minimum energy conformation would be a C₂ symmetry. However, dinitramide salts show a diversity of conformations with C₁, C_s, and predicted C₂ symmetry. No two dinitramide salts give isostructural conformers. The conformation adopted by the dinitramide anion is quite different, with different bent, twist, and torsional angles. The experimental results have been interpreted by and compared to extensive molecular orbital and electron density theoretical calculations.

XRD is the preferred tool for the investigation of the crystal structures of all energetic materials. Crystallite size and microstrain of ADN prills can be investigated by means of XRD [215, 216]. The investigations correlate the size/strain broadening with particle processing history and mechanical sensitivities. Compressibility can be different in different axes of the crystal. Shock loading may result in rapid compression in one axis but not in the other, leading to hot spots and accidental ignition of energetic materials. Anisotropic diffraction peak broadening was found for some of the energetic materials. Whereas 2 θ positions and intensities of XRD peaks yield information on crystal structures, peak profiles (e.g., width at half-height) are related to the real structure determined by crystallite sizes, shapes, and microstrains. Microstrains are left behind after grinding of the materials or as the result of imperfect (hastened) crystal growth. The size/strain broadening of ADN XRD peaks was measured and interpreted based on crystal geometry, contaminants, and internal crystal defects, and also in comparison to similar measurements on RDX and FOX-7 [217–219]. ADN microstrain broadening was moderate compared to FOX-7 or RDX; all values were below $0.02 \text{ \AA}^{-1}$ (reciprocal peak width).

Comparing the hygroscopicity of crystalline ADN and AP, it is noted that the unwanted hygroscopicity of crystalline ADN is more severe than that of AP, and it seriously affects its use. This quite different behavior is associated with their different crystal structures. XRD single-crystal diffraction data showed that vast hydrogen bond networks link the ADN structure [186]. The 3D structure of ADN joined by hydrogen bonds is an unusual twofold 3D interpropagation network structure, and the hydrogen bonds in the ADN crystal are much shorter than those in AP because of the special structure. The hydrogen bonds between ADN and H₂O were assayed by IR spectroscopy. DSC thermograms of moist ADN and AP crystals also confirm that, because of the stronger hydrogen bond between ADN and H₂O molecules, large amounts of bound H₂O are present in ADN crystals besides some unbound H₂O. All hydrogen atoms of the NH₄⁺ ions are involved in hydrogen bonds in the ADN crystal. All but one of the oxygen atoms participate in hydrogen bonding.

The melt crystallization behavior of ADN during cooloff in the course of prilling operations was observed by XRD and depends on ADN quality, humidity, maximum temperature of temperature cycles, and the type of liquid phase suspension agents [220]. Freshly prepared ADN prills undergo slow structural changes during storage following their preparation, in particular if they are not stored under absolutely dry conditions. Such changes can be followed by XRD [221].

3.10.1.2 Crystal Structure of Ammonium Dinitramide from Neutron Diffraction

Neutron diffraction measurements complement the information already obtained with XRD and confirm or sometimes contradict the XRD results. Neutron powder diffraction patterns of ADN were collected at pressures up to 4.03 GPa [222, 223]. All of the patterns could be indexed and fitted to a monoclinic unit cell based on that found at ambient pressure. Above 2.99 GPa, significant broadening of the diffraction peaks

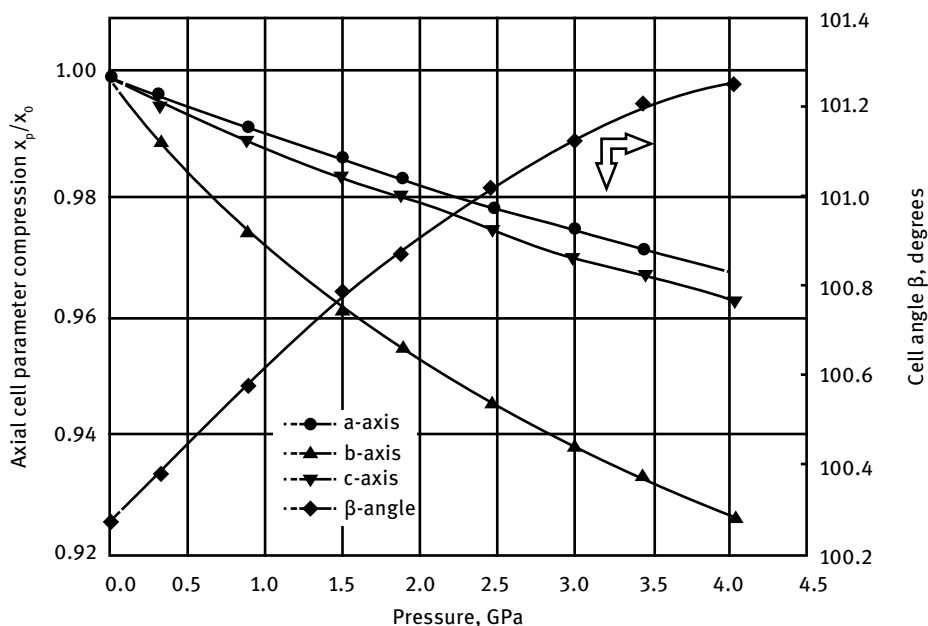


Figure 30: Variation of lattice parameters of ADN as a function of pressure. (Reproduced and modified from [222] with permission granted by Dr. Colin Pulham 15-Feb-2021)

was observed, indicative of the non-hydrostatic behavior of HT-70 (a perfluorinated polyether in which the crystals are suspended), and this prevented the collection of useful data above 4.03 GPa. Figure 30 shows the variation of ADN lattice parameters with pressure and highlights the higher compressibility along the *b* axis consistent with the weaker intermolecular interactions in that direction.

No sign of the first-order phase transition reported by Russell et al. was observed up to 4.03 GPa under these conditions. To test whether this apparent difference in behavior originated from the use of the perdeuterated compound, a separate experiment using $\text{NH}_4\text{N}(\text{NO}_2)_2$ was performed using angle dispersive powder XRD up to 5.5 GPa; this, too, showed no sign of a phase transition. At 2.5 GPa, several of the longer H-bonding interactions had substantially shortened, e.g., $\text{D4}\cdots\text{O2B}$ distance had decreased from 2.43 Å to 2.24 Å, and $\text{D2}\cdots\text{O3A}$ distance had decreased from 2.13 Å to 1.94 Å.

3.10.1.3 Molecular Structure of Ammonium Dinitramide from Computations

The molecular structure of energetic compounds is closely related to their thermal stability and energy content. Strong bonds and high symmetry result in a thermally stable molecule. What separates a potentially useful molecule from one that is not is the rate at which decomposition occurs, or the kinetic stability, which is

more difficult to predict than the heat of formation. Quantum chemical studies are a useful tool in predicting decomposition rates and should precede synthetic efforts. Ideally, a high-energy-density material (HEDM) suitable for safe handling at room temperature should have a free-energy activation barrier for decomposition that exceeds 125.5 kJ/mol (30 kcal/mol). This value is estimated assuming first-order decomposition kinetics and corresponds to a half-life of 35 years at room temperature.

Even prior to the publication of the (re)discovery of dinitramides outside the USSR, a series of *ab initio* self-consistent field (SCF) calculations of the structures of the dinitramide anion, $\text{N}(\text{NO}_2)_2^-$, and some related molecules, $\text{HN}(\text{NO}_2)_2$ and $\text{N}(\text{NO}_2)_3$, showed that several factors affect their stabilities [208]. The proton affinity of $\text{N}(\text{NO}_2)_2^-$ was predicted as a measure of the acidity of $\text{HN}(\text{NO}_2)_2$. The interaction energy of $\text{N}(\text{NO}_2)_2^-$ with NO_2^+ to yield $\text{N}(\text{NO}_2)_3$, an unknown nitrogen oxide, can be calculated, but this compound has not yet been found. It would be a good oxidizer. The proton affinity of $\text{N}(\text{NO}_2)_2^-$ was found to be considerably greater than that of NO_2^- . The computed interatomic distances and bond angles of the dinitramide anion are shown in Figure 31.

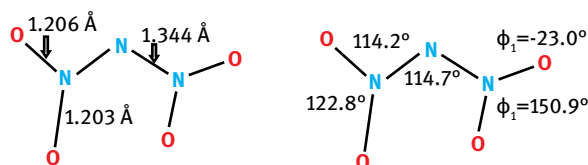


Figure 31: Bond lengths and bond angles of dinitramide predicted by computational chemistry. (Reproduced and modified from [224].)

Atom–atom distances, bond lengths, and bond angles of the dinitramide ion predicted by computational chemistry are in close agreement with XRD data [224]. With improved computing capabilities of desktop computers, existing programs for calculating the electron charge density and electrostatic potential between ions have been modified to produce output suitable for improved visualization, in particular using color and 3D computer graphics. As an example, the charge density and electrostatic potential of three dinitramide salts were calculated and published [225, 226]. The aim of this work was to obtain information about the redistribution of electrons in the dinitramide anion, $\text{N}(\text{NO}_2)_2^-$ due to effects such as chemical bonding, based on XRD measurements. Three dinitramide salts (ammonium, monoprotonated, and diprotonated biguanidinium) were selected for charge density analyses on the basis of the observed variations of the dinitramide anion in the room-temperature structures and the potential future applications of these compounds as rocket propellants.

There were two objectives for this project. The first was to see whether the difference in the geometries of the $\text{N}(\text{NO}_2)_2^-$ ion is reflected in the size and shape of the bonding electron density using experimental methods. The second objective was to obtain the electrostatic potential of the materials based on the experimentally determined electron density distribution in order to gain some insight into the reactivity of the dinitramide ion. The different geometries produced observable differences in the deformation density. The electrostatic potential derived from the experimental electron density also showed variations with respect to the geometry and environment. These potentials have different minima and are also different from potentials produced from gas-phase semi-empirical and *ab initio* calculations.

In continuation of this study, the same group of authors found that the flexibility of the dinitramide ion is the result of mutually opposed effects of resonance stabilization and steric repulsion [227]. Evidence for this claim was found in the structural trends discovered in the analysis of X-ray data and additional energy calculations. The X-ray data also showed structural distortions brought about by different crystal environments. The calculations gave the energy required to distort a single molecular anion from the minimum energy structure to that found in the crystal. From these results, it was found that the crystal environment causes geometric variations of the ion that are site specific. On the other hand, energetically opposed effects of resonance and steric repulsion were responsible for the typically non-planar geometry of the ion and a complete separation between the NNO angles involving “inner” and “outer” oxygens.

Sorescu and Thompson have studied the structural properties of ADN crystal at ambient pressure by using DFT with pseudopotentials [228]. The optimization of the crystal structure was done with full relaxation of atomic positions and lattice parameters under $P2_1/c$ symmetry. The calculations were performed using periodic boundary conditions in all three directions. The predicted crystal structure was in good agreement with X-ray data and indicated no internal symmetry for the dinitramide ion, in contradistinction to the gas-phase theoretical results. The two halves of the dinitramine ion are twisted with respect to each other, while the NO_2 groups are rotated out of the N—N—N plane. The thermal expansion coefficients calculated for the model indicated anisotropic behavior. Subsequently, the authors used the same method to investigate the structural properties of crystalline ADN under hydrostatic compression in the pressure range of 0–300 GPa [229]. It was found that the ADN crystal maintains its monoclinic structure with $P2_1/c$ symmetry for pressures up to 10 GPa. Above 20 GPa, there is a transition to a P triclinic symmetry. The crystalline phase transition involves reorientation of the ammonium ions relative to the dinitramide ions as well as additional rotations of the NO_2 groups relative to the N—N—N plane of dinitramide ions. The lattice compression induces electronic changes that are similar to those observed for AN. An excellent and very detailed summary of the achievements of computational chemistry in predicting the properties of energetic materials, including ADN, AN, AP, and HAN, was given in a book chapter [230].

The structural model is capable of accurately predicting the temperature of the solid-to-liquid transition in ADN and estimating temperature dependence of the diffusion and viscosity coefficient in the liquid temperature range [231]. The melting point of crystalline ADN could be predicted by calculating the temperature dependence of the density, enthalpy, and radial distribution functions. However, the melting temperature of the perfect crystal calculated from the change in density was predicted to be in the range of 474–476 K, compared to the experimentally determined range of 365–368 K. The difference is attributed to superheating of the perfect crystal. The superheating effect can be eliminated by introducing assumed voids in the crystal structure. Calculations of the temperature dependence of the density of a supercell with eight or more voids predicted a melting temperature in the range of 366–368 K, which is in excellent agreement with the experimental value. The computed dependence of the melting temperature on pressure is also in excellent agreement with experiments. Similar calculations were performed for AN [232].

The electronic structure, vibrational properties, absorption spectra, and thermodynamic properties of crystalline ADN and AP were compared using DFT in the local density approximation [214]. The results showed that the p states for the two solids play a very important role in their chemical reactions. From the low-frequency to the high-frequency region, ADN has more degrees of freedom of motion modes for the vibrational frequencies than AP. The thermodynamic properties showed that ADN is easier to decompose than AP as the temperature increases.

DFT and the *ab initio*-based CBS-QB3 method were used to study possible decomposition pathways of dinitraminic acid, $\text{HN}(\text{NO}_2)_2$ (HDN), a potential ADN decomposition product, in gas phase [233]. The proton transfer isomer of HDN, $\text{O}_2\text{NNN}(\text{O})\text{OH}$, and its conformers can be formed and converted into each other through intra-molecular and inter-molecular proton transfer. The latter has been shown to proceed substantially faster via double proton transfer. The main mechanism for HDN decomposition was found to be initiated by a dissociation reaction, the splitting of nitrogen dioxide from either HDN or the HDN isomer. This reaction has an activation enthalpy of 152.7 kJ/mol (36.5 kcal/mol) at the CBS-QB3 level, which is in good agreement with experimental estimates of the decomposition barrier. The decomposition barrier of polarized dinitramide anions on the surface of solid ADN is reduced by 67 kJ/mol (16 kcal/mol), which may explain the anomalous solid state decomposition of ADN [234]. The anomalous solid-state decomposition of KDN and ADN can be explained from quantum-chemical calculations on large clusters of the two salts [235]. The decomposition mechanisms of dinitramide alkali metal and ammonium salts are highly topochemical in nature. Unsymmetrical cation coordination at the surface causes dinitramide anions to polarize and lose their resonance stabilization, reducing the decomposition barrier by >67 kJ/mol (>16 kcal/mol), compared to an isolated dinitramide anion in gas phase, to 125.5 kJ/mol (30 kcal/mol). This corresponds to a rate increase by more than 11 orders of magnitude. Both ADN and KDN decomposition is initiated by homolytic rupture of a weakened

nitrogen–nitrogen bond and dissociation into NO_2 radicals and NNO_2 radical anions, followed by production of N_2O and the corresponding nitrate. The stabilizing effect of water can be explained by its ability to reduce the polarization by hydrogen bond donation. In a similar manner, surface-active species are likely to act as stabilizers for metal and ADN salts. Spectroscopy studies of ADN and KDN crystals suggest that their surfaces are entirely covered by the decomposition products, AN and KNO_3 , respectively. Decomposition is governed by surface chemical processes involving polarized (twisted) dinitramide anions of reduced stability [236]. Donation of hydrogen bonds, antioxidant character, and basicity are properties believed to correlate with a compound's ability to act as a stabilizer for dinitramide salts.

The molecular surface structure of ADN and KDN crystals was represented by vibrational sum frequency spectroscopy and quantum chemical modeling [237]. Identification of key vibrational modes was made possible by performing DFT calculations of molecular clusters. The surface of KDN was found to be partly covered by a thin layer of the decomposition product KNO_3 , which, due to its low thickness, was not detectable by IR or Raman spectroscopy. In contrast, ADN exhibited an extremely inhomogeneous surface on which polarized dinitramide anions were present, possibly together with a thin layer of NH_4NO_3 . The experimental verification of polarized and destabilized dinitramide anions points the way to surface-active polymer support, stabilizers, and/or coating agents in order to extend the useful temperature range of ADN.

In addition to the dinitramide anion, there are other energetic nitrogen-based anions that can be envisioned to make good propellants, but some so far exist only on paper (or on the computer screen). The kinetic stability of dinitramide, trinitrogen dioxide, pentazole, and oxopentazole anions was evaluated in the gas phase and in solution by using high-level *ab initio* and DFT calculations [207, 238]. Theoretical UV spectra, solid-state heats of formation, density, and propellant performance for the corresponding ammonium salts were predicted. All calculated properties for dinitramide were in excellent agreement with whatever little experimental data were available for comparison. The standard enthalpy of formation of solid ADN was predicted to be -151 kJ/mol (-36.2 kcal/mol) based on quantum mechanical calculations [207], but this is quite different from the recommended experimental value of 134.6 kJ/mol .

Comparison of the IR and Raman spectra of isotopically substituted dinitramide salts in the solid state and in solution has provided new information on the structure and topology of the electron charge density in the dinitramide $\text{N}(\text{NO}_2)_2^-$ anion [211]. The frequency assignments were made with the help of quantum-mechanical force-field calculations and normal-coordinate analysis. The harmonic vibrational spectrum of the dinitramide anion calculated at the B3LYP/6-31+G(d) level in the presence of solvent correlated best with the experimental data.

Researchers have attempted to predict the melting point of ADN and other nitramines based on theoretical molecular orbital calculations [171]. This method can be applied to calculating the melting point of complex molecular and ionic solids

and nanoparticles. Various approaches for simulating melting and computing the thermodynamic properties were described along with force-field calculations that have been used in simulations of the melting of molecular and ionic crystalline solids, and the different structural, energetic, and dynamical quantities used to characterize and predict the melting transition were described. See also [90, 178, 239, 240].

3.10.2 Optical Properties of Ammonium Dinitramide

3.10.2.1 UV-Visible Absorption Spectra of Ammonium Dinitramide

All dinitramide salts are photosensitive and may decompose while a UV spectrum is recorded. A solution of ADN in water shows UV absorption maxima at 212 and 284 nm (Figure 32). The peak at 284 nm is characteristic for the dinitramide ion. The intensity of the peak is concentration dependent. Dinitramides are not stable in acidic environment and thus the concentration will decline at low pH.

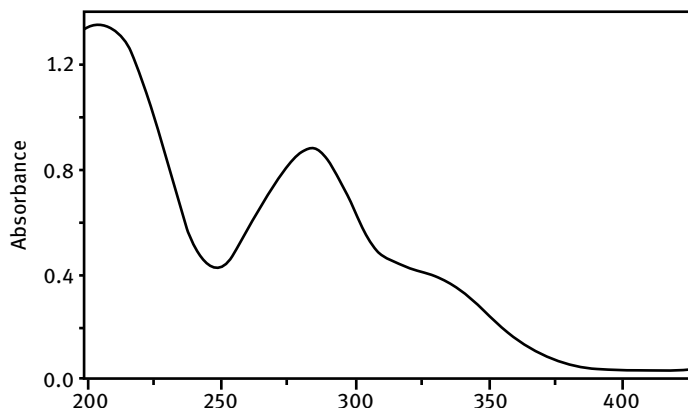


Figure 32: UV spectrum of ammonium dinitramide. (Reprinted and modified from [58] with permission granted by Dr. Santhosh 8-Feb-2021.)

The knowledge of the molar extinction coefficient ϵ of ADN is important for on-line process monitoring of the formation of ADN, for determining the yield, and also for verifying the purity of the ADN product. The molar extinction coefficient of ADN in different solvents such as water, acetonitrile, and methanol was determined [58]. The extinction coefficient at 284 nm in water is $5.258 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$. This value is comparable to one reported by Bottaro, Penwell, and Schmitt [20], who reported $5.207 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Figure 33). The extinction coefficient of ADN at 284 nm in methanol is $4.362 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$. The extinction coefficient at 284 nm in acetonitrile is $3.804 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$. For comparison, the extinction coefficient ϵ of KDN at 284 nm in water is $5.379 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$.

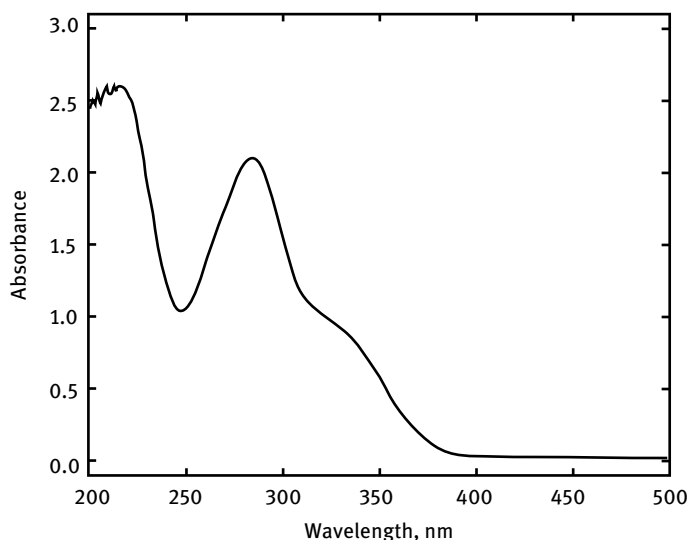


Figure 33: UV spectrum of aqueous ammonium dinitramide solution. (Reprinted and modified from [20] with permission from © 1997 American Chemical Society; permission conveyed through RightsLink.)

Other sources report that the aqueous solution of ADN has a maximum of absorption at 283.5 nm with an extinction coefficient $\sigma = 5600 \pm 100 \text{ L mol}^{-1} \text{ cm}^{-1}$ [241]. Other sources [169] give the molar extinction coefficient of ADN as $6680 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 214 nm and $5500 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 284 nm. The nature of the shoulder at 335 nm is somewhat dubious.

All dinitramide salts are sensitive to light. Some metal salts with complexed dinitramide are very light sensitive and will decompose while the UV absorption spectrum is being measured [242, 243].

3.10.2.2 IR Absorption Spectra of Ammonium Dinitramide

The IR absorption spectra of dinitramide salts either in the solid state or in solution are dominated by the absorption bands of the dinitramide ion. In the case of ammonium or hydrazinium dinitramide, the cation also contributes to the spectra and complicates the interpretation. Therefore, if one wants to study the dinitramide ion by itself, one will analyze the alkali metal dinitramides. IR spectra are available for ADN and various alkali metal dinitramides, but here we show only multiple spectra for ADN (Figure 34 and 36) and KDN (Figure 74 in Section 9.2.1). Infrared spectra of ADN show strong IR absorptions at 1526 cm^{-1} (asymmetric stretch of NO_2 in phase), 1181 cm^{-1} (symmetric stretch of NO_2 out of phase), 1025 cm^{-1} (asymmetric stretch of N_3), 3255 cm^{-1} (H_4N^+), and 1407 cm^{-1} (H_4N^+). We are comparing IR spectra of ADN from several sources.

IR Spectra at Atmospheric Pressure

Infrared spectra of ADN at atmospheric pressure are shown in Figure 34. A similar IR spectrum is in a book on dinitramide salts [3]. The assignment of IR absorption bands of ADN was made as shown in Table 15.

Table 15: Assignment of IR absorption band frequencies of ammonium dinitramide.

Assignment	Wavenumber, cm^{-1}			
Source	Santhosh [58]	Christe et al. [244]	Shlyapochnikov et al. [210]	Oliveira et al. [245]
ν N—H of NH_4^+	3124	3255	—	3132
ν_s NO_2 in phase	1343	1344	1340	1344
ν_s NO_2 out of phase	1178	1181	1180	1177
ν_{as} NO_2 in phase	1538	1526	1530	1537
ν_{as} NO_2 out of phase	1403	1455	1410	—
δ_{sciss} NO_2 in phase	827	828	825	828
δ_{sciss} NO_2 out of phase	761	761	755	762
δ_{rock} NO_2 out of phase	731	727	735	732
δ_{wag} NO_2 in phase	—	490	—	—
ν_s N3	952	954	—	954
ν_{as} N3	1022	1025	1038	1032

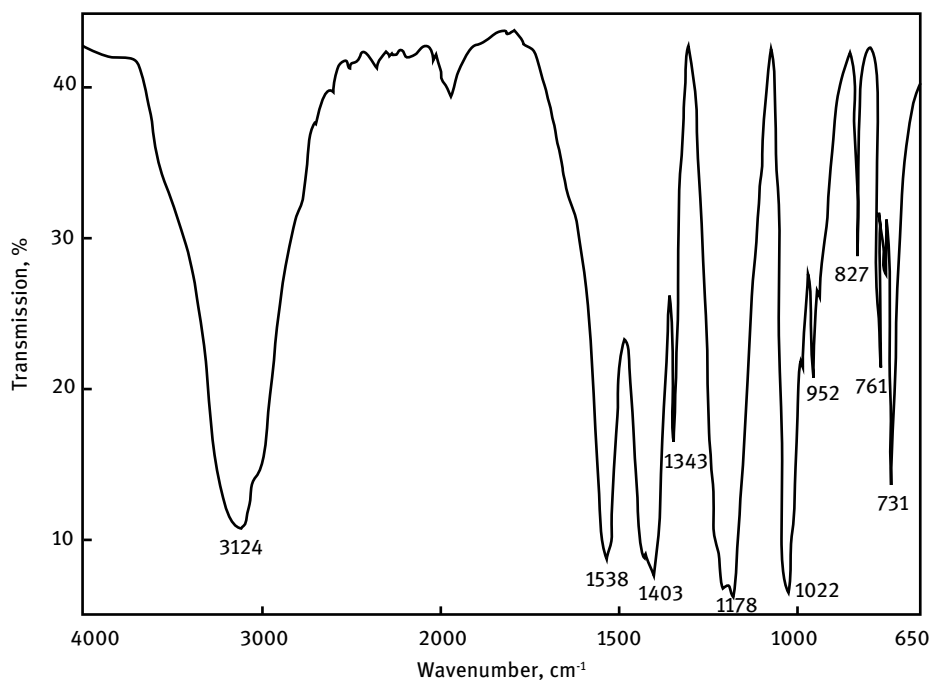


Figure 34: IR spectrum of ammonium dinitramide. (Reprinted and modified from [58] with permission granted by Dr. Santhosh 8-Feb-2021.)

The peak at 3124 cm^{-1} has been assigned to the valence vibration of N—H in NH_4^+ , the band at 1538 cm^{-1} is an asymmetric oscillation of N—O in NO_2 , and 1343 cm^{-1} is a symmetric oscillation of NO_2 .

The dinitramide ion IR spectrum (Figure 35) wavenumbers of a sample of ADN obtained by reaction of ammonia with dinitrogen pentoxide were in good agreement with literature data and were as follows: 1583, 1430, 1343, 1206, 1176, 1022, 953, 828, 762, and 732 cm^{-1} [44].

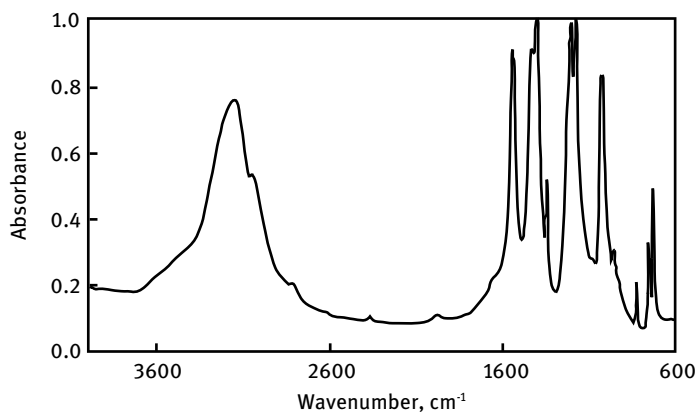


Figure 35: IR spectrum of ADN prepared by reaction of ammonia with dinitrogen pentoxide. (Republished and modified from [44], with permission of © 2002 John Wiley & Sons – Books; permission conveyed through Copyright Clearance Center Inc.)

There was concern that prilled ADN that was made by a two-phase emulsion process of molten ADN in paraffin oil might be contaminated by oil, but the IR spectrum of prilled ADN was essentially free of C—H and C—C bands (Figure 36).

Isotope substitution and the comparison of IR, Raman, and nuclear magnetic resonance (NMR) spectra of $^{14}\text{NH}_4^{15}\text{N}(^{15}\text{NO}_2)_2$ and $\text{K}^{15}\text{N}(^{15}\text{NO}_2)_2$ with those of natural ADN and KDN have enabled researchers not only to assign absorption bands to specific vibrations in designated parts of the molecule but also to predict spectra from theoretical quantum mechanical force-field calculations and normal-coordinate analyses [211]. The geometry, harmonic vibrational frequencies, and IR and Raman intensities of the dinitramide anion were calculated within DFT approximations. Figure 37 gives a comparison of the IR spectra of natural ADN and the analog compound made with $^{15}\text{N}(^{15}\text{NO}_2)_2$ anions.

Similar spectra for the potassium salt are provided in the same reference but are not shown here. Due to the structural variability of the $\text{N}(\text{NO}_2)_2^-$ anion observed in the solid state, a reliable interpretation of the IR and Raman spectra of its salts becomes much more difficult in comparison to the interpretation of spectra from solutions of

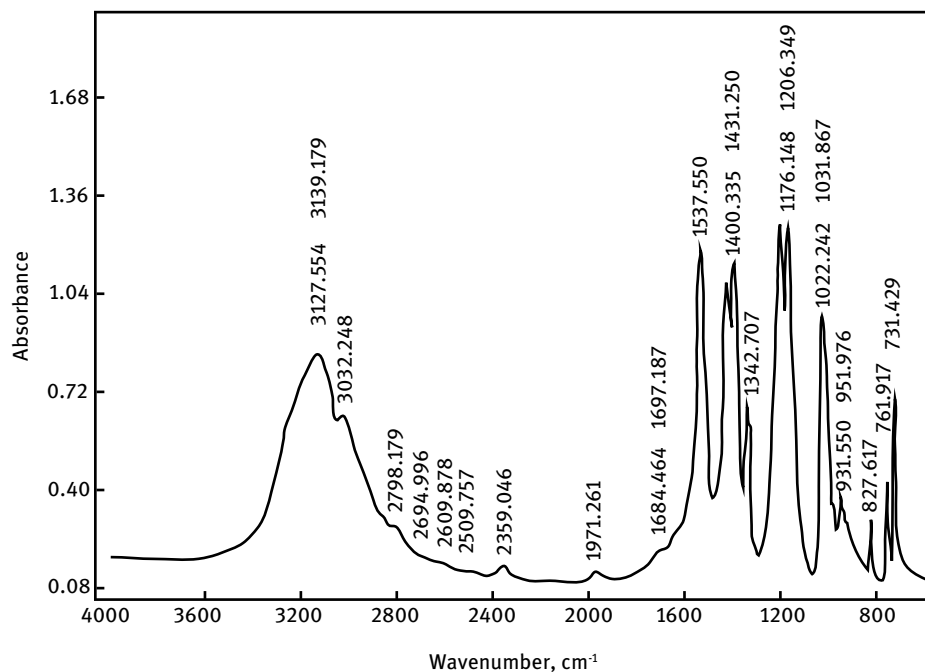


Figure 36: IR spectrum of recrystallized prilled ADN. (Republished and modified from [105], with permission of John Wiley & Sons – Books; permission conveyed through Copyright Clearance Center Inc.)

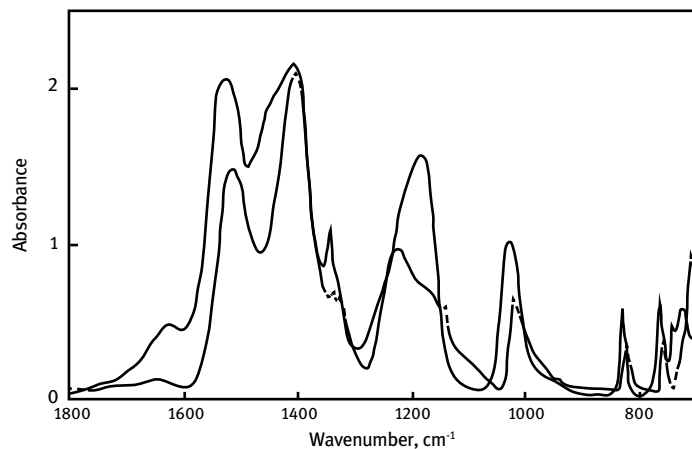


Figure 37: IR spectra of natural ammonium dinitramide (solid line) and its ¹⁵N-substituted analog (dashed line). (Republished and modified from [211], with permission of © 2001 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

the salts in water or acetonitrile. Vibrational spectra of the solids are dependent on the counterion present. The IR spectra were complemented by Raman spectra taken from the same samples (Section 3.10.2.3). It is possible that ADN crystals pressed into a KBr pellet (common practice for IR spectrometry) may undergo ion exchange in the solid state and that the spectrum will show some lines that are due to KDN. That is why we show spectra of both salts in this book.

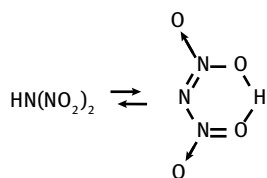
Samples of ADN were synthesized starting with ammonium sulfamate as the starting reactant and nitric acid as the nitrating agent. Sulfuric acid was used as a catalyst. IR spectra were evaluated by FTIR, in the near IR region and the middle IR region (MIR) [245]. The characteristic bands used to identify ADN in the MIR were 3132 cm^{-1} (stretching of NH_4^+), 1384 cm^{-1} (bending of NH_4^+), 1537 cm^{-1} (asymmetric stretching of NO_2 in phase), 1344 cm^{-1} (symmetric stretching), 1209 and 1177 cm^{-1} (symmetric stretching of NO_2 out of phase), 1032 cm^{-1} (asymmetric stretching of N_3), 954 cm^{-1} (symmetric stretching of N_3), 828 cm^{-1} (angular bending of NO_2 in phase), 762 cm^{-1} (angular bending of NO_2 out of phase), and 732 cm^{-1} (bending of NO_2 in phase). The MIR spectrum was compared to literature data and showed good agreement. In the near IR region analysis, only a few bands were observed, at 5185 and 4672 cm^{-1} , and they are typical for the region of combined bands of compounds that hold NH groups.

IR spectra were predicted using DFT calculations in the local density approximation and compared to experimental spectra and to those obtained for ADN [214]. The lattice mode spectra of AP and ADN display similar features in the region $28\text{--}220\text{ cm}^{-1}$. AP has seven frequencies in this region, which are in good agreement with the experimental reports [246]. The modes of 103.7 and 115.2 cm^{-1} in ADN correspond to the twist of NO_2 about the N—N bond. The 260.1 and 320.2 cm^{-1} modes corresponding to the lattice vibration appear in ADN but not in AP. In the region of $400\text{--}700\text{ cm}^{-1}$, AP has four frequencies. The molecular motion of the first frequency is the symmetric bending of ClO_4 , and the motions corresponding to the following frequencies are concentrated in the asymmetric bending of ClO_4 . Similarly, ADN also has four frequencies. The molecular motion of the first frequency is the symmetric bending of $\text{N}(\text{NO}_2)_2$, and the motions corresponding to the following frequencies are concentrated in the asymmetric bending of $\text{N}(\text{NO}_2)_2$. The modes of 739.7 , 822.1 , and 938.4 cm^{-1} in and, which do not appear in AP, correspond to the asymmetric bending of $\text{N}(\text{NO}_2)_2$. The calculated frequency 739.7 cm^{-1} for ADN is consistent with the experimental value 739.0 cm^{-1} . See also [174].

In the region of $1000\text{--}1200\text{ cm}^{-1}$, AP has five frequencies of absorption [214]. The molecular motions of the first two frequencies are the symmetric stretching of ClO_4 , and the motions corresponding to the following frequencies are the asymmetric bending of ClO_4 . The calculated frequencies for AP in this region have large deviations from the corresponding experimental values. The motions of these frequencies are concentrated in the ClO_4 moieties; thus, this discrepancy may be due to intermolecular hydrogen bonding interactions present in the crystal lattice, which are not well described by DFT. ADN also has five frequencies in this region. The molecular motions

of the first two frequencies are the symmetric stretching of $\text{N}(\text{NO}_2)_2$; the motions corresponding to the following two frequencies are the asymmetric bending of $\text{N}(\text{NO}_2)_2$, and the motion to the last frequency 1154.2cm^{-1} , which agrees with the experimental value, is the symmetric stretching of NO_2 . The modes of 1292.6 and 1311.8cm^{-1} in ADN correspond to the symmetric stretching of NO_2 . In the region of $1400\text{--}3300\text{cm}^{-1}$, the motion modes of NH_4 in AP and ADN present similar features. The motion of the first frequency involves the asymmetric bending of NH_4 , whereas those of the next two frequencies are concentrated in the symmetric and asymmetric stretching of NH_4 , respectively. The modes of 1706.6 and 1708.5cm^{-1} in ADN correspond to the asymmetric stretching of NO_2 . From the low-frequency to the high-frequency region, ADN has more motion modes for the vibrational frequencies than AP. The motions of the NO_2 groups in ADN are diffusely distributed. Since the torsional motions of the molecule's functional groups are usually supposed to be highly coupled to the other moiety of the molecule, it is possible that the torsion motions of the NO_2 groups act as doorways through which kinetic energy can flow into the molecule from its surroundings.

Although free dinitramidic acid is unstable and never used as such, it is of interest to compare the IR spectra of the free acid to that of the ammonium salt. The question about the free acid was whether it exists predominantly in the N–H form or the aci form with an intramolecular hydrogen bond (indicated by a dotted line) [212].



Depending on whether it is liberated from a salt in non-polar, water-free solvents or extracted from an acidified aqueous solution of KDN, the free dinitramidic acid may show different absorption spectra in the UV and the IR. Instead of a cyclic aci form with a hydrogen bond (dotted line in structure above), the proton may be shared equally between the two oxygen atoms.

Two different routes for making ADN were tested and their efficiency evaluated by IR spectroscopy [247]. One sample was made from sulfamic acid with a 40/20 ratio of WFNA/ H_2SO_4 at 243 to 238K (-30 to -35°C), and another sample was made from ammonium sulfamate at 238 to 236K (-35 to -37°C). The ADN was adsorbed on activated charcoal and desorbed with acetone. Analyzing the products by IR spectroscopy revealed some AN as a contaminant and potential decomposition product. This paper is very useful because it also contains the IR spectra of the starting reagents, sulfamic acid and ammonium sulfamate, so that their unwanted presence in the products can be identified by comparison. The product from the sulfamic acid process was of better quality than the product of the ammonium sulfamate process. The characteristic

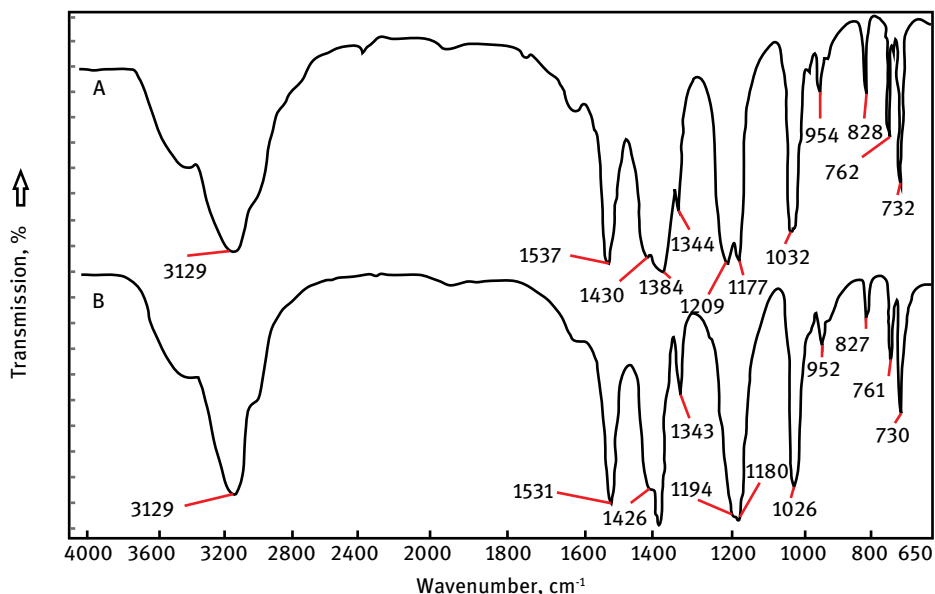


Figure 38: Infrared spectrum of ADN prepared from sulfamic acid 40/20 in comparison to a reference spectrum. (Reproduced and modified from [247].)

bands employed to identify ADN in the MIR were 3129 and 1384 cm^{-1} (NH_4^+); 1537, 1344, 1209, and 1177 cm^{-1} (NO_2); 1032 and 954 cm^{-1} (N3); 828, 762, and 732 cm^{-1} (NO_2). The near infrared analysis pointed out few bands at 5185 and 4672 cm^{-1} . Figure 38 is a comparison of the product from the sulfamic acid 40/20 process with a literature reference spectrum. The results showed excellent agreement between the two spectra.

IR Spectra at Very High Pressures

Raman and FTIR spectra for ADN crystals were measured as a function of pressure in an LN_2 hydrostatic medium [174]. No detectable changes were observed in spectra collected below 1.6 GPa or above 2.8 GPa. In the infrared spectra, significant pressure broadening was observed, which masked any potential subtle spectral changes due to the $\alpha \rightarrow \beta$ transformation.

Assignments for the observed Raman modes are as follows: The 1174 and 739 cm^{-1} shift modes correspond to the $-\text{NO}_2$ symmetric stretch and the rocking modes of the dinitramide anion.

IR Spectra of ADN Decomposition Products

The vapor space over ADN at 333–383 K (60–110 $^\circ\text{C}$) was pumped and condensed into a matrix of frozen argon for IR absorption spectra measurement [248]. The matrix spectrum had 22 absorption bands, which all seemed to be associated with one and the

same species, namely dinitraminic acid $\text{HN}(\text{NO}_2)_2$. UV irradiation of the matrix destroyed the species, and instead a new set of absorption bands was formed, which were assigned to *trans*- HNO_2 , N_2O , NO , and $(\text{NO}_2)_2$. There was no evidence for the aci form of $\text{HN}(\text{NO}_2)_2$ in the form of $\text{N}(\text{NO}_2)\text{NOOH}$, which, according to *ab initio* calculations by other authors, was predicted to be nearly as stable as $\text{HN}(\text{NO}_2)_2$.

3.10.2.3 Raman Spectra of Ammonium Dinitramide

Raman spectra of ADN and KDN with natural abundance of ^{15}N were compared to spectra of ADN and KDN made from ^{15}N -enriched dinitramide ion ([211]; Figure 39). The spectra were also compared to spectra from the isoelectronic dinitromethane anion. Calculated and experimental IR and Raman spectra were in reasonably good agreement.

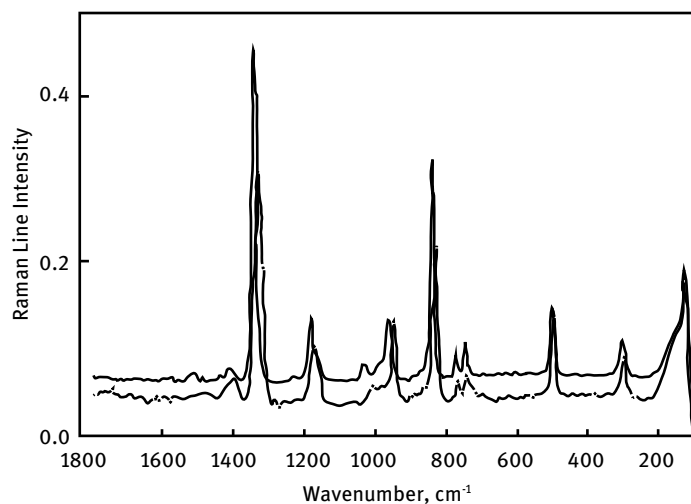


Figure 39: Raman spectra of natural ammonium dinitramide and its ^{15}N -substituted analog (dashed line). (Republished and modified from [211], with permission of © 2001 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

Earlier Raman studies of the structure of the $\text{N}(\text{NO}_2)_2^-$ anion in aqueous solution used *ab initio* calculations to interpret the measured spectra [244]. Measured spectra (Figure 40) agreed reasonably well with the harmonic vibrational frequencies calculated for the most stable C_2 conformation. However, the polarization properties of several Raman lines in ADN solutions (Figure 41) forced the spectroscopists to reduce the symmetry of the $\text{N}(\text{NO}_2)_2^-$ anion in solution to a C_1 conformation (i.e., no symmetry). This was attributed to the very small (< 3 kcal/mol) $\text{N}-\text{NO}_2$ rotational barrier in $\text{N}(\text{NO}_2)_2^-$, which allows for easy deformation. This was in contrast to theories by other investigators who had proposed a C_2 symmetric structure based on IR and Raman spectra [210].

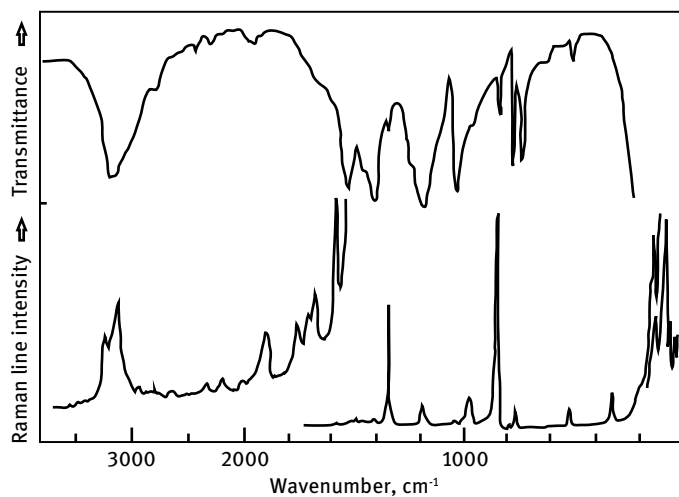


Figure 40: IR (top) and Raman (bottom) spectra of solid ADN. (Reprinted and modified from [244] with permission from © 1996 American Chemical Society; permission conveyed through RightsLink.)

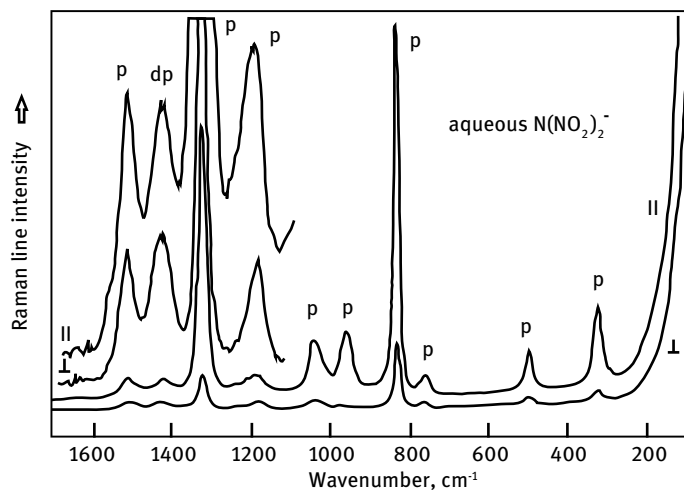


Figure 41: Raman spectrum of an aqueous solution of ammonium dinitramide at two different sensitivity levels. Where p, dp, ||, and ⊥ stand for polarized, depolarized, parallel, and perpendicular, respectively. (Reprinted and modified from [244] with permission from © 1996 American Chemical Society; permission conveyed through RightsLink.)

The vibrational and electronic IR and Raman spectra of dinitramide salts $\text{MN}(\text{NO}_2)_2$ [$\text{M} = \text{K}, \text{Na}, \text{Li}, \text{NH}_4, \text{Fe}, \text{Ag}, \text{Mn}, \text{Mg}, \text{Rb}, \text{or } \text{C}(\text{NH}_2)_3$] as solutions and melts were interpreted from the anion model with the C_{2v} symmetry [249]. The complication of the spectra in the crystalline phase was explained by a restructuring of the anion, which reduces its symmetry and makes the nitro groups nonequivalent. Table 16 is a compilation of the Fourier transform (FT)–Raman peak assignments for ADN.

FT-Raman spectroscopy employing near IR laser radiation at a wavelength of $1.064\text{ }\mu\text{m}$ (9394.5 cm^{-1}) as the light source was used to characterize ADN and several propellant formulations [250]. Raman spectra were measured over the region from 75 to 3000 cm^{-1} , relative to the laser line.

Table 16: FT-Raman peak assignments for ammonium dinitramide.

Assignments Source	Wavenumber, cm^{-1}			
	Shlyapochnikov et al. [210]	Fell et al. [250]	Christe et al. [244]	Oestmark et al. [169]
$\nu_s \text{ NO}_2$ in phase	1335	1335	1338	1338
$\nu_s \text{ NO}_2$ out of phase	1174	—	1175	1178
$\nu_s \text{ N3}$	1025	1043	1022	958
$\delta_{\text{sciss}} \text{ NO}_2$ in phase	830	830	832	833
$\delta_{\text{wag}} \text{ NO}_2$ in phase	493	493	492	495
$\delta_{\text{sciss}} \text{ N3}$	229	163	295	297

3.11 Electrical Properties of Ammonium Dinitramide

3.11.1 Dipole Moment of Ammonium Dinitramide Crystals

The hybridization of the central nitrogen of the dinitramide ion is sp^2 -like, as observed in the two biguanidinium salts $[(\text{NH}_2)_2\text{C}_2\text{N}][\text{N}_3\text{O}_4]$ and $[(\text{NH}_2)_2\text{C}_2\text{NH}][\text{N}_3\text{O}_4]_2$. Despite this robust topology, the dipole moment obtained from both experiment and crystal modeling is larger than that computed for a single dinitramide ion [196]. Significant differences in the direction of the dipole from theory and experiment were found, as were differences in the atomic charges. Strong hydrogen bonding polarizes the dinitramide ion, increasing the negative charge on the most strongly hydrogen bonded oxygen atom. Decomposition of the theoretical molecular dipole moment into atomic charge and atomic dipole contributions revealed that the atomic dipoles are nearly equal in both the crystal and single molecular ion. Changes in the atomic charge contribution to the molecular dipole moment principally account for the induced dipole.

3.12 Magnetic Properties of Ammonium Dinitramide

Nuclear magnetic resonance (NMR) spectra of ADN dissolved in D₂O were measured under high-resolution conditions with an NMR spectrometer at 400.13 MHz proton resonance frequency [251, 252]. In the same series of NMR measurements, HNIW shifts were compared to those of ADN. The ¹⁴N, ¹⁵N, and ¹⁷O NMR spectra of ADN were measured, and the signals were assigned to specific parts of the molecule. The chemical shifts are tabulated in Table 17. The atom highlighted in **bold** is the atom to which the shift was assigned. Because of proton/deuteron exchange, the ¹H spectrum of ADN could not be measured. The ¹⁴N spectrum in ADN has three lines, at $\delta = -12$ (nitro group), at $\delta = -60.2$ (central amino N), and at $\delta = -360.1$ (NH₄⁺ ion). As opposed to ¹⁴N NMR signals, the ¹⁵N atom gives very sharp lines, but due to the low natural abundance of this isotope, the scanning times are very long before one has a good spectrum. Three ¹⁵N lines were seen, one of which ($\delta = -60.8$, broadened) belongs to the amino nitrogen, the other ($\delta = -12.2$) belongs to the nitro group, and the last ($\delta = -360.1$) belongs to the nitrogen in the ammonium ion.

Table 17: NMR chemical shifts of ADN.

Nucleus	MHz	Shift, ppm	Assignment
¹⁴ N	28.91	-12.0	(N- NO ₂) $\Delta 1/2 = 12.4$ Hz
		-60.2	(N -NO ₂) $\Delta 1/2 = 940$ Hz
		-360.1	(NH ₄ ⁺) $\Delta 1/2 = 4.5$ Hz
¹⁵ N	40.56	-12.2	N- NO ₂
		-60.8	N -NO ₂
		-360.1	(NH ₄ ⁺)
¹⁷ O	54.24	469.6	(N- NO ₂) $\Delta 1/2 = 204$ Hz

Data source: [252]

A thorough examination of the IR and Raman spectra of ADN and KDN solids and the dinitramide ion in solution had already provided a fairly accurate description of the molecular structure of the three species [211]. These measurements were supplemented by NMR spectra of KDN in acetone-D₆. Three of the six possible isotopomers of the N(NO₂)₂⁻ anion, those with a ¹⁵N in the middle, represent the majority of the species seen in the NMR spectra (Figure 42). In the ¹⁵N NMR spectrum of KN(NO₂)₂ the most pronounced splitting patterns are a doublet at $\delta = -9$ ppm and a triplet at $\delta = -55$ ppm. They correspond to the ¹⁵N resonances of nitro groups in O₂¹⁵N-¹⁵N-¹⁴NO₂ and O₂¹⁵N-¹⁵N-¹⁵NO₂ (doublet) and to the central nitrogen atom in O₂¹⁵N-¹⁵N-¹⁵NO₂ (triplet).

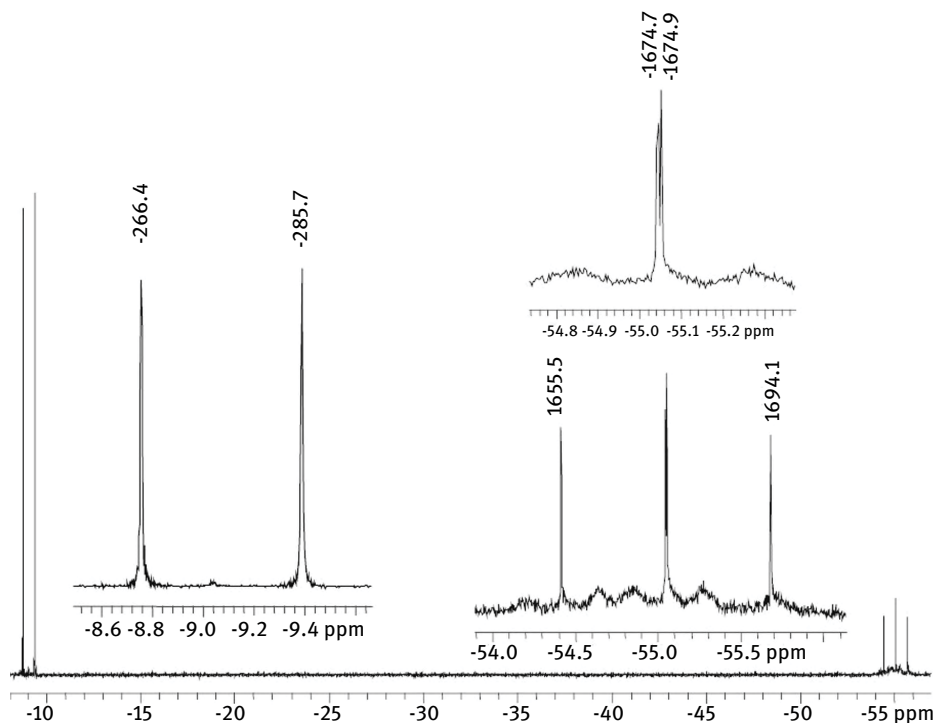


Figure 42: NMR spectra of the mixture of isotope ^{15}N -substituted dinitramide ion of $\text{KN}(\text{NO}_2)_2$ in acetone- D_6 . (Republished and modified from [211], with permission of Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

4 Chemical Properties of Ammonium Dinitramide

4.1 Reactions of Ammonium Dinitramide

4.1.1 Acid Strength of Hydrogen Dinitramide

Dinitramine (“dinitramidic acid,” hydrogen dinitramide) is one of the strongest inorganic acids, and therefore it can form salts not only with strong but also with weak bases. The $\text{p}K_{\text{a}}$ of dinitramidic acid is -5.62 , compared with -0.9 for nitric acid. It is thus a stronger acid than nitric acid or sulfuric acid and is weaker only in comparison to hydrochloric acid and perchloric acid.

Depending on the acidity of the solution, dinitramide is present in three different forms: $\text{N}(\text{NO}_2)^-$ anions, neutral $\text{HN}(\text{NO}_2)_2$ molecules, and protonated $\text{H}_2\text{N}(\text{NO}_2)_2^+$ cations. The rate of the thermal decomposition of dinitramide solutions is dependent

on the acidity of the solution. The temperature dependence of the equilibrium constant of dissociation (acidity constant) of $\text{HN}(\text{NO}_2)_2$ (K_a) is [253]:

$$K_a = 1.4 \times 10 \exp\left(-2.6 \times \frac{10^3}{T}\right)$$

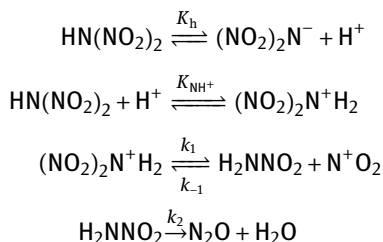
The temperature dependence of the equilibrium constant of the dissociation of the protonated dinitramide $\text{H}_2\text{N}(\text{NO}_2)_2^+$ is:

$$K_{a\text{-protonated}} = 1.1 \exp\left(6.4 \times \frac{10^3}{T}\right).$$

4.1.2 Acid Resistance of Dinitramide and Dinitramide Salts

Dinitramide salts are stable to base but slowly decompose in concentrated acids at room temperature [164].

Because dinitramide and dinitramide salts are often synthesized in acidic solutions, the yield of the desirable products is limited by simultaneous premature decomposition of the product due to the acidic medium. In a reacting mixture, there is a dynamic equilibrium concentration of dinitramide that peaks out and then disappears altogether if the reaction is not terminated at an opportune time. In 8-M H_2SO_4 , no loss is seen after 8 h, but in 11-M and above, the decomposition is quite rapid. Similarly, the decomposition in concentrated HNO_3 is found to be fast in 70% HNO_3 and above, and it is slow in HNO_3 treated with urea. Urea destroys the nitrous fumes in WFNA. The oxides of nitrogen in the untreated HNO_3 catalyze the decomposition of dinitramide. Dinitramide is hydrolyzed by acids [254]. The rate of this reaction was measured by spectrophotometry in aqueous H_2SO_4 , HClO_4 , and HNO_3 solutions over a wide temperature range and at various compositions of the medium. On the basis of the dependence of the apparent rate constants on the composition of the medium and of the UV spectra of solutions of nitramide NH_2NO_2 in concentrated nitric acid and its mixtures with H_2SO_4 , a mechanism was proposed for the acid-catalyzed decomposition of dinitramide. The proposed mechanism includes denitration of dinitramide to nitramide and nitronium cation; the subsequent decomposition of nitramide yields nitrous oxide and water:



Depending on the nitrating power of the medium, the rate-determining stage may be either denitration of dinitramide or decomposition of nitramide.

The half-life times of ADN at different temperatures in sulfuric acid solutions of different strengths are listed in Table 18.

Table 18: Decomposition of ADN in sulfuric acid solutions.

Acid concentration	Temperature		Rate constant	Half-life, $t_{1/2}$
	K	°C	min ⁻¹	min.
6.3M	303	30	No decomposition	—
6.3M	323	50	0.0003	2310.5
6.3M	338	65	0.0005	1386.3
6.3M	348	75	0.003	231.1
8.1M	303	30	No decomposition	—
8.1M	323	50	0.0048	144.4
8.1M	338	65	0.0194	35.7
8.1M	348	75	0.1291	5.4
10M	303	30	0.0057	121.6
10M	323	50	0.023	30.1
11M*	303	30	0.0074	93
12M*	303	30	0.0252	28
13M*	303	30	0.335	2.1

From [58], except those data marked with an asterisk*, which are from [20]

Dinitraminic acid is a colorless unstable liquid that decomposes to give HNO_3 and N_2O . Dinitraminic acid is the most acidic acid among the known gas-phase acids [255]. The gas-phase acidity of dinitramidic acid was found to be $\Delta H^\circ_{\text{acid}} < 1297 \text{ kJ/mol}$ ($< 310 \text{ kcal/mol}$). Dinitramide anion is extremely unreactive in the gas phase and is a poor nucleophile. It does not react with O_2 , CO_2 , CS_2 , or SO_2 .

4.1.3 Reactions of Dinitramides with Inorganic Substances

The main reactions of dinitramides with inorganic substances are those with metals with high heats of combustion, which are often added to solid propellants to increase performance and to reduce the tendency to combustion instabilities. Other mixtures of dinitramide oxidizers (mostly alkali metal dinitramides) and metal powders have also been proposed for pyrotechnic igniters.

Most solid propellants contain metals as a means to increase the energy output. Metal oxides have highly negative enthalpies of formation and high heats of combustion. If advanced solid propellants are formulated with ADN and metals, one needs to know the potential for premature reactions between ADN and metals during propellant processing and storage. Interaction between ADN and metals, in particular Be, Mg, B, and Al, can be determined by experiment or can be predicted by quantum chemical density-functional theory (DFT) model calculations [256]. The results indi-

cate that Be and Mg are oxidized by ADN in close contact but that B and Al are not. In the case of Be and Mg, the reduction of ADN is accompanied by the removal of NO_2 moiety, which has negative total charge. On the other hand, the interaction pattern of these elements with dinitramidic acid in the presence of ammonia is different from the ADN + metal reaction.

An unusual synthetic application of dinitramide salts is the controlled stage-by-stage substitution of fluorine atoms with oxygen in interhalides [257]. In these reactions, the $\text{N}(\text{NO}_2)_2^-$ anion is preferable to the nitrate that has been used in other cases. For example, $\text{KN}(\text{NO}_2)_2$ smoothly reacts with BrF_5 at 228 K (-45°C) to quantitatively give KBrOF , N_2O , and FNO_2 , and its interaction with ClF_5 at 260 K (-13°C) yields an equimolar mixture of KClOF_4 and KClF_4 . It is remarkable that KClOF_4 is formed as an intermediate product because with most other exchange reagents, e.g., NO_3^- , it is difficult to terminate the process in this stage, and FCIO_2 is the only product.

4.1.4 Reactions of Dinitramides with Organic Substances

The main concern about reactions of dinitramides with organic substances is about those occurring prematurely with binders and curing agents during the production of solid propellants [258]. After the propellant is cured, other reactions, often undesirable, continue at a slow rate at room temperature and cause the propellant to age more rapidly. Reactions of ADN with binders and curing agents will be discussed in a future volume on solid propellants. Other organic reactions are discussed here.

It was difficult to find suitable curing agents for ADN-based solid propellants because dinitramide reacted with many isocyanates commonly used in the past to cure AP-based propellants.

The reactivity of dinitramide and its aci-isomer (if it exists) toward alkenes was theoretically studied using electron density functional B3LYP/6-31+G(d,p) and non-empirical *ab initio* CBS-QB3 methods [259]. It was concluded that the rate of 1,3-dipolar cycloaddition to the double bond of the N—N—O fragment is comparable to the rate of interactions of nitrile oxides and azides with olefins but that *I* decreases in the presence of electron-acceptor substituents at the double bond. The observed reactivity trends support the design of unsaturated compounds that are highly reactive toward azides and chemically inert toward dinitramides. This may be helpful for the development of binders for ADN-based propellants.

Combustion reactions of ADN with organic binders and additives as they will occur in solid propellants in a rocket motor will be described in a future volume. Several combustion experiments were conducted with ADN and a combustible solid (binder, binder surrogate) sandwiched together with or without a gap between the two reactants. Section 4.11.2.1 ("Experimental Study of ADN Combustion in Model Solid Propellants") contains some information on combustion reactions of ADN with polymeric binders in model propellants.

The interaction and compatibility of ADN with various propellant compositions, including binders, curing agents, plasticizers, and energetic fillers, were investigated by means of pressurized differential scanning calorimetry (PDSC) [260]. Results showed that the onset of decomposition temperature of ADN/polyethylene glycol (PEG)/toluene diisocyanate (TDI) and ADN/PEG/hexamethylene diisocyanate (HDI) mixtures was 16–26°C lower than that of ADN by itself. The interactions between them are dangerous, and ADN is incompatible with PEG, TDI, and HDI. The decomposition temperature of ADN-NG/butanetriol trinitrate (BTTN), ADN-TEGDN, ADN-Bu-NENA, and ADN-HMX mixtures was 0.5–7.5°C higher than that of ADN. The difference of decomposition temperatures of ADN-glycidyl azide polymer (GAP), ADN-PBT, ADN-PET, ADN-IPDI, ADN-N-100, ADN-NG, ADN-trimethylolethane trinitrate (TMETN), ADN-BDNPA-F, and ADN-Al mixtures was less than 2°C, and ADN should be compatible with those compositions.

4.1.4.1 Reactions of Dinitramides with Nitrate Esters

Nitrate esters are contained in double-base propellants and many energetic plasticizers. ADN may or may not be compatible with nitrate esters.

The thermal stability and safety properties of two ADN-based propellants containing different relative amounts of ADN crystals, TMETN, 1,2,4-BTTN, and GAP were measured by differential scanning calorimetry (DSC), TGA-FTIR, and accelerating rate calorimetry (ARC) [165, 261].

The interactions of double-base propellant ingredients nitrocellulose and nitroglycerin (NC/NG) with ADN were investigated by PDSC, thermogravimetry-derivative thermogravimetry (TG-DTG), and a vacuum stability test (VST) [262]. The results showed that the decomposition exothermic peak temperature of NG in the NC/NG is 480 K (207°C), but it drops to 433 K (159.8°C) in the (NC/NG)/ADN system at atmospheric pressure and drops further to 427 K (153.6°C) at higher pressure. It was shown that ADN is less compatible with NC than with NG. The rate of gas evolution of ADN/NC/NG as evaluated by VST was excessive.

The interaction of ADN and mixtures of NC and NG at high temperatures was investigated by a gasometric method [263]. Results showed that compared with the sum of the maximum standard volume of evolved gas from ADN and (NC + NG) systems, the maximum standard volume of evolved gas from the ADN/(NC + NG) mixture (626.8 mL/g) decreased, but the decomposition rate evidently increased, and the activation energy decreased to 82.58 kJ/mol, which showed that there is a strong interaction between ADN and (NC + NG).

On the basis of the study of thermal behavior of ADN and the interaction between ADN and NC, the influences of stabilizers, such as *N*-methyl-*p*-nitroaniline (MNA), 1,3-dimethyl-1,3-diphenylurea (Centralite 2 = C2), 2-nitrodianiline(2-NDPA), hexamethylenetetramine (HMT), and mixtures of MNA/C2, MNA/2-NDPA, and MNA/HMT, on the nascent interactions between ADN and NC were investigated by DSC [264]. The results showed that the interaction between ADN and NC can be decreased to

a certain extent by mixing MNA and C2, and the nascent interaction between ADN and NC can be inhibited by mixing the complex of MNA/C2, MNA/2-NDPA, and MNA/HMT. Comparing the binary system of ADN/NC, the value of ΔT_p , which is the DSC exothermic peak temperature difference between ADN/stabilizer and NC, can be decreased from 19.2 to 11.9 degrees by using the mixtures of stabilizers.

4.2 Photolysis of Ammonium Dinitramide

All dinitramides are sensitive to light and are best stored in the dark.

4.2.1 Photolysis of Solid Ammonium Dinitramide

Prilled ADN was photolyzed by exposure to sunlight and was analyzed by IR, and the purity and apparent storage life of photolyzed ADN were tested by high-performance liquid chromatography (HPLC) [265]. Photolysis products are NO_3^- , NO, N_2O , and N_2 , along with small amounts of NO_2^- . The results indicated that the primary solid product of ADN photolysis is AN, and the apparent storage life of ADN photolyzed with sunlight is 756 d. Further decomposition of ADN is restrained because ADN grains are coated by the AN formed as photolysis product.

4.2.2 Photolysis of Ammonium Dinitramide Solutions

ADN solutions were kept in side-by-side clear and amber glass bottles, and samples were taken periodically and analyzed [58]. The decay of ADN as a function of time is shown in Figure 43 for three solutions with three different starting concentrations. Solutions in clear glass bottles decomposed much faster than those kept in amber glass bottles.

Solutions of ADN in water are sensitive to light. While the sensitivity to light may complicate the handling and storage of ADN in the laboratory and may affect the storage life of formulated propellants, this is a blessing in disguise because if ADN is accidentally spilled into surface waters, it decays under the influence of sunlight before it can do much environmental damage.

In the wake of the realization that AP production wastes and accidental spills from AP fires are quite persistent in the environment and that AP contamination had found its way into agricultural products and drinking water, the environmental chemistry of ADN was investigated in detail to make sure that ADN, a potential AP replacement, would not cause the same problems downstream. As part of such a study, the photolysis of ADN in natural waters was analyzed and modeled [266, 267]. Dark solutions of ADN were stable indefinitely, and indirect photolysis did not provide a significant decay mechanism. Photolytic rate constants for the photolysis of ADN were determined in order to better understand the fate of ADN in natural bodies of water. Quantum

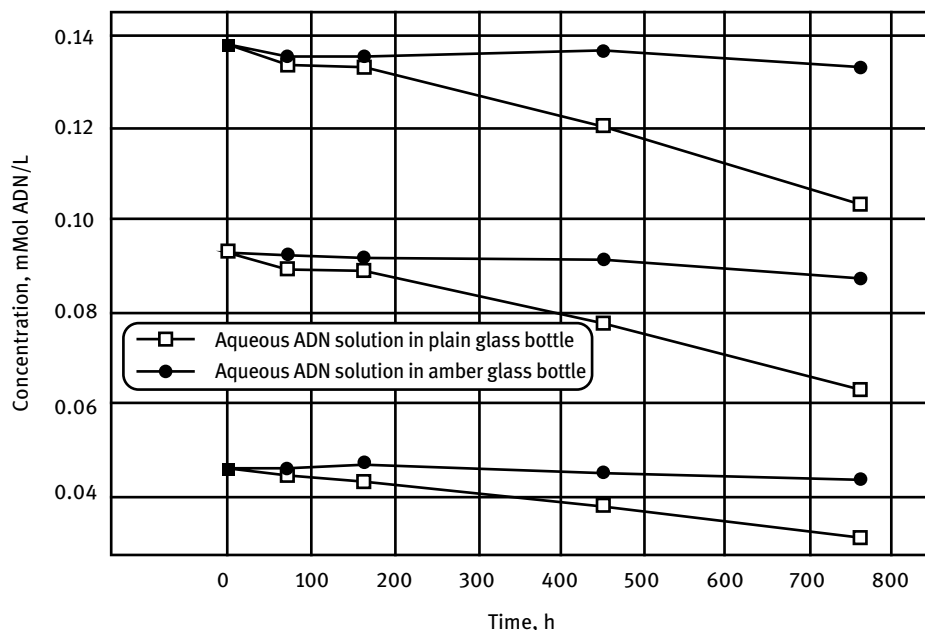


Figure 43: Decomposition of ADN solutions stored in clear and amber glass bottles. (Reprinted and modified from [58] with permission granted by Dr. Santhosh 8 February 2021.)

yields were measured between 290 and 400 nm using a filtered light system, and these values were combined with absorption of light in a water column to model photolysis rates as a function of water depth. The validity of this model was tested in field trials in Onondaga Lake, Syracuse, New York, USA. For summertime irradiation, half-life times ranged from ~6 min at the surface to ~15 years at a depth of 2 m. The predicted and observed degradation rates of ADN were quite similar. It was also found that the degradation of ADN was not enhanced to any measurable degree by sensitized photoreactions in humic solutions.

Free-radical and thermal and photolytic decomposition products of ADN were compared to those of cyclic nitramines and AP [268]. Photochemical formation of NO_2 by UV photolysis of ADN at 77 K followed first-order kinetics, whereas photolysis of cyclic nitramines (RDX, HMX, HNIW) formed NO_2 via zero-order reactions. If ADN is caused to decompose thermally at 463 K (190 °C), free radicals can be trapped by radical scavengers and identified by electron spin resonance (ESR) [269].

ADN in aqueous solution absorbs light in the UV region and decomposes photolytically to form nitrate ion, nitrite ion, and nitrous oxide [270]. The rate of photolysis and the product distribution are dependent on the pH of the solution. At pH 11, the ratio of $\text{NO}_2^-/\text{NO}_3^-$ is about 20, but at pH 2, the ratio is only 0.5. Dilute (10–50 μM) ADN solutions in water have a half-life time of ~3–4 min in sunlight.

4.3 Electrolysis of Ammonium Dinitramide

The electrolysis of ADN does not result in formation of tetranitrodiazane ($(\text{NO}_2)_2\text{NN}(\text{NO}_2)_2$), which is unstable and unknown. The electrolysis of ADN in dimethyl sulfoxide (DMSO) was studied by cyclic voltammetry trials with a platinum electrode [271]. The associated mechanisms were predicted based on a quantum chemical calculation. ADN exhibited three redox peaks at -0.69 , -1.16 , and -1.52 V, and two oxidation peaks at 0.34 and 0.50 V (vs Ag/AgCl) at a scan rate of 50 mV/s. Quantum chemistry calculations identified possible pathways for the electrolysis of ADN in DMSO and indicated that reduced ADN rapidly decomposes to form NH_3 , N_2O , NO_2 , and OH^- .

4.4 Analysis of Ammonium Dinitramide

Because ADN is very sensitive to contamination, it is important to have accurate analysis methods to determine the types and quantities of contaminants that might reduce the thermal stability of this rocket propellant oxidizer.

ADN is intended as a replacement for AP, which has been the cause of widespread drinking water pollution. In order to make sure the same will not happen again with ADN spilled and leaked into the groundwater, sensitive methods have been developed to analyze for traces of ADN in the wastewater leaving the propellant processing plants.

4.4.1 Volumetric Analysis Methods for Ammonium Dinitramide

A rapid and simple method to determine the purity of ADN is non-aqueous potentiometric titration [272]. A quaternary ammonium salt was used as the titrant, while AN, the major impurity present in ADN that tends to cause serious interference, was removed. The standard deviation of the method was 0.001 g, and its coefficient of variation was 0.19% .

4.4.2 Spectroscopic Analysis Methods for Ammonium Dinitramide

Nitrate and nitrite ion are common contaminants in ADN and need to be tightly controlled to prevent instability of the propellant products. UV spectrophotometric methods can give only a partial answer [273]. ADN and other energetic additives in solid propellants can be detected and quantified by laser Raman spectroscopy [250].

At the time when the propulsion community became aware of widespread contamination of groundwater by perchlorate, there was a need for sensitive perchlorate ion analysis. It is unlikely that dinitramide will ever become an environmental contaminant like the perchlorate it is intended to replace, but sensitive analysis methods are now available for dinitramide analysis in water. This method converts the

dinitramidate to nitrite by UV photolysis and determines the nitrite by reaction with 4-aminothiophenol and *N*-(1-naphthyl)ethylene diamine, forming an azo dye that can be determined colorimetrically [274].

4.4.3 Chromatographic Analysis Methods for Ammonium Dinitramide

Anionic impurities in ADN can be analyzed by either ion chromatography with UV detection [275] or capillary ion electrophoresis with UV detection [276]. The presence of ADN in the IC eluent can be detected by its UV absorption at 214 nm. The disadvantage of UV detection is that sulfate ions cannot be detected this way because they do not absorb light in the UV. The analyses could be completed in <20 min or <6 min, respectively. For capillary ion electrophoresis, Oehrle [276] used a chromate and a phosphate electrolyte. In this case, dinitramide ion was measured at 254 and 185 nm. Good separation of ADN and its degradation products was achieved with the phosphate electrolyte. An example of dinitramide/nitrate separation by capillary ion electrophoresis is shown in Figure 44, where the small peak on the left is nitrate and the large main peak is dinitramide.

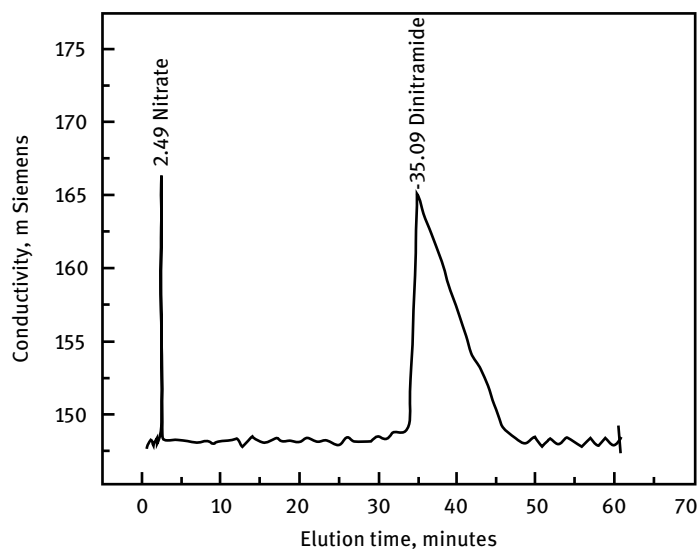


Figure 44: Analysis of nitrate and dinitramide by capillary ion electrophoresis. (Reprinted and modified from [58], with permission from Dr. Gopalakrishnan Santhosh granted 8 February 2021.)

For evaluating the purity of the synthesized and/or treated or aged pure or formulated ADN, the AN content needs to be known. AN is known to be a by-product of ADN synthesis as well as a possible decomposition product of ADN. Heated ADN decomposes mainly to N_2O , H_2O , NO_2 , and AN, which further reacts to N_2O and NH_3 . Determining only the nitrate contents, assuming the rest to be intact ADN, will not lead to correct

values because there may be other contaminants. Depending on how it was made, another possible contaminant in ADN is ammonium nitrourethane (ANU), which is an intermediate in the production of ADN from urethane. The ANU concentration carried over into the product must be kept as low as possible. Therefore, a quick and accurate method for detecting nitrourethane besides nitrate and dinitramide is needed.

The best method is an IC method for the direct analysis of all anions concerned [277–280]. The IC instrumentation (Alltech/GAT) used at the ICT was a so-called single-column ion chromatography (SCIC) technique that used no suppressor in combination with the electrical conductivity detector. Here the ground level of the conductivity of the used eluent is compensated electronically. Alternative systems using the suppressor technique reduced the ground conductivity of the eluent, chemically yielding to a greater usable detection range of the detector. For standard anions, cations, and organic acids, the SCIC system has been a well-suited technique making measurements possible at the ppm or even the ppb level. Different ion exchanger phases were tested in the IC columns with organic and/or inorganic eluants. Best results were obtained with a special IC anion exchange column from DIONEX (IonPac 11 HS) in combination with the UV detector. This separation phase could be used with sodium hydroxide as the eluent also at very high concentrations. Moreover, NaOH shows essentially no UV absorption in the possible wavelength region. The ionic strength and flow rate of the eluant was optimized to get an acceptable resolution for nitrite and nitrate combined with a short run-time for the whole analysis. Detection was either by electrical conductivity or UV absorption, whereby the UV measurement wavelengths were tuned in order to get a small signal-to-noise ratio and simultaneously a suitable sensitivity (especially for NO_3^- and nitrourethane). The UV detector was adjusted at 214 nm for the analysis of NO_2^- and NO_3^- and at 285 nm for the detection of dinitramide. Limits of detection (LOD) of 0.05 to 0.01 ppm were realized for NO_3^- and NO_2^- , respectively, measured at 214 nm. Using 220 nm as the detection wavelength resulted in a worse LOD of about 0.3 ppm for nitrate. Using a wavelength between 210 and 220 nm resulted in an LOD for ADN of about 1 ppm. The linearity range for the analysis of dinitramide anion (at 285 nm) was found to be very broad (up to 700 ppm). All anions could be analyzed at the same time in one run, taking no more than 30 min.

An HPLC-UV method has been developed for the analysis of dinitramide and the anionic impurities nitrate and nitrite in commercial ADN [281]. All of these anions can be analyzed on a porous graphitic carbon column.

ADN crystals and prills were analyzed by IC [165]. Three different measurements were performed on each sample: **(1)** cation analysis (Na^+ , K^+ , NH_4^+), **(2)** trace anion analysis (NO_3^- , SO_4^{2-} , Cl^- , NO_2^-), and **(3)** dinitramide ion analysis. A Dionex DX-600 IC and a Dionex DX-320 IC, both equipped with conductivity detectors, were used for the cation and the trace anion analysis, respectively. For the selective measurement of dinitramide, a Dionex AD25 UV absorption detector was used in addition to the conductivity detector. Na^+ , K^+ , and NO_3^- were detected in both ADN samples. Trace amounts of SO_4^{2-} but no Cl^- or NO_2^- were found in the crystals.

Analysis of ADN in pure form as well as in mixtures can be carried out by IC [282]. The purity of ADN was directly determined by estimating the dinitramide ions and indirectly by estimating the impurities. Both methods gave results comparable with those determined by DSC and UV spectroscopy. The chemical composition of ADN in mixtures containing nitrate, chromate, chlorate, perchlorate, and thiocyanate ions was quantitatively estimated in the same solution without any interferences or prior separation of analyte ions. The ion chromatographic methods for the analysis of ADN are simple and fast, with good accuracy and precision compared to other wet chemistry analytical techniques. The IC methods were found to be highly suitable for quality-control analysis of ADN containing compositions and for the online process monitoring of the formation of ADN in the reaction mixture.

The purity of ADN was determined by an HPLC method using an Agilent C18 column (150×4.6 mm, $5\mu\text{m}$) at 303 K (30°C) with acetonitrile-phosphoric acid as the binary mobile phase with a pH value of 3.0 (volume ratio 10:90) at a flow rate of 1.0 mL/min. and UV detection wavelength of 210 nm [283]. Results showed that when the concentration of ADN was in the range of 0.1–1 mg/mL, there was a linear relationship between the peak area of the chromatogram and ADN concentration: $A = 51.73C + 5.442$. The linear correlation coefficient was 0.9980, average recoveries were 98.33–99.67%, and the relative standard deviation was $\pm 0.49\%$.

The performance and durability of ADN as an oxidizer in rocket propellant compositions depend on its purity. The presence of undesired impurities would be detrimental to its performance and storability. During ADN production, the overall yield of the product depends on the purity of the precursors. Hence, it becomes essential to analyze both the precursors and the final product using suitable analytical techniques prior to application in propellant compositions. ADN and its precursors such as guanylurea dinitramide (GUDN) and potassium dinitramide (KDN) were characterized using UV/visible, FTIR spectroscopy, and DSC [284]. The ions involved in GUDN, KDN, and ADN were analyzed using IC for the direct analysis of anions and cations. The compounds were also characterized using atomic absorption spectrometry to estimate their purity.

4.4.4 Mass Spectrometric Analysis Methods for Ammonium Dinitramide

ADN sublimation and dissociation have been investigated using high-energy xenon atoms to sputter ions directly from the surface of the neat crystalline solid [285]. Tandem mass spectrometric techniques were used to study dissociation pathways and products of the sputtered ions. Among the sputtered ionic products were NH_4^+ , NO^+ , NO_2^- , N_2O_2^- , $\bullet\text{N}_2\text{O}_2^-$, N_3O_4^- , and an unexpected high abundance of NO_3^- . Tandem mass spectra of the dinitramide anion revealed the uncommon situation in which a product ion (NO_3^-) is formed in high relative abundance from metastable parent ions but is formed in very low relative abundance from collisionally activated parent ions. It was proposed that the NO_3^- anion is formed in the gas phase by a rate-determining

isomerization of the dinitramide anion that proceeds through a four-centered transition state. The formation of the strong gas-phase acid, dinitraminic acid (HN_3O_4), the conjugate acid of the dinitramide anion, was observed to occur by dissociation of protonated ADN and by dissociation of ADN aggregate ions with the general formula $[\text{NH}_4(\text{N}(\text{NO}_2)_2)_n]\text{NH}_4^+$, where n was 1 to 30.

4.4.5 Electrochemical Analysis Methods for Ammonium Dinitramide

A graphene modified glassy carbon electrode (GMGCE) was developed to investigate the electroreduction of ADN using cyclic voltammetry and differential pulse voltammetry techniques [286]. ADN was reduced with higher rates at low potentials on GMGCE compared to GCE. The GMGCE exhibited fast response toward ADN with a detection limit of 2.0×10^{-6} M and a linear range of 2.5×10^{-6} to 8.5×10^{-4} M. The possible interference from several common ions was tested, and the method was successfully applied in the determination of ADN in water samples.

4.5 Thermal Stability and Decomposition Reactions of Ammonium Dinitramide

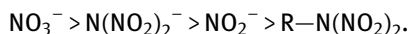
ADN may decompose at elevated temperatures in the solid (crystalline), molten (liquid), vapor (sublimed), and dissolved states. The mechanisms may be different depending on what the environment of the molecules is like. The study of the thermal stability of ADN includes experiments in the laboratory, development of kinetic models to fit the experimental data, and *ab initio* molecular dynamics calculations from scratch to predict the thermal stability of ADN and other nitramines without ever getting one's hands dirty.

All energetic compounds decompose slowly, although the more stable ones decompose only immeasurably slowly. What separates a potentially useful energetic oxidizer from one that is not is the rate at which the transformation occurs, or the kinetic stability. Quantum chemical studies are a useful tool in predicting decomposition rates and should precede synthetic efforts. Ideally, a high-energy-density material (HEDM) suitable for safe handling at room temperature should have a free-energy activation barrier for decomposition that exceeds 125 kJ/mol (30 kcal/mol). This value is estimated assuming first-order decomposition kinetics and corresponds to a half-life of 35 years at room temperature. The thermal decomposition of ADN and its parent acid and its anion can be predicted based on quantum mechanical calculations (see later paragraphs).

The first publications referenced in the following section contain information on thermal decomposition of ADN. The first sections in the following chapter discuss just the thermal effects without any chemistry involved. Subsequent sections will not only discuss the thermal effects but will also analyze the intermediates involved in the reaction leading to the ultimate decomposition products. It was suggested that the chemical transformation of ADN during decomposition and combustion includes two main

pathways (mechanisms): an ionic heteropolar pathway and a dissociative homopolar pathway.

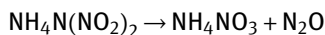
ADN is less stable thermally than KDN, but it is much more stable than NH_4NO_2 and alkyl dinitramides ($\text{R}-\text{N}(\text{NO}_2)_2$). Among ammonium salts, the order of anion stability is



The higher stability of $\text{N}(\text{NO}_2)_2^-$ is attributed to stabilization of the overall negative charge through the electron resonance effect. The thermal stability of dinitramide metal salts depends on the metal cation electronegativity, thus the higher electronegativity results in a higher decomposition rate. In dinitramide onium salts, such as hydrazinium, guanidinium, anilinium, and tetramethylammonium dinitramide, basicity of the cation strongly influences the decomposition rate [287]. Salts of bases with $\text{p}K_a < 5$ have an order-of-magnitude greater decomposition rate than bases with $\text{p}K_a > 8$.

The stability of dinitramide salts is a highly complex issue, and the experimentally determined decomposition barrier of solid-state ADN is typically reported in the range of 29–42 kcal/mol. However, the decomposition barrier for the free dinitramide anion has been theoretically estimated to be 197 kJ/mol (47 kcal/mol). The larger barrier can be attributed to stabilization of the anion through considerable electron resonance delocalization. The actual real-life stability of dinitramide anion is strongly coupled to its ability to polarize charge, and its chemical environment has been shown to be of great importance.

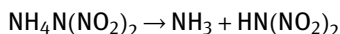
An excellent summary of the decomposition reactions and burning rates of ADN with 89 literature references was published by Yang in 2005 [288]. The list of references is very useful because it also gives the complete titles of the papers referenced, not only the author name and the source. The basic thermal properties, chemical pathways, and reaction products in both the condensed and gas phases were summarized over a broad range of temperature and pressure conditions. Detailed combustion-wave structures and burning-rate characteristics were compared with other types of energetic materials. In particular, the influence of various condensed-phase and gas-phase processes in affecting the pressure and temperature sensitivities of the burning rate was explained. In the condensed phase, decomposition proceeds through the reactions



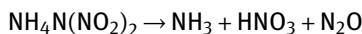
and



the former mechanism being the basic one. In the gas phase, the mechanisms



and



are prevalent. The gas-phase combustion-wave structure in the range of 0.5–2.03 MPa (5–20 atm) consists of a near-surface primary flame followed by a dark-zone temperature plateau at 873–1273 K (600–1000 °C) and a secondary flame followed by another dark-zone temperature plateau at 1273–1673 K (1000–1400 °C). At higher pressures (6.08 MPa = 60 atm and above), a final flame is observed at about 2073 K (1800 °C) without the existence of any dark-zone temperature plateau. The Yang 2005 paper [288] also contains an extensive discussion of the kinetics of NO_2/NH_3 reactions, which are not included in our review.

The most detailed summary of literature on the thermal decomposition of ADN was published in 2016, and it contains all of the references offered here and even more [289]. This paper would be a valuable resource to have in everybody's library. Another excellent review of ADN thermal stability includes 102 literature references [290].

4.5.1 Thermal Stability, Decomposition Reactions, and Autoignition of Solid or Molten Ammonium Dinitramide

ADN has not been around very long, and once it became available, most of it was used up right away for characterization or burning-rate experiments. Hardly any ADN was set aside for controlled storage tests in which samples were taken about once a year to monitor the stability of the material during storage in a closed container in the dark at room temperature.

Aging can change the performance of energetic materials. Freshly synthesized ADN (ADN-2009) was compared with a sample that had been stored in the dark for 11 years (ADN-1998) [291]. Characterization was conducted using IR, Raman, and UV spectroscopy, sealed cell differential scanning calorimetry (SC-DSC), and a thermal activity monitor (TAM). The results of IR, Raman, UV spectroscopy, and SC-DSC suggested that ADN-1998 had an altered composition and was a mixture of ADN and AN, showing that some of the ADN had degraded to AN during storage. The amount of ADN in ADN-1998 was 57 mass-% in the surface region and 89 mass-% in the core region, showing that more aging had occurred on the surface than in the core region. The results of DSC and TAM analysis showed the influence of aging on the thermal decomposition of ADN. It appeared that the presence of AN generated by the aging of ADN mainly caused the difference of thermal properties.

ADN is known to degrade to AN during storage, which will affect its performance. The effects of aging on the thermal decomposition mechanism of ADN and thermal behavior of ADN and ADN/AN mixtures were studied by analyzing the gases evolved during their decomposition, using DSC, TGA-DTA-IR, and TGA-DTA-MS [292]. The results of these analyses demonstrated that the decomposition of ADN occurred via a series of distinct stages in the condensed phase. The gases evolved from ADN decomposition were N_2O , NO_2 , N_2 , and H_2O . In contrast, ADN mixed with AN (to simulate aging)

did not exhibit the same initial reaction. It was concluded that aging inhibits early-stage, low-temperature decomposition reactions of ADN. Two possible reasons were proposed, these being either a decrease in the acidity of the material due to the presence of AN, or inhibition of the acidic dissociation of dinitraminic acid by NO_3^- .

4.5.1.1 Experimental Studies of Thermal Decomposition of Condensed Phase Ammonium Dinitramide

This section deals only with the slow, controlled decomposition of ADN as it might occur in a DSC or ARC. There is also an additional section on the catalytic (as opposed to purely thermal) decomposition of ADN and ADN solutions. Another section deals with the flash pyrolysis of ADN, which is typically done by a rapidly heated filament or by laser illumination. Further down in that section is a section on the actual combustion of ADN in solid propellants and the strand burning rate of ADN. Slow decomposition of ADN is evident by the evolution of gas bubbles from the melt, which begins immediately after melting.

Initial melting of impure grades of ADN containing varying amounts of AN occurred at 328 K (55 °C). An ADN/AN eutectic-phase diagram was constructed from melting-point observations that is useful in studying the effects of AN contamination in ADN decomposition [293]. N_2O evolution was observed at modest temperatures as low as 333 K (60 °C). Some ADN sublimates near its melting point, and then N_2O and AN evolution are very active. At 503 K (130 °C), a small amount of NO_2 was detected in the gas phase, followed by stronger NO_2 evolution at 523 K (150 °C). It was theorized that the ADN decomposition is initiated by proton transfer. Above 503 K (130 °C), dinitraminic acid in the vapor phase decomposes by N–N bond cleavage, evolving NO_2 and initiating a very exothermic reaction sequence.

The sublimation products of ADN contain free dinitraminic acid, which can be trapped in a frozen matrix and identified by IR spectroscopy [294]. Twenty-two absorption bands were identified in the trapped matrix, which were assigned to $\text{HN}(\text{NO}_2)_2$. No evidence was obtained for the presence of structural isomers of hydrogen dinitramide. A suspected but not found isomer was the *aci* form $\text{O}_2\text{N}=\text{NOOH}$, which, according to some molecular orbital calculations, was predicted to be only slightly less stable than the secondary amine structure.

The kinetics of ADN decomposition were studied by a manometric method [241]. The initial decomposition of ADN proceeds via monomolecular cleavage of the N–N bond in the anion. This experiment was supported by the spectrophotometric analysis of the $\text{N}(\text{NO}_2)_2^-$ anion. Gaseous products were analyzed by gas-liquid chromatography (GLC) and mass spectrometry, water was analyzed by the Karl Fisher method, and nitric acid in the products was analyzed by titration with caustic. Thoroughly dried ADN samples with less than 0.2% H_2O showed anomalous decomposition kinetics. At 333 K (60 °C) in the solid state, the decomposition proceeded faster than in the melt at 373 K (100 °C) (abnormal Arrhenius behavior). To avoid the unusual solid-state de-

composition, it is necessary to keep ADN absolutely dry and to control its moisture content.

The autoignition temperature was determined to be 433 K (160 °C) by Wood's metal bath. The thermal stability, measured with microcalorimetry, showed that ADN is stable to at least 353 K (80 °C) and that impurities cause decreased thermal stability. It was also found that ADN in aqueous solution is sensitive to light. Microcalorimetric measurements showed that ADN is thermally stable to 353 K (80 °C), but contaminants will lower the threshold of decomposition. Based on DSC data obtained in accordance with ASTM E698-79, the pre-exponential factor of ADN decomposition is $A_0 = 6.0 \times 10^{15} \text{ s}^{-1}$ and the activation energy is 158 kJ/mol [4].

Slow decomposition of ADN may begin in the solid phase at 333 K (60 °C) to produce gaseous N_2O . ADN begins to decompose rapidly at 403–408 K (130–135 °C), and the DTA/DSC shows an exothermic peak maximum at 453–463 K (180–190 °C) [170]. The thermal decomposition of ADN was studied by DSC and TGA combined with mass spectrometry (TG-MS) and infrared spectroscopy [295]. ADN decomposed in the range 403–503 K (130–230 °C), with an overall heat release of $240 \pm 40 \text{ kJ/mol}$ with pre-exponential coefficients of the order of $A = 10^{21} \text{ s}^{-1}$. The product gases were identified by MS as NH_3 , H_2O , NO , N_2O , NO_2 , HONO , and HNO_3 . The infrared experiments showed that the primary decomposition products are N_2O and NO_2 . No evidence has been found for the participation of dinitraminic acid in the reaction mechanism, and a mechanism involving ionic reactions in the liquid phase was proposed. The global activation energy determined from TGA experiments decreased from $175 \pm 20 \text{ kJ/mol}$ at the beginning of the reaction to $125 \pm 20 \text{ kJ/mol}$ when the reaction neared its completion. Experiments conducted at different carrier gas flow rates indicated that the reaction was catalyzed by product gases released during the reaction. If the product gases are purged fast enough, the decomposition is slowed down. A condensed-phase ionic reaction mechanism was proposed, in which AN and ammonium mononitramide (NH_4NHNO_2) are formed as intermediates in two competing pathways.

Subsequently, temperature-controlled gas cell and thin-film laser pyrolysis techniques have been used to investigate the condensed phase thermal decomposition of ADN [296]. Gas cell experiments were performed at heating rates of $0.02\text{--}0.1 \text{ °C s}^{-1}$ over a temperature range of 293–523 K (20–250 °C). Pulsed CO_2 laser heating of thin ADN films achieved very rapid heating rates of 10^7 °C s^{-1} , and temperatures of about 903 K (630 °C) could be reached in short time. The thermal decomposition products were analyzed in real time by FTIR spectroscopy. Both experimental techniques showed that the primary decomposition products are N_2O and NO_2 . Nitric oxide is produced only at a later stage in the reaction. Surprisingly, no evidence was found for participation of dinitramidic acid in the reaction mechanism. The fact that the same initial products are observed over a wide range of temperatures and heating rates shows that this mechanism can be used to model the initial stages of combustion of ADN.

At 415 K (142°C) in air, ADN will ignite and burn. Other experimenters using a Wood's metal bath for immersing ADN have reported the ignition temperature as 433 K (160°C). Thermogravimetric analysis of ADN decomposition shows that it is a single-stage process. Typical decomposition products are NH_3 , NO , N_2O , H_2O , NO_2 , HONO , and HNO_3 .

The thermal behavior of ADN was characterized by thermomicroscopy, modulated DSC (MDSC), and TGA [167, 297]. The gaseous decomposition products of ADN were captured and analyzed in different heatable optical cells. The decomposition gases were detected in real time on-line during the sample heating by rapid-scan FTIR spectroscopy. All experiments were performed under an argon atmosphere at isothermal conditions or at linear heating rates between 0.5 K min^{-1} and 10 K min^{-1} in the temperature range of 298–548 K (20–275°C). Figure 45, 46, and 47 show three typical DSC thermograms for the decomposition of pure ADN from different sources. There is quite a bit of variation in the onset of exotherm and in the peak temperature. These differences are obviously caused by different purities of the ADN samples used. The sample used by Loebbecke et al. [297] had the lowest melting point and the lowest onset of exotherm and peak exotherm temperature of several data sets published in the literature. The thermograms at a slow heating rate of 0.5 K/min showed the onset of thermal decomposition at 400 K (126.8°C) followed by a symmetrical exothermic peak.

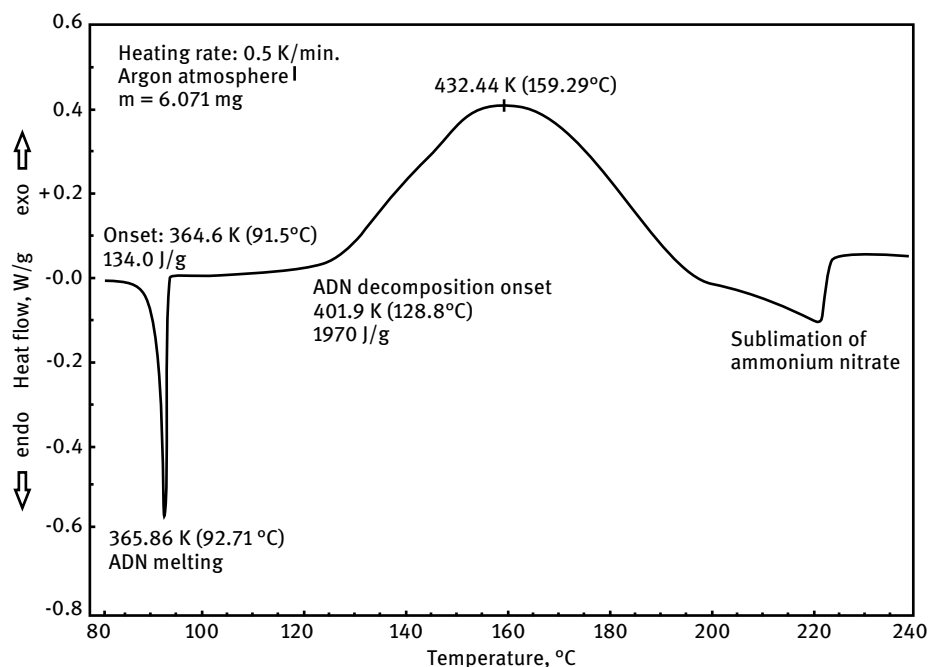
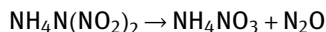


Figure 45: DSC Thermogram of ADN decomposition. (Reprinted and modified from [297], with permission from Elsevier; permission conveyed through RightsLink.)

The exothermic decomposition of ADN proceeded in two steps. The first step resulted in a ~30% mass loss at $T = 433\text{ K} = 160^\circ\text{C}$, and the second step consumed the remaining ~70% of mass at $T = 433\text{--}503\text{ K}$ ($160\text{--}230^\circ\text{C}$). For the reaction $\text{ADN} \rightarrow \text{N}_2\text{O} + \text{AN}$, we would expect a mass loss of 35%. Therefore, the two steps are possibly related to ADN decomposition, first into AN and subsequently to AN decomposition. The two-step thermal decomposition of ADN observed by DSC was confirmed by TGA and high-resolution TGA measurements, showing a mass decrease of 30% in the first step followed by a 70% mass decrease in the second step. There was no residue after completion of the reaction. These results are consistent with a simplified proposed reaction for the first decomposition step of ADN into AN and nitrous oxide with a theoretical mass loss of 35% (Figure 46):



The heat of decomposition was $255 \pm 12.5\text{ kJ/mol}$, and the onset of the exothermic decomposition was at 400 K (127°C). The evaporation curves of NH_4NO_3 and NO_2 pass a maximum, whereas the formation of N_2O is increasing continuously throughout the two steps. See also [298–300].

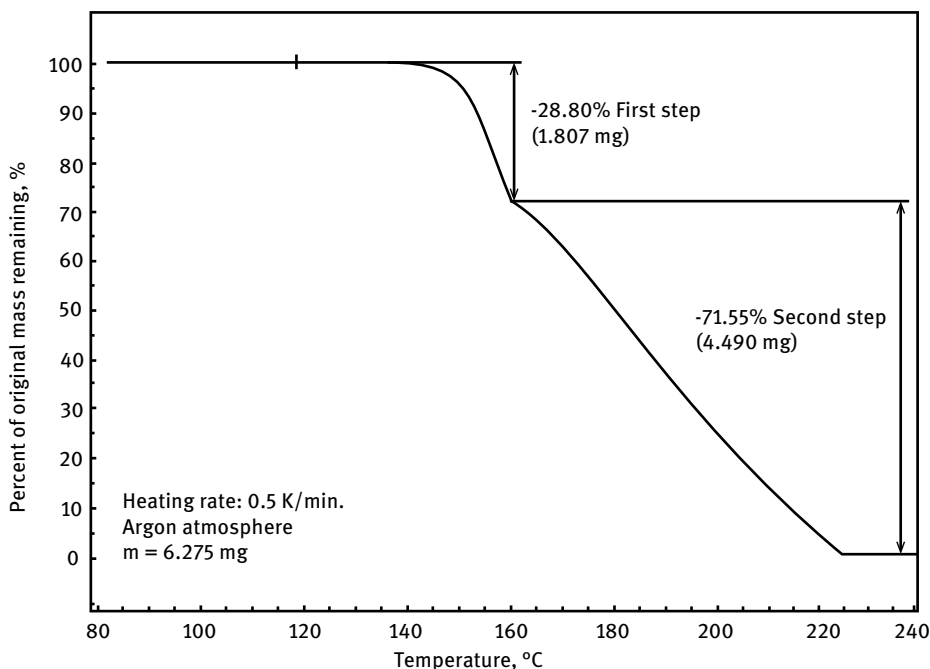


Figure 46: TGA thermogram of ADN decomposition. (Reprinted and modified from [297], with permission from Elsevier; permission conveyed through RightsLink.)

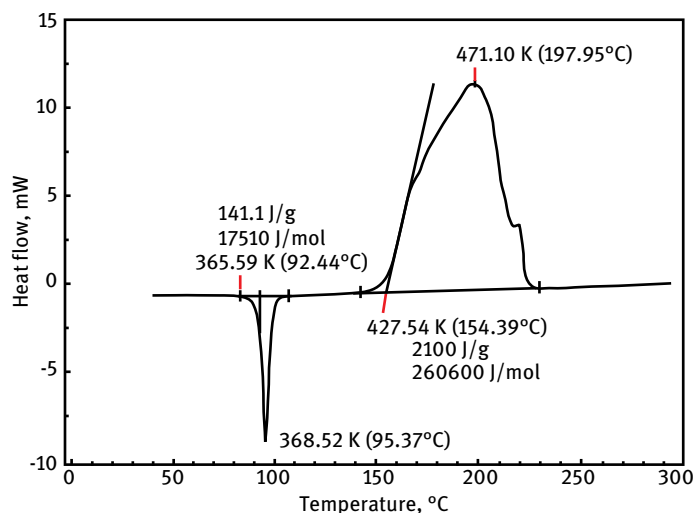


Figure 47: DSC thermogram of ADN decomposition. (Reprinted and modified from [20] with permission from the American Chemical Society; permission conveyed through RightsLink.)

The thermal decomposition of ADN was measured by TGA, DTA, and MS [301] The DTA/TGA data indicated that the activation energy was 110 kJ/mol in the initial stage and 150 kJ/mol in the terminal stage. Based on analysis of the mass spectra of decomposition products, ADN decomposed to form NO_2 , NH_2OH , and NH_3 above the melting point (365 K = 92°C). This is the only instant where experimenters reported the detection of hydroxylamine free base.

Isotope effects can be observed if the atom that has been substituted by an isotope with a different atomic mass participates in a rate-determining step of decomposition reactions (or any other chemical reactions). The isotope effect is most pronounced when replacing hydrogen ^1H with deuterium ^2H . It is less pronounced when replacing ^{14}N with ^{15}N .

The thermal decomposition of ADN and KDN were examined in the solid state and in solution [166]. Isothermal kinetic rates were measured at 433–493K (160–220°C) by monitoring dinitramide ion disappearance. The reactions were found to be first-order in dinitramide ion. Ammonium ion loss and gas formation were not useful for monitoring ADN decomposition since they reflect the fate of the ADN decomposition product AN. The kinetics of decomposition were nearly identical for ADN neat (proteo- and deuterio-), ADN in water (1 or 20 mass-%), ADN in various pH aqueous buffers, and aqueous KDN (1 mass-% in water or deuterium oxide). The activation energy of ADN decomposition was about 167 kJ/mol (40 kcal/mol) for solid ADN and 155 kJ/mol (37 kcal/mol) for aqueous solutions of ADN. Decomposition of ADN in aqueous buffers proceeded at about the same rate at pH 3, pH 5, and unbuffered, but it decreased by

about 40% at pH 9. Solid KDN was unique in that it decomposed about an order of magnitude slower than ADN, but its decomposition increased to be comparable to that of ADN when KDN was aqueous or when any ammonium salt was mixed in with KDN. Nitrous oxide and nitrate (or nitric acid) were the principal decomposition products of any dinitramide. Nitrogen gas was also formed to a significant extent in the decomposition of ADN and to a small extent in the decomposition of KDN. Isothermal decomposition of ADN in a sealed glass tube showed a tendency to produce more N_2 . For decomposition of neat ADN at $503\text{ K} = 230^\circ\text{C}$, the amount of N_2 was nearly the same as that of N_2O (mol ratio) $N_2/N_2O = 0.6\text{--}0.8$; for ADN in an aqueous solution at $473\text{ K} = 200^\circ\text{C}$, the amounts of N_2 and N_2O were 0.15 and 0.69 mol per ADN mol, respectively. The ^{15}N isotope analysis showed that 90% of N_2 came from a combination of one N atom in ammonium and one N atom in the nitro group, and 90% of N_2O consisted of one N atom in the amine and one N atom in the nitro group. Based on isotope exchange, nitrogen gas resulted from the interaction of ammonium or ammonia with the nitrate or gaseous nitrogen oxides. Studies of ^{15}N -labeled ADN confirmed that one N--NO_2 bond remains intact, forming nitrous oxide, while the other nitro group combines with the nitrogen from ammonium to form nitrogen gas.

The thermal decomposition of dinitramide in aqueous and sulfuric acid solutions was studied over a wide temperature range [253, 302]. Depending on the acidity of the solution, dinitramide is present in three different forms: $\text{N}(\text{NO}_2)^-$ anions, neutral $\text{HN}(\text{NO}_2)_2$ molecules, and protonated $\text{H}_2\text{N}(\text{NO}_2)_2^+$ cations. The rate of the thermal decomposition of dinitramide is dependent on the acidity of the solution. In different experiments, the initial acidity was increased. The sequence in which species decompose is first $\text{N}(\text{NO}_2)^-$ anions, then $\text{HN}(\text{NO}_2)_2$ molecules, and, finally, protonated $\text{H}_2\text{N}(\text{NO}_2)_2^+$ cations. The temperature dependences of the rate constants of the decomposition of $\text{N}(\text{NO}_2)^-$ (k_{anion}) and $\text{HN}(\text{NO}_2)_2$ (k'_{acid}) and the equilibrium constant of dissociation (acidity constant) of $\text{HN}(\text{NO}_2)_2$ (K_a) are as follows:

$$\begin{aligned}k_{\text{anion}} &= 1.7 \times 10^{17} \exp\left(-20.5 \times \frac{10^3}{T}\right), \text{ s}^{-1} \\k'_{\text{acid}} &= 7.9 \times 10^{16} \exp\left(-16.19 \times \frac{10^3}{T}\right), \text{ s}^{-1}, \text{ and} \\K_a &= 1.4 \times 10 \exp\left(-2.6 \times \frac{10^3}{T}\right).\end{aligned}$$

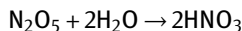
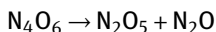
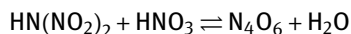
The temperature dependences of the decomposition rate constant of $\text{H}_2\text{N}(\text{NO}_2)_2^+$ ($k_{\text{protonated}}$) and the equilibrium constant of the dissociation of $\text{H}_2\text{N}(\text{NO}_2)_2^+$ ($K_{\text{a-protonated}}$) were estimated as

$$k_{\text{protonated}} = 10^{12} \exp\left(-7.9 \times \frac{10^3}{T}\right), \text{ s}^{-1}$$

and

$$K_{\text{a-protonated}} = 1.1 \exp \left(6.4 \times \frac{10^3}{T} \right).$$

The kinetic and thermodynamic constants obtained make it possible to calculate the decomposition rate of dinitramide solutions in a wide range of temperatures and acidities of the medium. The protonation of the $\text{HN}(\text{NO}_2)_2$ molecules should not affect the strength of the N—N bond, and the orders of the N—N bond in $\text{H}_2\text{N}(\text{NO}_2)_2^+$ and $\text{HN}(\text{NO}_2)_2$ are close. However, when a second proton is added to $\text{HN}(\text{NO}_2)_2$, the protonated form gains the possibility of decomposing via a dehydration reaction. In continuation of these experiments, the decomposition of dinitramide in nitric acid and acetic acid was studied [303]. It was hypothesized that the decomposition in nitric acid occurs via a mixed anhydride N_4O_6 as an intermediate:



Thermal decomposition of ADN and melting points of the ADN/AN binary system and eutectic point were measured by programmed DSC and TGA [168]. The influence of AN on ADN decomposition was studied in detail. When AN was added to ADN, multiple exotherm peaks fused into a single peak at high pressure. The eutectic point is at 30 mass-% AN, with a melting point of 333 K (60 °C). ADN decomposition is retarded by the addition of AN. At high pressures, ADN accelerated the AN decomposition.

A richly illustrated report with 20 DSC and TGA thermograms for several types of ADN samples (prilled, unprilled (Figure 48), and recrystallized) under various experimental conditions (in aluminum and gold-coated aluminum pans; in sealed glass ampoules; under vacuum and pressure) showed asymmetrical or double exothermic peaks with an endothermic peak at a higher temperature [304, 305].

In another test in which the ADN sample was first subjected to an isothermal 325–335 K (52–62 °C) TGA aging process to obtain a residue, followed by the ramp-up DSC, the residue analysis revealed an endothermic peak at 332 K (59 °C) and a lower melting point of 356 K (83 °C) attributed to the presence of AN. It was noted that the first endothermic peak was near the melting point (442.7 K = 169.6 °C) of AN, and the additional exothermic peak was at 310 °C, close to the common AN decomposition temperature of 553–592 K (280–320 °C). Kinetic constants of decomposition were determined for ADN and prilled ADN by DSC and TG. DSC and TG runs in open (pinholed) sample pans in nitrogen or helium had higher activation energies and frequency factors, namely 167–180 kJ/mol (40–43 kcal/mol) and 18–20 min^{−1}, respectively, than in sealed pans. Thus, it appears that confinement of the ADN decomposition gases either under pressurization or a sealed environment accelerates the decomposition of prilled ADN. Kinetics of decomposition of unprilled ADN at atmospheric pressure in

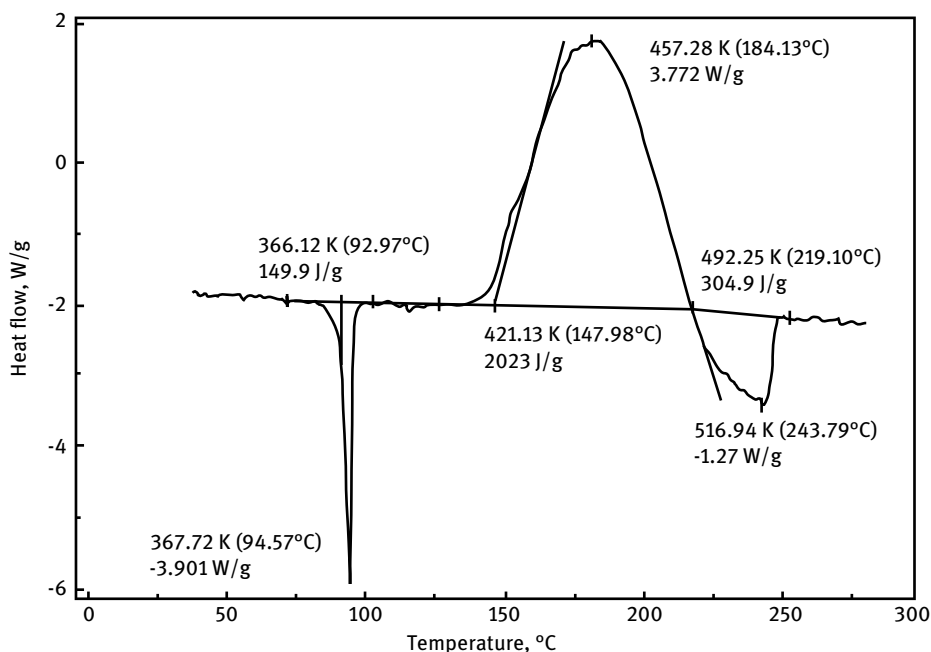


Figure 48: DSC of Bofors ADN under nitrogen at 5 °C/min. (Reprinted and modified from [304], with permission from Elsevier; permission conveyed through RightsLink.)

nitrogen or helium by DSC and TG were $E_a = 154.8 \text{ kJ/mol}$ (37 kcal/mol) and $\log A = 17 \text{ min}^{-1}$. Unprilled ADN had a lower activation energy and frequency factor for decomposition than prilled ADN that contained stabilizers. The effect of sample containment (i.e., aluminum, coated aluminum, gold, and glass ampoules) on the shape of the DSC curve of ADN was investigated. Isothermal TG in vacuum of ADN in the 318–348 K (45–75 °C) region and the DSC analysis of the TG residues showed unusual results in the 333 K (60 °C) region. The rate and enthalpy of decomposition of four other dinitramide salts (ammonium [ADN], hexamethylenetetramine⁺ [HDN], potassium [KDN], and sodium [NaDN]) and their dielectric relaxation were related to the basicity of the cation. The DSC results also suggested that ADN decomposition has a low activation energy in vacuum.

ADN decomposes at 393 K (120 °C). The main pathway is the formation of NH_4NO_3 and N_2O , followed by the thermal decomposition of NH_4NO_3 to N_2O and H_2O at higher temperatures [306, 307]. Gas chromatography/mass spectrometry analysis shows formation of NO_2 , NO , N_2 , and O_2 .

It is known that ADN decomposes at temperatures above its melting point (365 K = 92 °C). The thermal stability of ADN below its melting point had not received much attention until the thermal stability of ADN was studied at temperatures ranging from

328 to 353 K (55 to 80 °C) by using microcalorimetry and TGA at isothermal conditions [308]. The results showed that very dry as-received ADN had a poor thermal stability at 333 K (60 °C), whereas the stability improved at higher temperatures of 343 and 353 K (70 and 80 °C). This anomalous behavior had been observed by other researchers. In more humid samples, the stability at 333 K (60 °C) improves. A possible explanation of the instability of as-received Bofors-ADN at 333 K (60 °C) is that organic impurities, from the 2-propanol used in the last step of the synthesis, may be present. By purification, the ADN becomes substantially more stable at 333 K (60 °C). At higher temperature the organic impurities in as-received ADN volatilize, making the ADN more stable at 343 and 353 K (70 and 80 °C). As-received ADN stored at 353 K (80 °C) showed improved stability when later analyzed at 333 K (60 °C).

For linear pyrolysis under vacuum at 370 K and 0.3–0.5 mbar, an extremely high activation energy of $E_a = 237 \text{ kJ/mol} = 56.7 \text{ kcal/mol}$ with a frequency factor of $1.2 \times 10^{26} \text{ sec}^{-1}$ was obtained using DSC [309]. This is much different from any other reported E_a data for ADN.

Based on differential thermal analysis (DTA) data, the activation energy of ADN decomposition was $E_a = 164 \text{ kJ/mol} = 39.2 \text{ kcal/mol}$, with a frequency factor of $1.52 \times 10^4 \text{ min}^{-1}$ [57]. Based on TGA data, the activation energy calculated from the slope of the Arrhenius curve was 135.7 kJ/mol. The natural logarithm of the pre-exponential factor A was 33.62 [58]. TGA data revealed that E_a changed from 174 to 68.6 kJ/mol (41.6 to 16.4 kcal/mol), while the conversion extent varied from 10 to 90%. The mass loss TGA of ADN at four different temperatures above its melting point is shown in Figure 49. An intermediate step (expected if the decomposition goes to AN first) is barely recognizable from a change in slope after 100 min.

Similar data were obtained for the thermal decomposition of four samples of KDN-ADN mixtures with weight ratios of 90:10, 50:50, 25:75, and 10:90. A thermogram was obtained on a sample of ADN that had been prepared by nitration of ammonium sulfamate [57], shown in Figure 50. The melting points of the samples in Figure 50 and 51 agree quite well, 92.71 °C max and 93.4 °C max.

The thermal decomposition of ADN was studied using TG and DSC for better understanding of the thermal decomposition behavior of ADN [310]. The main variables included the effect of GN_2 purge gas flow rate, ammonium ethyl *N*-nitrocarbamate (AUN, a contaminant from the manufacturing process) content, and AN. Several of these have a strong effect on the ADN decomposition process and influence the activation energy curve of ADN thermal decomposition represented by a model-free isoconversion method. The results showed that the decomposition process of ADN is affected by GN_2 flow rate and AN content but not by AUN content.

In order to study the decomposition mechanisms occurring during the adiabatic self-heating of ADN, a procedure was developed to remove the decomposition gases from the accelerating rate calorimeter system [311]. The main reaction products of ADN were nitrate, nitrogen, and dinitrogen monoxide, which were measured as a function of the degree of ADN conversion.

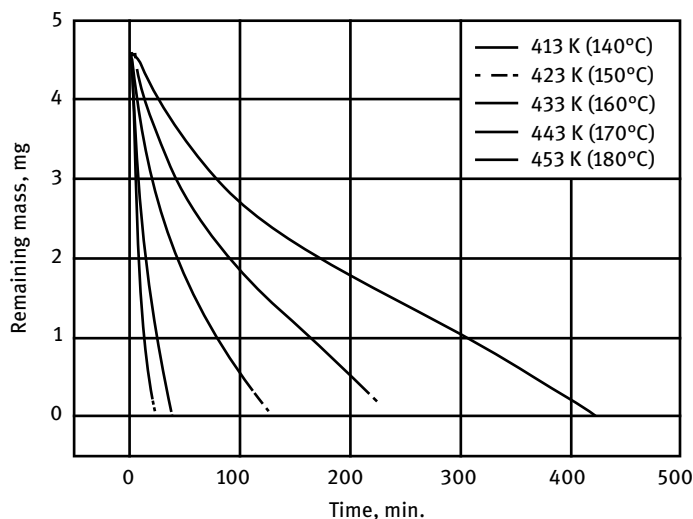


Figure 49: Mass loss TGA of ADN under isothermal conditions. (Reprinted and modified from [58] with permission granted by Dr. Santhosh 8-Feb-2021.)

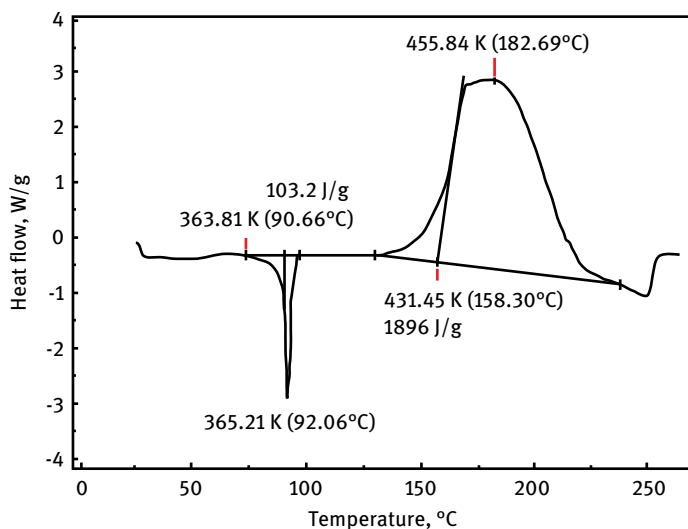


Figure 50: DSC thermogram of ADN decomposition. (Reprinted and modified from [58] with permission granted by Dr. Santhosh 8-Feb-2021.)

A variety of thermal analysis equipment was used to study the decomposition of ADN crystals and ADN prills by themselves and also in contact with binders, using DSC, TGA, TGA-FTIR-MS, ARC, heat flux calorimetry, and isothermal nanocalorimetry [165, 261]. The average diameters for the crystals and prills were 148 and 154 μm ,

respectively. The prills were coated with 2.4% bis-(2-ethylhexyl)-sebacate (DOS) and 0.6% hydroxyl-terminated polybutadiene (HTPB). In the DSC, two endotherms and two exotherms were obtained for both ADN samples. The first endotherm, which was observed at an onset temperature of about 363 K (90 °C), was due to the melting of ADN, where the melting point may be depressed by impurities. The melting temperature of ADN prills was lower than that of the crystals. The slightly lower melting points of the prills were due to the presence of coating agents. The major exotherm ($\sim 403\text{ K} = \sim 130\text{ °C}$) resulting from the decomposition of liquid ADN was followed by a second exotherm ($\sim 473\text{ K} = \sim 200\text{ °C}$) from the decomposition of AN formed during ADN decomposition. The second endotherm ($\sim 523\text{ K} = \sim 250\text{ °C}$) can be attributed to the formation and vaporization of water during AN decomposition. No second exotherm was observed from the TG-DTA results. With ARC, an exotherm was detected at a true onset temperature of 373 K (100 °C). The onset temperature was 30° lower than that obtained by DSC. This difference was mainly due to the larger sample size used in ARC measurements. All of the ARC runs were stopped automatically at 388–398 K (115–125 °C), when the self-heating rate exceeded 1°/min. The activation energy and pre-exponential coefficient were $E_a = 257 \pm 9\text{ kJ/mol}$ and $\ln Z = 80 \pm 3\text{ min}^{-1}$, which is different from the ARC results reported by SRI ($E_a = 571 \pm 113\text{ kJ/mol}$; $\ln Z = 180 \pm 35\text{ min}^{-1}$).

In one set of experiments, ADN melted at $363.52 \pm 0.49\text{ K}$ ($90.37 \pm 0.49\text{ °C}$), and the onset of exotherm was at $393.80 \pm 0.77\text{ K}$ ($120.65 \pm 0.77\text{ °C}$) [252]. The heat of decomposition was $234.06 \pm 5.55\text{ kJ/mol}$. AN, a frequent contaminant and a decomposition product of ADN, has a pronounced effect on the melting behavior of ADN. A sample contaminated with 3.8% AN showed a new endothermic peak at 331 K (58 °C). AN contamination lowers the thermal stability of ADN, and the AN content should be kept below 0.5%. A very similar DTA thermogram is shown in Figure 51 [7].

In an effort to explain a mechanism for the anomalous decomposition of ADN at 333–338 K (60–65 °C), the ADN decomposition at moderate temperatures was analyzed by a time-of-flight (TOF) mass spectrometer (MS) equipped with a fused silica capillary column inlet. The sample chamber was connected to the ionization chamber of the TOF-MS by a long capillary line [312, 313]. The results from the mass spectrometric studies of decomposition products from solid and molten (100 °C) ADN for two different batches of neat ADN, MgO stabilized neat ADN and prilled ADN showed that stabilization by MgO also retards the formation of N_2O . For the liquid ADN test, the sample was heated to 373 K and kept at that temperature while mass spectra were recorded for several hours. A peak at m/e 45 was attributed to contamination by 2-propanol, which is a solvent used in crystallization of ADN. It disappeared after 3 h. After 21 h at 373 K, the MS showed mostly N_2O with some N_2 and H_2O . There was no signal at m/e 15, and there was no evidence for formation of NH_3 (contrary to what others have reported). After 36 h, water with m/e 18 and 17 was the dominating species in the MS. If 2-propanol can be eliminated as a potential source of the peak at m/e 43, it has been theorized that it could come from hydrogen azide HN_3 , which has not been detected by any previous investigators of ADN decomposition. A sample heated

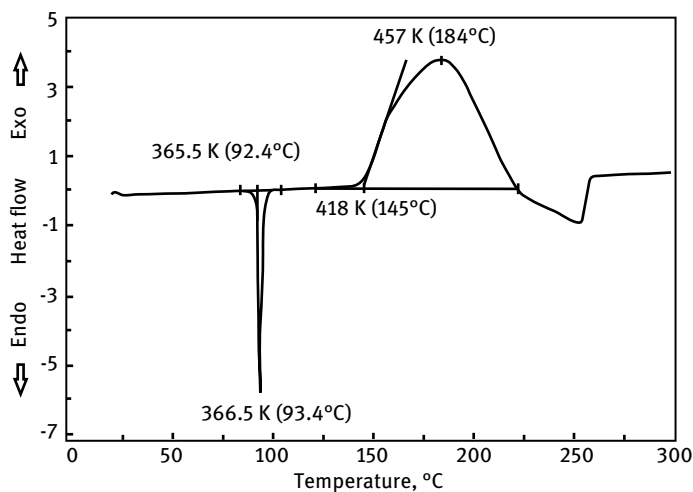
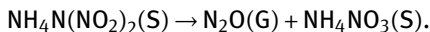


Figure 51: DSC thermogram of ADN decomposition. (Republished and modified from [7], with permission of John Wiley & Sons Books; permission conveyed through Copyright Clearance Center Inc.)

only to 338 K (65 °C) instead of to 373 K showed some N₂O but no H₂O or NH₃ formed. It was suggested that ADN in the solid state decomposes directly to AN and H₂O:



Under those conditions, the proton transfer mechanism, wherein the first step is a transfer of a proton from the ammonium ion to the dinitramide ion, is not likely to take place. Instead, it has been proposed (as supported by theoretical studies) that the direct formation of N₂O and AN is facilitated by a rearrangement of the dinitramide group, which has a very unsymmetrical electron distribution. The presence of traces of water decreases polarization, smoothens the asymmetry, and thereby prevents an intramolecular rearrangement responsible for the anomalous decomposition. In ADN with 1% MgO added as stabilizer and heated to 368 K, the autocatalytic reaction as measured by heat flow calorimetry was delayed by several days. Prilled ADN (prilled from the melt) contained less (if any) 2-propanol and had a slower onset of decomposition at 373 K than any of the neat (freshly crystallized) ADN samples. The ADN anomalous decomposition is best illustrated by the heat flow calorimeter measurements of samples kept at constant temperatures between 328 and 348 K (55 and 75 °C). Figure 52 shows that the shortest life span is at 338 K (65 °C), with a little longer life span at 333 K (60 °C), but that samples kept at 328, 343, 348, or 353 K (55, 70, 75, or 80 °C) did not decompose measurably within the duration of the experiment (7 d).

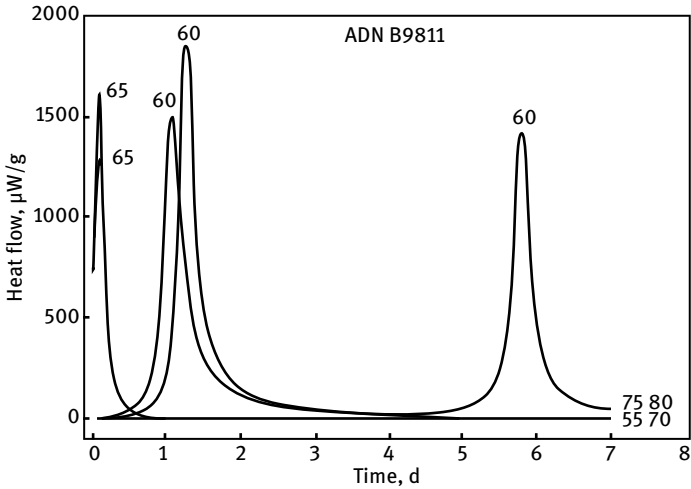


Figure 52: Anomalous decomposition of ADN as illustrated by heat flow calorimetry of elevated temperature storage test. (Reproduced/printed/used from [313], with permission from FOI Sweden, 6 June 2020, from FOI-R-1639-SE and/or AIAA 2005-4468) Legend: The numbers shown adjacent to the exotherm peaks and in the right corner are the storage temperatures in degrees Celsius (°C)

Based on the species detected in the mass spectrogram of decomposition products in a dynamic flow reactor, the following equations were proposed to describe the decomposition of ADN (Table 19):

Table 19: Balanced equations for decomposition reactions of ADN.

Equation no.	Balanced equation	Enthalpy of reaction kJ/mol	Entropy of reaction J mol ⁻¹ K ⁻¹	Adiabatic temperature °C
1	$\text{NH}_4\text{N}(\text{NO}_2)_2(\text{S}) \rightarrow \text{O}_2(\text{G}) + 2\text{H}_2\text{O}(\text{G}) + 2\text{N}_2(\text{G})$	-335.7	791	1811
2	$\text{NH}_4\text{N}(\text{NO}_2)_2(\text{S}) \rightarrow 2\text{N}_2\text{O}(\text{G}) + 2\text{H}_2\text{O}(\text{G})$	-172.5	643	987
3	$\text{NH}_4\text{N}(\text{NO}_2)_2(\text{S}) \rightarrow 2\text{NO}(\text{G}) + 2\text{H}_2\text{O}(\text{G}) + \text{N}_2(\text{G})$	-155	816	924
4	$\text{NH}_4\text{N}(\text{NO}_2)_2(\text{S}) \rightarrow \text{NO}_2(\text{G}) + 2\text{H}_2\text{O}(\text{G}) + 1.5\text{N}_2(\text{G})$	-302.6	730	1648
5	$\text{NH}_4\text{N}(\text{NO}_2)_2(\text{S}) \rightarrow 4/3\text{HNO}_2(\text{G}) + 4/3\text{H}_2\text{O}(\text{G}) + 4/3\text{N}_2(\text{G})$	-278.9	671	1501
6	$1.25\text{NH}_4\text{N}(\text{NO}_2)_2(\text{S}) \rightarrow \text{HNO}_3(\text{G}) + 2\text{H}_2\text{O}(\text{G}) + 2\text{N}_2(\text{G})$	-346.3	647	1807
7	$\text{NH}_4\text{N}(\text{NO}_2)_2(\text{S}) \rightarrow \text{HN}(\text{NO}_2)_2(\text{G}) + \text{NH}_3(\text{G})$	+184		

Data source: [314]

The results were compared to those obtained for AN and hydroxylammonium nitrate decomposition. In either case, nitric acid formation competes with oxygen formation. Based on equilibrium calculations using HSC Gibbs, nitric acid is a very stable inter-

mediate kinetic product up to about 523 K (250 °C). Above 573 K (300 °C), HNO_3 decomposes into H_2O and NO_2 .

Samples of ADN prills were prepared by emulsion crystallization and characterized by optical microscopic observation, TGA and DSC [102]. The particle size of ADN prills as measured by optical microscopy was in the range of 100–300 μm . The isothermal and non-isothermal decomposition kinetics were studied using TGA. The differential isoconversional method of Friedman (FR) and integral isoconversional method of Vyazovkin (VY) were used to calculate the dependence of activation energy (E_a) on the degree of conversion (α), and the results were compared to literature data. The dependence of E_a was also derived from isothermal data. A strong dependence of E_a on α was observed for the ADN prills. All the methods showed an initial increase in E_a up to $\alpha \approx 0.2$ and a later decrease over the remaining reaction time, indicating that more than one reaction may be rate determining. However, TGA and DTG showed only one decomposition step. The apparent E_a values of FR method were higher than those of the VY method up to $\alpha \approx 0.45$. The calculated mean E_a values by FR, VY, and standard isoconversional method for α between 0.05 and 0.95 were 211, 204, and 157 kJ/mol, respectively. The TGA measurements showed that ADN prills undergo a single-stage decomposition with a 100% mass loss in the temperature range from 418 to 503 K (145 to 230 °C). The well-defined DTG curve with a peak maximum at $T \approx 454$ K ($T \approx 181$ °C) also indicated that ADN decomposes in a single step. A generalized decomposition mechanism was proposed, based on the assumption that the decomposition of ADN produces various oxides of nitrogen where the formation of ammonia and dinitramidic acid [$\text{HN}(\text{NO}_2)_2$] dominate in the first step (below 373 K = 100 °C), followed by further decomposition of the latter and AN formed by the recombination of NH_3 and HNO_3 at higher temperatures (greater than 373 K = 100 °C).

The rate of thermal decomposition and mechanism of ADN decomposition were investigated using DSC/TGA-MS-FTIR technology [315]. During the thermal decomposition of ADN, N_2O , NO_2 , NH_3 , H_2O , and N_2 were detected and measured in the gas phase by simultaneous TG-DSC-FTIR-MS techniques. The kinetic parameters, activation energy E_a of the evolution of N_2O , NO_2 , and NH_3 gas products were 157, 159, and 100 kJ/mol, respectively. The decomposition mechanism closely resembled a genuine elementary microcosmic process.

Exothermic behavior during thermal decomposition of fresh and aged ADN was measured by isothermal high-sensitivity calorimetry tests and non-isothermal tests using DSC [316]. Figure 53 shows a typical DSC thermogram for fresh ADN. The endothermic peak that was observed at an onset temperature of about 363 K (90 °C) was due to the melting of ADN. Two exothermic peaks are evident at 403–493 K (130–220 °C) (first exothermic peak) and 492–563 K (220–290 °C) (second exothermic peak). The integrated heat value was ~ 1.8 kJ/g for the first exothermic peak and 0.6 kJ/g for the second exothermic peak.

Figure 54 shows heat evolution at different constant temperatures as a function of time. The heat evolution peaked during the first 1–3 d and then subsided.

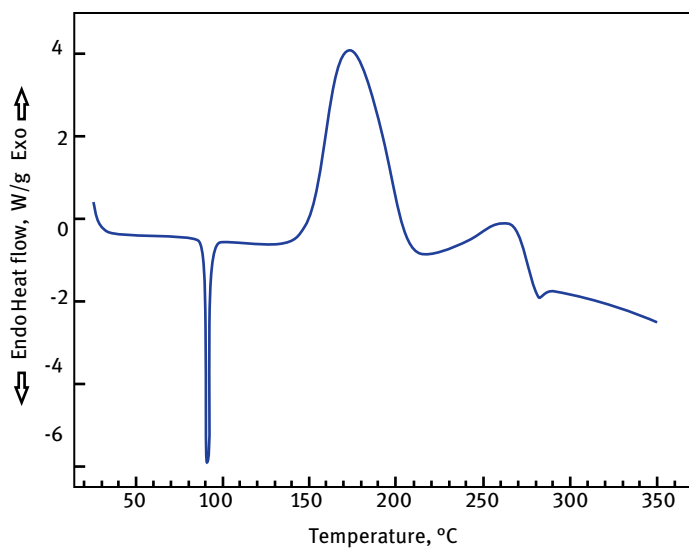


Figure 53: DSC trace of fresh ADN. (Republished and modified from [317], with permission of Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

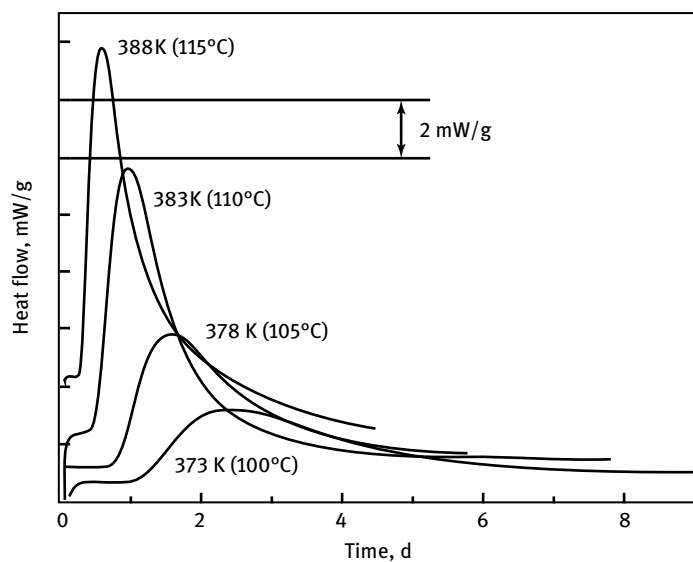


Figure 54: Heat flow from decomposing fresh ADN during isothermal tests in a microcalorimeter. (Republished and modified from [317], with permission of Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

Based on these results, an analysis of the decomposition kinetics was conducted. The activation energy determined by calorimeter tests was lower than that from DSC tests. The value of E_a from calorimeter tests was 80–120 kJ/mol, whereas E_a from DSC tests was 145–165 kJ/mol. That indicated that the decomposition path in calorimeter tests was different from that in DSC tests. The amount of ADN decomposition predicted from calorimeter tests was closer to that found under real storage conditions than the amount of decomposition predicted from DSC tests. Non-isothermal tests may not be able to precisely predict the lifetime of materials with a decomposition mechanism that changes with temperature, such as ADN. The lifetime predicted from DSC results was much longer than that from calorimeter tests, especially at low temperatures. It will be necessary to use isothermal tests to predict the long-term stability at low temperature. Two different samples of ADN were used for the experiments: a fresh sample of ADN-2011 and an aged sample of ADN-1998 (Hosoya Pyro-Engineering) that had been stored in a dedicator for 11 years at room temperature in the dark. The effects of light, heat, moisture, and other factors on the samples vary depending on the area of the sample tested. Therefore, ADN-1998 was separated into a surface-layer sample and a bulk sample from below, which were characterized separately. Based on UV analysis of nitrate ion at 284 nm, the amount of ADN surviving in ADN-1998 was only 36 mass-% ADN at the surface and 57% in the bulk.

ADN was heated at a constant rate, and the exothermic behavior and the decomposition products in the condensed phase during heating were measured simultaneously by Raman spectroscopy, revealing multiple stages of exothermic reactions [317]. In the condensed phase, AN was formed in the primary decomposition at lower temperature, and it further decomposed at higher temperature.

The products and chemical pathways of ADN decomposition reactions under different ambient conditions (pressure, temperature, isothermal or non-isothermal, heating rate, sealed or unsealed) in both the condensed and vapor phases, the thermal stability, and the combustion mechanism were analyzed [318]. It is generally believed that ADN decomposition reaction in the condensed phase will undergo a solid-state molecular rearrangement to form N_2O and AN (or $NH_3 + HNO_3$) at low temperature. However, the decomposition proceeds through N– NO_2 bond cleavage mechanism to form NO_2 at high temperature. For the gas-phase decomposition of ADN, decomposition proceeds mainly via proton transfer in the intramolecular or intermolecular to form dinitraminic acid, $HN(NO_2)_2$, and then dinitraminic acid dissociates following the four pathways:

- $HN(NO_2)_2$ dissociates into NO_2 and $HNNO_2$ radicals, which in turn dissociates to produce various species such as HNO , H_2O , N_2O , and $HONO_2$;
- $O_2NN=N(O)OH$, one of $HN(NO_2)_2$ isomers, decomposes into $NN(O)OH$ and NO_2 radicals;
- $O_2NN=N(O)OH \rightarrow NO_2 + OH + N_2O$; and
- $O_2NN(OH)NO$, another isomer of $HN(NO_2)_2$, which undergoes a four-member molecular rearrangement or possibly proceeds through other transition states, finally dissociates into N_2O and HNO_3 .

4.5.1.2 Effect of Pressure on Thermal Decomposition of Solid Ammonium Dinitramide

Pressure DSC at 3.78 MPa (550 psi) air or helium had similar kinetic constants for prilled ADN, namely 121.3 kJ/mol (29 kcal/mol) activation energy and a log frequency factor of $\sim 14.0 \text{ min}^{-1}$ [304, 305]. These values were similar to those found in sealed sample pans in which the decomposition gases were confined. DSC and TG runs in open sample pans in nitrogen or helium had higher activation energies and frequency factors, namely 167–180 kJ/mol (40–43 kcal/mol) and $18\text{--}20 \text{ min}^{-1}$, respectively. Thus, it appears that confinement of the ADN decomposition gases either under pressurization or a sealed environment accelerates the decomposition of prilled ADN.

For studying the thermal decomposition mechanism of ADN under pressurized conditions from 0.1 to 6 MPa while ADN was heated at a constant rate, the exothermic behavior and the decomposition products in the condensed phase during heating were measured simultaneously using PDSC and Raman spectrometry [319]. PDSC analyses showed multiple stages of exotherms after melting. The exothermic behavior at low temperatures varied with pressure. Analysis of the decomposition products indicated that AN was generated during decomposition of ADN at all pressures. At normal pressure, AN was produced at the same time as start of exotherm. However, the temperature at which the ratio of ADN in chemical species in the condensed phase began to decrease under high pressure was higher than that at atmospheric pressure despite the existence of a significant exotherm.

The main reaction under all pressure conditions was the decomposition of ADN to AN and N_2O . The relative amount of NO_2 decreased with pressure. Condensed phase reactions involving NO_2 take place during early stages of the decomposition process. The reaction mechanism changed in the presence of AN [320].

4.5.1.3 Effect of Moisture on Thermal Decomposition of Solid Ammonium Dinitramide

Moist ADN containing 0.4–0.5% of water was more thermally stable than “dry” ADN containing 0.02–0.05% of water. The kinetics of thermal decomposition of ADN were studied using a manometric method. The thermal decomposition of dinitramide onium salts proceeds via the dissociative mechanism when the $\text{p}K_{\text{a}}$ of the base is lower than 5.0 and via the monomolecular decay of the anion at $\text{p}K_{\text{a}} > 7.0$ [321]. Going from the melt to the solid state, the reaction mechanism of alkali metal dinitramide decomposition does not change, and the rate decreases by 1–2 orders of magnitude. Unusual irregularities are observed for decomposition of ammonium salt and some metal salts in the solid phase: The solid-phase reaction can be $10\text{--}10^4$ times faster than that in the melt. The ADN decomposition rate has a sharp peak at 333 K (60 °C) in the region of eutectics melting with the decomposition product (AN), and it is instantly inhibited by traces of water vapor. In the inhibited regime, the rate in the solid phase is lower than that in the liquid phase. This is related to a change

in the reactivity of the anion due to the violation of its symmetry on going to the solid state. When the nitro groups of the anion are non-equivalent, and the charge is concentrated predominantly on one of them, its reactivity increases, and a new fast pathway of decay is opened: elimination of NO_3^- with elimination of N_2O . Further, the absence of hydrogen bonds between the anion or cations and water molecules is an additional prerequisite for the fast decay [322]. The hydrogen bonds between the anion and H-containing cations in moist samples or direct solvation by water molecules decrease polarization of the anion, smoothen its electronic asymmetry, and prevent intramolecular rearrangement. When water is added to the $\text{NH}_4\text{N}(\text{NO}_2)_2$ melt, the rate of thermal decomposition of the salt first decreases and begins to increase only when the water content is $> 5 \text{ mol-\%}$.

In contrast, no anomalous effects inherent in dinitramide ammonium salt and metal salts in the solid phase were observed during decomposition of onium salts from organic amines [287].

4.5.1.4 Effect of Acids on Thermal Decomposition of Solid Ammonium Dinitramide

It was shown by direct methods that ADN decay can be accelerated by HNO_3 and NO_2 . Both of these both products, as well as water, are highly soluble in molten, liquid ADN. They form during ADN decomposition and cause the process to be self-accelerating. Thermal decomposition of ADN and other dinitramide salts is sensitive to acid catalysis. HNO_3 is one of the decomposition products of ADN, and the addition of HNO_3 aqueous solution to the ADN melt accelerates decomposition [323]. In strong acids, such as H_2SO_4 and HNO_3 , ADN decomposes more rapidly at room temperature, and the rate of acid-catalyzed decomposition is proportional to acidity. Kinetic data for decomposition of different forms of dinitramide and the influence of water on the rate of decomposition of $\text{NH}_4\text{N}(\text{NO}_2)_2$ at 375–412 K (102.4–138.9 °C) show that the contributions of the decomposition of $\text{N}(\text{NO}_2)_2^-$ and $\text{HN}(\text{NO}_2)_2$ to the initial decomposition rate of the reaction at temperatures of about 373 K (100 °C) are approximately equal. The decomposition has an autocatalytic character. The analysis of the effect of additives of HNO_3 solutions and the dependence of the autocatalytic reaction rate constant on the gas volume in the system shows that the self-acceleration is due to an increase in the acidity of the $\text{NH}_4\text{N}(\text{NO}_2)_2$ melt owing to the accumulation of HNO_3 and the corresponding increase in the contribution of the $\text{HN}(\text{NO}_2)_2$ decomposition to the overall rate. At a certain point, the self-acceleration ceases because of the accumulation of NO_3^- ions decreasing the equilibrium concentration of $\text{HN}(\text{NO}_2)_2$ in the melt. The accumulation of HNO_3 in the system is the most probable reason for the self-acceleration of the thermal decomposition during the initial stages of the reaction. The effect of a 26% aqueous solution of HNO_3 (which corresponds to the content of HNO_3 with respect to the sum of HNO_3 and H_2O in the melt at the moment of achievement of the maximum decomposition rate) on the kinetics of thermal decomposition of the $\text{NH}_4\text{N}(\text{NO}_2)_2$ melt was studied by adding known amounts of acid. The acid was introduced in amounts of 3.86 and 1.34 mass-% HNO_3 of the weight of $\text{NH}_4\text{N}(\text{NO}_2)_2$, i.e.,

1.97 and 0.68 mol-% HNO_3 , respectively, with respect to the number of moles of the salt. When pure $\text{NH}_4\text{N}(\text{NO}_2)_2$ decomposes, 0.5 mol-% HNO_3 is present in the system at the moment of achievement of the maximum rate. The increase in the initial rate is proportional to the molar concentration of the added HNO_3 , and its 2.8-fold increase results in a 2.7-fold increase in the rate of decomposition.

NO_2 gas, one of the decomposition products, was found to catalyze ADN decomposition, whereas basic substances, such as NH_3 , amines, and urea, may restrain ADN decomposition.

4.5.1.5 Effect of Contaminants or Additives on Thermal Decomposition of Solid Ammonium Dinitramide

Ammonium nitrate, which is a common contaminant in and decomposition product of ADN, can affect the rate of thermal decomposition of ADN in the solid and molten states [322]. Figure 55 shows the rate of gas evolution (an indicator of ADN decomposition) as a function of time for two ADN samples with different AN content. The sample with the higher AN content (10% AN) evolves gas at a similar rate compared to the sample with only a trace of AN (0.3% AN).

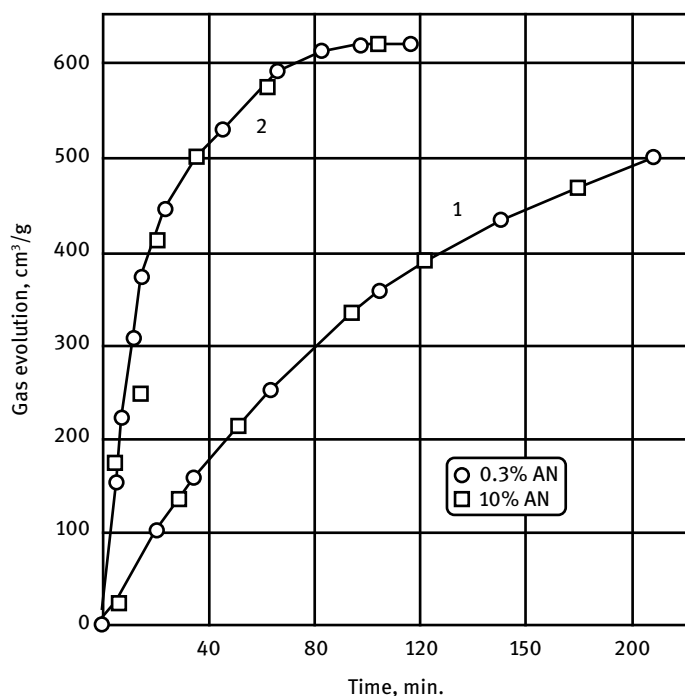


Figure 55: Gas evolution from ADN at $m/V_f = 4 \times 10^{-4} \text{ g/cm}^3$ and temperatures of 150 (curve 1) and 170 °C (curve 2). (Reprinted and modified from [322], with permission by Springer Nature; permission conveyed through Copyright Clearance Center Inc.)

It has been proposed that the effect of higher concentrations of AN in the decomposing ADN is mostly due to the formation of low melting eutectics in the AN/ADN system. This effect is most prominent if the decomposition proceeds at 333 K (60 °C).

The thermal decomposition of ADN and the interaction of ADN with HMX or RDX were investigated by means of DSC and TGA-DTG [324]. The results showed that there existed strong interaction among ADN and HMX or RDX. Because HMX partially dissolved in the molten ADN, the exothermic decomposition peak temperature of ADN increased with the increase of pressure, while that of HMX appeared as a double decomposition peak. A large amount of RDX was liquefied prior to ADN melting, and then it decomposed together with ADN. The decomposition peak temperature of RDX in the mixture at normal pressure would be delayed because of inhibition caused by gaseous products from ADN, while the decomposition peak temperature of RDX at high pressure would be accelerated because of the catalytic effect of gaseous products from RDX decomposition.

4.5.1.6 Effect of Stabilizers on Thermal Decomposition of Solid Ammonium Dinitramide

The thermal stability of ADN is worse than that of AP or AN; therefore, a wide range of stabilizers have been tested in the hope of improving its thermal stability [325].

4.6 Autoignition and Ignition Delay of ADN

The thermal initiation by electron beam heating of single crystals and prills of ADN on a calibrated hot stage has been filmed and recorded in an environmental scanning electron microscope all the way from the formation of microscopic “reaction sites” (0.01 μm in diameter) to full crystal consumption [326]. The transformations of the ADN prills and crystals were compared and recorded in real time at various magnifications (10000 $\times$ to 100 $\times$) and under different atmospheres (pure nitrogen and nitrogen/water vapor mixtures). The initiation characteristics of the prills were found to differ and are related to the microstructural characteristics produced by different prilling techniques, such as the “prilling tower” technique (Thiokol) and the “melt-stir” technique (United Technology Corp. Chemical Systems Division, CSD).

A model with two-phase subsurface reactions was developed to study the physical and chemical processes involved in ADN autoignition [327]. The model was based on the conservation equations of mass, species concentration, and energy for both the condensed phase and the gas phase, and it takes into account finite-rate chemical kinetics and real thermophysical properties. A kinetics scheme containing 35 species, two global ADN decomposition reactions in the condensed phase, and 166 reactions in the gas phase was used to describe the process. The ignition model was applied to predict ADN autoignition delay time (induction period) at various initial temperatures at 0.1 MPa. The agreement between calculation predictions and experimental results

was satisfying, which indicated that the model can predict the ADN ignition process accurately. The results showed that ADN ignition delay time decreased rapidly with an increase of initial temperature. An extension of this model was used to model the linear burning rate of ADN once it has ignited.

4.6.1 Fitting ADN Thermal Decomposition Rate Data to Kinetic Models

Comparative decomposition studies on KDN and HDN are helpful in investigating the key chemical processes involved with ADN decomposition. A widely used model-fitting method gave excellent fits to the experimental data for the thermal decomposition of ADN (ADN), but yielded highly uncertain values of the Arrhenius parameters when applied to non-isothermal data because temperature and extent of conversion are not independent variables [328]. Therefore, a comparison of model-fitting results from isothermal and non-isothermal experiments is practically meaningless. On the other hand, model-free isoconversional methods of kinetic analysis yield similar dependencies of the activation energy on the extent of conversion for isothermal and non-isothermal experiments. Analysis of synthetic data generated for a complex kinetic model suggests that, in the general case, the identical dependencies are unlikely to result from experiments obtained under isothermal and non-isothermal conditions.

The model-free and model-fitting kinetic approaches were applied to data for non-isothermal and isothermal thermal decompositions of HMX and ADN [329]. The popular model-fitting approach gave excellent fits for both isothermal and non-isothermal data but yielded highly uncertain values of the Arrhenius parameters when applied to non-isothermal data. These values could not be used to reasonably predict the isothermal kinetics, but the dependence derived from non-isothermal data enabled reliable predictions of the isothermal kinetics.

One of the intermediates in ADN decomposition in the gas phase may be nitroamine, which was already discussed as a potential intermediate in the production of ADN. The decomposition of nitroamine can be modeled using the same set of kinetic parameters as those that will be needed for modeling ADN decomposition [46].

4.6.2 Modeling the Thermal Decomposition Reactions of Solid Ammonium Dinitramide from Scratch (ab initio)

The initial step in the thermal decomposition of ADN was the subject of vigorous discussions during the decade following its discovery. The first decomposition step could be as follows:

- (a) conversion to AN and NO_2
- (b) sublimation to NH_3 and $\text{HN}(\text{NO}_2)_2$
- (c) dissociation of the dinitramide ion $\text{N}(\text{NO}_2)_2^-$ through the loss of either NO_2 or NO_2^-
- (d) conversion of the dinitramide ion to N_2O and NO

It is, of course, quite possible that two or more of these processes are occurring simultaneously. These initial steps are followed by some series of subsequent reactions, leading eventually to products that may include combinations of HNO_3 , N_2O , NO_2 , NH_3 , H_2O , NO , HNO_2 , N_2 , and more. Figure 56 illustrates the multitude of decomposition pathways and subsequent reactions in the decomposition of solid ADN.

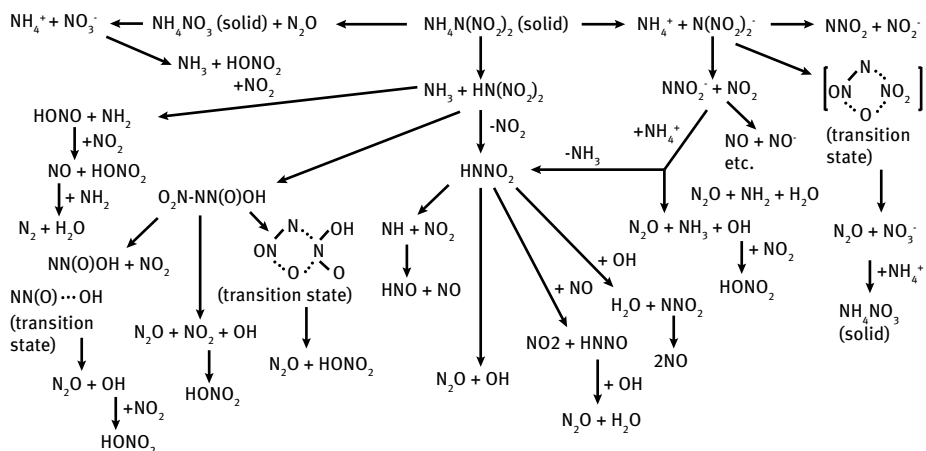


Figure 56: Possible pathways and subsequent reactions in the decomposition of solid ADN (Adapted from Politzer, Seminario, and Concha [330].)

In addition to using computational chemistry to model the thermal decomposition of ADN and other energetic materials, the same methods can also be used to model the actual combustion of ADN either by itself or in combination with a combustible fuel (Section 4.11.2.2).

With the advances of computational chemistry came the ability to calculate and predict not only the thermodynamic properties of energetic materials but also the paths taken by thermal decomposition reactions. Nitramide H_2NNO_2 , closely related to dinitramide, is an intermediate in the production and decomposition of ADN and its decomposition into amino radicals and nitrogen dioxide or water and nitrous oxide, and rearrangement has been modeled based on quantum chemical calculations (also for dimethylnitramide) [331].

Aside from the exothermic decomposition of hydrogen dinitramide (dinitramidic acid) to N_2O and HNO_3 , the gas-phase oxidation of NH_3 by NO_2 seems to be responsible for the exothermicity of the ADN decomposition. The kinetics and mechanisms of the $\text{NH}_3 + \text{NO}_x$ ($x = 1, 2$) reactions have been systematically studied by pulsed laser photolysis/mass spectrometry (PLP/MS) and pyrolysis/FTIR spectrometry (P/FTIRS) [332]. In the PLP/MS experiment, the total rate constants and product-branching ratios of the $\text{NH}_2 + \text{NO}_x$ ($x = 1, 2$) reactions were tested by measuring the time-resolved

concentrations of H_2O , N_2O , and NO_2 in the laser-initiated reaction of NH_3 with NO in the presence of varying amounts of NO_2 in the temperature range of 300–725 K. Agreement between the kinetically modeled and experimentally measured concentrations was quite satisfactory for the reactants and products. A remote hope is that once the $\text{NH}_3 + \text{NO}_x$ reactions are better understood, they might be tuned (high pressure?) and aimed at the synthesis of ADN in reversal of the decomposition reaction.

The structures, energetics, and decomposition mechanisms of gaseous ADN and ammonium nitrite (NH_4NO_2) have been studied theoretically by different *ab initio* molecular orbital (MO) approaches [333]. Ammonium nitrite, an unstable compound, was chosen because it has some structural similarity with ADN. In the gas phase, both species have the structures not of ionized salts but rather of molecular complexes $[\text{NH}_3] \bullet [\text{HX}]$, which are stable after vaporization. For NH_4NO_2 , $[\text{NH}_3] \bullet [\textit{trans}\text{-HONO}]$ is the most stable isomer. The $[\text{NH}_3] \bullet [\textit{cis}\text{-HONO}]$ and $[\text{NH}_3] \bullet [\text{HNO}_2]$ structures lie higher by 5.8 and 35 kJ/mol (1.4 and 8.4 kcal/mol). For the gaseous ADN, $[\text{NH}_3] \bullet [\text{HN}(\text{NO}_2)_2]$ is the most stable structure, while the $[\text{NH}_3] \bullet [\text{HON}(\text{O})\text{NNO}_2]$ isomer is 9.6 kJ/mol (2.3 kcal/mol) less favorable. The calculated dissociation energies of the $[\text{NH}_3] \bullet [\text{HX}]$ complex to NH_3 and HX are 33.5–37.7 and 50.2–58.6 kJ/mol (8–9 and 12–14 kcal/mol) for NH_4NO_2 and ADN, respectively. The energies for elimination of the NO_2 group from $\text{HN}(\text{NO}_2)_2$ and $\text{HON}(\text{O})\text{NNO}_2$ are found to be 159–167 kJ/mol (38–40 kcal/mol), while the barrier for $\text{HON}(\text{O})\text{NNO}_2$ dissociation is about 176 kJ/mol (42 kcal/mol). The following values of the heats of formation, $\Delta H_f^0(0)$, in the gas phase were predicted as follows: –148.5 kJ/mol (–35.5 kcal/mol) for $[\text{NH}_3] \bullet [\textit{trans}\text{-HONO}]$, +104 kJ/mol (+24.9 kcal/mol) for $\text{HN}(\text{NO}_2)_2$ and +13.4 kJ/mol (+3.2 kcal/mol) for $[\text{NH}_3] \bullet [\text{HN}(\text{NO}_2)_2]$. Based on these *ab initio* MO calculations, a realistic mechanism for the decomposition of ADN was proposed, which is fully consistent with the decomposition products measured by Brill, Brush, and Patil [334]. It was concluded that $[\text{NH}_4]^+ [\text{N}(\text{NO}_2)_2]^-$ is not a local energy minimum, and the ionic structure of ADN does not exist in the gas phase. Dinitramidic acid can exist in two isomeric forms:

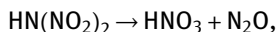


Accordingly, the energy levels of two different isomers of the ADN molecular complex were calculated, and the most favorable structure and two less favorable structures were drawn in 3D. $[\text{NH}_3] \bullet [\text{HN}(\text{NO}_2)_2]$ is the most stable structure in the gas phase at all the levels of calculation, while $[\text{NH}_3] \bullet [\text{HON}(\text{O})\text{NNO}_2]$ and the unstable $[\text{NH}_4]^+ [\text{N}(\text{NO}_2)_2]^-$ ionic structure lie higher by 9.6 and 50.6 kJ/mol (2.3 and 12.1 kcal/mol), respectively. The heat of formation of ADN in the gas phase was calculated to be +13.9 kJ/mol (+3.2 kcal/mol). In order to estimate $\Delta H_f^0(0)$ for ADN in the solid phase, one has to add the sublimation energy to this value. The theoretical research by Michels and Montgomery [209] and Politzer et al. [335] largely supported the case for dissociation of $\text{HON}(\text{O})\text{NNO}_2$ into N_2O and HNO_3 , while the results of Mebel et al. [333] tend to support the N– NO_2 bond cleavage of $\text{HN}(\text{NO}_2)_2$ forming NO_2

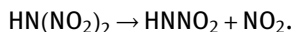
with no acid catalysis. All calculations predict that the ion-pair $[\text{NH}_4]^+[\text{N}(\text{NO}_2)_2]^-$ is not stable in the gas phase. A more stable configuration is the H-bonded acid-base pair $[\text{NH}_3][\text{HN}(\text{NO}_2)_2]$ similar to the isomeric $[\text{NH}_3] \bullet [\text{HON}(\text{O})\text{NNO}_2]$, which is only 9.6 kJ/mol (2.3 kcal/mol) less stable.

Proton transfer in gaseous ADN clusters up to $(\text{ADN})_2$ was studied using DFT [336]. A similar study had been conducted a year earlier on AN clusters [337]. Proton transfer between the hydrogen dinitramide and ammonia units does not occur in the ADN monomer. Instead, the ammonia-hydrogen dinitramide complex is stabilized by strong hydrogen bonding. However, proton transfer between hydrogen dinitramide and ammonia is predicted in the following three clusters: ADN dimer $[\text{NH}_3\text{HN}(\text{NO}_2)_2]_2$, ADN solvated with a single ammonia molecule $\text{NH}_3 \bullet [\text{NH}_3\text{HN}(\text{NO}_2)_2]$, and ADN solvated with a hydrogen dinitramide molecule $[\text{NH}_3\text{HN}(\text{NO}_2)_2]_2 \bullet [\text{HN}(\text{NO}_2)_2]$. The binding energies of the clusters and total electrostatic interaction energy in each cluster were calculated using population analysis. The electrostatic energy is a measure that distinguishes between the ionic or hydrogen-bonded nature of the clusters. Proton transfer in ADN clusters can have a significant influence on the decomposition mechanism of ADN and its parent acid, HDN, as shown in a subsequent paper by the same authors:

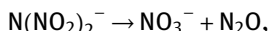
According to those calculations [338], gas-phase dinitramidic acid (HDN) decomposes along two pathways, one involving a molecular rearrangement,



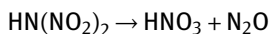
and a second initiated by N—N bond fission,



A molecular rearrangement pathway for the gas phase dinitramide ion,



can also occur. The reaction rates and pathways for the decomposition of HDN and the corresponding dinitramide ion were calculated using DFT calculations. The energy levels of the geometries, vibrational frequencies, and zero-point energies of the reactants, products, and transition states involved in the gas-phase decomposition of $\text{HN}(\text{NO}_2)_2$ were calculated. The lowest energy pathway for N_2O formation initially involves an internal proton transfer in the HDN molecule. The system then passes through a four-center transition state that has a protonated bridge oxygen atom. The energy of this geometry is 147.3 kJ/mol (35.2 kcal/mol) higher than the reactant from which it is formed. This path had not been previously identified. The rates of N_2O elimination were calculated, and the rates of HDN and $\text{N}(\text{NO}_2)_2^-$ decomposition were compared with each other and with the rate of N—N bond fission in dinitraminic acid. The reaction



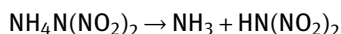
could not proceed by a simple bond cleavage. It needs to undergo a four-member molecular rearrangement ($\text{O}_2\{\text{NONN}\}\text{O}$) or proceed through other transition states.

Non-local DFT is an effective means for determining the energetics and mechanisms of decomposition processes of energetic materials such as ADN, nitramine, and substituted nitramines of real chemical interest and practical significance [335, 339]. It can be viewed as a tool that is available as a useful supplement to existing experimental techniques but with the additional advantage that it can be applied to hypothetical, envisioned molecules that may not yet have been synthesized. A non-local density functional procedure (DF/GGA/DZVPP) was used to compute the structure of the dinitramide anion $\text{N}(\text{NO}_2)_2^-$ and the energetics of some possible decomposition paths. The NO_2 groups can be rotated out of the N—N—N plane, with a considerable difference between the two N—N—O angles of each NO_2 group. Of three possible N—N bond-breaking reactions, the least energy is required to yield NNO_2^- and NO_2 ($208 \text{ kJ/mol} = 49.8 \text{ kcal/mol}$). It is possible that NNO_2^- and NO_2 form a loosely knit complex. Nitramine $\text{H}_2\text{N}-\text{NO}_2$ is an intermediate in the formation as well as the decomposition of ADN. Gaussian-2 (G2) and non-local DFT (DFT-GGA) were used to calculate the energy requirements for (1) $\text{H}_2\text{N}-\text{NO}_2$ dissociation (through N—N bond scission), (2) inversion of the amine group, and (3) isomerization through the nitro–nitrite rearrangement [340].

The structures, zero-point energies at 0 K, and enthalpies at 298 K of 37 gaseous molecules, fragments, free radicals, ions, and transition states that have been implicated as intermediates and products in the thermal decomposition of ADN have been computed using a density functional procedure DF/B3P86/6-31 + G** [330]. $\Delta H(0 \rightarrow 298)$ is the enthalpy change in going from 0 to 298 K; it includes the zero-point contribution. These data permit the calculation of ΔH_{298} for a large number of possible decomposition steps. The lattice enthalpy of ADN is $\Delta H_{298} = 602 \text{ kJ/mol} = 144 \text{ kcal/mol}$. This seems quite reasonable when compared to literature values for other ammonium salts, e.g., NH_4NO_3 , 163 kcal/mol , and NH_4ClO_4 , 140 kcal/mol . The heat of sublimation of ADN with proton transfer to molecular $\text{NH}_3^+\text{HN}(\text{NO}_2)_2$ is $\Delta H_{298} = 184 \text{ kJ/mol} = 44 \text{ kcal/mol}$, and the gas-phase heat of formation of $\text{HN}(\text{NO}_2)_2$ is $\Delta H_{298}^f = 79.5 \text{ kJ/mol} = 19 \text{ kcal/mol}$. The decomposition rate of $\text{HN}(\text{NO}_2)_2$ is 10^7 – 10^8 times higher than that of $\text{N}(\text{NO}_2)_2^-$ for $t = 273$ – 373 K (0 – 100°C) since the anion $\text{N}(\text{NO}_2)_2^-$ has a higher activation energy than $\text{HN}(\text{NO}_2)_2$. Further, the protonated $\text{H}_2\text{N}(\text{NO}_2)_2^+$ has a more rapid decomposition rate than $\text{HN}(\text{NO}_2)_2$. The poor stability of $\text{HN}(\text{NO}_2)_2$ may be attributed to a weaker N—N bond in $\text{HN}(\text{NO}_2)_2$ as compared with $\text{N}(\text{NO}_2)_2^-$. The N—N bond in $\text{N}(\text{NO}_2)_2^-$ has a bond order between the double ($\text{N}=\text{N}$) and single ($\text{N}-\text{N}$) bonds, whereas N—N in $\text{HN}(\text{NO}_2)_2$ and in protonated $\text{HN}(\text{NO}_2)_2^+$ has a bond order closer to a single N—N bond.

Molecular dynamics simulations are useful for predicting the thermal stability of energetic compounds as well as their sensitivity toward other stimuli [341]. This can provide a better understanding of how factors related to the crystal lattice, e.g., defects, influence the initiation and propagation of detonation.

Earlier experiments revealed two important channels of ADN decomposition: The first one is associated with the formation of AN in the melted ADN layer, and the second one is based on ADN sublimation (evaporation) at low pressures. In order to clarify the kinetic mechanism proposed previously for the description of the structure and reactant concentration profiles of ADN flames, the chemical processes in thermal decomposition products and ADN flame with a pressure of 10 mm Hg and 3–40 atm were modeled numerically [342]. Results of numerical simulation of pyrolysis of undissociated ADN sublimation products in a flow reactor in a temperature range of 373–920 K for a pressure of 10 mm Hg were compared with a numerical simulation of NH_3 reaction with $\text{HN}(\text{NO}_2)_2$ under conditions of high temperatures and low pressures. The reasons for significant differences in results calculated with the use of one-dimensional models were not quite understood. Adaptation of one-dimensional numerical algorithms to fast processes and qualitative estimation of the contribution of the heating zone to chemical processes may lead to a better understanding of the decomposition process. Based on a comparison of numerical and experimental data, the contributions of individual stages and components to the pyrolysis process and the values of rate constants were estimated. It was concluded that the ADN sublimation process follows the dissociative mechanism

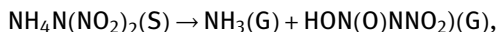


followed by reaction of NH_3 with $\text{HN}(\text{NO}_2)_2$ in the gas phase. The Ermolin 2004 paper [342] contains a long list of 218 (!) individual, fundamental reactions that may contribute to the $\text{HN}(\text{NO}_2)_2/\text{NH}_3$ reactions, complete with pre-exponential factor, activation energy, and literature source. This very complete list is also useful for any other kinetic studies involving only oxygen, nitrogen, and hydrogen in the absence of any carbon species.

In order to get a more detailed molecular insight and to correlate the experimental data with bond-dissociation processes, quantum mechanical calculations were performed with the DMol³ program from Biovia (previously named Accelrys) to get bond-dissociation energies and bond-dissociation enthalpies for possible involved bonds in ADN [343].

The mechanism for sublimation of ADN has been investigated quantum-mechanically with generalized gradient approximation plane-wave DFT calculations [197]. The solid surface was represented by a slab model, and periodic boundary conditions were applied. The calculated lattice constants for the bulk ADN, which were found to consist of $\text{NH}_4^+[\text{ON}(\text{O})\text{NNO}_2]^-$ units instead of $\text{NH}_4^+[\text{N}(\text{NO}_2)_2]^-$, agreed quite well with experimental values. Results showed that three steps were involved in the sublimation/decomposition of ADN. The first step was the relaxation of the surface layer with 6.7 kJ/mol (1.6 kcal/mol) energy per $\text{NH}_4\text{ON}(\text{O})\text{NNO}_2$ unit, and the second step was the sublimation of the surface layer to form a molecular $[\text{NH}_3]^+[\text{HON}(\text{O})\text{NNO}_2]^-$ complex with a 123 kJ/mol (29.4 kcal/mol) sublimation energy, consistent with the experimental observation of Korobeinichev et al. The last step was the dissociation of

the $[\text{NH}_3]^- [\text{HON}(\text{O})\text{NNO}_2]$ complex to give NH_3 and $\text{HON}(\text{O})\text{NNO}_2$ with a dissociation energy of 58 kJ/mol (13.9 kcal/mol). Direct formation of $\text{NO}_2(\text{G})$ from solid ADN would require a higher energy, 244 kJ/mol (58.3 kcal/mol). The calculated total sublimation enthalpy for



188 kJ/mol (44.9 kcal/mol) via three steps, was in good agreement with the value of 176 kJ/mol (42.1 kcal/mol) predicted for the one-step sublimation process in this work and the value of 184 kJ/mol (44.0 kcal/mol) computed by Politzer et al. using experimental thermochemical data. The sublimation rate constant for the rate-controlling step 2 could be represented as

$$k_2 = 2.18 \times 10^{12} \exp\left(-30.5 \frac{\text{kcal/mol}}{RT}\right) \text{s}^{-1},$$

which agreed well with available experimental data within the temperature range studied. For other quantum mechanical and *ab initio* treatments of ADN decomposition, see also [230, 344].

Ionization and decomposition pathways of ionized ADN have been analyzed using DFT methods, coupled cluster theory, and the composite complete basis set CBS-QB3 method [345]. The $\text{NH}_4\text{N}(\text{NO}_2)_2^+$ ion dissociates into the stable dinitramide radical and NH_4^+ with a dissociation enthalpy of 50 kJ/mol. The subsequently formed $\text{N}^+(\text{NO}_2)_2$ ion has an activation enthalpy of 102 kJ/mol for decomposition into N_2O , O_2 , and NO^+ . A competing pathway for ionization and decomposition of ADN involves the $\text{HN}^+(\text{NO}_2)_2$ ion, which dissociates into NO_2^+ and HNNNO_2 with a barrier of only 17 kJ/mol. The ionization product HN^+NO_2 is stable toward further decomposition, and the barrier for isomerization to HONNO^+ is 167 kJ/mol. The computed adiabatic ionization potentials of ADN, $\text{HN}(\text{NO}_2)_2$, $\text{N}^-(\text{NO}_2)_2$, and HNNNO_2 are 9.4, 11.5, 10.2, and 10.9 eV, respectively.

The effect of solvents on the decomposition of ADN was analyzed theoretically, including a path for decomposition of different proton transfer isomers via dinitramidic acid (HDN), $(\text{HDN})_2$, and $(\text{ADN})_2$ clusters and the effects of an intramolecular and intermolecular double proton transfer process on the decomposition reactions of different isomers [346]. The effect of trace water in $(\text{H}_2\text{O})_n \cdot \text{NH}_4^+ [\text{N}(\text{NO}_2)_2]^-$ ($n = 1, 2, 3$) and $(\text{ADN})_2$ clusters on the abnormal decomposition behavior of ADN was discussed. The kinetic parameters obtained in the larger $(\text{ADN})_n$ clusters agreed with some experimental results. The study showed that the introduction of the QM-MM method, which was suitable for the larger $(\text{ADN})_n$ clusters and solvation model in the liquid phase and gas phase, enabled prediction of relevant thermodynamic and kinetic parameters of ADN decomposition.

A detailed chemical kinetics model for the liquid-phase reactions of ADN based on quantum chemical calculations was used to calculate the thermal corrections, entropies, and heat capacities of chemical species from the partition function using sta-

tistical thermodynamic methods [347]. Rate coefficients were determined to allow the application of transition state theory and variational transition state theory to reactions identified in previous studies. The new model simulated the thermal decomposition of ADN under specific heating conditions and successfully predicted heats of reaction and the gases that resulted from decomposition under those conditions. The thermal behavior predicted from this model was an excellent match with the experimental behavior observed from thermal analysis using DSC and Raman spectroscopy.

Results from an overall decomposition mechanism computation of ADN in the gas phase via DFT calculations were compared with experimental TGA-FTIR and TGA-MS results [348]. In the thermal decomposition of gaseous ADN [ADN(G)], ADN(G) first decomposed into dinitraminic acid $[\text{HN}(\text{NO}_2)_2]$ and NH_3 , followed by $[\text{HN}(\text{NO}_2)_2]$ decomposition into other products with smaller molecules. $[\text{HN}(\text{NO}_2)_2]$ was found to isomerize into five isomers in the gas phase. For the initial decomposition of $[\text{HN}(\text{NO}_2)_2]$, the favorable decomposition pathway via a structure of $\text{HON}(\text{O})\text{NNO}_2$ was more likely to form HNO_3 and N_2O with a large release of energy (approximately 188 kJ/mol [45 kcal/mol]). HNO_3 and NH_3 can first combine to form NH_4NO_3 , which is relatively stable but will decompose in subsequent steps. Both calculated and experimental results indicated that the product N_2O is first formed in the thermal decomposition of ADN(G). Other products are NH_3 , H_2O , NO , NO_2 , HONO , and HNO_3 .

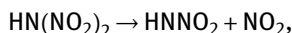
4.7 Thermal Decomposition of Vapor-Phase Ammonium Dinitramide

Because ADN may sublime and exist in the vapor phase in the form of molecular additives, the discussion of experimental studies of the decomposition process in this book has been separated into condensed-phase decomposition studies and vapor-phase decomposition studies. This is in addition to the computational chemistry studies summarized in the previous section. Reactions of decomposition products of ADN in the gas phase are very similar to NO_x/NH_3 reactions such as those that take place in the DeNO_x process for stack gas decontamination to reduce air pollution from power plants. There are numerous publications on this subject, but they are not included in our review of the ADN decomposition reactions in the gas phase. The same reactions also limit the yield of dinitramide during the reaction of dinitrogen pentoxide or other nitryl salts with ammonia during ADN production.

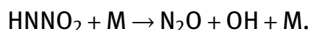
Mass spectrometric analysis of ADN decomposition products at low pressure showed the appearance of the NH_3 peak much earlier than decomposition experiments at atmospheric pressure [349]. ADN pyrolysis is dominated by decomposition into NH_3 and $\text{HN}(\text{NO}_2)_2$ (hydrogen dinitramide, HDN) in analogy to NH_4NO_3 , with a maximum rate of decomposition under these conditions at approximately 428 K (155 °C). The two vapor-phase components regenerated ADN on cold cryostat surfaces in addition to deposition of the pure acid HDN and H_2O . Condensed phase HDN was found to be stable for indefinite periods of time at ambient temperature and

vacuum conditions, whereas fast heterogeneous decomposition of HDN at higher temperature led to N_2O and HNO_3 . The HNO_3 then underwent fast (heterogeneous) decomposition. Gas-phase HDN also underwent fast heterogeneous decomposition to NO and other products, probably on the internal surface (about 333 K [60 °C]) of the vacuum chamber before mass spectrometric detection. Other nitramines studied under similar conditions and compared to ADN decomposition products were NH_4NO_3 , NH_2NO_2 , RDX, and $\text{AgN}(\text{NO}_2)\text{CH}_2\text{CN}$ [350].

The thermal decomposition of ADN in the gas phase has been studied at 373–920 K by pyrolysis/mass spectrometry under low-pressure (10-mm-Hg) conditions [351]. The reaction of the sublimed mixture of NH_3 and $\text{HN}(\text{NO}_2)_2$ (hydrogen dinitramide, dinitraminic acid) was found to be initiated by the unimolecular decomposition of dinitraminic acid,



followed by the rapid decomposition reaction



The measured absolute yields of NH_3 , H_2O , N_2 , and N_2O could be satisfactorily modeled by employing the theoretically computed values of

$$k_2 = 6.79 \times 10^{48} T^{-11.0} \exp(-21780/T) \text{ s}^{-1}$$

and

$$k_3 = 7.53 \times 10^{24} T^{-2.9} \exp(-12958/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

by high-level *ab initio* molecular orbital and canonical variational calculations. It was concluded that ADN is unstable in its ionic form, $\text{NH}_4^+\text{N}(\text{NO}_2)_2^-$, and its sublimation leads to the formation of two molecular complexes, $\text{H}_3\text{N} \bullet \text{HN}(\text{NO}_2)_2$ and $\text{H}_3\text{N} \bullet \text{HON}(\text{O})\text{NNO}_2$, which are more stable than the dissociated states, $\text{NH}_3 + \text{HN}(\text{NO}_2)_2$ and $\text{NH}_3 + \text{HON}(\text{O})\text{NNO}_2$, by 51.9 and 59.0 kJ/mol (12.4 and 14.1 kcal/mol), respectively. The yields of N_2 , N_2O , H_2O , and NH_3 measured in the thermal decomposition of ADN could be satisfactorily accounted for with a mechanism consisting of 152 reactions, assuming that initial concentrations of NH_3 are approximately equal to that of $\text{HN}(\text{NO}_2)_2$.

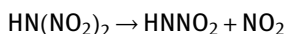
In another study [352] of ADN thermal decomposition by TOF-MS at pressures of about 0.000001 Hg, 100 mm Hg, and 1 atmosphere within a temperature range of 373–573 K (100–300 °C) at isothermic and non-isothermic conditions, the rate of reaction was expressed as

$$W = \frac{d\alpha}{dt} = 3.5 \times 10^{15} [\exp(-32000/RT)](1 - \alpha) \text{ s}^{-1}.$$

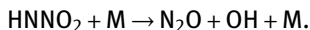
Peaks were observed at $m/e = 17$ (NH_3^+ , OH^+), 18 (H_2O^+), 28 (N_2^+), 30 (NO^+), 46 (NO_2^+), and 63 (HNO_3^+). The data indicated that mass spectra of ADN decomposition

products at 1 atm or 100 mm Hg differ significantly from mass spectra of ADN decomposition products in vacuum, especially at the m/e ratio 146/117, which is 1.5–1.7 in the first case, while in vacuum it is in the range of 0.06–0.16. For comparison, thermal decomposition of AN was measured in the same apparatus at 10^{-6} mm Hg. In this case, the reaction products were ammonia and nitric acid. The rate of ADN decomposition increased with decreasing pressure, and the HNO_3 mol fraction in the decomposition products decreased. One reason is that the process of ADN dissociative sublimation into NH_3 and HDN followed by decomposition of the latter to give N_2O , NO , and H_2O becomes dominant with decreasing pressure. During a test at 10^{-3} atm, 90% of the ADN sublimed and deposited on the cold wall of the tube. See also [353–355]. Temperature profiles through the flame front of burning ADN/HTPB propellant with 3% binder indicated that the dark zone contains ADN decomposition products [356, 357].

The thermal decomposition of ADN in the gas phase has been studied at 373–920 K by pyrolysis/mass spectrometry under low-pressure conditions using a Saalfeld reactor [344, 358]. The reaction of the sublimed mixture of NH_3 and $\text{HN}(\text{NO}_2)_2$ was found to be initiated by the unimolecular decomposition of dinitraminic acid:



followed by the rapid decomposition reaction



The measured absolute yields of NH_3 , H_2O , N_2 , and N_2O , calibrated with standard mixtures, at 10 mm Hg He carrier gas pressure could be quantitatively modeled by employing the theoretically calculated values of

$$K_2 = 5.0 \times 10^{15} \exp(-17620/T) \text{ s}^{-1}$$

and

$$K_3 = 7.53 \times 10^{24} T^{-2.9} \exp(-16600/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

A mechanism involving 152 reactions with recommended rate constants is presented that can be programmed into a program such as CHEMKIN.

The vapor pressure at temperatures of 353–413 K (80–140 °C), the heat of vaporization, and the thermal decomposition of ADN were studied using a two-temperature flow reactor [359]. ADN vapors were formed in the first stage of a flow reactor at 353–413 K (80–140 °C) and ducted into the second stage, where they would either condense or decompose, depending on the temperature in the second stage. Based on these results, a mechanism for the thermal decomposition of ADN was proposed that included the ADN vaporization stage, i.e., the transition from the condensed to the gaseous state in the form of a molecular complex $\text{NH}_3 \cdot \text{HN}(\text{NO}_2)_2$, followed by dissociation into NH_3 and $\text{HN}(\text{NO}_2)_2$. The composition of the products from the thermal decomposition of ADN vapor at temperatures of 433–1173 K (160–900 °C) was determined by molec-

ular beam mass spectrometry, but no HNO_3 was observed at $m/e = 63$. The effective rate constant for the dissociation of ADN vapor was determined by repeating the experiments at different temperatures from 433 to 593 K (160 to 320 °C). After completion of the experiments, the overall thermal decomposition of ADN vapor in a flow reactor was modeled theoretically using the proposed mechanism and the reaction rate constant for ADN vapor dissociation, and the agreement between experimental and theoretical results was satisfactory. See also [360].

4.8 Rapid Heating Thermal Decomposition and Flash Pyrolysis of ADN with Analysis of Intermediate Products

The mechanisms of ADN decomposition can be identified by analyzing the off-gassing during rapid thermolysis (pyrolysis) of ADN crystals. Depending on the rate of heat application, the surface of the crystals may decompose before it has a chance to melt. The methods for analysis must have a short response time such that a time-resolved sequence of the various intermediate species and reaction products as well as their momentary concentrations can be obtained. The rapid-response methods of analysis used most often are FTIR (T-Jump FTIR) and TOF-MS. The methods of rapid heating consist of either placing a thin film of the sample on a resistance-heated platinum ribbon or zapping the sample with a laser.

4.8.1 Mass Spectrometric Analysis of Intermediate Products During Rapid Decomposition

Mass spectrometry is useful for analyzing ADN decomposition products during slow, low-temperature decomposition as well as during rapid, high-temperature decomposition. There are several methods to flash-pyrolyze ADN and other energetic materials in order to analyze the decomposition products by MS or other fast-analysis methods. The resistance-heated hot metal foil method has been described elsewhere. Another fast method is laser flash pyrolysis, in which the amount and the intensity of energy delivered to the surface can be accurately dosed.

The results of CO_2 laser-induced deflagration of ADN were presented as a function of pressure (0.1–3.0 atm of argon) and incident laser heat flux (20–300 W/cm^2) [361]. Spatial and temporal profiles of gaseous species concentrations were obtained by microprobe sampling and MS analysis. Both gas-phase temperature profiles and surface temperatures were measured with fine-wire thermocouples. Visual observations of the laser heating event recorded with a high-magnification fast video recording system allowed a direct view of the process and revealed a surface melt layer with tiny gas bubbles that was evident at pressures of 1 atm or lower. A luminous flame was observed only when the pressure was raised to greater than 3 atm, where a quasi-stable flame could be established. A significant number of fine pale-white particles, believed to be

the higher-melting AN, evolved from the melt layer when no flame existed, but they were not observed once a flame was established. Other models have included the modeling of aerosol particles. Gas-phase processes for RDX and ADN were modeled with CHEMKIN as a one-dimensional, premixed flame. A kinetic mechanism consisting of 21 species and 110 reactions was compiled to model the deflagration of ADN. Additional work included the study of RDX, XM39, and M43 [362, 363]. The microprobe mass spectrometer (MP-MS) system was used to study the gas-phase chemical reactions occurring above solid propellant ingredients and actual solid propellants when they are heated and/or ignited by the heat flux from a CO₂ laser.

Using a tandem-flowing, afterglow-selected-ion flow tube, the basicity, reactivity, electron-binding energy, and collision-induced dissociation of dinitramide ion $[\text{N}(\text{NO}_2)_2]^-$ and nitroacetylide ion $[\text{O}_2\text{NC}\equiv\text{C}]^-$ were investigated [255]. Dinitraminic acid is among the strongest known gas-phase acids with $\Delta H^\circ_{\text{acid}} < 1297 \text{ kJ/mol}$ ($< 310 \text{ kcal/mol}$). The conjugate base, dinitramide anion, has a high electron-binding energy, is extremely unreactive, and is a very poor nucleophile. Collision-induced dissociation of dinitramide anion generated the $\text{O}_2\text{N}=\text{N}^-$ anion.

In laser-pyrolysis experiments under argon at 10–505 kPa (0.1–5 atm) with flux densities of 20–300 W/cm², the microprobe MS indicated only 1–1.5% or barely detectable NH₃ [363]. Three distinct regions of laser-induced decomposition were observed: **(1)** laser-induced pyrolysis (LIP), **(2)** laser-induced regression (LIR), and **(3)** laser-assisted combustion (LAC). LIP was observed at subatmospheric pressures and low heat fluxes ($< 50 \text{ W/cm}^2$). At or above atmospheric pressure and with higher heat fluxes, LIR (i.e., regression without a flame) could be observed. LAC required pressures of at least 303 kPa (3 atm) and heat fluxes of at least 100 W/cm². True ignition and self-sustained burning were not observed for any of the experiments. Of the three distinct categories of laser-induced behavior (LIP, LIR, LAC), the latter two categories were characterized by stable regression of the surface but with a luminous flame observed only for LAC. Under LIR conditions, ADN evolved N₂O, H₂O, N₂, NO₂, and NH₃ (in order of decreasing mol fraction) and numerous particles of AN. LAC was observed for ADN at 3 atm with an unstable flame, whereas tests at 5 atm produced a more stable flame with individual flamelets just above the surface. The flame produced significant amounts of NO and H₂O and a gas temperature of about 1350 K. During LIP, and before the onset of rapid pyrolysis, ADN bubbled vigorously, and primarily N₂O and H₂O and no other species were detected in the gas phase. After the onset of rapid pyrolysis, a fair amount of NO₂ and NH₃ along with small amounts of N₂ and NO were detected. At high pyrolysis rates, AN particles were thrown into the vapor space. The pyrolysis regression rate was relatively insensitive to incident heat flux. In addition to the MPMS system, direct and Schlieren photography were used to study the flame structure, and 25- μm thermocouples were used to measure the gas-phase temperature profile [364].

The thermal decomposition of ADN has been studied by thermal gravimetry combined with mass spectrometry (TG-MS) and by infrared spectroscopy [295]. Arrhenius parameters obtained from TG data by an isoconversional method are $E_a = 200 \pm 20 \text{ kJ/mol}$ and $A = 10^{21} \text{ s}^{-1}$. ADN decomposes entirely to gaseous products that have been identified by MS as NH_3 , H_2O , NO , N_2O , NO_2 , HONO , and HNO_3 . The infrared experiments showed that the primary decomposition products are N_2O and NO_2 . No evidence was found for the participation of dinitraminic acid as an intermediate in the reaction mechanism. Instead, a mechanism involving ionic reactions in the liquid phase is proposed. The fact that the same initial products have been observed over a wide range of temperatures (333–673 K [60–400 °C]) and heating rates (10^{-2} – 10^7 °C/s) suggests that this mechanism can be used to model the initial stages of combustion of ADN.

Vyazovkin and Wight [170, 296], in the range $T = 298$ – 523 K [25–250 °C] at a heating rate of 5 °C/min, found that NH_3 appeared only above 100 °C, much later than NO_2 and N_2O . NH_3 was not detected until 453 K [180 °C] in the TGA/FTIR analysis at a heating rate of 5 °C/min [293]. NH_3 and dinitramidic acid were possibly being absorbed in the condensed phase at low temperatures.

Probing mass spectrometry (PMS) is a very useful method based on microprobe and molecular-beam MS probing for the study of solid propellant flame structures at high (10 atm) and low (≤ 1 atm) pressures; it has been applied to the study of AP and ADN decomposition flames [365]. This apparatus allows the study of thermal decomposition of ADN or other oxidizers at high heating rates up to 100 °C/s under conditions approximately similar to those present in the condensed phase in the vicinity of the burning surface in a rocket motor. In this apparatus, a strand of burning material (propellant, pressed ADN pellet) is moving toward a stationary probe at a rate greater than the regression rate, and the probe measures a profile through the flame and dark zone. The ADN grains decomposed without flames at 101 and 303 kPa (1 and 3 atm, respectively) and with a flame at 606 kPa (6 atm). The regression rates were 3.4 mm/s at 1 atm, 12 mm/s at 3 atm, and 19 mm/s at 6 atm. Profiles of the species concentrations in ADN flames helped in identifying main reactions in high temperature zones of ADN decomposition at 1, 3, and 6 atm. In addition to flame studies, the non-deflagrating, non-flame thermal decomposition of ADN was investigated by molecular-beam MS on a sample that was heated rapidly from 433 K (160 °C) to 573 K (300 °C) with heating rates of 20 °C/s, giving a time-resolved profile of the products of ADN thermal decomposition and product release rates. A peak at $m/e = 72$ has not yet been identified and was tentatively assigned to nitramide H_2NNO_2 . There were no peaks at 106, 107, or 124, where one would expect the nitramide molecular ion or ADN clusters.

The structure of ADN combustion zones at 1–6 atm was studied using molecular-beam MS as well as a microthermocouple technique [355]. Three combustion zones were observed, and gaseous ADN was discovered in the first cool flame zone at 3 atm. Gaseous ADN dissociation to NH_3 and dinitraminic acid followed by dinitraminic acid

decomposition in the near-surface zone were key reactions, resulting in a temperature rise of about 150 K. The second high-temperature zone was found within 6–8 mm from the ADN burning surface at 6 atm. The main reaction in this zone was ammonia oxidation by nitric acid, and the combustion temperature was 1400 K. The third zone was observed at 40 atm, where the measured final temperature was ~2000 K. Based on these data, a chemical mechanism of reactions in both the ADN flame and combustion was proposed.

Mass spectrometric analysis of evolved gases during the decomposition of ADN revealed the formation of ions having a mass to charge m/e ratio of 17, 30, 44, and 46 amu [58]. Since ADN contains only nitrogen, oxygen, and hydrogen, the ions formed in the isothermal decomposition were identified as NH_3 , NO, N_2O , and NO_2 . The analysis of complete mass spectra showed that no other reaction products were observed. The other possible products looked for in the mass spectrometry included H_2O , HNO_3 , and HONO in the range of 10–250 amu, but none of those were observed. Figure 57 gives the TGA curve as well as the ion signal strength for the species detected, namely NH_3 (amu 17), NO (amu 30), N_2O (amu 44), and NO_2 (amu 46). The superimposed TGA trace of ADN shows that the majority of ADN decomposition takes place in the range of 413–493 K (140–220 °C). The

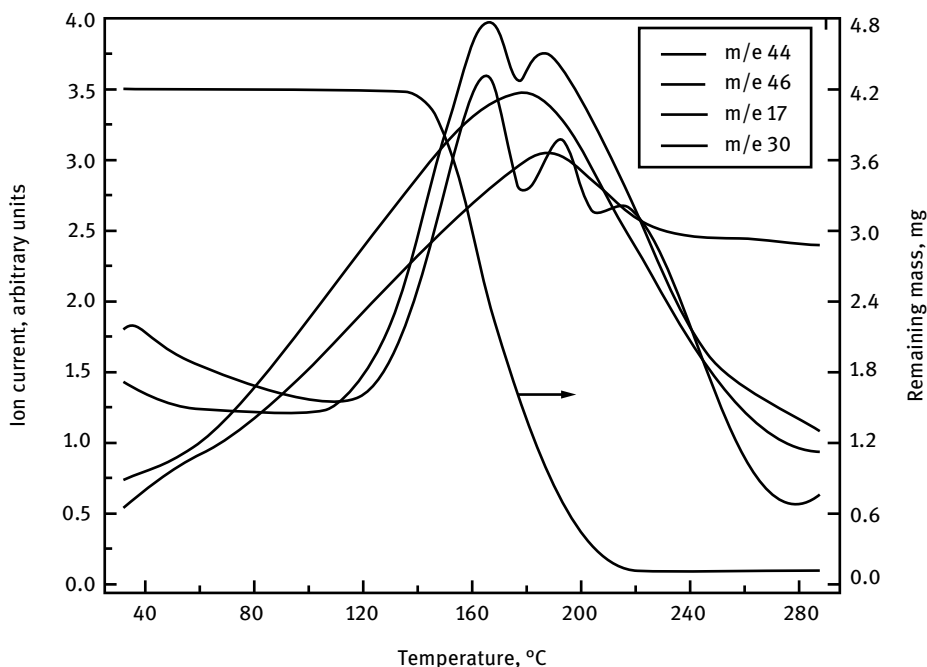


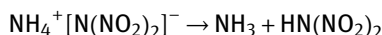
Figure 57: Mass spectrometric and thermogravimetric analysis of ADN decomposition products at a heating rate of 5 °C/min. (Reprinted and modified from [58] with permission granted by Dr. Santhosh 8 February 2021.)

mass spectral data show that the predominant species in the initial stage of ADN decomposition are N_2O and NO_2 , while those in the latter stage are NH_3 and NO . This is inconsistent with the thermal decomposition mechanism for ADN by Vyazovkin et al. [170].

4.8.2 Infrared Spectrophotometric Analysis of Intermediate Products

Mass spectrometry and IR spectrophotometry are the two primary fast-response methods used to analyze transient phenomena occurring on the surface of decomposing energetic materials. These methods can be applied to oxidizers by themselves, to formulated solid propellants, or to slabs of oxidizer sandwiched between two layers of fuel binder. The methods for rapid heating in either case can be a laser pyrolysis or the thin-film sample heating on a rapidly heated metal ribbon (T-jump/FTIR spectroscopy). The rapid pyrolysis chemistry of thin films of AN and ADN at temperatures approximating a burning surface was studied using T-jump/FTIR spectroscopy [334]. It is very valuable to study these two oxidizers next to each other using the same equipment because AN is one of the intermediate decomposition products of ADN. The sequence of appearance and amounts of each gas product combined with the net endothermicity and exothermicity of the process at each time gave the necessary information to develop multi-step reaction schemes. The decomposition of the condensed phase of AN is net endothermic up to at least 33 atm. Although dissociative sublimation and the formation of N_2O and H_2O dominate the overall process, the superposition of two additional reactions is needed to account for all of the products observed from AN. ADN becomes highly exothermic very early in the decomposition process. The superposition of two overlapping stoichiometric reaction branches explains this behavior. The spectra and thermal responses are consistent with the assumption that the reaction of NH_3 with NO_2 is the major source of heat released during the decomposition of AN above 33 atm and ADN at 1 atm and higher.

The decomposition mechanism



suggests that NH_3 evolution should occur early, but the experimental measurements have shown inconsistent results. When ADN was heated to 260 °C at a rate of 2000 °C/s on a platinum filament, FTIR detected NH_3 , N_2O , and HNO_3 in similar amounts in the initial spectra; then, the amounts of N_2O and NO_2 increased, and the amounts of NH_3 and HNO_3 decreased sharply [334].

Because HNO_3 may react with the inlet materials on a mass spectrometer and attach itself to the walls, MS is not the best method for detecting HNO_3 . FTIR seems to be more effective in detecting HNO_3 . Vyazovkin and Wight [170, 296] found that at $T = 50^\circ\text{C}$, HNO_3 evolved almost simultaneously with NO_2 , and its concentration increased.

4.9 Thermal Stability and Decomposition Reactions of Ammonium Dinitramide Solutions

The thermal stability of ADN solutions intended to be used as a liquid oxidizer was studied by microcalorimetry [366]. Additional heat evolution rate measurements were made with solid and liquid ADN mixtures containing Al powder, with and without addition of stabilizers [367], and with gelled ADN solutions [368]. Fumed silica is commonly used as a gelling agent for liquid oxidizers, but it may adversely affect the thermal stability of ADN solutions [369]. Several silica types have been investigated with regard to their compatibility with ADN: hydrophilic and hydrophobic silica, hydrophilic mixed oxide (SiO_2 and Al_2O_3), and very fine particle precipitated silica. Silica adsorption columns are used for separation of dinitramides from the mixture of reactants and by-products from which ADN is made.

4.9.1 Catalytic Decomposition of Ammonium Dinitramide Solutions

Although it is well known that dinitramides are energetic compounds, the thermal and catalytic decompositions of aqueous dinitramide solutions have not yet been studied extensively. In a study of the thermal and the catalytic decomposition of ionic oxidizers in aqueous solution such as ADN, HAN, AN, and HNF, the decomposition was followed by DTA-TGA, constant volume batch reactor and dynamic flow reactor coupled with a mass spectrometer [370]. The gaseous products were analyzed by mass spectrometry, whereas the condensed products were analyzed by Raman spectroscopy and acid-base titration to establish a balanced equation of the thermal or catalytic decomposition of these oxidizers. A 10% Pt/ Al_2O_3 / SiO_2 catalyst initially developed for HAN-water decomposition achieved only a low catalytic activity toward ADN-water mixtures. Other monometallic and bimetallic catalysts based on Pt, Fe, Cu, and Zn were prepared and tested to decompose these mixtures.

Binary HAN and ADN aqueous solutions have been decomposed thermally and catalytically [371]. Binary ADN/ H_2O mixtures were prepared with different concentrations: 75, 60, and 50 mass-% ADN. The catalysts were prepared by impregnation of alumina/lanthanum oxide with $\text{Cu}(\text{NO}_3)_2$, followed by calcination and characterized by transmission electron microscopy with a resolution of 3.5 Å, XRD, and hydrogen chemisorption. The decomposition processes were followed by DTA in a constant-volume batch reactor. In the constant-volume batch reactor, 50 μL of monopropellant was added to 80 mg of catalyst at room temperature under 1 bar of argon flow, using a micro syringe through a septum, and was then heated at a rate of 10 °C/min. The pressure and temperature were recorded versus time. This reactor can be used to simulate cold starts or injection by pulses, but not stationary monopropellant flow (steady-state studies). This work was done to study the effect of monopropellant concentrations on the activity of green propellants for rocket applications. The (10%)CuO/ Al_2O_3 / La_2O_3

+ 75% ADN mixture showed a lower onset of decomposition temperatures, higher reaction rates, and higher amounts of gas-phase products than other systems tested.

The thermal decompositions of solid ADN and aqueous ADN solutions were studied, and the products of decomposition were identified using a thermogravimetric analyzer connected to an FTIR spectrometer [372]. A study of the decomposition of aqueous ADN solutions in contact with CuO nanocatalysts showed that the decomposition of aqueous ADN was influenced by CuO nanocatalysts, leading to the formation of higher concentrations of NO_2 , which in turn autocatalyzed the remaining ADN decomposition.

4.10 Thermal Stability and Decomposition Reactions of Solid Mixtures Containing Ammonium Dinitramide

ADN can form eutectics and other solid solutions with a wide range of other oxidizers and energetic materials. These mixtures may have improved properties (increased explosive power, improved stability) than the ingredients by themselves.

Melting-point diagrams of binary mixtures containing ADN were described in Section 3.4.2. We will now look at the thermal stability of such mixtures with fuels and other oxidizers.

An ADN mixture that is of particular interest is that with AN. AN is an intermediate decomposition product of ADN and plays a major role in ADN decomposition. It has been observed that eutectic mixtures of ADN and AN decompose much faster than pure ADN.

DSC data showed that ADN in contact with AN was compatible up to 393 K (120 °C) [373]. A mixture of ADN with AP, however, was incompatible. This was confirmed by evaluating the neat ingredients and their mixtures using several different heating rates to obtain decomposition kinetics. A higher frequency factor and rate constant were found for the ADN/AP mixture compared to the neat ingredients, which indicated incompatibility.

Because decomposing ADN and other dinitramide salts are quite acidic, there is concern about their interaction with metals that are often added to solid propellants to increase specific impulse and suppress combustion instability.

The dinitramide salts of ammonia (ADN), hexamethylenetetramine (HDN), potassium (KDN), and sodium (NaDN) showed a linear relationship between the DSC rate of decomposition at the peak maximum and the slope value at the low temperature transition peak [374, 375]. As the cation basicity increased in the series $\text{ADN} < \text{HDN} < \text{KDN} \leq \text{NaDN}$, there was an increase in the low temperature transition peak, the energy barrier for dielectric relaxation, and the decomposition peak temperature, and there was a decrease in the loss tangent $\tan \omega$ value at the low temperature transition peak, specific heat capacity, and the rate and enthalpy of decomposition. Five aluminum powders of different surface areas were analyzed by DSC in platinum sample

pans, and it was found that the enthalpy and rate of oxidation increased as the particle size of Al decreased, whereas the enthalpy of the Al melt decreased. TGA showed a two-step weight gain in the oxidation of Al, with plateaus in the 338 K (65 °C) and 386 K (113 °C) regions, and the percent weight gain increased as the particle size of Al decreased. Variable DSC and TGA heating-rate studies showed that the activation energies for the first step in the oxidation process increased as the particle size of Al increased.

The thermal decomposition of ADN/potassium dinitramide (KDN) mixtures was investigated by combined thermogravimetry-differential thermal analysis (TGA-DTA) and compared to the decomposition of the two salts by themselves [376]. ADN melts at 364 K (91 °C) followed by a single-step decomposition (100%) in the temperature range of 408–493 K (135–220 °C). KDN melts at 403 K (130 °C) prior to a two-stage decomposition reaction, with an onset of decomposition at 433 K (160 °C). The mass loss corresponding to the first stage was ~38%. The non-isothermal decomposition of ADN, KDN, and mixtures of KDN/ADN (90 : 10, 50 : 50, 25 : 75, 10 : 90 ratios by mass) was studied at a heating rate of 5 °C/min. The kinetic parameters, such as activation energy E and the logarithm of the pre-exponential factor A , for the thermal decomposition reactions were evaluated by two integral equations (Coats-Redfern, Madhusudanan-Krishnan-Ninan) for comparison. The calculated activation energy was 120 kJ/mol for ADN and 143 kJ/mol for KDN, while that of the mixtures was in between, and the corresponding $\ln(A)$ values were ~35 and 25 min⁻¹.

One of the ADN mixtures of particular interest is the mixture of ADN and guanurea dinitramide (GUDN). GUDN can be used to separate dinitramide ion from the reaction mixture and can later be converted to other dinitramide salts. The thermal decomposition kinetics of a mixture of ADN and GUDN were studied by non-isothermal differential scanning calorimetry [377]. An isoconversional method is a method to measure activation energies by taking timed data points at the same level of conversion α instead of doing isothermal tests and repeatedly measuring α as a function of time. Advanced isoconversional methods were used to investigate the dependence of activation energy (E_a) on conversion (α). A strong dependence of E_a on α was observed, indicating a complex decomposition process. E_a is close to 165–175 kJ/mol at the start of the reaction, and then reaches a maximum of ~196–199 kJ/mol at $\alpha = \sim 0.4$, followed by a strong decrease to ~135 kJ/mol near the end. The results suggest that the decomposition of ADN greatly influences the observed E_a dependence on α . This was further supported by FTIR results and enthalpy values of the exothermic decomposition.

ADN crystals, prills, and two ADN-based propellants having different relative amounts of ingredients were characterized by DSC, TGA-DTA-FTIR-MS, ARC, heat flux calorimetry, and isothermal nanocalorimetry [378]. Decomposition of ADN was observed in all of the samples at temperatures above the melting point of ADN (~365 K = ~92 °C). Formation of N₂O, NO₂, H₂O, CO₂, CO, N₂, and NO was detected during the ADN decomposition. Even at temperatures below the melting point of

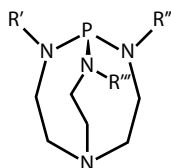
ADN, early solid decomposition of ADN, which generated N_2O and H_2O , was detected at 333 K (60 °C).

4.10.1 Stabilizers for Ammonium Dinitramide

Although pure solid ADN has sufficient thermal stability to be used as an oxidizer in solid propellants (or in dissolved form in liquid monopropellants), the effect of minute contaminants that might catalyze the decomposition and lower the thermal stability can be counteracted by the addition of stabilizers. Numerous stabilizers have been evaluated for this purpose, similar to the search for stabilizers for HAN. Since the first step of ADN decomposition is a proton transfer and formation of free, unstable dinitramidic acid, it was proposed that basic additives such as urea, hexamethylene tetramine, cyanoguanidine, or tetraethylenepentamine/acrylonitrile (HX-879, TEPAN) should inhibit the dissociation and stabilize the ADN [379, 380].

Because ADN has a higher energy content in comparison to AN, the exothermic decomposition already takes place under low pressures. Fortunately, phase transitions effecting changes in volume and density are lacking. Suitable additives are required for an effective stabilization of ADN at lower temperatures. The thermal stability of pure ADN and ADN with 2% of different stabilizers was investigated using DSC and TGA [381]. The DSC measurement showed melting onset at 91.5 °C followed by thermal decomposition all the way up to 200 °C. Although the addition of 2% MgO (usually effective for AN) or NaBO_2 showed no effect, the addition of 2% urotropine (hexamethylenetetramine), 2-nitrodiphenylamine (often used for double-base propellants), or akardite II (methyldiphenylurea) shifted the onset of ADN thermal decomposition to higher temperatures.

Prophosphatranes are adamantane-like spherical molecules in which the bridge joints are nitrogen and/or phosphorus atoms. Prophosphatranes have been patented as stabilizers for ADN and other dinitramide salts [382].



Prophosphatranes have been described in which R' , R'' , and R''' are the same or different substituents such as aryl or alkyl groups.

In search of stabilizers for molten ADN, at first the decomposition mechanism was studied by using ^{15}N isotope-labeled ADN with the isotope markings in the cation or the anion [383]. ADN with the ^{15}N label in the NH_4^+ cation was prepared by neutralizing a 2% solution of HDN in ether with liquid ammonia (97% enriched in $^{15}\text{NH}_3$) at 233 K (−40 °C). The crystals were washed with ether and recrystallized from isopropanol. ADN with the ^{15}N label in the anion was prepared by reaction of acrylonitrile

with $^{15}\text{NH}_3$ and nitration of iminodipropionitrile. Then 0.5-g samples of ADN were evacuated and sealed in glass ampules and immersed in a constant temperature bath at 120 °C for test durations from 30 min to 10 h. The gas released from the ampules was analyzed by GC and MS. Residual nitrate was analyzed spectrophotometrically after the residue was dissolved in water, and nitric acid was measured by pH. The experiments were then repeated with various stabilizers, including 0.78% potassium bromide, 0.58% potassium iodide, and various organic amines, carboxylic acids, and amides, as well as their dinitramide salts (22 different compounds tested). The most effective reduction of the gas-evolution rate was achieved by the addition of 1 mol-% hexamethylene tetramine, semicarbazide, oxalylhydrazide, aminotriazole, urea, or 1H-benzotriazole. In the decomposition of ADN with the ^{15}N label in the cation, current understanding of the decomposition mechanism would lead one to expect that half of the nitrogen atoms in the N_2 formed come from the ammonium cation and the other half is derived from the anion. The experiments showed that the percentage of ^{15}N in the N_2 formed increased with progression of the decomposition reaction, starting at 40% and ending at 90%. In the decomposition of ADN with the label in the anion, the ^{15}N label was found mostly in N_2O , which evolved only in the form of $^{15}\text{N}^{14}\text{NO}$ and only a little in N_2 and NO . The ratio of $\text{N}_2\text{O} : \text{N}_2$ changes during progressing decomposition. Initially the amounts are the same, but then the rate of N_2O evolution increases while that of N_2 evolution remains the same. The oxidation of the ammonium cation is responsible for the formation of N_2 and an autocatalyst. It was hoped that the addition of readily oxidizable stabilizers would scavenge the autocatalyst and prevent oxidation of the NH_4^+ cation.

The isothermal decomposition rates of ADN were measured at 333, 343, 353, and 363 K (60, 70, 80, and 90 °C, respectively) by measuring the amount of AN and N_2O formed by their UV absorption [384]. The tests were then repeated at 363 K after the addition of 1–2 mass-% of stabilizing additives, such as KDN, KF, a phenylphosphorus polymer, or perhydro-1,3,5-triazine-2,4,6-trione (also known as Verkade superbase). Hexamethylene tetramine was also considered as a potential stabilizer. Perhydro-1,3,5-triazine-2,4,6-trione was found to be the most effective additive, but KF showed no effect, and KDN worsened the stability. Free radical scavengers such as 2,2-diphenyl-1-picryl hydrazyl did not improve the stability of ADN, but 2-nitro-diphenylamine (commonly used as a stabilizer in double-base propellants) slowed the rate of decomposition somewhat.

Several stabilizers were evaluated for solid and liquid ADN mixtures containing Al powder [367] and for gelled ADN solutions [368]. See also [293]. Stabilizers that are free radical scavengers (e.g., butylhydroxytoluene) showed no beneficial effect on ADN decomposition; 2-nitrodiphenylamine, widely used as a stabilizer for double-base propellants, at the 1% level inhibited N_2O formation at 348 K (75 °C) for the first 6 h, but once it was depleted, the ADN decomposition proceeded uninhibited.

ADN has a more positive enthalpy of formation, 1208 versus –2518 J/g, and a higher heat of explosion than AP, 3337 versus 1972 J/g. One disadvantage of ADN is its much

lower thermal stability compared to that of AP. If it is possible to find stabilizers, ADN could be considered as a substitute candidate for AP. An extensive investigation was made with eight substances to find out their stabilization effect on ADN [385, 386]. ADN was mixed with 12 mol-% of each of these candidate stabilizers, and mass loss as function of time and temperature at 338, 343, 348, and 353 K (65, 70, 75, and 80 °C, respectively) and adiabatic self-heating was measured by isothermal TGA. The stabilization effectiveness changed with temperature. With well-stabilized solid-phase ADN, the rate-determining step was N—N bond cleavage in the dinitramide anion. In unstabilized ADN, the protonation of hydrogen dinitramide accelerated its decomposition autocatalytically. Various other organic and inorganic compounds were tested as stabilizers for ADN [387]. MgO, SiO₂, and hexamethylenetetramine did not show any improvements, but TiO₂, *N*-methyl-*p*-nitroaniline, and 2,4,6-triaminopyridine did have some stabilizing effect.

All ADN stabilizer candidates that work to any extent are weak to moderately strong bases, capable of reaction with acid moieties. ADN-stabilizing additives are also capable of reacting with NO_x and sequestering it before it can do any more damage. Pyridine and pyridone have been described as stabilizers for hydroxylammonium nitrate (HAN) and hydroxylamine in U.S. patent 5703323 (Rothgery et al. [388]), and similar compounds have been evaluated for stabilization of ADN [389]. Other stabilizers claimed are purine, pyrimidine, and triazine derivatives such as aminopyridines, aminopyrimidines, aminopyrazines, aminotriazines, aminoquinolines, aminoquinoxalines, aminocinnolines, aminopteridines, aminoacridines, and aminophthalazines.

ADN that is intended for melt casting (as well as in mixtures with aluminum powder) can be stabilized by the addition of 1% MgO [139].

The effect of four different stabilizers, by themselves and in various mixtures with each other, on the thermal decomposition of ADN and the interaction between ADN and NC was measured using DSC [264]. The candidate stabilizers included *N*-methyl-*p*-nitroaniline (MNA), 1,3-dimethyl-1,3-diphenylurea (C2), 2-nitrodiphenylamine (2-NDPA), and hexamethylenetetramine (HMT) and their mixtures MNA/C2, MNA/2-NDPA, and MNA/HMT. The results showed that the interaction between ADN and NC can be retarded to a certain extent by mixing MNA and C2, and the nascent interaction between ADN and NC can be inhibited by mixing the complex of MNA/C2, MNA/2-NDPA, and MNA/HMT.

4.10.2 Catalyst-Enhanced Decomposition of Solid Ammonium Dinitramide

The effect of catalysts on thermal decomposition of ADN is studied for several reasons: There are many unwanted contaminants that can have an adverse catalytic effect on the thermal decomposition of ADN. One needs to know which of these contaminants are the worst actors in order to prevent premature decomposition of ADN. On the other hand, we are looking for catalysts that can enhance the burning rate of ADN-based

solid propellants (Section 4.11.1 and a future volume on solid propellants). Some of these catalysts may even be useful for the decomposition of ADN solutions in liquid monopropellants.

The effects of ten different combustion catalysts on the thermal decomposition of ADN were studied using DTA and TGA experiments under linear temperature-increase conditions and isothermal TGA conditions [390]. The kinetic parameters of the thermal degradation of ADN and mixtures of ADN and catalysts were calculated for the DTA results at heating rates of 2, 5, 10, or 20 degrees per minute. The results showed that the catalysts containing Fe or Cu (except Fe_2O_3) distinctly affected the thermal decomposition of ADN and caused a decrease of the thermolysis peak temperature and an increase of the rate of mass loss of ADN. The effects of the catalysts containing Cu were more salient, and their catalytic mechanism can be attributed to coacervation phase catalysis, while the catalytic mechanism of the catalysts that contain Fe is a type of gas-phase catalysis. In contradistinction, additives containing ammonium salts or Ca achieve better thermal stability during the thermal decomposition of mixtures of ADN/additives as a result of the NH_3 produced, which absorbs protons. They shift the thermolysis peak temperature (T_p) to a higher temperature and increase the activation energy (E_a) of ADN, restraining the thermal decomposition of ADN.

Monodispersed cobalt metal nanoparticles were prepared by means of a hydrogen arc plasma method in an inert atmosphere and were characterized by particle size, morphology, and specific surface area [391]. ADN samples containing varying amounts of Co nanoparticles were prepared, and the effect of different Co nanoparticle concentrations on the decomposition of ADN was investigated using DTA. The decomposition exotherm peak temperature of ADN decreased with increasing Co addition, which indicated that the Co nanoparticles have a strong catalytic effect on ADN decomposition.

Copper(II) oxide is not a normal contaminant of ADN, but it may be added for other reasons, for instance as a burning-rate catalyst. Copper(II) oxide has been added to AN for phase stabilization, but ADN does not undergo phase changes at room temperature as AN does. The effect of copper(II) oxide on the thermal decomposition of ADN was investigated to gain a better understanding of the thermal decomposition mechanism of ADN [392]. The thermal behavior and activation energy associated with the decomposition of ADN/CuO mixtures were analyzed using sealed-cell DSC. DSC results showed that CuO affects the thermal stability of ADN and promotes its decomposition. TGS/DTA-evolved gas analysis was also performed, and in addition, the decomposition behavior was observed visually using hot-stage microscopy. From the results, a thermal decomposition mechanism was proposed for ADN/CuO. In this mechanism, copper dinitramide $\text{Cu}[\text{N}(\text{NO}_2)_2]_2$ is generated at the surface of the CuO almost simultaneously with the melting of the ADN. Next, a significant exothermic reaction occurs, associated with the decomposition of $\text{Cu}[\text{N}(\text{NO}_2)_2]_2$, followed by decomposition via $[\text{Cu}(\text{NH}_3)_2](\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$.

4.11 Combustion of Ammonium Dinitramide

This section describes the laboratory studies of the linear rate of combustion of ADN by itself in the absence of any fuel. Later sections also describe the combustion of ADN with fuel additives or with binders. The combustion of ADN by itself in the absence of any fuel is sometimes also called self-deflagration.

ADN burns without any luminous emission at low pressure, forming copious white vapors that condense as a fine white powder inside the tube and on the cold surfaces of the bomb. As the pressure increases, small flamelets emanating from local hot spots can be observed. Above 1–2 MPa, the gases become almost transparent, a luminous flame appears, and the condensed products of (partial) combustion are no longer observed. The burning-rate data display a considerable scatter, especially in the pressure range below 10 MPa.

According to several authors [353, 393, 394], ADN is capable of sustained burning at atmospheric pressure, whereas according to Denisjuk, Kuleshova, and Shepelev [395], ADN does not burn at pressures below 0.5 MPa. Sinditskii [396, 397] failed to obtain self-sustained burning of pure ADN at atmospheric pressure either by decreasing the sample density to 1.35 g/cm³ or by increasing the sample diameter to 12 mm. A sample 12 mm in diameter and 14 mm in height, having a density of 1.67 g/cm³, burned through a length of only 8 mm but then extinguished. Even at an initial temperature of 353 K (80 °C), samples of pure ADN were incapable of complete burning at atmospheric pressure. Samples of molten ADN at a temperature of 373 K (100 °C), however, were capable of complete burning, with the burning rate varying from 6.7 to 9.1 mm/s [293, 361, 363]. All of these investigators observed the emission of a solid aerosol of AN above the surface of burning ADN [334], noted a white cloud of AN particles leaving the surface of ADN during their pyrolysis studies, but attributed its appearance to the recombination of NH₃ and HNO₃ upon entering the cool-gas phase. They postulated that AN would not be present if combustion were taking place because NH₃ and HNO₃ would decompose to other species instead of recombining to AN.

Sinditskii et al. [397, 398] observed profuse amounts of white vapor that condensed as a fine white powder inside their experimental apparatus and at cold surfaces of their constant-pressure window bomb. After examining the white powder, they noted that it consisted not only of AN but also of some ADN.

4.11.1 Strand Burning Rates of Ammonium Dinitramide

Strand burning of ADN by itself in the absence of any fuel is sometimes also called self-deflagration. In most experiments, the burning behavior of this new oxidizer is compared to that of the most frequently used oxidizer, AP.

4.11.1.1 Experimental Studies of Solid ADN Strand Burning

At low pressure, ADN burns without any luminous emission, forming copious white vapors that condense as fine white powder at cold surfaces of the bomb. As pressure increases, small flamelets emanating from local reaction sites are observed, and above 1–2 MPa, flowing-off gases become almost transparent. Above 2 MPa, a luminous flame appears, resulting in elimination of the condensed combustion products. Nevertheless, photographic records frequently reveal segments with a lack of luminescence, suggesting that the flame is not very stable and often exhibits random patterns. Burn-rate data display a considerable scatter, especially in the pressure range below 10 MPa. The appearance of a region of strongly pronounced data scatter is indicative of combustion instability at these pressures.

In some sandwich burner experiments, ADN was able to burn by itself, leaving the unburnt fuel lamina behind if a non-energetic binder had been used instead of an energetic binder [399, 400]. More of these experiments will be discussed in a future volume on solid propellants.

The combustion behavior of ADN was studied in the form of both pressed strands and single crystals [401]. Self-sustained combustion of ADN pressed into plexiglass tubes 4 mm in internal diameter was found to begin at 0.2 MPa. Within the pressure intervals of 0.2–1.5 and 10–36 MPa, the combustion process was stable, whereas at 2.8 MPa and below the burning rate turned out to be unsteady through the length of the strand, and its value might vary by more than twice the rate at the same pressure. Small amounts of paraffin added to ADN substantially reduced the low-pressure limit of ADN combustion to the subatmospheric region. The temperature distribution in the ADN combustion wave was measured at 0.1–4.1 MPa using thin bare tungsten-rhenium thermocouples. The ADN decomposition reaction in the condensed zone to form AN and N_2O is supposed to play a dominant role in burning at low pressures. The ADN surface temperature corresponds to the temperature of AN dissociation to yield NH_3 and HNO_3 . Heat feedback from the gas to the surface is negligibly small. Temperature measurements suggest that the flame structure of ADN is subdivided into three zones. Thermocouple-aided experimental studies on the combustion of different energetic materials have shown that the surface temperature is equal to the boiling point or, in the case of salts like ADN, the dissociation temperature [402, 403].

The self-deflagration of pressed pellets of ADN was studied in preparation for later experiments with the combustion of sandwiches with ADN laminae on both sides of a binder lamina [404]. Results obtained with ADN were then compared to those obtained with AP. Burning-rate measurements of ADN obtained from three different sources resulted in quite different curve shapes when the burning rate versus pressure was plotted on double-logarithmic graph paper. In comparison to AP, all three ADN samples burned faster, and the slope was less steep.

ADN from three different sources was recrystallized from isopropanol and compacted into 7-mm polycarbonate tubes under a pressure of ~250 MPa, and the burning rate was measured between 0.5 and 30 MPa [395]. The burning-rate curve as a function

is very complex and consists of four different regions with quite different pressure exponents (Figure 58). In the range of 0.5–4 MPa, the burning rate increased with a pressure exponent of 0.55. In the range of 4–6 MPa, the burning rate decreased, and the slope was -0.55 . Between 6 and 10 MPa there was little change of the burning rate, and beyond 10 MPa (data available up to 30 MPa) it increased again, and the pressure exponent was 0.48.

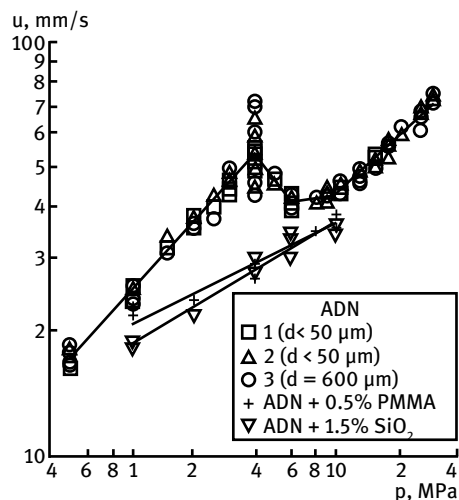


Figure 58: Burning rate of ADN and ADN mixtures. (Reprinted and modified from [395]; Reprinted with permission from Pleiades Publishing Inc.)

At all pressures, the charges burned to the end and left a whitish residue on the walls. The residue has been analyzed and consists mostly of AN with a little undecomposed ADN. In the vicinity of the burning-rate maximum, the combustion was very unsteady, and the burning rate fluctuated between 45 and 70 mm/s. The burning rate, particularly in the area of the burning-rate maximum, is very sensitive to additives. Adding 0.2 to 0.5% of polymethylmethacrylate (PPMA) powder or 1.5% fumed silica eliminated the up-and-down behavior and allowed the burning-rate data to fit nicely on a straight line, as the Robert deVeuille law would predict.

The burning rate of ADN is also very sensitive to moisture. Leaving the ADN exposed to air (20 min at 293 K and 90% relative humidity) caused the ADN to pick up moisture, and the maximum burning rate of the pressed samples was decreased by 15%. Leaving the ADN out in moist air for 240 min caused it to gain 2.5% by weight, the burn-rate maximum disappeared, and the straight line was shifted downward. Surprisingly, even ADN with very high water content was still capable of burning at high pressures. A sample with 8% H_2O had a paste-like consistency and burned with a regression rate of 11 mm/s at 4 MPa. An aqueous solution containing 75% ADN burned with a regression rate of 4 mm/s at 4 MPa. The temperature profile through the combustion zone was measured with a thermocouple probe. At 0.5 MPa, the temperature close (1 mm) to the solid surface was ~ 950 K, and at a greater distance (6 mm) it

was ~1300 K. ADN burns much faster than other propellant ingredients. For instance, at 2 MPa, it burns twice as fast as RDX and 14 times faster than AP.

Data on ADN combustion were obtained in 1976 in the Soviet Union but could not be published at that time. These data eventually surfaced in 1999 [393]. Strands were prepared by pressing ADN under a pressure of 300 MPa into polymethylmethacrylate (PMMA) tubes with a wall thickness of 1 mm and a length of 20 mm. The burning rates were measured in a combustion bomb at nitrogen pressures up to 10 MPa. The temperatures in the burning wave were measured with W-Re thermocouples with a wire diameter of 5 μm . The temperature results are summarized in Table 20.

Table 20: Flame temperature characteristics of ADN combustion.

Pressure MPa	Burning rate r_b (measured experimentally) cm/s	Temperature (measured experimentally)	
		Surface temperature K	Flame temperature K
0.066	0.22	530	685
0.1	0.27	560	720
2	1.82	700	2640
6	2.26	715	2770

Data source: [393]

The samples of ADN burned steadily at room temperature throughout the range of pressures studied (0.025–10 MPa). At pressures of up to 1 MPa, combustion proceeded without a luminous flame, but with the formation of a great amount of white smoke (AN). Above this pressure, a bright flame became visible. At a pressure of 2 MPa, a high-temperature zone, separated from the surface by a dark zone, appeared. The heat released as a result of ADN decomposition in the condensed phase was consumed in heating the substance and for subliming the decomposition product AN. However, as estimates showed, the heat was insufficient for a complete evaporation of AN, and some of it escaped as smoke. AN did not decompose under the conditions of ADN decomposition in the condensed phase, and the rate constant for AN decomposition was four orders of magnitude smaller than that of ADN. The dependence of the burning rate of ADN on pressure is shown in Figure 59.

The burning rates were very similar for the samples of 5 and 7-mm inner diameters at 0.025–2 MPa and could be described by Robert-deVielles law with a pressure coefficient of about 0.7, but above 2 MPa the curves for samples with different diameters diverged. The combustion peculiarities of ADN correlated with high rates of ADN decomposition, low reactivity of gas products, and the formation of a large amount of intermediate product (AN) at low pressures. Cu_2O accelerated ADN combustion, whereas Al and AN slowed it down, sidetracking the heat needed for heating up the

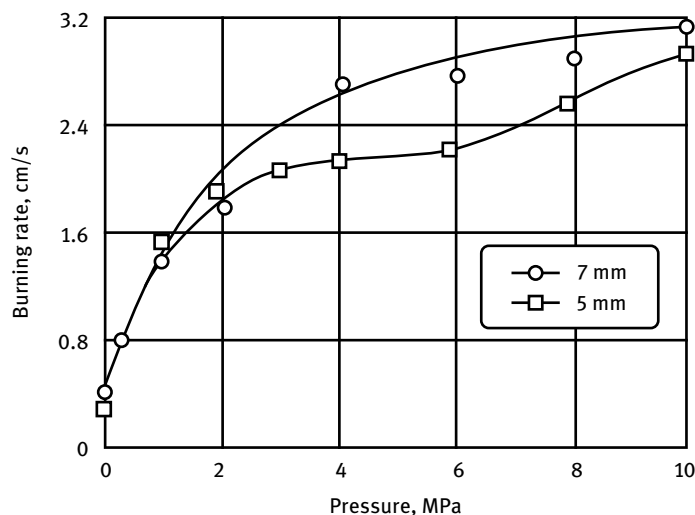


Figure 59: Strand burning rate of ADN pellets pressed into tubes with different internal diameters. (Republished and modified from [393], with permission of © 1999 Elsevier; permission conveyed through Copyright Clearance Center, Inc.)

reactants and sustaining endothermic processes. However, the very marked inhibiting effect of small amounts of organic materials on ADN combustion was a surprise. The addition of AN to ADN caused a strong decrease in the burning rate even at small concentrations of this additive, but the burning-rate retarding effect of AN diminished at the higher pressures; see Figure 60.

The thermal structure of combustion waves of ADN was profiled by W+5Re/W+20Re microthermocouple techniques and enhanced by data processing [394]. Temperature profiles and burning wave parameters (burning rate, burning surface temperature, heat feedback from gas to solid, heat release in solid, zone dimensions and temperatures in solid and gas phases) were obtained for ADN samples at pressures of 0.1–8.08 MPa (1–80 atm) and at sample temperatures of 123 K (–150 °C), 293 K (20 °C), and 353 K (80 °C) in nitrogen atmosphere. Characteristic features of the physics of ADN combustion are a large heat release in the solid phase and a weak heat feedback from gas to solid (due to low emissivity of the flame), low burning surface temperatures, and the two-zone structure of the gas phase above the solid (molten) surface. A surprising observation was irregular temperature pulsations (~5 Hz) in the gas phase; however, temperature traces are smooth in the solid phase. At 101 kPa (1 atm), averaged temperature profiles had only one zone in the gas phase, with a dark zone temperature of 723 K (450 °C). Only at pressures greater than 101 kPa (1 atm) did a two-zone structure in the gas phase develop. The mass burning rates $\dot{m}$ and surface temperatures T_s for burning ADN at three different initial sample temperatures and seven chamber pressures are summarized in Table 21.

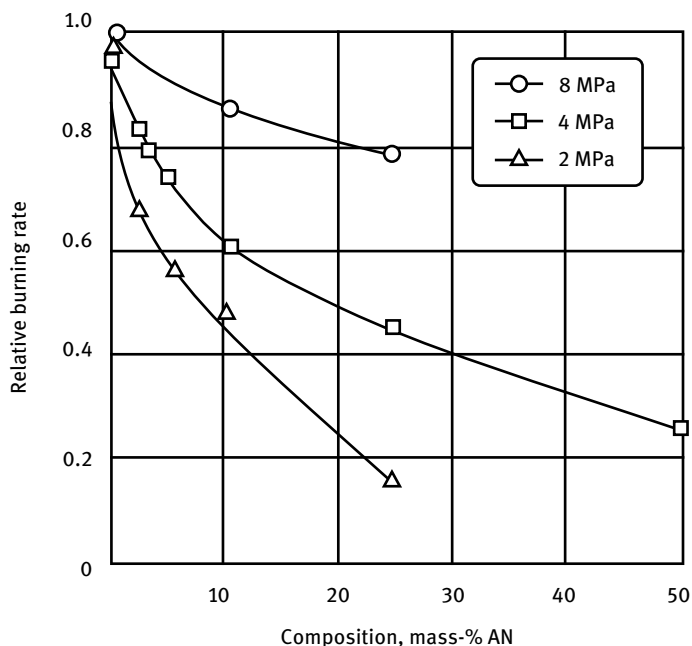


Figure 60: Effect of AN addition on the strand burning rate of ADN. (Republished and modified from [393], with permission of Elsevier; permission conveyed through Copyright Clearance Center, Inc.)

Table 21: Mass burning rates $\dot{m}$ and surface temperature for burning ADN.

Initial temperature			Pressure, atm						
°C			1	3	5	10	20	40	60
-150	$\dot{m}$	$\text{g cm}^{-2} \text{s}^{-1}$	0.32	0.43	0.56	0.80	1.32	2.4	3.4
	T_s	°C	260	270	279	294	312	342	355
+20	$\dot{m}$	$\text{g cm}^{-2} \text{s}^{-1}$	0.63	1.83	2.5	3.9	4.2	4.5	4.8
	T_s	°C	291	325	341	360	362	368	376
+80	$\dot{m}$	$\text{g cm}^{-2} \text{s}^{-1}$	1.4	5	6.2	8.2	9.4	12	13.8
	T_s	°C	369	370	380	392	397	410	417

Data source: [394]

The macrokinetic law of ADN gasification in combustion waves has the form

$$m = 13.6 \times 10^6 \exp(-38000/2RT)$$

where T is the temperature in kelvin and m is the mass burning rate in $\text{g cm}^{-2} \text{s}^{-1}$.

The strand burning rates of ADN were compared to those of HNF, RDX, HMX, CL20, and AP [405]. Samples of ADN powder were dry-pressed at 621 MPa and held for

10 min. The density of the resulting rectangular pellets was 97–98% of the theoretical maximum density. The sample sources of ADN consisted of small batches synthesized at the U.S. Naval Air Warfare Center, Weapons Division, as well as a sample from SRI International.

The ADN burning rates at ambient temperature are quite high, with a relatively low burning rate pressure exponent; however, the data displayed considerable scatter in the pressures between 2 and 10 MPa. The ambient temperature ADN data are compared to those of Fogelzang et al. [401] in Figure 61, where the data scatter is also observed. Fogelzang et al. attributed this data scatter to unstable combustion, but it may also be due to the deconsolidation and spalling of the material due to thermal stresses in the crystalline sample.

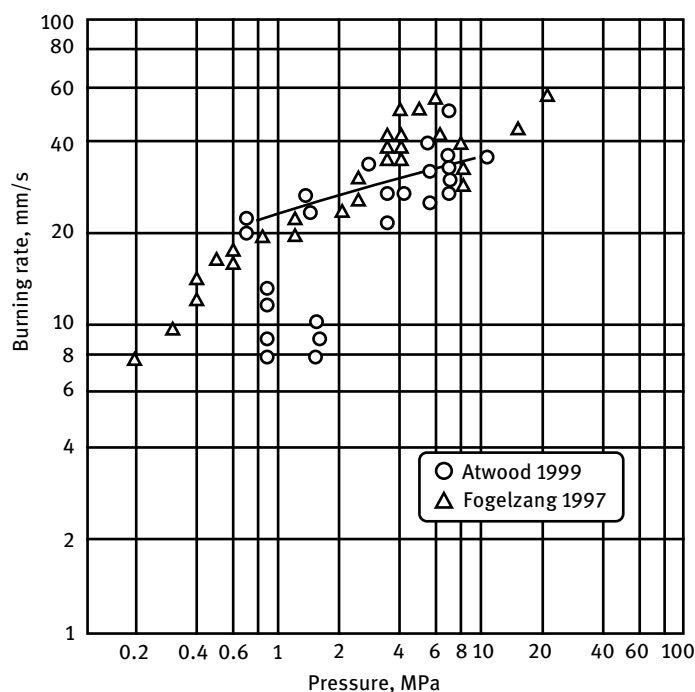


Figure 61: Strand burning rate of ADN at room temperature; comparison of U.S. Naval Air Warfare Center Weapons Division and Mendeleev University Russia data. (Republished and modified from [406] with permission of American Institute of Aeronautics & Astronautics; permission conveyed through Copyright Clearance Center, Inc.)

ADN burning rate data at two initial temperatures (298 K, circles; 348 K, triangles) over the pressure range of 0.69–10.3 MPa are presented in Figure 62. There is a significant amount of data scatter, and it takes a good amount of imagination to recognize a linear trend in these data.

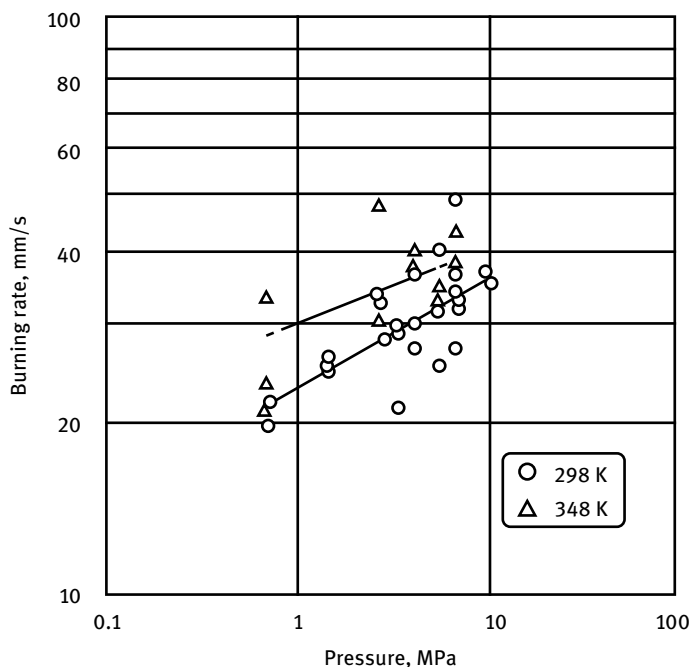


Figure 62: ADN strand burning rate data at two initial temperatures. (Republished and modified from [406] with permission of American Institute of Aeronautics & Astronautics; permission conveyed through Copyright Clearance Center, Inc.)

In extending conventional burning-rate and pressure-exponent measurements, additional data were used to determine the temperature sensitivity coefficient σ_p of the burning rate of ADN and four other oxidizers [406]. The simplest means of determining a value of σ_p is to measure the burning rate of a particular material as a function of initial temperature, take the natural logarithm of the burning rate values, and determine the burning-rate temperature sensitivity as the slope of the line through a plot of the natural logarithm of the burning rate versus the initial temperature. The main requirement is to obtain a consistent and reliable set of burning rate data at various initial temperatures and pressures. In the case of ADN, the temperature sensitivity decreases with increasing pressure. A comparison of the temperature sensitivity coefficients of ADN and AP is shown in Figure 63. The temperature sensitivity coefficient of ADN decreases, while that of AP goes through a minimum.

Previously, at 1–6 atm, only two zones had been observed in the flame front of ADN combustion [401]. Then the work was extended to 4 MPa (40 atm) chamber pressure, and a wide third zone was detected and studied using probing mass spectrometry and microthermocouples [407]. Pressed ADN pellets 10 mm in diameter and 15 mm high were burned in an argon atmosphere. A cooled stainless steel probe was inserted

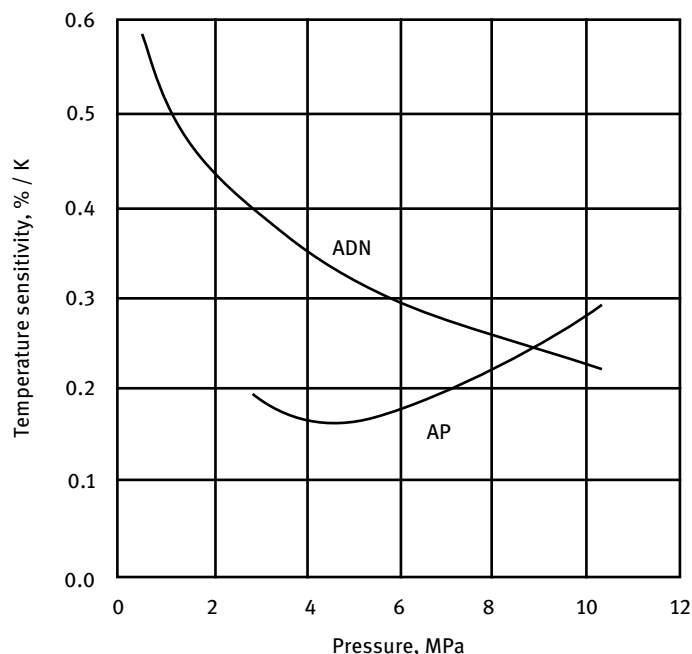


Figure 63: Comparison of the temperature sensitivity coefficients of the burning rates of ADN and AP. (Republished and modified from [406], with permission of © 1999 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

into the flame, and gas samples were drawn into a mass spectrometer. The probe was moved from 1.2 to 16 mm above the surface of the burning ADN pellet, and intensity profiles for key fragments at m/e of 28, 30, 32, and 44 amu were recorded. A decrease in N_2O concentration and an increase in N_2 and O_2 concentration were observed within a zone that is 8–10 mm wide. The NO concentration did not vary a lot within this zone. At the same time, temperature profiles were measured using un-sheathed Pt/Pt10Rh microthermocouples that were only 50 μm in diameter. The temperature increased from 1400 to 1800 K from 1.5 to 8 mm above the burning surface at 4 MPa (40 atm). It was attempted to reproduce the species and temperature profile using the CHEMKIN code with 170 reactions for 29 species. Experimental data and calculated numbers showed satisfactory agreement. The calculated adiabatic temperature at a sufficient distance from the surface was close to that expected for thermodynamic equilibrium.

Samples of pure ADN and ADN mixtures with paraffin were prepared by pressing strands with $40 \times 5 \times 5$ -mm dimensions [408–410]. The mixture (mass ratio 90 : 10) corresponded to the maximum specific impulse. The burning rates were measured in the pressure range from 0.1 to 10 MPa. Above 2 MPa, the burning rates of ADN were close

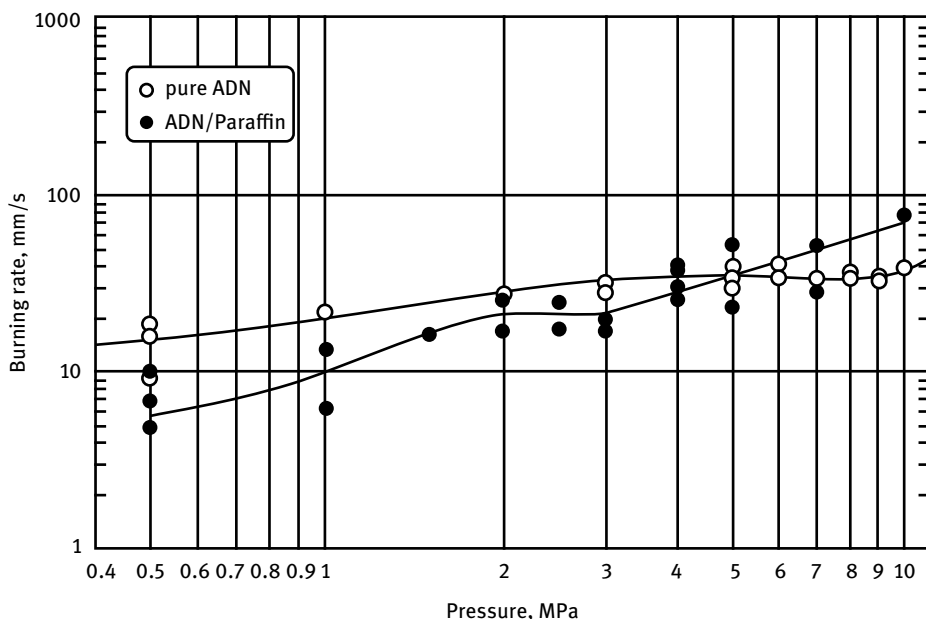


Figure 64: Burning rates of ADN and ADN/paraffin strands. (Republished and modified with permission of American Institute of Aeronautics and Astronautics, Inc. from [410]; permission conveyed through Copyright Clearance Center, Inc.)

to those of ADN/paraffin mixtures but unexpectedly exceed those above 4 MPa where the two curves cross each other (Figure 64). Similar data are presented in Figure 68 and 69.

In addition to burning-rate measurements, UV and IR spectra of flame zones allowed the identification of reactant profiles through the length of the flame zone, which were then compared to theoretical predictions based on kinetic models. Burning of ADN starts with the decomposition of the material at the surface, followed by chemical reactions in the gas phase. Therefore, the burning of ADN would have to be modeled by two separate reactions. The results of CHEMKIN calculations for the gas-phase reaction at 1100 K are shown in Figure 65.

It is interesting to compare the peculiar behavior of ADN deflagration with that of other ammonium salts of oxidizing acids, AN and AP, [411] and with dinitramide salts of other bases [412]. Burn-rate studies were carried out on dinitramide salts of common formula of $L_n\text{HN}(\text{NO}_2)_2$ (where $n = 1$ or 2 ; L = methylamine, trimethylamine, *tert*-butylamine, tetramethylammonium, urea, guanidine, aminoguanidine, triaminoguanidine, ethanolamine, diethanolamine, ethylenediamine, hexamethylenediamine, aniline, 3-nitroaniline, 2-toluidine, benzylamine, phenylhydrazine, morpholine, piperazine, pyridine, 3,5-dimethylpyridine, or 5-aminotetrazole), as well

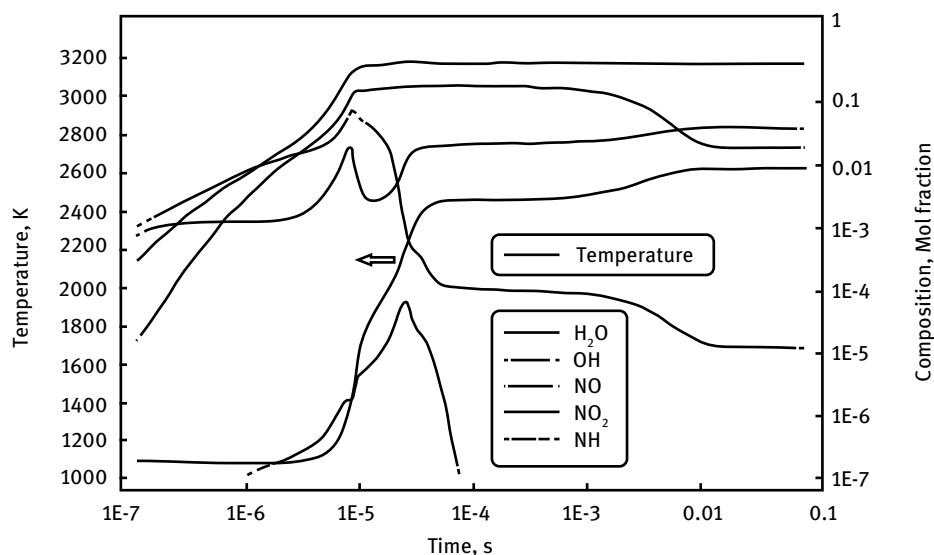


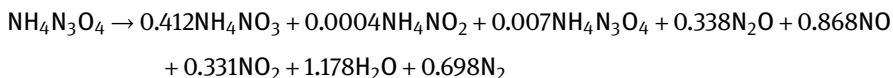
Figure 65: Calculated temperature and species profiles for pure ADN combustion. (Republished and modified with permission of American Institute of Aeronautics and Astronautics, Inc. from [410]; permission conveyed through Copyright Clearance Center, Inc.)

as lithium and barium salts of dinitramide. Most of the salts exhibited either combustion instability (like ADN) or a transition region on their $r_b(p)$ curves. The occurrence of this region depended on the fuel reactivity and, largely, the surface temperature, which was assumed to be dissociative and dependent on the amine basicity. In order to study the combustion mechanism, the flame structure of hexamethylene diamine bis(dinitramide) was investigated with tungsten-rhenium microthermocouples. The burn-rate study of this compound over a wide initial temperature range was used to evaluate the temperature sensitivity of the combustion rate.

The relationships between ADN burning rate and pressure were examined by measuring combustion phenomena under different pressure conditions in a combustion bomb [413]. Experimental temperature profiles in ADN combustion waves were taken with thermocouple probes in an effort to identify initial thermal decomposition reactions and dark-zone formation mechanisms in ADN combustion. At atmospheric pressure, the decomposition temperature barely exceeds 800 K, and the profile is flat out to 10 mm away from the surface, but above 2 MPa, a high temperature zone appears between 5 and 12 mm from the surface.

ADN is unique among the ammonium salts in that its autodecomposition can proceed even at subatmospheric pressures. Chemical analysis of the decomposition products at subatmospheric pressures showed that the amounts of NO, N_2O , NO_2 , and HNO_3 remain constant over the lower pressure range, and the proportions of NH_4NO_3 ,

NH_4NO_2 , and $\text{NH}_4\text{N}_3\text{O}_4$ decrease with increasing pressure. The stoichiometry of ADN decomposition at subatmospheric pressures can be approximated by the following equation:



In spite of the efforts by many investigators, there still remain a number of unresolved issues about ADN combustion. In particular, a well-grounded theory needs to be established to help in understanding the irregular burning phenomenon in the pressure range of 2–10 MPa (20–100 atm).

ADN combustion is stable in the range from 0.5 to 2 MPa (5–20 atm), and the pressure sensitivity of the burning rate has the form

$$r_b = 20.72p^{0.604}$$

where r_b is the burning rate in mm/s and p is the pressure in MPa [288]. This equation is valid for the pressure range from 0.5 to 2.0 MPa. The burning characteristics are controlled by exothermic decomposition in the condensed phase. Above 10 MPa (100 atm), the burning rate is well correlated with pressure as

$$r_b = 8.50p^{0.608}$$

where r_b is the burning rate in mm/sec and p is the pressure in MPa. This equation is valid for the pressure range from 10 to 36 MPa. Combustion of ADN pressed grains is stable, and intensive heat feedback from the gas phase dictates the burning rate. The pressure dependence of the burning rate, however, becomes irregular in the range of 2–10 MPa (20–100 atm). This phenomenon has been attributed to the competing influence of the condensed-phase and gas-phase exothermic reactions in determining the propellant surface conditions and the associated burning rate.

ADN and hexamethylenediamine(2+) dinitramide (HMDADN) both have a condensed-phase combustion mechanism that may be responsible for occasional combustion instability [414]. The Zeldovich and Novozhilov criteria have been calculated for these two salts in an effort to explain the combustion instability.

In spite of the fact that ADN is an oxidizer, combustible surroundings have been found to exert practically no effect on the burning rate of ADN pressed strands. In contrast, minor amounts of organic and inorganic additives intimately mixed in were found to have a strong effect on ADN burning behavior, extending considerably the pressure limit of sustained combustion to the vacuum area [397]. Burning-rate measurements over the pressure range of 0.1–36 MPa were carried out in a constant-pressure windowed 1.5-L combustion bomb with a motion picture camera aimed at the burning pellets and single crystals. Within the pressure range of 1–10 MPa, a decrease in the strand cross-sectional size caused a decrease in the ADN burning rate, accompanied by a notable burning-rate data scatter. Within this pressure range, the burning

rate of strands with a diameter of 4 mm or less could differ by more than a factor of two. Small amounts of organic substances added to ADN appeared to suppress the scatter and strongly affected the burning rate. The burning-rate law $r_b = bp^n$ constants for recrystallized ADN pressed into plexiglass tubes 7 mm in diameter, covering all of the pressure range studied, is given in Table 22.

Table 22: Burning-rate law for pure ADN pressed into 7-mm plexiglass tubes.

Pressure interval, MPa	<i>b</i>	<i>n</i>
0.2–5.8	18.98	0.60
5.8–10	213.18	−0.80
10–36	9.06	0.60

$r_b = bp^n$ where r_b is the burning rate in mm/s
and p is the pressure in MPa.

Data source: [397]

In Figure 66, the $r_b = f(p)$ curve for pure ADN with its maximum and minimum of the burning rate is very similar to those reported earlier.

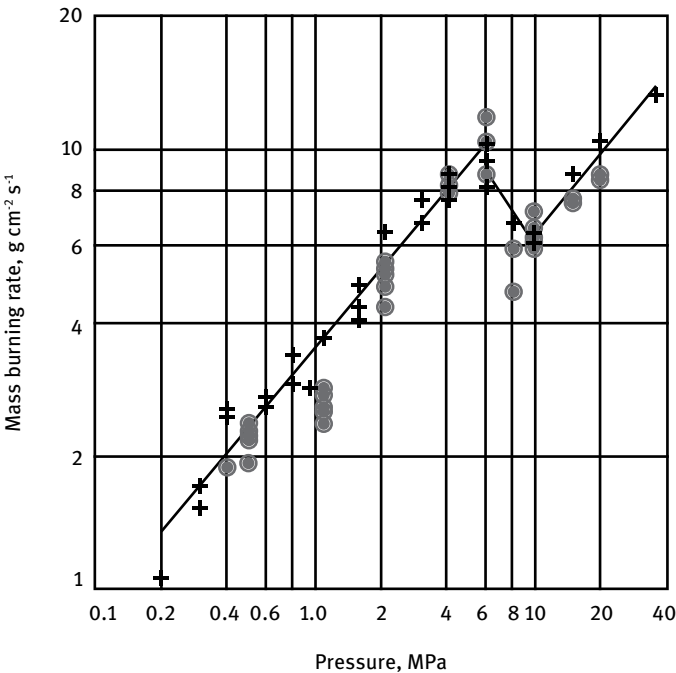


Figure 66: Effect of pressure on the mass burning rate of ADN pressed into 7-mm combustible plexiglass tubes with density of 1.79 g/cm³ (+) and 8.5-mm non-combustible quartz tubes with density of 1.54 g/cm³ (light points). (Reproduced and modified from [397].)

Surprisingly, a 90% supersaturated ADN solution in water can be ignited and sustains burning at 1 MPa at a rate less than the burning rate of neat solid ADN at this pressure. As the pressure increases, however, the burning rate of the solution rises very rapidly and has a maximum at 4 MPa, surpassing the neat ADN. As with ADN monocrystals, in this case the combustion instability area is distinguished very distinctly. However, the turbulent combustion of the supersaturated water solution reveals a local maximum on the burning rate versus the pressure curve in this area, whereas the crystals are incapable of sustained burning within the same pressure range.

Temperature profiles in combustion waves propagating into pressed ADN pellets were measured in the 0.04–10 MPa pressure range using thin tungsten-rhenium thermocouples [398]. The temperature profile data suggested that the ADN decomposition reaction in the condensed phase zone plays a dominant role in burning at low pressures. The heat feedback from the flame front to the surface appeared to be negligibly small. It was concluded that the reaction of AN dissociation to form NH_3 and HNO_3 controls the ADN burning surface temperature. The flame front of the ADN combustion wave consists of three zones, and theories explaining the main chemical reactions occurring in the three zones were proposed. One of the steps in the temperature profiles coincides with the dissociation temperature of AN, an intermediate in the ADN decomposition. The ADN surface temperature corresponds to the temperature of dissociation of AN, a decomposition product of ADN in the melt. Temperature just above the surface (the aerosol zone) is controlled first by the reaction of AN dissociation at the surface of small droplets, followed by dissociation of remaining ADN droplets tossed into the flame front. The first flame is due to NH_3 oxidation by nitric acid decomposition products. In the second flame, the complete thermodynamic heat release is attained. At low pressures (less than 1 MPa), the burning of ADN could be satisfactorily described by a condensed-phase combustion model with the rate-controlling reaction being the ADN decomposition in the melt. A gas-phase model with the rate-controlling reaction being HNO_3 decomposition in the first flame can be used to explain high pressures (greater than 10 MPa) burning. In the medium pressure interval (2–10 MPa), ADN showed combustion instabilities caused by a deficiency of heat produced in the condensed material. In this range, the fast but energy-limited heat-release process in the condensed phase has to adapt itself to the slow but energy-rich heat-release process in the gas phase. At 0.1 MPa, temperature measurements were carried out with molten ADN and paraffin-doped ADN (both capable of sustained burning at this pressure) and showed surface temperatures T_s for both materials in the range of 593–608 K.

Thermocouple studies showed that the lack of heat flux from the gas at least up to 4 MPa led to consideration of the condensed-phase chemistry as determining ADN combustion at low pressures [398]. It was proposed that it is AN formed in the decomposition of ADN in the melt, which dissociates from the ADN burning surface, thus controlling the surface temperature. Rate constants of the dominant combustion reaction of ADN in the pressure range of 0.02–1 MPa were obtained from Zel-

dovich's expression for the burning rate, taking the surface temperature, T_s , as the AN dissociation temperature. The average specific heat, c_p , was taken as $2.05 \text{ kJ kg}^{-1} \text{ K}^{-1}$ ($0.49 \text{ cal g}^{-1} \text{ K}^{-1}$); the thermal diffusivity of the condensed phase, χ , as $1.78 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$; heat of reaction, Q , as 1674 kJ/kg (400 cal/g); and heat of melting, H_m , as 14.2 kJ/mol (3.4 kcal/mol) [415].

As seen in Figure 67, the results derived from the combustion model,

$$k = 10^{16.37} \cdot \exp(-19630/T),$$

where k is the rate constant in s^{-1} and T is the temperature in kelvin, are in satisfactory agreement with ADN decomposition kinetics found by different ways, such as from dinitramide anion and ammonium cation disappearance rates [166],

$$k = 10^{16.94} \cdot \exp(-20080/T) \quad \text{and} \quad k = 10^{15.56} \cdot \exp(-19020/T)$$

and from rates of formation of gaseous decomposition products [241],

$$k = 10^{14.4} \cdot \exp(-17866/T) \quad \text{and} \quad k = 10^{15.4} \cdot \exp(-17765/T).$$

All of the data can be described fairly well in the temperature interval of 370–705 K by a general line, which is shown as a solid line in Figure 67.

$$k = 10^{16.16} \cdot \exp(-19375/T).$$

Figure 67 shows rate constants versus reciprocal temperature for the leading reaction of ADN combustion and the kinetics of ADN decomposition found from dinitramide anion and ammonium-cation disappearance rates, as well as from rates of formation of gaseous decomposition products. A solid line was then drawn through all the points. See also [416].

The thermal and combustion characteristics of ADN were measured by a pressure thermogravimetric analysis at pressures below 8 MPa [417]. The burning rates of pure ADN and ADN/AN mixtures were measured in the range of 0.2–12 MPa, and the burning temperature profiles were obtained using thermocouples with diameters of 5 and $25 \mu\text{m}$ in order to study the condensed-phase behavior in the vicinity of the burning surface as it progressed into the unburned material. Measurement of the temperature profiles was complicated because the ADN decomposition and AN dissociation competed in the condensed phase, and the bubbles of the decomposition gases and gas-phase flame also affected the surface temperature.

A study of the influence of various condensed-phase and gas-phase processes in determining the pressure and temperature sensitivities of the burning rate showed that ADN combustion is stable in the range of 0.5–2 MPa [318]. The pressure sensitivity of the burning rate has the form $r_b = 20.72p^{0.604} \text{ mm/s}$, and the burning characteristics are controlled by exothermic decomposition in the condensed phase. At 10–36 MPa, the burning rate can be correlated with pressure as $r_b = 8.50p^{0.608} \text{ mm/s}$. The pressure dependence of the burning rate, however, becomes irregular in the range of 2–10 MPa. This phenomenon may be attributed to the competing influence of the

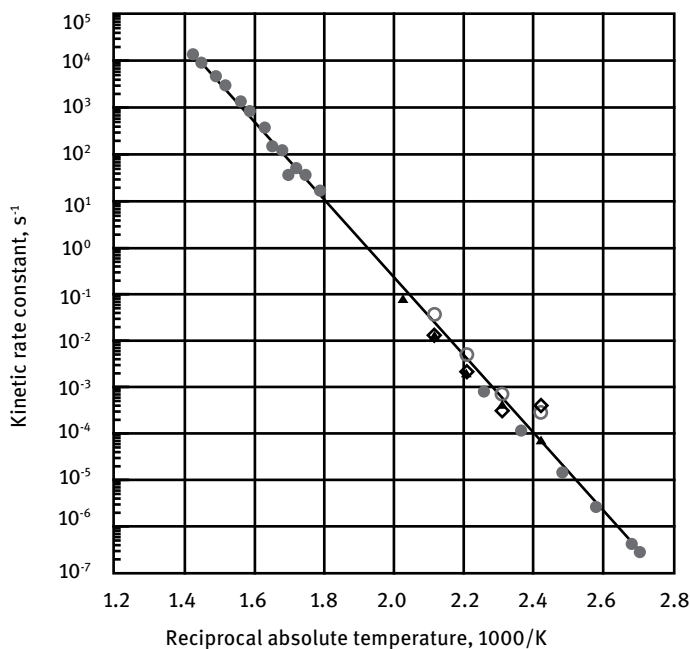


Figure 67: Rate constants vs. reciprocal temperature for the leading reaction of ADN combustion. (Republished and modified from [415], with permission of © 2009 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

condensed-phase and gas-phase exothermic reactions in determining the propellant surface conditions and the associated burning rate.

4.11.1.2 Lower Pressure Limit of ADN Deflagration

The lower pressure limit of combustion of recrystallized ADN pressed into acrylic tubes 7 mm in diameter was found to be 0.2 MPa. The ability of pure ADN pellets to burn at atmospheric pressure has been disputed, and different interpretations have been offered for the disparate observations. An addition of an amount of paraffin as small as 0.2% to crystalline ADN extended the low-pressure limit of ADN-sustained combustion from 0.2 to 0.02 MPa (Figure 68; [418]).

In the subatmospheric pressure region (at 0.04 and 0.06 MPa), the temperature profiles for paraffin-doped ADN were typical of flameless combustion: a sharp temperature increase in the condensed zone followed by the gas zone of practically constant temperature, i.e., with practically zero temperature gradient above the burning surface [397, 398]. This temperature remained almost constant over all of the length studied (~6 mm) and was equal to 553–563 and 583–603 K at 0.04 and 0.06 MPa, respectively.

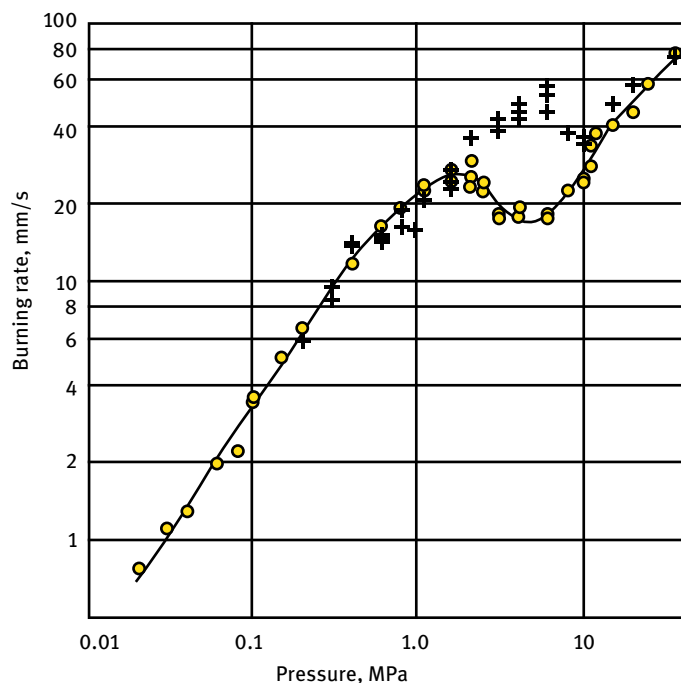


Figure 68: Burning rate of pure ADN (black + signs) and ADN doped with paraffin wax (open circles). (Reprinted and modified from [418], with permission from © 2007 Begell House, Inc.)

4.11.1.3 Effect of Initial Temperature on the Burning Rate

Burning-rate measurements at atmospheric pressure at different initial temperatures were conducted with samples of ADN pressed into plexiglass tubes 7 mm in diameter (Figure 69; [397]).

Although only a few experimental data points are available, the condensed-phase combustion model can be successfully used to describe combustion of ADN in a wide range of initial temperatures and at pressures less than 1 MPa. Figure 70 shows a comparison of experimental and calculated burning rates of ADN at different pressures and initial temperatures based on data from two different laboratories [402]. Note that in order to fit all five curves on one graph, four of the data sets were multiplied by an adjustment factor shown adjacent to the curves in the right-hand section of the graph. It can be seen that the burning rate coefficient (the slope of the curves) remained independent of temperature.

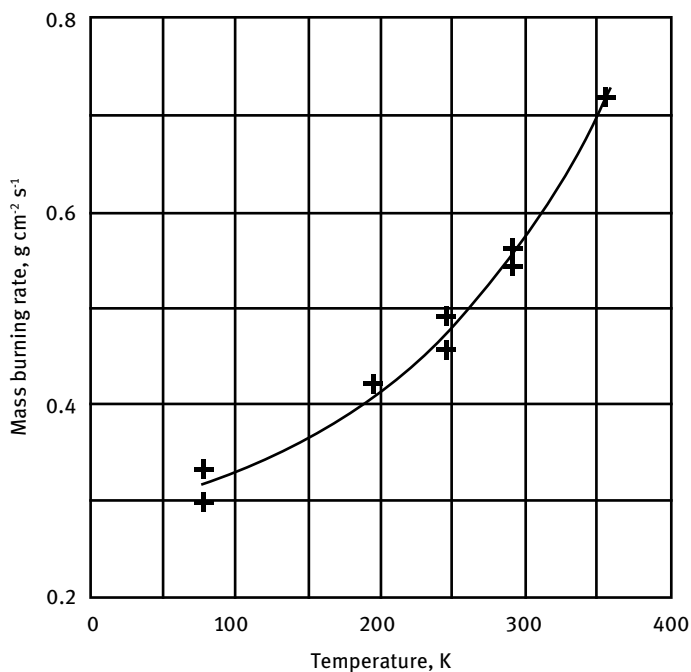


Figure 69: Effect of initial temperature on the burning rate of paraffin-doped ADN at 0.1 MPa. (Reproduced and modified from [397].)

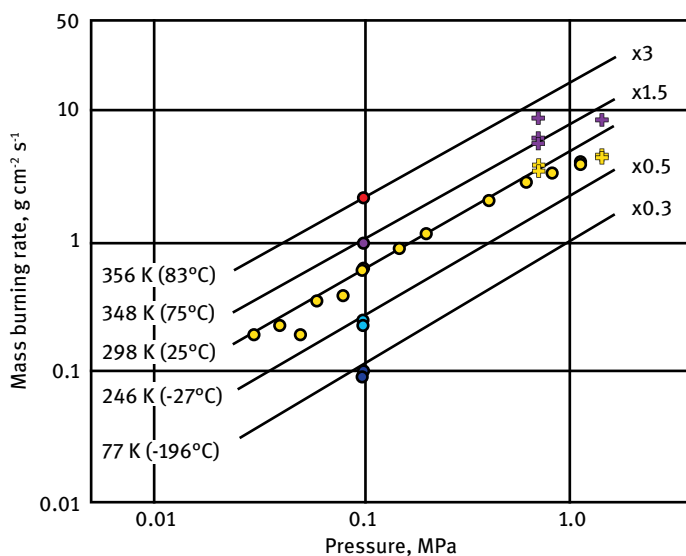


Figure 70: Comparison of experimental and calculated burning rates of ADN at different pressures and initial temperatures. (Reprinted and modified from [402]; AD-A517253 is in public domain)

4.11.1.4 Computer Modeling of ADN Strand Burning

ADN not only has a very high burning rate, but it also has a very unique burning rate versus pressure behavior. This complex behavior is extremely difficult to model mathematically. An unstable region exists between 20 and 100 atm in the ADN monopropellant burning-rate curve. It has been attempted to develop computer models based on kinetic codes, computational fluid dynamics, and heat and mass transfer calculations to predict the strand burning rate of ADN by itself and eventually also the burning rates of actual solid propellants based on ADN as the oxidizer (Section 4.11.2.2). With the advances in computational chemistry, various aspects of ADN molecular structure, energy levels, decomposition, and burning have become accessible for theoretical studies, and the computer predictions have been compared to experimental results (not always with full success). It would be relatively easy to restrict the computations to the gas-phase burning, but mass and heat transfer in the boundary zone between the solid (molten) surface and the gas phase makes calculations more difficult. Similar calculations have been performed for other solid propellant oxidizers with and without the presence of a combustible binder.

A numerical method was developed to study the physical and chemical processes involved in ADN combustion [419, 420]. The analysis was based on the well-known conservation equations of mass, species concentration, and energy for both condensed and gas phases, and it considered finite-rate chemical kinetics and variable thermophysical properties. A chemical kinetics scheme, containing 33 species and more than 180 reactions, was established to investigate the gas-phase flame structure. The analysis was applied to ADN self-deflagration (in the absence of combustible binders) at 6 atm, with the measured surface composition used as the boundary condition. Results showed good agreement with experimental data in terms of the temperature and species concentration profiles in the gas-phase flame. Sublimation and dissociation of ADN to NH_3 , $\text{HN}(\text{NO}_2)_2$, N_2O , and HNO_3 are believed to be the major initial decomposition steps. However, surface conditions derived from these processes failed to accurately model the measured gas-phase flame structure if a different kinetics scheme was employed.

The theoretical burning-rate equation of ADN and its mixtures with various additives was derived based on the chemical structure [421]. The calculated values showed good agreement with experimental results. Based on the chemical structure and reaction, the mechanism of plateau combustion in pure ADN remains to be explained. The formation and disappearance of the intermediate product NH_4NO_3 play a key role in plateau or mesa combustion of ADN.

Data (species concentrations and temperature profiles) obtained from mass spectrometric analysis of the decomposition products of ADN can be applied to modeling the combustion of ADN in a flame, either ADN burning by itself or ADN burning in mixtures with solid propellant binders. Molecular-beam MS and thermocouple measurements were used to study ADN flame structures at pressures from 0.3 to 0.6 MPa [422, 423]. Based on these experimental studies and literature data, a general mecha-

nism for describing the chemical reactions in an ADN flame (including 172 reactions and 31 species) was developed and compared to data reported by earlier investigators, including [358]. The correlation between experimental and theoretical results was satisfactory. The scheme included a submechanism (98 reactions and 22 species) for propellant combustion suggested by Yetter and Dryer. The latter was further supplemented by a set of 74 reactions, including 63 steps suggested by Lin and Park and the ADN dissociation reactions suggested by Korobeinichev, Bolshova, and Paletsky [423]. The correlation between the experimental and calculation results was satisfactory.

The book on thermal decomposition and combustion of explosives and propellants by Manelis et al. [424] contains chapters devoted to strand burning of individual oxidizers such as AP, AN, and ADN, as well as a more general chapter on developing a model that can be applied to all of those oxidizers that decompose in the condensed phase [424]. That chapter describes the different modes of reactions in the condensed phase of burning pure substances, dealing mostly with solid propellant oxidizers such as AP, AN, and ADN. The models describe different paths, depending on whether the substance burns with dispersion of the condensed phase (spattering, geysering), foaming, or a combination of condensed-phase reaction and evaporation or sublimation. These models are then applied to the study of strand burning of AP, HAP, AN, HN, hydrazinium(1+) chloride, and ADN. It was concluded that for ADN and a few other onium salts, the exothermic decomposition in the condensed phase and evaporation are the determining factors in determining the surface temperature and the regression rate. Dispersion (particle ejection, spattering, or foaming) plays only a secondary role. Gas-phase reactions contribute to the decomposition energy release only at high pressures. It is estimated that in the case of ADN decomposition, the contribution of gas-phase reactions is only 3% of the overall energy release.

Subsequent to and based on a thorough review of the ADN decomposition literature through 2006, a multi-phase model for the combustion of ADN in the absence of fuel additives has been developed using the BYU PHASE3 combustion code [425]. The model uses a single, global condensed-phase reaction and assumes that ADN evaporates to form the molecular complex $(\text{ADN})_{\text{associated}}$. The proposed mechanism is a parallel decomposition path in which ADN is converted to AN via one path and ADN is converted to NH_3 and dinitramidic acid by way of a second, competing path. The proposed condensed-phase decomposition reaction schematic is illustrated in Figure 71.

Very good results were obtained using a single, global condensed-phase reaction for the first segment of the burning rate curve. The model accurately predicted burning rates, temperature and species profiles, and other combustion characteristics of ADN at pressures below the unstable region ($2\text{--}10\text{ MPa} = 20\text{--}100\text{ atm}$) of combustion. Burning rates were also predicted halfway accurately in the unstable pressure regime and at higher pressures. The decomposition of AN must be included when designing an ADN combustion model because ADN is converted to AN in the first stage. The majority of AN is assumed to decompose in the condensed phase.

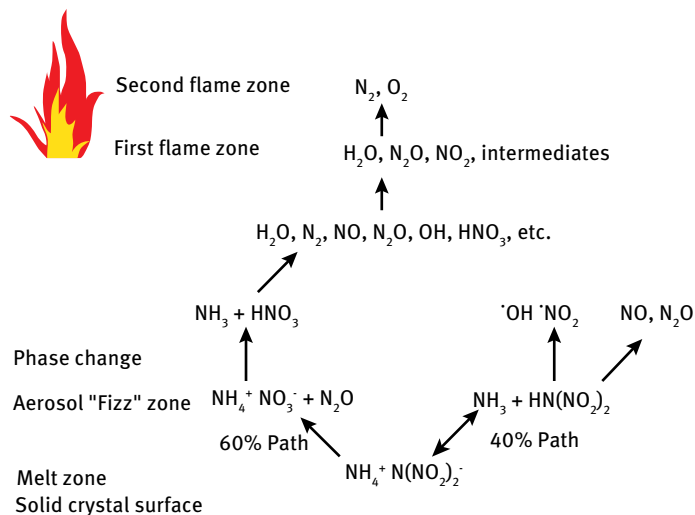
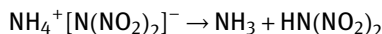
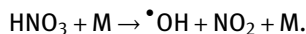


Figure 71: Proposed condensed-phase ADN decomposition pathway. (Adapted from [425].)

In order to verify the adequacy of various models of heat release in ADN flames proposed by other authors and to compare the results to real-world processes, the chemical processes in products of thermal decomposition at a pressure of 10 mm Hg and in ADN flames at pressures from 0.04 to 6.06 MPa (0.4–60 atm) were numerically simulated [426]. The calculations were performed on the basis of a detailed kinetic mechanism, and the boundary conditions were correlated with experimental data, thermodynamic properties, and initial chemical composition of ADN. The kinetic mechanism included sub-mechanisms that describe high-temperature chemical processes in $\text{N}_2\text{O}/\text{NO}/\text{NO}_2/\text{HNO}_2/\text{HNO}_3/\text{NH}_3$ and $\text{NH}_3/\text{HN}(\text{NO}_2)_2$ mixtures and the global stages of aerosol decomposition. Based on calculated and experimental data, the roles of dinitraminic acid $\text{HN}(\text{NO}_2)_2$, AN aerosols, ADN aerosols, and ADN vapor in heat release in the ADN flame zone adjacent to the burning surface were examined. The calculations predicted that the main source of heat release in the cold flame zone at $p \geq 3$ atm would be dinitraminic acid, which is formed by dissociative evaporation



from the burning surface. In the second high-temperature flame zone, heat release is caused by reactions that occur in the $\text{N}_2\text{O}/\text{NO}/\text{NO}_2/\text{HNO}_2/\text{HNO}_3/\text{NH}_3$ mixture. At moderate pressures, the high-temperature and low-temperature zones are separated by an induction zone. The stage that governs production of the OH radical, which plays an important role in combustion of ADN, is the reaction



Because of the high activation energy of this stage, small temperature perturbations in the induction zone at low pressures lead to a finite change in the stand-off distance between the high-temperature flame zone and the burning surface. Therefore, small temperature perturbations in the induction zone, which are caused by admixtures in the sample or by heat transfer between the reacting gas and the ambient medium, may be responsible for disagreement between various experimental data and between experimental and calculated data of the stand-off distance between the high-temperature flame zone and the burning surface. This can be measured by high-speed cameras through the windows of a combustion bomb.

A numerical calculation model with a coupled condensed-phase/gas-phase kinetics mechanism was developed to study the physical and chemical processes involved in ADN combustion and to predict the characteristics of combustion waves [427–429]. The model was based on the conservation equations of mass, species concentration, and energy for both the condensed phase and the gas phase, and it takes into account finite-rate chemical kinetics and real thermophysical properties. Finally, an equation of state for a multicomponent system was employed to connect the equations. A chemical kinetics scheme, containing 34 species, one condensed-phase global ADN decomposition reaction, and 165 detailed reactions in the gas phase, was established and employed in the model. The gas-phase mechanism model was applied to predict species mole-fraction profiles and temperature profiles in ADN gas-phase flames at 0.6 MPa. The coupled condensed-phase/gas-phase mechanism was employed to predict ADN strand burning rates and burning surface temperatures at pressures from 0.2 to 36 MPa. The agreement between calculation results and experimental data was satisfactory. The results indicated that the coupled condensed-phase/gas-phase kinetics mechanism can predict ADN combustion with reasonable accuracy. See also [430].

The surface temperature in the combustion wave of ADN, as well as in AN, HNF, and AP, is controlled by a dissociation process similar to that postulated for other onium salts [431].

A comprehensive multi-phase combustion model describing the physiochemical processes involved in the autodecomposition combustion of ADN was based on the conservation equations of mass, species concentration, and energy, and it took into account finite-rate chemical kinetics in both the condensed and gas phases [432]. Based on an extensive review of the literature on ADN thermal decomposition, three global decomposition reactions in the condensed phase of ADN were selected. A detailed chemical kinetics scheme involving 34 species and 165 reactions was employed to describe the gas phase. Detailed combustion-wave structures and burning-rate characteristics of ADN can be described by this model. The optimized gas-phase kinetics mechanism was able to predict the multi-stage flame structure of ADN self-deflagration flames. Good agreement between the predicted and measured profiles of temperature and species mol fractions was obtained at different pressures, and moderate agreement between calculated and measured values of

propellant burning rates and surface temperatures was obtained over a broad range of pressures from 70 kPa to 3.53 MPa (0.7–350 atm). The burning rate increased with pressure, except in the middle range of ~6.06–10.1 MPa (~60–100 atm). The coupled condensed-phase/gas-phase analysis employed in the current model was able to capture this irregular/unstable combustion behavior in the middle range, where the burning rate decreased with the increase in pressure, which is quite unusual.

4.11.1.5 Strand Burning of ADN Solutions

ADN solutions in water or formamide ignited in glass tubes 4–6 mm in diameter display a transition from laminar to turbulent burning initiated by a steep rise in the burning rate [396, 433]. At pressures greater than 15 MPa, this turbulent burning regime seems to undergo a transition to another more stable combustion regime marked by a weak dependence of the burning rate on pressure, as well as smooth burning of the entire charge for the entire length of the sample holder tube. In this range, most additives decrease the burning rate. An aqueous solution containing 75% ADN burned with a regression rate of 4 mm/s at 4 MPa [395].

4.11.2 Ammonium Dinitramide Combustion in Solid Propellants

Several sections in this chapter have already dealt with the thermal decomposition and combustion of pressed ADN pellets in the absence of a combustible binder. There is some inevitable overlap between those sections and other works studying the combustion of ADN in the presence of a combustible binder. We are trying to avoid repetition, but several publications are referenced in both locations, here and elsewhere. The papers discussed in the following sections deal with experimental as well as theoretical-computational studies of ADN as the oxidizer in the combustion of fuels in solid propellants. Sometimes the only combustible material in contact with ADN is the straw or thin tubing into which the oxidizer has been tamped or pressed to form the shape of a long cylinder for strand burning tests. Quite often the straw is polymethylmethacrylate, which has good see-through characteristics for high-speed photography in a windowed combustion bomb.

4.11.2.1 Experimental Study of ADN Combustion in Model Solid Propellants

Quite often the oxidizer/fuel combinations used for academic combustion studies do not meet all of the mechanical and structural requirements for a good propellant. These are only models for the real thing, but they are easier to deal with.

Sometimes a combustible non-polymeric substance is dry-mixed with the oxidizer and pressed into pellets for burning-rate studies. This is done because it is much easier to dry-mix the ingredients than to mess around with sticky pre-polymers and wait for several days until a formulation has cured. Pressing the samples into pellets in a hydraulic press is much faster and allows more variables. Particle size must be controlled, though.

In contrast to AP, an addition of any fuel to ADN did not appear to increase the burning rate. This is an unlikely result, but a 1000 °C increase in the flame temperature upon addition of the fuel did not cause the burning rate to increase. Moreover, the burning rate of the oxygen-balanced mixture with 7% of paraffin is actually less than that of neat ADN.

Several types of instruments based on microprobe and molecular beam mass spectrometric sampling have been developed and applied to ADN, AP, and double-base propellant combustion as examples [434]. TOF mass spectrometers connected to a skimming inlet can study combustion at high (>10 atm) or low (<1 atm) pressures.

The effect of fuels on the burning rate of ADN was studied by varying the O:F stoichiometric ratio and the pressure [395]. The fuels tested included anthracene, phenantrene, succinic acid, phthalic acid, hydroquinone, resorcinol, diphenylamine, hexamethylenetetramine, dinitrobenzene, dinitrophenol, and RDX. All fuels, with the exception of oxamide, had a similar effect on the burning rate of ADN. Minor amounts (0.5–1%) of fuel additives actually decreased the burning rate of ADN, particularly in the area where pure ADN had a maximum in its burning rate curve. Mixtures with oxamide burned the slowest, and mixtures with dinitrophenol burned the quickest.

When a burning pressed ADN pellet is surrounded by a combustible environment, this has practically no effect on the burning rate of pressed strands [433]. However, when the organic material is intimately mixed with the ADN before pressing it, this will allow ADN to burn even at very low pressures. In the pressure range from 2 to 20 MPa, a decrease in the strand diameter will cause a decrease in ADN burning rate, and the data are plagued by more data scatter. ADN single crystals (as opposed to pressed strands) did not burn at all at these pressures. The reason for this burning behavior is assumed to be a dominant role of condensed-phase decomposition reactions taking place in burning ADN. The ADN surface temperature is controlled by dissociation reactions, which are dependent of pressure. Since the amount of heat that can be released in the condensed phase is limited, combustion of ADN occurs on the verge of condensed-phase energy levels. Because ADN has such a low melting point and the surface layer is liquid, burning is accompanied by significant spattering of the melt layer that consists of ADN and some AN (the first decomposition product). Entrainment of condensed-phase droplets into the gas zone reaches its maximum in the pressure regime of unstable combustion (2–10 MPa), resulting in more scatter of burning-rate data. However, at the lower pressure limit of ADN deflagration, where the fraction of ADN ejected into the gas phase is larger, the dispersion retards the burning process because the energy release is scattered over a wider area. If the surface tension of the polar melt is reduced by the addition of organic compounds, the lower pressure limit of deflagration is lowered, and there is less data scatter.

The strand combustion of pure ADN suffers from combustion instability in the pressure range of 2–10 MPa. However, even small amounts of organic additives (<1%) result in a reduction of both burning rates and their scatter in this pressure range. Polycaprolactone (PCL) is not the best binder for solid rocket propellants, but it burns

cleanly and can be used in academic settings where the use of isocyanates and more toxic curing agents must be avoided. Combustion studies of ADN with PCL showed that PCL inhibits the reactions of ADN decomposition in the condensed phase [435, 436]. This leads to a decrease in the burning rate. The ADN used in this study contained 2% of AN as an impurity. It was shown that the particle size of the oxidizer influences the burning rate of ADN/PCL. The pressure exponent for propellant with bimodal oxidizer decreased to 0.72 in comparison with propellant on a base of fine oxidizer within a pressure range of 3–8 MPa. Burning rates of the 98% ADN/2% CuO mixture at pressures of 4–8 MPa were compared with those for pure ADN; the burning rates of this mixture were in a straight line beneath the lower boundary of the burning rates of pure ADN, which were scattered all over the graph grid. CuO catalyst increased the rate of reactions and heat release in the condensed phase and in the gas phase near the burning surface.

Sandwich combustion of laminated layers of oxidizers and fuels is one of the many methods to study and model heterogeneous solid propellant combustion. In some of these experiments, the deflagration of the oxidizer (AP or ADN) by itself (without addition of a fuel lamina) was examined as the baseline [437].

In addition to measuring burning rates and combustion temperatures, it is also of interest to analyze exhaust gases and to compare the results with theoretical predictions. Again, the ADN/PCL combination was used as the model propellant to demonstrate the operation of a new exhaust-gas sampling system. A new probe method for determining the quantitative composition of solid-propellant combustion products at temperatures of 2500–3200 K and pressures of 4–8 MPa under conditions typical of rocket motor conditions allows a sample to be frozen without passing through the main shocks inside the sampler and to be saved for later analysis [438]. See also [439].

4.11.2.2 Computer Modeling of ADN Combustion in Solid Propellants

This section is an expansion and continuation of Section 4.11.1.4, with the addition of combustible substances. With the advances in computational chemistry, various aspects of ADN molecular structure, energy levels, decomposition, and burning have become accessible for theoretical studies, and the computer predictions have been compared to experimental results (not always with full success). It would be relatively easy to restrict the computations to the gas-phase burning, but mass and heat transfer in the boundary zone between the solid (molten) surface and the gas phase makes calculations more difficult. Similar calculations have been performed for other solid propellant oxidizers with and without the presence of a combustible binder.

The combustion process of ADN has been modeled in two different situations: decomposition in an open environment, with a flow of abundant air transporting the products, and decomposition in rocket-motor internal environmental conditions surrounded by the decomposition products [440]. The rate of combustion and concentration of species in the open-air environment were higher than those in the rocket-motor environment, showing the effect of the different atmosphere in the reactions kinetics.

4.11.3 Burning-Rate Catalysts for Ammonium Dinitramide Combustion in Solid Propellants

Future volumes in this series may contain the general discussion of the effect of additives on the strand burning rates of pressed oxidizer pellets or formulated solid propellants. The current section deals specifically only with ADN in the absence of combustible binders. Many of the additives tested here are the same that have historically been used for AP-based solid propellants with moderate success. The burning rates of pressed pellets of ADN are much higher than those of AP; therefore, burning-rate catalysts are rarely needed.

4.11.3.1 Metals as Burning-Rate Catalysts for ADN

Metals can affect the burning rates of solid propellants only if they are finely divided. This is where the new nanometal powders are finding new applications.

4.11.3.2 Metal Oxides as Burning-Rate Catalysts for ADN

Finely divided nano-size iron(III) is a very effective burning-rate catalyst for all types of solid propellants. A nanocomposite iron(III) oxide freshly hydrolyzed and precipitated on ADN is a high-performance, high-burning-rate oxidizer [441]. By using 1,2-epoxypropane (propylene oxide) as the agent for controlling the rate of hydrolyzation of Fe^{3+} ions, an ADN/ Fe_2O_3 composite wet gel was prepared by a sol-gel method under mild conditions. An ADN/ Fe_2O_3 aerogel was obtained by means of supercritical CO_2 fluid dehydration. Transmission electron microscopy

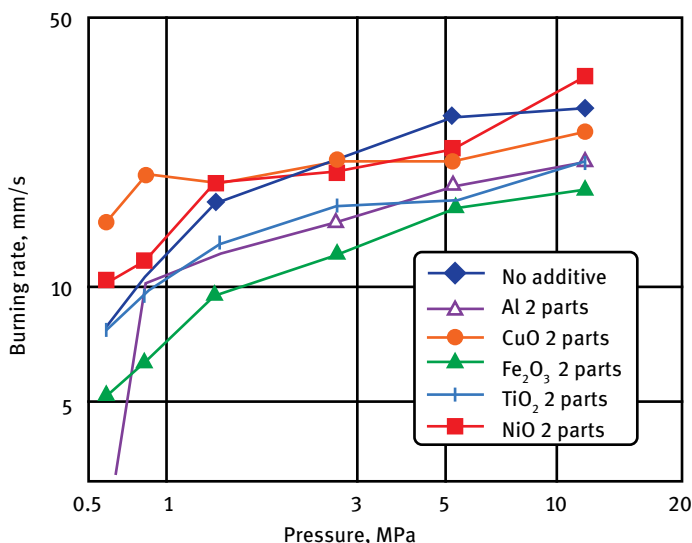


Figure 72: Effect of additives on burning rate of pressed ADN pellets. (Reprinted and modified from [443]. This image is in public domain.)

(TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), IR, DSC, and sensitivity tests were employed to characterize the appearance, structure, thermal behavior, and mechanical sensitivity of the samples. The results indicated that the as-prepared ADN/ Fe_2O_3 nanoparticles are about 50–100 nm in diameter and are much less sensitive to mechanical stimuli. Moreover, the ADN/ Fe_2O_3 nanoparticles decompose at a lower temperature with the disappearance of the melting endothermic peak.

Micrometer-sized particles of Al, Fe_2O_3 , TiO_2 , NiO, $\text{Cu}(\text{OH})\text{NO}_3$, Cu, and CuO, and nano-meter-sized Al (Alex) and CuO (nanoCuO) were employed as the additives for pelletized ADN in the absence of binders [442] and with added binders [443]. The burning rates of pelletized ADN were measured at pressures ranging from 0.6 to 6.2 MPa. Nanosized CuO enhanced the burning rate of pelletized ADN, but only below 3 MPa. Alex-incorporated ADN burned with flames even at 0.55 MPa, under which pure ADN does not support combustion by itself. Figure 72 illustrates the effects of additives on the strand burning rate of pelletized ADN. The burning rates of most of the other samples with additives were lower than those of pure ADN pellets under those conditions.

4.11.3.3 Metal Carbonates as Burning-Rate Catalysts for ADN

The effect of lead(II) carbonate (PbCO_3) on the combustion characteristics and thermal decomposition behavior of ADN was investigated using burning-rate measurements, DSC, and TGA [444]. Results showed that the burning rate of an ADN + 5% PbCO_3 + 0.2% paraffin system is higher than that of an ADN + 0.2% paraffin system in the pressure range of 3–12 MPa, and PbCO_3 causes the mesa combustion effect in the ADN + 0.2% paraffin system to disappear. TGA and DSC curves of ADN and ADN + 5% PbCO_3 indicated that the onset of decomposition temperature of ADN can be decreased by the addition of PbCO_3 . Kinetic analysis for DSC data showed that the apparent activation energy of thermal decomposition of ADN decreased when 5% PbCO_3 was added into ADN.

4.11.3.4 Metal Complexes as Burning-Rate Catalysts for ADN

The effect of organometallic compounds on the combustion and thermal decomposition of ADN was investigated using burning-rate measurements, DSC, and TGA [445]. It was shown that organometallic compounds can increase the burning rate of ADN within the pressure range of 1–12 MPa. TGA and DSC tests for ADN and ADN+1% organometallic compounds indicated that the initial decomposition temperature of ADN can be noticeably decreased. The initial onset of decomposition temperature of ADN is dependent on the number of organometallic compounds added. Kinetic analysis of DSC and TG data showed that the activation energy of thermal decomposition of ADN was decreased by about 30% by the addition of only 1% of organometallic compounds to ADN.

4.11.3.5 Nanomaterials as Burning-Rate Catalysts for ADN

Bismuth oxide is rarely used as a burning-rate catalyst for any rocket propellant, and even less so for ADN. Nevertheless, the catalytic activity of bismuth oxide deposited on carbon nanotubes (CNTs) has been tested. CNTs supporting bismuth oxide (Bi_2O_3) nanometer particles were prepared by a microwave radiation method and characterized by means of SEM, X-ray photoelectric spectroscopy, and XRD [446]. The catalytic activity of Bi_2O_3 nanometer particles on the thermal decomposition of ADN was investigated by TG and DSC. The results showed that nanometer Bi_2O_3 was coated uniformly on the surface of the nanotubes.

The catalytic activity of CNTs, CNTs supporting ferric oxide ($\text{Fe}_2\text{O}_3/\text{CNT}$), and CNTs supporting iron and copper ($\text{Fe}\bullet\text{Cu}/\text{CNT}$) for the combustion and thermal decomposition of ADN were investigated through burning-rate measurements and TGA [447, 448]. Results showed that all three catalysts increased the burning rate of ADN. The burning rates were related to combustion pressure by an exponential burning-rate function, and the pressure exponents decreased with the amount of catalyst for all of the three catalysts. When 3 mass-% of catalyst was used, the burning rate of ADN at 4 MPa increased from 30 to 50 mm/s, 40, and 39 mm/s and the pressure exponents decreased from 0.81 to 0.36, 0.67, and 0.75 for the CNTs, $\text{Fe}_2\text{O}_3/\text{CNTs}$, and $\text{Fe}\bullet\text{Cu}/\text{CNTs}$, respectively. TGA tests showed that all three catalysts decreased the onset of thermal decomposition temperature of ADN. When 1 mass-% catalyst was added to the ADN, the thermal decomposition onset temperatures of ADN decreased by 18.3, 12.1, and 11.6 °C for the CNTs, $\text{Fe}_2\text{O}_3/\text{CNTs}$, and $\text{Fe}\bullet\text{Cu}/\text{CNTs}$, respectively.

4.11.4 Burning-Rate Studies with Alkylammonium Dinitramide Salts

A large number of dinitramide salts of organic amines were synthesized, and their physical properties and strand burn rates were measured [412, 449]. It was attempted to obtain a correlation between the basicity constant of the amine and the burning rate of its dinitramide salt, but not all data fit into the same scheme. The burning rates of the dinitramide salts of various aliphatic, aromatic, and heterocyclic amines were compared to the corresponding perchlorates. The advantages due to the ability of dinitramides to burn at lower pressures and over a wider pressure range disappear at higher combustion pressures.

5 Toxicity of Ammonium Dinitramide

As soon as ADN became available, several studies were performed by the U.S. Air Force Toxicology Division to evaluate the toxicity of this new chemical [450, 451]. These studies included acute and subacute toxicity screening, a 90-d reproductive screen and three follow-on reproductive studies, electron paramagnetic resonance (EPR) spectroscopy studies, mutagenicity assays, and a study evaluating the effects of ADN on hepatocytes *in vitro*. The results of the *in vivo* studies indicated that ADN is a female

reproductive toxicant in rats, causing implantation failure during early gestation. The follow-on studies implied that ADN is even embryotoxic. EPR studies indicated that ADN can decompose to form reactive nitrogen metabolites that can be harmful in biological systems. The hepatocyte studies suggested that ADN has the potential for directly affecting cellular DNA *in vitro*. Additional traditional genotoxicity assays indicated that ADN is potentially mutagenic.

Eurengo Bofors started analyzing environmental and toxicological effects of ADN and GUDN (also called FOX-12) [452]. The tests were performed by independent and accredited test institutes (Research and Consulting Company, Itingen, Switzerland), and they are in full accordance with the requirements in the European Registration, Evaluation and Authorisation of Chemicals (REACH) regulations. The products have been registered and have all received ELINCS-numbers (i.e., they are on the European List of Notified Chemical Substances according to REACH). ADN is registered according to REACH and has received the ELINCS-number 453-090-2. The results of the tests are shown in Table 23.

Table 23: Results of toxicity and environmental screening of ADN.

Type of test	Results
Toxicity LD50 (oral rat)	832 mg/L
Toxicity to aquatic organisms EC50	> 10000 mg/L (15 min)
Acute inhalation	May cause irritation
Sensitizing	Not sensitizing
Effect on skin	Not irritating
Effect on eyes	Not irritating
Lipophilicity	$\log P_{o/w} < -2.8$
Mutagenicity mammalian cell	Negative
Biodegradability COD	0.2 g/g
BOD7/COD	0.5

Data source: Stenmark and Sjoekvist [452]

According to these tests, ADN is considered to be non-carcinogenic and non-allergenic. It is not irritating when in contact with skin or eyes but may cause irritation if inhaled. ADN is harmful if swallowed.

5.1 Oral Toxicity of Ammonium Dinitramide

Because the most significant exposure route expected for ADN would be accidental ingestion, acute oral toxicity animal tests were conducted [453]. In preparation for a reproductive screen on ADN, stability and palatability studies were also conducted. Oral administration of ADN at 5 g/kg body weight (the U.S. Environmental Protection

Agency [EPA] limit dose) produced convulsions and rapid death in all treated rats. Subsequent studies indicated an acute LD₅₀ in F-344 rats of 823 mg/kg. Administration of either 12, 25, 50, or 100 mg ADN/mL of drinking water on a continuous basis for 2 weeks to male and female Sprague-Dawley rats produced no apparent effect on body weight gain, water consumption, organ weights, hemoglobin concentration, or methemoglobin formation. Dermal application of 2 g/kg (EPA limit dose) produced no toxic signs in rabbits.

It was hypothesized that ADN decomposes in the body to form free radicals that would then destroy living cells. This hypothesis was tested on liver cells *in vitro* [454]. Liver cells were chosen because, regardless of the mode of administration, ADN will enter the bloodstream and ultimately pass through the liver. Leakage of the enzymes aminotransferase, alanine aminotransferase, and lactate dehydrogenase was taken as an indication of cell damage in WB344 hepatocytes after a 24-h exposure to ADN. Incubation of hepatocytes with 2.8 mM of ADN solutions for 24 h was toxic to 50% of the cells. Cells exposed to ADN produced free radicals that could be trapped chemically by two free-radical scavengers ("spin traps") and sensed by EPR, but not in all of the tests. EPR can detect free radicals in concentrations down to 10^{-10} M. Three of the four tests showed that increasing the ADN concentration will cause reduced cell viability.

In an evaluation of acute and subacute toxicity of ADN, oral gavage of ADN solutions greater than 1 g/kg resulted in mortality preceded by convulsions for male rats [455]. An oral LD₅₀ of 823 mg/kg was determined for male Fischer 344 rats. Rats receiving non-lethal doses of ADN showed no treatment-related effects when necropsied following a 14-d observation period.

In studies to try to determine a mechanism of action of ADN in biological systems, the interaction of ADN and its decomposition reaction intermediates on deoxyribose nucleic acid (DNA) was analyzed *in vitro* [456]. Some of the intermediates of ADN decomposition are free radicals. Free radicals can alter the genetic code in living cell propagation and induce cancer. EPR spectroscopy was used to determine whether radiation induces chemical changes in ADN by formation of free radicals. Irradiated ADN powder generated two superimposed EPR spectra, which were tentatively identified as NO₂ and NH₃ radicals. An electron nuclear double resonance (ENDOR) method was then used to verify the EPR results. The initial results of these experiments suggested a proton interaction proximal to the NH₃ radical center. Both reactive oxygen metabolites (ROMs) and reactive nitrogen metabolites (RNMs) play an important role in normal physiology and pathophysiology in biological systems. In order to identify the free radicals, they were made to react with a spin-trapping agent (*N-tert*-butyl- α -phenylnitron [BPN], 10-mM solution) that, in the presence of ADN, yielded overlapping spin adduct EPR spectra [457]. Precision-cut human liver slices were incubated in the presence of BPN with and without 10 mM ADN solutions. The liver slices were then homogenized, frozen in liquid nitrogen, and lyophilized. ADN oxidized the BPN

in human liver within 5 min of exposure to form a yellow compound that was no longer paramagnetic. The reaction of ADN with liver caused acute injury.

High-pressure liquid chromatography studies revealed the formation of ADN-fragmented DNA [458, 459]. Damage to DNA in solution was caused by at least two major pathways, one arising from reactions of NO_2 with oxygen and the other arising from a reaction with superoxide (O_2^-). The radical species generated when ADN was incubated with standard solutions of DNA, pH 7.5, in the presence of the spin-trap agent BPN was compared to the BPN-radical adducts generated in the presence of ADN and O_2^- or of ADN and H_2O_2 . The synergistic effect of ADN with O_2^- may provide an understanding of the sensitivity of rat blastocysts to ADN at the preimplantation stage of development and the lack of toxicity in *in vivo* studies in tissues that are high in catalase.

5.2 Cutaneous Toxicity of Ammonium Dinitramide

Preliminary field reports from exposed personnel have indicated that the chemical is readily absorbed into the skin, resulting in numbness of the fingers. Because the most significant exposure route expected for ADN would be dermal exposure, acute dermal toxicity tests were conducted [453, 455]. Dermal toxicity in New Zealand white rabbits, performed at the EPA's limit dose level of 2 g/kg body weight, resulted in no mortality and no clinical signs or differences in clinical pathology following a 14-d post-treatment observation period.

5.3 Mutagenicity of Ammonium Dinitramide

ADN was examined for its genetic toxicology effects using a combination of short-term mutagenicity screening assays, which included Salmonella/microsome mutagenesis (Ames test), mouse lymphoma cell mutagenesis (L5178Y-TK test), and an *in vivo* mouse bone marrow micronuclei assay [460, 461]. Results of Ames testing indicated that ADN is a base-pair substitution mutagen, causing about twofold (without S9) or threefold (with S9) increases of revertants in TA100, while there was zero increase of mutants in TA1535, TA1537, and TA98. ADN also induced mutation at the TK locus of mouse lymphoma cells, causing 40–95% (without S9) or 130–220% (with S9) increases of mutants. The *in vivo* micronuclei examination revealed a dose-dependent increase of micronucleated cells in the bone marrow of both male and female mice treated with ADN in a dose range of 62.5–750 mg/kg (single dose for 3 consecutive days), with a maximal induction of threefold increase at the highest dose. These tests demonstrated that ADN is mutagenic to both bacteria and mammalian cells and causes chromosomal damage in mouse bone marrow cells *in vivo*.

5.4 Carcinogenicity and Genotoxicity of Ammonium Dinitramide

In vitro toxicity, stress gene induction, and genotoxicity of ADN were determined as part of the initial phase of toxicity testing and evaluation of ADN [462]. First, the liver enzymes alanine aminotransferase (ALT) and aspartate aminotransferase (AST) were measured to estimate the membrane integrity of WB 344 hepatocytes. It was found that ADN increased leakage of both of these enzymes at all concentrations studied. Normalized EC_{50} s were determined at percentage of controls: ALT $EC_{50} = 2.7$ mM and AST $EC_{50} = 3.2$ mM. Next, to measure interactions of ADN with cellular regulatory transcription factors, genetically engineered human cell lines with fused human and bacterial stress-inducible genes were observed for the stress gene induction followed by *in vitro* ADN treatment. The stress reporter gene induction profile reflected that ADN induced the promoted sequences for all genes observed in the assay. Finally, preliminary assays to determine genotoxicity/mutagenicity of ADN were performed. These studies measured damage caused by DNA to living cells, potentially giving rise to mutations and subsequent tumors, and indicated that ADN has the potential for directly affecting cellular DNA. The results of the yeast recombination assay indicated that ADN may be a genotoxin but possibly not a direct-acting genotoxin. The assay uses two criteria: survival of the yeast cells and the recombination frequency. ADN may act through an oxidative challenge that may directly or indirectly damage nuclear DNA.

5.5 Teratogenicity and Reproductive Toxicity of Ammonium Dinitramide

Initial studies had shown that ADN is a female reproductive toxicant, causing implantation failure in Sprague-Dawley rats when it was administered during the preimplantation period of gestation. Male and female rats received drinking water containing 0.0, 0.2, 1.0, or 2.0 g ADN/L throughout the study. Mating occurred following 14 d of treatment. [463, 464].

The potential of ADN to produce alterations in paternal fertility, maternal pregnancy and lactation, and growth and development of offspring was studied in male and female rats that received drinking water treated with 200, 100, or 20 mg ADN/100 mL throughout the study [465]. Mating occurred following 14 d of treatment. All dams, one-half of the males, and representative pups were maintained for a total of 90 d of treatment. No mortality occurred in parental animals during the study. Adverse treatment-related decreases were noted in the maternal and paternal fertility indices, gestational indices, and live birth indices of the high-dose and mid-dose groups. Litter sizes in the high-dose and mid-dose groups were significantly smaller than those of the low-dose and control groups. Gross and histopathologic examination of the animals failed to identify the cause for the decrease in litter production in the high-dose and mid-dose dams. This study indicated that ADN is a reproductive toxicant. The no observable effect level (NOEL) was 29 mg/kg/day, the median dose of the low-level female rats.

In a study of preimplantation effects of ADN administered in the drinking water of Sprague-Dawley rats, in phase I, mated female rats were treated with 2 g/L ADN in their drinking water for 24, 48, 72, or 96 h before preimplantation embryos were harvested from the oviducts or uterine horns [466, 467]. In phase II, 2-cell embryos were harvested from the oviducts of superovulated mated B6C3F1 mice. The embryos were cultured for 72 h in medium supplemented with 0, 1, 4, 6, 10, or 20 mM ADN. The development of embryos cultured at <4 mM ADN was not affected compared to the control group. Culture in medium containing >4 mM ADN either slowed or arrested development of the embryos. These data suggest that the implantation failure seen in animals treated with ADN was due to embryo lethality.

A 90-d general toxicity/reproductive screen performed with ADN in rats at doses of 162, 103, 29, and 0.0 mg ADN kg⁻¹ d⁻¹ resulted in a distinct treatment-related adverse effect on litter production [468, 469]. Incidences of animals producing litters increased (1/11, 3/12, 12/12, and 11/12, respectively), and the mean number of pups per litter increased (7, 7, 16, and 15, respectively), both statistically significant differences. In a follow-up study, mated dams treated with ADN at the same doses and examined at gestation days 10 and 20 showed a similar effect in fetus loss as those in the reproductive screen. A pre-implantation versus post-implantation dosing regimen indicated that implantation is vulnerable to ADN effects during the pre-implantation period (gestation days 1–3). The pituitary gland was not specifically identified as a site of primary action, but serum progesterone was reduced by 27%, which may have resulted in reduced fertility.

The purpose of a follow-up study was to identify the mechanism(s) associated with implantation failure following exposure to ADN [470]. Mated female rats were treated with 2.0 g/L ADN in their drinking water for 24, 48, 72, or 96 h before preimplantation embryos were harvested from the oviducts or uterine horns. On gestation day 1 (GD-1), comparable numbers of morphologically normal two-cell embryos were harvested from the oviducts of the treatment and control groups. On GD-2, the development of the embryos harvested from the treated animals was either slowed or halted compared to the control embryos. By GD-4, 98% of the embryos harvested from the control group had developed to the morula or blastocyst stage; these were collected from the uterine horns. On GD-4 in the treated group, 41% of the harvested embryos remained at the two-cell to six-cell stage, and 59% were degenerate; 82% of these embryos were collected from the oviducts. These data suggest that the implantation failure seen in animals treated with ADN is due to embryo lethality.

A follow-up pre-implantation study indicated that ADN exerts its effects during the preimplantation period in rats during gestation days 1–3. The number of corpora lutea was consistent in each group, indicating that ovarian function was not affected by ADN treatment. Serum progesterone, prolactin, and estradiol were affected by ADN treatment compared to the control group. These hormone levels were also driven by maternal signals and normal implantation/embryonic development, so these data are somewhat ambiguous. The cause of implantation failure could occur at a number of

other points during the reproductive process: 1) oviduct mobility, which affects sperm, ova, and embryo transport, 2) uterine receptivity, or 3) ova/embryo lethality.

5.6 Aquatic Toxicity of Ammonium Dinitramide

Because ADN is intended as a replacement for AP, which turned out to be very persistent once it entered the groundwater and aquifers, the authorities made an extra effort to make sure that the AP replacement was not plagued by the same environmental problems as the oxidizer it was intended to replace. Thus, the aquatic toxicity of ADN and its photolysis products were tested under laboratory and field conditions.

The *Hydra attenuata* assay exposes both adult hydra and “artificial embryos” composed of disassociated hydra cells to test compounds to investigate developmental toxicity. Results from the hydra assay of ADN indicated that the minimal effective concentrations required to elicit a toxic response in the adult hydra and in the regenerating hydra were 750 mg ADN/L in both cases [471]. The developmental hazard index (A/D ratio) of 2.14 determined for ADN showed that ADN should not be considered a primary developmental toxin in the context of this assay.

In addition to ADN, the aquatic toxicity of *N*-GUDN, or FOX-12, was tested under the same conditions in the water flea, *Daphnia magna* [472]. The calculated acute toxicity (EC_{50}) value of ADN in the water flea was 405 mg/L after 48 h of exposure. With reference to the concentration of ammonium in the water, ADN is equally acutely toxic to *D. magna* as ammonium chloride. The solubility of FOX-12 in water is very low. A saturated solution of FOX-12 was not acutely toxic to the water flea. Additional work compared the aquatic toxicity of ADN and FOX-12 and their photolysis products to that of CL-20 and FOX-7 and used a different water flea (*Ceriodaphnia dubia*) as the test species [473]. The highest concentration tested (83 mg/L) of FOX-7 was not acutely toxic on its own or in combination with UV-A. The 48-h EC_{50} values for CL-20, FOX-12, and ADN were 6.4, 61, and 463 mg/L, respectively. In combination with UV-A, the toxicity was significantly enhanced for these three explosives.

5.7 Toxicity of Ammonium Dinitramide to Soil Bacteria

Cultured tests of bacteria in media amended with ADN indicated that dinitramide is not used by aerobic bacteria (*Pseudomonas*) as a sole source of nitrogen [474]. Similar results were obtained with pure cultures of anaerobic bacteria (*Pseudomonas denitrificans* grown under nitrate-reducing conditions). In contrast, *Pseudomonas aeruginosa* is able to convert dinitramide to nitrite, but only when NH_4^+ is present as a source of nitrogen. Dinitramide is biodegradable under anaerobic conditions when amended to a sulfate-reducing consortium taken from a lake sediment and sustained with lactate as the energy source.

6 Safe Handling of Ammonium Dinitramide

6.1 Disposal of Ammonium Dinitramide

During the first decade after ADN was discovered, chemists were mostly concerned about how to manufacture ADN in large quantities. Only after it became apparent that ADN might become a high-volume item did people start looking into the potential disposal problems when large quantities of ADN waste had accumulated in some locations. Propellant chemists had just witnessed the discovery of widespread pollution caused by perchlorates. ADN was intended as an environmentally friendly replacement for AP, and propellant chemists had to make sure that ADN would not cause the same type of environmental problems if it was spilled and found its way into the groundwater. For this reason, chemists started looking into safe disposal methods for ADN much earlier than their predecessors did for AP in the 1960s.

Demilitarization, neutralization, and disposal of energetic materials, including ADN and RDX, by hydrothermal hydrolysis methods in supercritical water has been studied extensively [475, 476]. This work was conducted with liquid water at autogenous pressures at temperatures over the range of 343–623 K (70–350 °C). The reactors included simple cuvettes placed in a thermostatted cell holder in either a UV spectrophotometer, sealed quartz bulbs, or stainless steel reactor bombs, and a spectrophotometric cell for work in the hydrothermal regime designed and built specially for this study. This has the advantage of water being a cheap reactant, with the ability to dilute the energetic materials to below the explosive threshold.

Various perchlorate cleanup methods are currently in use to remove perchlorate from surface waters, underground pollution plumes migrating in aquifers, and drinking water sources. One of these methods, bioremediation, has also been tested for disposal of dinitramide.

ADN can be destroyed through biodegradation by a mixture of denitrifying bacterial species. ADN was effectively mineralized in the anaerobic mixed culture, and the initial ADN concentration of 250 mg/L was reduced to non-detectable levels (>99% removal efficiency) by incubation under anaerobic conditions within 5 d [477]. Final products generated from anaerobic degradation of dinitramide by anaerobic metabolism were innocuous NH_4^+ , CH_4 , and CO_2 . The activity of denitrifiers was inhibited by high concentrations of ammonia generated through the degradation reactions of nitrite present as an additional contaminant.

Another method to destroy dinitramide and RDX is by reduction in alkaline solution (dispersion) at a pH of 12 with aluminum powder, accelerated by ultrasound sonication [114]. In the presence of 5 mg/mL aluminum powder and at a pH close to 12 (10 mM NaOH), 74% of the RDX and 86% of the ADN in near-saturated solutions decomposed within the first 20 min of sonication (20 kHz; 50 W). Sonication without Al powder and base caused minimal degradation of either RDX or ADN (~5–10%). Sonication at high pH in the presence of dispersed aluminosilicate, zeolite, alumina, or titanium dioxide also achieved only minimal degradation.

6.2 Environmental Fate of Ammonium Dinitramide

The environmental fate chemistry of ADN was investigated in detail to make sure that spilled ADN, a potential AP replacement, would not cause the same long-term problems as AP in the groundwater and aquifers [478]. The melting point of ADN is 365 K (92 °C), but it contrasts sharply with the melting point predicted with EPI Suite (518 K [245 °C]). However, empirical and modeled values for water solubility and vapor pressure agreed moderately well.

As part of such a study, the photolysis of ADN in natural waters was analyzed and modeled [267]. Photolytic rate constants for the photolysis of ADN were determined in order to better understand the fate of ADN in natural bodies of water. The validity of computer predictions was tested in field trials in Onondaga Lake, Syracuse, New York, USA. For summertime irradiation, half-life times of dinitramide anion ranged from ~6 min at the surface to ~15 years at a depth of 2 m.

ADN has a photolysis half-life on the order of minutes [479]. Based on a computer prediction, ADN is hydrolytically stable in water at all environmentally relevant pH levels from 2–10 at 25 °C, with an estimated half-life of about 370 years at pH 7. Bio-transformation of ADN in water and soil, under aerobic and anaerobic conditions, was not observed. Aqueous and solid ADN photolyzed in sunlight very rapidly, with half-lives of a few minutes in the summer and fall seasons, making photolysis the dominant loss mechanism for ADN in surface waters in all seasons. Quantum yields for ADN photolysis at 285–370 nm were 0.1 ± 0.02 for aqueous ADN solutions and 0.3–0.04 between 300 and 325 nm for solid ADN. Major decomposition products included nitrite and nitrate ions and N_2O , and their proportions were unaffected by oxygen, other cations present, or wavelength. Solid ADN gave NO, N_2O , N_2 , and nitrate ion. Co-metabolism with glucose did lead to rapid biodegradation of ADN over 65 h.

7 Safety Properties of Ammonium Dinitramide

Drop weight sensitivity, friction sensitivity, and electrostatic discharge (ESD) tests of four different types of ADN crystals were performed [30]. It was noted that powdered and prismatic crystalline ADN were less sensitive than a coagulated and a needle-type crystalline form. Drop weight test, friction test, DSC, bullet impact, ignition temperature by Wood's metal bath, and Koenen testing were reported in this paper [480]. The ADN used for this work was synthesized at the Swedish Defense Research Establishment (FOA) by a new method that is much less expensive than the conventional (SRI) method and is now in use by Bofors Explosives. The friction sensitivity of ADN is much lower than that of RDX. The impact sensitivity of ADN is of the same magnitude as that of RDX but varies a great deal with the shape of the particles; e.g., prilled ADN is nearly twice as insensitive as RDX. The reaction of ADN is also less violent. The ignition temperature was determined to be 160 °C (by Wood's metal bath). The ther-

mal stability, measured with microcalorimetry, showed that ADN is stable to at least 353 K (80 °C) and that impurities cause decreased thermal stability. The activation energy ($E = 158 \text{ kJ/mol}$) and frequency factor were determined from DSC data using the ASTM method E 698-79. It was also found that ADN in aqueous solution is sensitive to light.

To date, efforts to produce desensitized ADN and desensitized ADN propellants continue. In one such solicitation [481], the objective was to develop a process for desensitizing ADN or synthesis of an insensitive version of ADN containing comparable energy as prior art ADN. The objective would be to scale up the ADN desensitization process and produce material to conduct testing to demonstrate the desensitized nature of the newly developed ADN. One would then produce and test ADN-based formulations as AP replacements to show improved or at least comparable performance compared to currently fielded formulations. Such formulations could be used as propellants in base-bleed or rocket-assisted projectiles such as Excalibur 1b and XM1128, replacing AP-based base-bleed propellants with environmentally friendly ADN formulations.

Scaling up ADN production operations is not without hazards [482]. Three ADN synthetic methods were studied in order to estimate process safety for a planned increased production scale: from ammonia (method I), from urea (method II), or from potassium sulfamate (method III). The intermediates formed in these processes were identified, and their thermal stability was examined. DSC analysis showed that the intermediates in method II are unstable, readily decompose, and pose an explosion hazard. The intermediate in method III is more thermally stable and less hazardous than its counterparts in method II. The most suitable methods for large-scale processes are methods I and III. The preferred method for commercial large-scale ADN production, in terms of safety, would be method III.

7.1 Drop Weight Sensitivity of Ammonium Dinitramide

Although ADN has the advantage of lower friction sensitivity than RDX, ADN has the disadvantages of increased shock sensitivity and sensitivity to light and moisture. In the Bundesanstalt für Materialforschung und -prüfung (BAM) machine, the impact sensitivity of ADN was 50% point at 31 cm with a 2-kg weight, which was of the same magnitude as that of RDX but varied substantially with the shape of the particles. Prilled ADN was only half as sensitive as RDX and had a 50% point at 59 cm with a 2-kg weight [4].

The effect of hygroscopicity of ADN on its sensitivity was studied with samples conditioned at various controlled relative humidity levels ([123]; Table 24). For dry ADN, the investigators found that ADN is slightly more sensitive to impact and friction than RDX. ADN samples containing 0.5% H_2O were less sensitive than ADN containing only 0.02% H_2O . ADN containing only 0.3% hexamine as stabilizer was not much

different, but prilled ADN containing 2% hexamine was much more friction sensitive in the ABL friction test machine, close to the sensitivity of pentaerythritol tetranitrate (PETN).

Table 24: Drop weight, friction, and electrostatic discharge sensitivity of ADN.

Sample	Impact, 2.5 kg, 50% point, cm drop height	ABL friction, 50% point, lb _f	ESD sensitivity, 0.25 J
Neat ADN			
Dry (0.25% H ₂ O)	11–12	295–355	10/10 no fire
Not quite dry (0.5% H ₂ O)	11–12	295–355	10/10 no fire
Prilled ADN			
0.3% hexamine	11–12	295–355	10/10 no fire
2% hexamine	11	87	10/10 no fire

For comparison: HMX impact 20 cm, ABL friction 398 lbf

Data source: Chan et al. [123]

A high-speed photographic study was performed of the rapid deformation and possible initiation of ADN and GAP by drop-weight impact [483]. ADN was found to be more impact sensitive than AP, and it can be sensitized by both hard high-melting point grits (60-micron borosilicate or Pyrex glass shards) and brittle polymers, but high-density polyethylene powder would suppress deflagration.

Mixtures of ADN with CL-20 (30/70) have 10% more expansion energy than HMX but are very sensitive, comparable in sensitivity to lead azide [484].

ADN samples with a melting point of 363–365 K [90–92°C], decomposition point of 525 K [252°C], and density of 1.80 g/cm³ had an impact sensitivity H 50% of 24 cm with a 2-kg weight and a sample size of 30 mg [79].

The impact sensitivity of ADN was listed as 5 Nm (as synthesized) and 7.5 Nm (after emulsion crystallization) [105]. It is assumed that this is the 50% sensitivity point.

Both a Bureau of Explosives Impact Machine and a BAM Fallhammer apparatus were used in side-by-side tests to determine the sensitivity of ADN crystals, prills, and two propellants to drop-weight impact [165]. In the Bureau of Explosives impact test, about 10 mg of sample was subjected to an impact of a 3.6-kg mass dropped from a height of 102 mm. A positive reaction was recorded when the impact produced an audible report, visible flame, or smoke. Ten trials were performed on ten fresh samples while the drop height was held constant. The sample was considered as impact sensitive when positive events were observed in at least five out of ten trials. In the Bureau of Explosives Impact Machine, ADN crystals gave five positives out of ten, and ADN prills gave seven positives out of ten trials and thus is marginally sensitive. For the BAM Fallhammer Impact Test, about 40 mm³ of ADN was subjected to the impact of a mass (1 or 5 kg) dropped from a height of 15–50 cm. The limiting impact energy

for each sample was determined to be the lowest energy at which an explosion was obtained from at least one out of 6 six trials. An explosion was characterized by an audible report and/or a deformation of the impact assembly. Samples were considered impact sensitive if the limiting impact energy was equal to or less than 2 J. In the case of ADN in the BAM Fallhammer apparatus, the lowest energy at which a reaction was obtained was 4 J for both crystals and prills, and that is above (safer than) the 2-J limit. Some mixtures of ADN with solid fuels were much more impact sensitive than ADN by itself [485].

7.2 Friction Sensitivity of Ammonium Dinitramide

The friction sensitivity of ADN is much lower than that of RDX [4]. In the BAM friction sensitivity tester, the 50% point was above 35 kg_f (343 N). ADN samples with a melting point of 363–365 K (90–92 °C) and a density of 1.80 g/cm³ had a 14% friction sensitivity of 2.45 MPa (at 339 K [66 °C] with a 20-mg sample) [79]. Other sources report the friction sensitivity (point of beginning reaction) of ADN as 72 N [105]. For comparison, the impact sensitivity of the same sample of ADN was 5 Nm. The friction sensitivity of ADN was listed as >350 N [127]. A stabilized sample of ADN had a friction sensitivity of 54 N [110]. For comparison, the impact sensitivity of the same sample of ADN was 4 Nm. Additional friction sensitivity data are shown in Table 24.

7.3 Electrostatic Discharge Sensitivity of Ammonium Dinitramide

The ESD sensitivity of ADN is 0.45 J. The sensitivity to electrostatic discharge of ADN crystals, the prills, and two propellants was determined using an ESD apparatus manufactured by Franklin Applied Physics [165]. About 30 mm³ of sample was placed in a sample holder made from a nylon washer backed with a stainless steel disk. The sample holder was closed with a layer of adhesive tape. The limiting energy for ESD initiation was determined by subjecting fresh samples to sparks of varying energies. The test was also repeated with an open sample holder. Positive reaction was defined when the sample burned completely. Samples with limiting energies below 25 mJ were considered to be sensitive to ESD. All four ADN samples had limiting ignition energies greater than 156 mJ, and therefore they are not sensitive to ESD in either the closed or open sample holder. Additional ESD sensitivity data are given in Table 24.

7.4 Explosive Performance of Ammonium Dinitramide

7.4.1 Detonation Velocity of ADN

The detonation velocities of ADN were determined using cylinders of three different diameters of pressed ADN [484]. These were lightly confined in tubes of plexiglass and further enclosed in a larger-diameter tube of plexiglass. The cylinders of ADN were pressed axially to a density of 1.568 g/cm^3 , with a diameter of 25.1 mm and length 25 mm, and similarly to a density of 1.658 g/cm^3 for the larger cylinder with a diameter of 43.9 mm and a length of 40 mm. A 10-mm charge, similar in design to those described above, was also fired in an effort to determine the critical diameter, but no reaction at all could be measured. One can therefore assume that the critical diameter is $10 < d_{\text{crit.}} < 25.1\text{ mm}$. The detonation velocity in the 25-mm charge was $5.013 \pm 0.0407\text{ mm}/\mu\text{s}$, and the detonation velocity in the 43.9-mm charge was $5.260 \pm 0.0630\text{ mm}/\mu\text{s}$. Table 25 gives a comparison of the calculated and measured detonation properties of ADN.

Table 25: Detonation properties of ADN.

Density g/cm^3	Diameter mm	Detonation properties, measured		Chapman-Jouguet detonation properties, calculated	
		Velocity $\text{mm}/\mu\text{s}$	Pressure GPa	Velocity $\text{mm}/\mu\text{s}$	Pressure GPa
1.568	25	5.013 ± 0.0407	~ 16	6.950	16.45
1.658	43.9	5.260 ± 0.0630	18 ± 2	7.310	18.8

Data source: [484]

If you have some spare low-carat diamonds in your jewelry box and want to get rid of them really fast, try to mix them with ADN and measure the detonation velocity, as was done with ADN and nano-diamonds [486]. Detonation velocities of confined cylinders of melt-cast ADN/ZnO (99.5/0.5 by weight), ADN/nano-diamond/ZnO (92.4/

Table 26: Experimental and theoretical detonation characteristics of ADN.

Density, g/cm^3	Detonation velocity, m/s		Chapman-Jouguet pressure, GPa		Charge diam- eter, mm	References
	Experimental	Theoretical	Experimental	Theoretical		
1.568	5013 ± 60	6950	16.0	16.45	25.1	[487]
1.658	5260 ± 80	7310	18 ± 2	18.8	43.9	[487]
1.820	Failed	7960	Failed	23.6	43.9	[487]
		8074		23.72		[7]

7.2/0.4), ADN/AN/ZnO (95.5/4.0/0.5); and ADN/AN/ZnO/nano-diamond (88.0/4.5/0.5/7.0) ranged from 3.9 to 4.5 mm/ μ s in 1.3-cm diameter samples confined by steel and a 2.5-cm diameter ADN/AN/ZnO unconfined cylinder. Measured detonation velocities of ADN at different loading densities and charge diameters gave fairly good agreement with calculated values (Table 26).

7.4.2 Critical Density of ADN Detonations

Explosives can be classified into two types. For compounds of the first type, which includes high explosives (TNT, RDX, and others), the detonation velocity (D) increases linearly with an increase in density (ρ). Explosives of the second type are characterized by **non-monotonic** dependence $D(\rho)$. The detonation velocity for this type first increases with density and then passes through a maximum, and then detonation fails to propagate past a certain distance from the booster. These explosives of the second type are referred to as *non-ideal* explosives. The second type of explosives includes individual chemical compounds (AN, AP, **ADN**, nitroguanidine, HN) and many explosive compositions of the oxidant/fuel type. The reasons for such a behavior of $D(\rho)$ for individual explosives and explosive compositions are different [488]. An increase in density to 1.4–1.5 g/cm³ leads to the failure and termination of detonation propagation in ADN. This limit is diameter dependent.

7.4.3 Critical Diameter of ADN Detonations

The critical diameter of lightly confined ADN is $10 < d_{\text{crit.}} < 25.1$ mm [484].

7.4.4 ADN-Based Explosives

ADN is not a useful explosive by itself, but ADN is a very energetic oxidizer and can be combined with fuels or other explosives to form melt-castable explosives as potential replacements for TNT, tritonal, and amatol. The low melting point of ADN is usually a disadvantage for many of its applications as rocket propellant, but for melt-cast explosives, the low melting point makes it easier to safely process and pour the molten material.

One family of such melt-castable explosives is described in [489], where molten ADN forms the matrix in which other finely divided (but insoluble) explosives (RDX, HMX, CL-20) and metals (aluminum) can be suspended.

The shape of ADN for explosives is preferably prilled (spherical) particles. Although porosity of the prills may be undesirable for solid propellants, it may be acceptable for prills that are intended to be filled with organic oils and used as explosives [115]. See also [490]. Viton is a suitable binder for pressed ADN-based explosives [491, 492]; see Table 27.

Small-scale detonation velocity and plate-push tests were performed on ADN and aluminum (ADN/Al) pressed-powder composites [493]. The effects of varying the Al

Table 27: Explosive properties of ADN and pressable ADN/Al-based explosive compositions.

Composition	ρ , g/cm ³	D , km/s	$\rho/\rho_{\max}$, %
ADN	1.69	4.24	92.2
ADN	1.604	4.19	87.2
72/25 ADN/Al (3 μ m Al)	1.794	4.10	90.5
73/23/3 ADN/Al/Viton (50 μ m Al)	1.714	5.03	86.3
97/3 ADN/Viton	1.752	4.25	95.0
97/3 ADN/Viton	1.735	4.06	94.0

Data source: [491]

particle size in this mixture between 50 nm and 60 μ m revealed a large particle size dependency on the observed detonation velocities and the plate-push terminal velocities. The calculated detonation velocity for ADN was nearly twice the measured value. This discrepancy was explained on the basis that the major products of ADN decomposition are HNO₃ and NH₃ and that H₂O is only a minor constituent.

If AN in common emulsion explosives (which are typically sensitized by the addition of glass microballoons) is replaced with ADN, the brisance of the resulting explosive is increased by 60% [494]. That is comparable to or even higher than the explosive output of maximum-density trotyl.

Thermodynamic calculations of explosive performance of emulsion explosives containing energetic additives – propellants of various sorts and ADN – showed that the additives improved the properties of explosives: In the ideal-detonation approximation, AN-water-propellant-aluminum mixtures provided detonation velocities greater than 7000 m/s and detonation pressures of about 18 GPa [495]. ADN is more efficient: Replacement of AN in a model AN-water-saturated hydrocarbon-oleic acid mixture by ADN and replacement of glass microballoons by propellant enhanced the work function of industrial emulsion explosives by 60%.

The detonation velocity of melt-cast ADN was measured at charge diameters of 25–100 mm [193]. The detonation velocities were as follows: 25 mm, no detonation; 40 mm, 4.3 mm/ μ s; 60 mm, 5.4 mm/ μ s; 100 mm, 6.0 mm/ μ s. All data were taken at a density of 1.72 g/cm³. The 25-mm charge did not detonate, which indicates that the critical diameter for cast ADN is between 25 and 40 mm. The radius of the detonation curvature is dependent on the charge diameter and was 59, 76, and 137 mm, respectively. A cylinder test with a 51.95-mm inner diameter, 5-mm wall thickness and 300-mm length was also conducted. FOI Sweden has developed a method for melt-casting ADN that enables the melt casting of multi-kilogram charges at up to 99% of theoretical maximum density. After preliminary work with small charges, the casting process was scaled up to 6-kg charges. ADN proved to be relatively easy to cast when 1% of finely divided magnesium oxide (MgO) was added as nucleation kernels and stabilizer. It was found that melt casting in vacuum produced charges with lower densities. A number of basic parameters of importance to melt-casting

ADN were also determined: Shrinkage on solidification was 14%. A comparison with thermochemical equilibrium calculations (Cheetah 2.0) showed a large discrepancy between measured and predicted detonation velocity and Chapman-Jouguet (CJ) pressure, and the conclusion was that ADN is a strongly non-ideal explosive or even behaves as a non-CJ explosive. The detonation velocity in the cylinder test was low enough that CJ conditions at the front were probably never established.

ADN in mixture with aluminum powder makes a very powerful explosive [487]. The critical pressure of explosion initiation of ADN by itself is 0.80 ± 0.05 GPa for crystalline ADN and 1.12 ± 0.04 GPa for prilled ADN. The density at which a maximum detonation velocity was measured was between 1.4 and 1.6 g/cm³.

A melt-casting technique for ADN and ADN/aluminum was developed for cast explosive charges [139]. ADN proved relatively easy to cast when 1% of magnesium oxide was used as a stabilizer and crystallization kernels. Densities of ADN/MgO 99/1 were 92 to 97% of theoretical mean density, and those of ADN/Al/MgO 64/35/1 were between 95 and 99% of theoretical mean density. Sedimentation of Al in the melt was prevented and particle wetting was ensured by selecting a suitable particle size for Al. No gelling agents or surfactants were used to retard the settling of the Al particles. See also [496].

8 Applications of Ammonium Dinitramide

ADN is a useful oxidizer for solid propellants and monopropellants. Unconfirmed information indicated at one time that the Soviet Union may have fielded a weapon with an ADN-based solid propellant shortly after this oxidizer was discovered. No other fielded solid propellant application has become known in the interim. While HNF has insufficient thermal stability and a tendency to self-accelerating decomposition and therefore is less likely to ever find application in a solid propellant formulation, ADN can be qualified as medium-stable at lower temperatures, similar to nitrocellulose-based products. One must be aware that ADN also shows self-accelerated decomposition, but it can be stabilized. Some stabilizers are very effective. From the results presented, one can conclude that ADN has a chance to replace AP in propellants designed for selected applications [24]. A “universal” replacement application does not seem realistic at this time. Special measures such as coating of ADN particles may improve the situation, but the limited inservice temperature range will not be changed [497, 498].

ADN-based monopropellants can take credit for being the key ingredient in the first “green” less-toxic monopropellant to have flown in a satellite propulsion application (see *Encyclopedia of Monopropellants*, chapter “Ammonium Dinitramide-Based Monopropellants”).

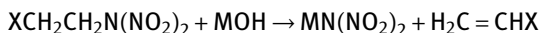
9 Alkali Metal Dinitramide Salts

It is unlikely that alkali metal dinitramide salts will ever be used as rocket propellants. However, they are under consideration as replacements for KClO_4 (less corrosive exhaust products) and KNO_3 (more energetic) in pyrotechnic formulations such as igniters and charges for pyrovalves [499]. In the past, some alkali metal dinitramides have been used as intermediates in the preparation of ADN, but usually the preparations now go the opposite way because ADN is now the most readily available dinitramide salt (although it is rarely listed in chemical supply catalogs).

9.1 Production of Alkali Metal Dinitramide Salts

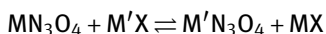
Alkali metal dinitramides can be prepared by at least three different methods [500]:

1. Reaction of metal hydroxides with β -substituted *N*-alkyl-*N,N*-dinitramines in ethanol:



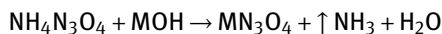
where $\text{X} = -\text{CN}, -\text{CHO}, -\text{COR}, -\text{COOR}$, and $\text{M} = \text{K}, \text{Rb}, \text{Cs}$. This reaction works best for potassium, rubidium, and cesium dinitramide, which are poorly soluble in ethanol.

2. Cation exchange starting with potassium dinitramide obtained by the method above:



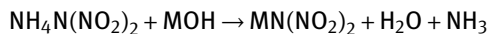
If the silver dinitramide is available, it can be reacted with any metal chloride or metal iodide to shift the equilibrium in the desired direction because the silver halogenide will precipitate.

3. Treatment of ADN with the metal hydroxide, allowing the liberated ammonia to escape:



Sodium, potassium, rubidium, and cesium dinitramide were synthesized in yields >70% by adding the corresponding alkali metal hydroxide starting from commercially available ADN, which was dissolved either in water or in methanol [501, 502]. First, a highly concentrated ADN solution (4.29 mol/L) was prepared. The synthesis of the salts was then done by adding the corresponding alkali metal hydroxide dissolved in

water or methanol to the ADN solution. The basic equation for the metathetical reaction is as follows:



where M = Na, K, Rb, Cs

The equilibrium can be shifted to the right by driving off the ammonia as a gas. Removal of water and liberated ammonia gas by freeze-drying gave the salts as white powders. Recrystallization gave the salts as crystalline plates (NaDN from nitromethane) or needles (KDN, RbDN, and CsDN from methanol). The lithium salt could not be recrystallized, and the freeze-dried material was used directly for analysis. The purification by recrystallization can be carried out from a highly concentrated water solution or in methanol as a solvent. Three of the alkali metal dinitramides (K, Rb, Cs) could be recrystallized from saturated water solutions. The yields of small (214 mmol) batches were 71–88%. The procedure of recrystallization out of a saturated water solution did not work for the very hygroscopic $\text{NaN}(\text{NO}_2)_2$ compound. It could be crystallized only by using the freeze-drying method described in the literature. The dinitramide salts were characterized by determining the melting point, by elemental analysis, by DSC, TGA (see more to follow), IR spectroscopy, and light microscopy investigations of the crystal shape. The recrystallized KDN consisted mainly of small cubes with a typical edge length of 0.2–0.3 mm. The results were in good agreement with the values mentioned in the literature. However, the DSC and TGA measurements showed some significant differences from previously published results. The X-ray structure analysis of $\text{RbN}(\text{NO}_2)_2$ showed an isomorphic structure in comparison to $\text{CsN}(\text{NO}_2)_2$.

In conventional metathetical reactions, product separation is based on solubility product differences (often using silver iodide as the insoluble product), and the resulting products are often impure and require purification by recrystallization. A new approach to product separation relies on the formation of an unstable, volatile by-product, such as ammonium methoxide $\text{NH}_4^+\text{CH}_3\text{O}^-$. This method provided very pure and anhydrous products in high yield and was demonstrated successfully for the syntheses of anhydrous cesium salts such as cesium perchlorate and cesium dinitramide [503].

Operating parameters in the synthesis of potassium dinitramide, an intermediate in the ADN synthesis, were optimized to reduce the costs of the ADN synthesis [504]. The optimal conditions for the synthesis of KDN, including nitrating agent:reagent molar ratio, nitration time, and temperature, were determined, and KDN was obtained in an approximate 48% yield.

9.2 Physical Properties of Alkali Metal Dinitramide Salts

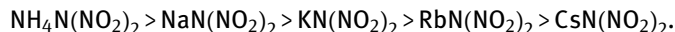
Tables 28 and 29 present a summary of melting points of metal dinitramides and their CAS Registry Numbers.

Table 28: Melting points and CAS Registry Numbers of alkali metal dinitramide salts.

Compound	CAS RN	Melting point		References
		K	°C	
Li N(NO ₂) ₂	154962-43-3	424	151	[505]
		431	158 (dec.)	[506]
Li N(NO ₂) ₂ •H ₂ O		341–346	68–73	[500]
Na N(NO ₂) ₂	160150-82-3	370	97	[505]
		374	111	[506]
		374–380	101–107	[500]
K N(NO ₂) ₂	140456-79-7	401	128	[505]
		400	127	[2]
		403	130	[376]
Rb N(NO ₂) ₂	162760-50-1	377	104	[505]
		381	108	[506]
Cs N(NO ₂) ₂	140456-77-5	355	82	[505]
		360	87	[164]
		361	88	[506]
For comparison:				
[NH ₄][N(NO ₂) ₂]	140456-78-6	365.6	92.44	[102]

Cesium dinitramide has a melting point of 360 K (87°C) followed by the onset of exothermic decomposition at 448 K (175°C) (as observed by DSC). Its density is 3.05 g/cm³. The dinitramide ion in Cs N(NO₂)₂ is stable to base. Cesium dinitramide dissolved in water has a UV maximum at 284 nm with an absorption coefficient of $\epsilon(\text{H}_2\text{O}) = 4.24 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ [501].

The solubility of the alkali metal dinitramides in water decreases in the following order:



The densities of alkali metal dinitramides are summarized in Table 30.

Table 29: Melting temperatures of the alkali metal dinitramides compared with literature data.

Substance	Small scale		Large scale		Lukyanov et al. [78]		Pavlov and Nazin [321]		Konkova et al. [201]	
	K	°C	K	°C	K	°C	K	°C	K	°C
NaN(NO ₂) ₂	<363	<90	—	—	374–380	101–107	384	111	374–380	101–107
KN(NO ₂) ₂	398–402	125–129	399–404	126–131	400–404	127–131	400	127	397–399	124–126
RbN(NO ₂) ₂	378–380	105–107	375–379	102–106	375–379	102–106	381	108	—	—
CsN(NO ₂) ₂	357–360	84–87	359–361	86–88	358–360	85–87	361	88	358–361	85–88

Data source: [502]

Table 30: Densities of alkali metal dinitramides.

Compound	Density, g/cm ³	References
LiN(NO ₂) ₂	2.15–2.19	[501]
LiN(NO ₂) ₂	2.175	[195]
NaN(NO ₂) ₂	2.09	[501]
KN(NO ₂) ₂	2.25	[501]
KN(NO ₂) ₂	2.201	[195]
RbN(NO ₂) ₂	2.63	[501]
CsN(NO ₂) ₂	3.07	[501]
CsN(NO ₂) ₂	3.055	[195]
For comparison:		
NH ₄ N(NO ₂) ₂	1.81	[501]

9.2.1 Optical Properties of Alkali Metal Dinitramide Salts

The vibrational IR spectra and electronic spectra of KN(NO₂)₂ and other salts (Na, Li, NH₄, Fe, Ag, Mn, Mg, Rb, guanidinium [⁺C(NH₂)₃]) were first reported by Shlyapochnikov et al. [249] and later refined by the same author Shlyapochnikov et al. [211]. Dinitraminic acid salts of metal ions (with the exception of the mercury salt) have an ionic structure. Each possesses characteristic absorptions in the IR (1520–1540, 1430, 1180–1210, 1010–1035 cm⁻¹) and the UV ($\lambda_{\text{max}} = 223$ nm and 285 nm with a shoulder at 335 nm; $\epsilon = 5640$ L mol⁻¹). The IR and Raman spectra of solutions and melts of the salts indicate a C_{2v} symmetry. The complication of the spectra in the crystalline phase was explained by restructuring of the anion, which reduces its symmetry and makes the two nitro groups non-equivalent.

However, a KN(NO₂)₂ sample measured in the U.S. gave different results ([244]; Figure 73). The complication of the spectra in the crystalline phase has been explained by restructurization of the anion that reduces its symmetry and makes the nitro groups non-equivalent.

A comparison of the Christe et al. [244] results with those given previously by Shlyapochnikov for KN(NO₂)₂ shows significant discrepancies. Raman bands at 583 cm⁻¹ in the aqueous solution and at 640 and 204 cm⁻¹ in the solid state were not observed in the U.S. and most likely do not belong to the KDN sample. The previous polarization data given for the 1520 and 1436 cm⁻¹ bands are reversed: The 1520 cm⁻¹ band should be polarized, and the one at 1436 cm⁻¹ should be depolarized. Other Raman frequencies, relative intensities, and polarization ratios were also in poor agreement with the U.S. KDN data, while the agreement of the corresponding infrared data was somewhat better.

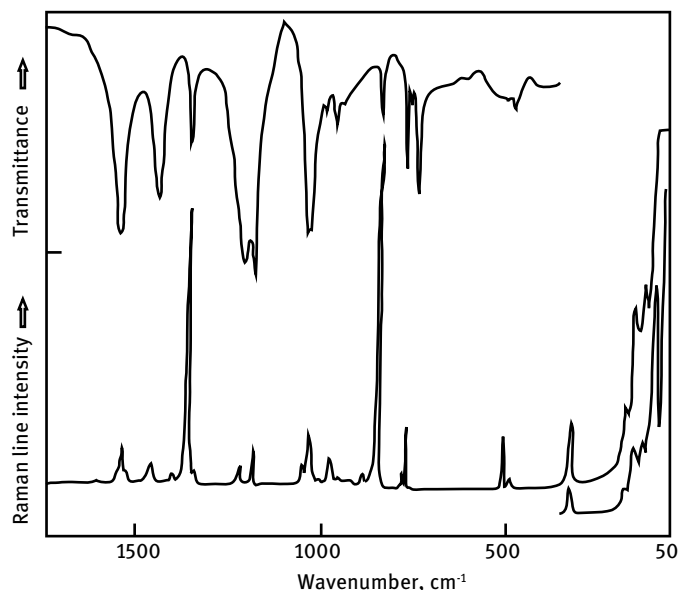


Figure 73: IR (top) and Raman (bottom) spectra of solid KDN. (Reprinted and modified from [244] with permission from © 1996 American Chemical Society.)

Some of the Shlyapochnikov assignments were later reexamined by Berger et al. [502]. According to Berger, the measured IR spectrum of $\text{KN}(\text{NO}_2)_2$ was comparable to the spectrum given by Shlyapochnikov et al. [210]. All described peaks were confirmed with a deviation of $\pm 5 \text{ cm}^{-1}$. The only deviation was a peak at 490 cm^{-1} , which was found by the Russian authors at a wavelength of 480 cm^{-1} . The IR spectrum of a Swiss $\text{KN}(\text{NO}_2)_2$ sample showed an additional small peak at a wave number of 1384 cm^{-1} . This could be the signal of the $-\text{O}-\text{H}$ vibration due to humidity. The IR spectrum of pure ADN did not show such a signal. A third type of IR spectrum of KDN is shown in Figure 74. The following assignments were made to the eight absorption bands seen in this spectrum (Table 31).

Similar salts are formed between methylnitroamine (methylnitramine) and alkali or alkaline earth metals. The IR and Raman frequencies of the K^+ , Rb^+ , Cs^+ , Me_4N^+ , Ca^{2+} , Ba^{2+} , and Mg^{2+} salts of MeNHNO_2 were not appreciably affected by the cation or by transition from the crystalline state to solution [507].

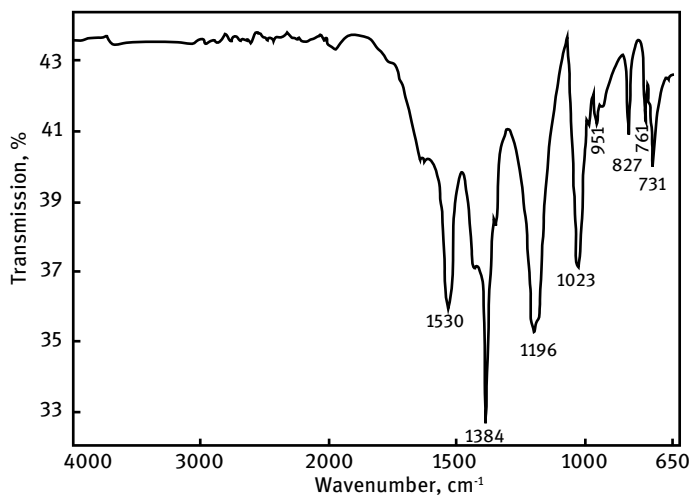


Figure 74: FTIR spectrum of potassium dinitramide. (Reprinted and modified from [58] with permission granted by Dr. Santhosh 8-Feb-2021.)

Table 31: Characteristic absorption peaks in IR spectrum of KDN.

Assignment	Wavenumber (cm ⁻¹)
ν_{as} NO ₂ in phase	1530
ν_s NO ₂ in phase	1384
ν_s NO ₂ out of phase	1196
δ_{sciss} NO ₂ in phase	827
δ_{sciss} NO ₂ out of phase	761
δ_{rock} NO ₂ out of phase	731
ν_{as} N3	1023
ν_s N3	951

Data source: [58]

9.2.2 Thermodynamic Properties of Alkali Metal Dinitramide Salts

The enthalpies of formation and the enthalpies of solution in water of three alkali metal dinitramides are summarized in Table 32. Similar data are available for ammonium, guanidinium, and mono- and tri-aminoguanidinium dinitramides (See Table 40). Substitution of nitrate ion by dinitramide ion increases the enthalpy of formation of the alkali metal salts by approximately 230 kJ/mol (55 kcal/mol) (more positive, i.e., less-negative number). See also [508].

Table 32: Enthalpies of formation and enthalpies of solution of alkali metal dinitramides.

Compound	Enthalpy of formation		Enthalpy of solution	
	kJ/mol	kcal/mol	kJ/mol	kcal/mol
Sodium dinitramide	-230 ± 0.5	-54.94 ± 0.13	24.8 ± 0.04	5.93 ± 0.01
Potassium dinitramide	-264 ± 0.5	-63.14 ± 0.13	47.2 ± 0.08	11.28 ± 0.02
Cesium dinitramide	-274 ± 0.8	-65.38 ± 0.18	50.7 ± 0.08	12.12 ± 0.02

Data source: [201]

9.2.3 Molecular Structure of Alkali Metal Dinitramide Salts

The crystal structures of lithium, potassium, and cesium dinitramides are summarized in Table 33, as well as in comparison to ADN [195].

Table 33: Crystal structures of alkali metal dinitramides and ADN.

Compound	$\text{LiN}(\text{NO}_2)_2$	$\text{KN}(\text{NO}_2)_2$	$\text{CsN}(\text{NO}_2)_2$	For comparison: $\text{NH}_4\text{N}(\text{NO}_2)_2$
System	Tetragonal	Monoclinic	Orthorhombic	Monoclinic
Space group	$I4_1/a$	$P2_1/n$	$Pc2_1/b$	$P2_1/c$
$a, \text{\AA}$	5.9164(4)	6.614(1)	7.740(2)	6.914(1)
$b, \text{\AA}$	5.9164(4)	9.280(2)	9.059(2)	11.787(3)
$c, \text{\AA}$	19.712(3)	7.198(1)	14.818(4)	5.614(1)
$\beta, ^\circ$	—	97.58(1)	—	100.40(2)
$V, \text{\AA}^3$	689.99(12)	437.94(13)	1038.9(4)	450.0(2)
Z	8	4	8	4
$D_c, \text{g/cm}^3$	2.175	2.201	3.055	1.831

Data source: [195]

With the exception of the lithium salt, there are similarities in the structural parameters of the dinitramide ions. All have inequivalent N—N and N—O bond distances and nitro groups, which are twisted from the central NNN plane by varying amounts. Both the N—N distances and the NNN angles are intermediate between expected values for an sp^3 -hybridized or sp^2 -hybridized central nitrogen atom. It has been postulated that the twisting of the nitro groups is necessary to maximize the potential for conjugation with the lone pairs of the central nitrogen atom.

Diaquo-dinitramidato-lithium(I), $[\text{Li}(\text{N}_3\text{O}_4)(\text{H}_2\text{O})_2]$ and pyridinium dinitramide, $[\text{C}_5\text{H}_6\text{N}^+][\text{N}_3\text{O}_4^-]$, differ significantly in their cation-anion contacts [509]. The Li⁺ atom of the first is coordinated by two O atoms of the dinitramide anion in a chelate and by four additional water molecules, with the Li and central N atom of the anion on a twofold rotation axis. The pyridinium cation of the second exhibits a contact with the dinitramide anion via an intermolecular N—H $\cdots$ N hydrogen bridge. These

interactions are comparable to those found in anhydrous lithium dinitramide and ADN salts.

9.3 Chemical Properties of Alkali Metal Dinitramide Salts

9.3.1 Reactions of Alkali Metal Dinitramide Salts

The reactions of ADN with metals in solid propellants were discussed in Section 4.11.3.1. Additional applications of such mixtures with alkali metal dinitramides are in pyrotechnic igniters.

9.3.2 Thermal Stability of Alkali Metal Dinitramide Salts

The thermal behavior and hazards assessment of lithium, sodium, potassium, rubidium, and cesium dinitramide were studied using differential scanning calorimetry, thermal gravimetric analysis, differential thermal analysis, and hot-stage microscopy [501]. The metal dinitramides quantitatively decomposed to their respective metal nitrates, which were identified by mass spectrometry and X-ray diffraction [510]. The thermal stability study of the dinitramide salts of lithium, sodium, potassium, rubidium, and cesium revealed a complex set of DSC exothermic decays with the exception of the lithium salt, which showed two simple exothermic decomposition reactions [505]. The DSC trace of lithium dinitramide (LiDN) displayed two exotherms at 398 K (125 °C) (−298 J/g) and 455 K (182 °C) (−101 J/g). The melting endotherm occurred between the two exotherms at 430 K (157 °C) (+83 J/g) and corresponds to the melting of an initial decomposition product rather than LiDN itself. Sodium dinitramide (NaDN) gave a melting endotherm at 370 K (97 °C) (+54 J/g), followed by major and minor exotherms at 429 K (156 °C) (−946 J/g) and 483 K (210 °C) (−105 J/g) respectively. The potassium dinitramide (KDN) DSC trace displayed a large endotherm at 401 K (128 °C) (+96 J/g) corresponding to melting of KDN; however, it was preceded by a smaller exotherm (378 K [105 °C], −10.5 J/g) and endotherm (381 K [108 °C], +5.3 J/g). The observed endotherm at 381 K (108 °C) corresponds to the melting point of a KDN/KNO₃ eutectic. All five alkali metal dinitramide salts thermally decomposed to the equivalent nitrate salt as evidenced by DSC melting endotherms and TGA stoichiometric mass losses. Physical changes due to thermal heating were able to be followed by hot-stage microscopy. Thermal decay was usually accompanied by gas evolution.

All dinitramide salts, with the exception of LiDN, reacted violently under *temperature of ignition* test conditions (duplicate runs of 200-mg samples heated at 5 °C/min). Ignition occurred at 396–431 K (123–158 °C) for sodium, potassium, rubidium, and cesium dinitramide and was accompanied by an explosion or smoke. LiDN showed no ignition at temperatures up to 673 K (400 °C), but DSC for LiDN showed exothermic behavior at temperatures of 398 K (125 °C), yet no violent ignitions were observed under *temperature of ignition* test conditions.

DTA and X-ray photoelectric spectroscopy were used to investigate the thermal stability of KDN [511]. It was found that the decomposition product KNO_3 formed a eutectic system with KDN and decreased the liquefaction temperature of KDN. In continuation of this work, the thermal decomposition of KDN was investigated by DTA and FTIR [512]. The results showed that the decomposition of KDN in the solid state is different from that in the liquid state. The main condensed-phase product of the solid-state decomposition is KNO_3 . Some KNO_2 can also form. The melting point of the KNO_3 /KDN eutectic is about 382 K (109 °C).

The thermal stability of $\text{NaN}(\text{NO}_2)_2$, $\text{KN}(\text{NO}_2)_2$, $\text{RbN}(\text{NO}_2)_2$, and $\text{CsN}(\text{NO}_2)_2$ was measured by DSC and TGA [502]. The measured endothermicities of the dinitramide salts (melting of the dinitramide salts and the corresponding nitrates) were in good agreement with older literature data. However, some exothermicities showed significant differences compared with literature data. It was shown that the crystal modification influences the exothermic decomposition. Different crystallization and drying processes give crystals of varying stability. All dinitramide salts, with the exception of LiDN, reacted violently under temperature of ignition test conditions (duplicate runs of 200-mg samples heated at 5 °C/min). Ignition occurred at 396–431 K (123–158 °C) for sodium, potassium, rubidium, and cesium dinitramide and was accompanied by an explosion or smoke. LiDN showed no ignition at temperatures up to 673 K (400 °C).

The thermogram of $\text{KN}(\text{NO}_2)_2$ (Figure 75) showed a melting endotherm peaking at 398 K (125 °C), a decomposition exotherm peaking at 518 K (245 °C), and KNO_3 melting at 611 K (338 °C) [502]. According to the literature, KNO_3 has a melting temperature of 607 K (334 °C). Further investigations showed that the decomposition products of $\text{KN}(\text{NO}_2)_2$ are KNO_3 (90 mass-%) and KNO_2 (10 mass-%). A DSC thermogram of KDN at the heating rate of 10 K/min showed two endothermic peaks at 401 K (128 °C) and 611 K

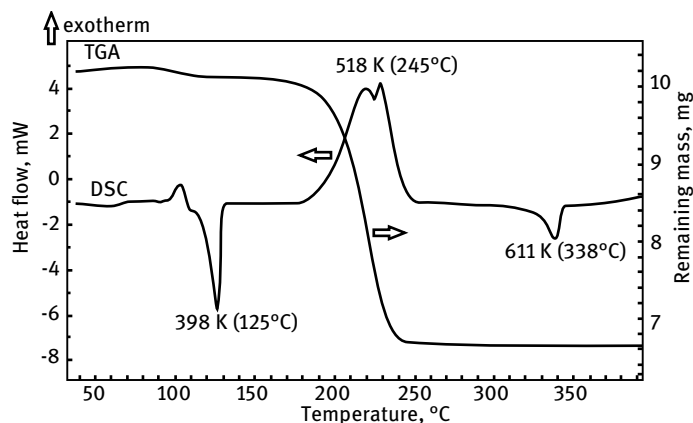


Figure 75: DSC thermogram of KDN under argon. Heating rate 5 °C/min. (Republished and modified from [502], with permission of John Wiley & Sons Books; permission conveyed through Copyright Clearance Center Inc.)

(338 °C), the first one corresponding to melting of KDN (127 °C) and the second one to melting of KDN decomposition products, as well as a broad exotherm composed of two overlapping peaks, which were attributed to the decomposition of KDN.

ADN and KDN have similar structures, but KDN is more stable. After it was noted that the thermal stability of ADN is very sensitive to the presence of traces of moisture, it was suspected that a similar sensitivity might be found with KDN. Two types of KDN were synthesized and recrystallized in methanol with and without water and were tested for thermal stability [513]. A moist, not entirely dried sample melted at 404.0 K (130.9 °C). The thermal stability of both samples was evaluated by a pressurized DSC and TGA with heating rates of 10 to 30°/min. The PDSC pressure was either atmospheric pressure or elevated pressure at 3 or 6 MPa. In contrast to molten KDN, solid KDN decomposed rapidly. The absolutely dry KDN decomposed more rapidly than the partially moist KDN, an anomaly similar to what has been observed with ADN. For dried KDN, there was an exothermic peak at 364 K (91 °C) prior to the two endothermic peaks. At high pressures, the thermal decomposition of dry KDN was restrained. The exothermic peak at 364 K (91 °C) contracted gradually as the pressure was increased, and at 7 MPa it disappeared altogether. Pressure also had a distinct effect on the decomposition of liquid KDN. See also [514, 515] for information on the thermal stability of KDN and [516] for information on rubidium dinitramide. See also papers on the thermal decomposition of potassium dinitramide in the liquid state [517] or the solid state [518] or additional information by the same authors about other alkali metal dinitramides [519].

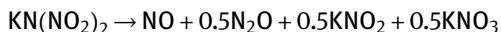
Unusual irregularities were observed for the decomposition of dinitramide metal salts in the solid phase: the solid-phase reaction was 10 to 10³ times faster than that in the melt, its rate had a sharp peak in the region of eutectics melting with the decomposition product (metal nitrates), and it was instantly inhibited by water vapor [506]. The addition of 10–15 mm Hg of water vapor at any stage of the dinitramide salt decomposition in vacuum immediately stopped the reaction. The injection of moist air acted in the same way. In the inhibited regime, the rate in the solid phase was lower than that in the liquid phase. No indications of such anomalous behavior were observed for the decomposition of guanidinium dinitramide. The formation of eutectics of dinitramide salts and the corresponding nitrates was studied using DSC. Rubidium, cesium, and guanidinium salts give these eutectics with melting points of 357.6 K (84.5 °C), 354.6 K (81.5 °C), and 401 K (128 °C), respectively. Li, Na, Rb, Cs, Ba, and guanidinium dinitramides were synthesized using literature methods [78, 520]. The products were twice recrystallized from ethanol or aqueous isopropanol and dried over P₂O₅ in a vacuum desiccator. These procedures rapidly decreased the water content to 0.2 to 0.4%, after which the drying process was sharply retarded. More drastic drying conditions (333–343 K [60–70 °C], vacuum) lowered the water content to 0.05% H₂O but were often accompanied by partial decomposition of the substance. Lithium and barium salts were synthesized only as low-melting crystal hydrates. They were dehydrated to 0.5% H₂O by drying over P₂O₅ at 253 K (–20 °C) in vacuum (0.01 mm Hg).

9.3.2.1 Radiolysis of Alkali Metal Dinitramide Salts

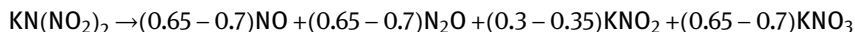
ADN-based propellants used for interplanetary missions may be exposed to cosmic radiation. No specific data exist for ADN, but KDN solutions 8.8×10^{-4} to 1.7 M, with a pH from 3.5 to 4.5, were used in dinitramide radiolysis experiments [521]. The solutions were prepared using bidistilled, deaerated water; were saturated with argon; and were irradiated in sealed glass tubes 1 cm in diameter. The samples were irradiated with ^{60}Co γ rays and with 4.8-MeV electrons from an accelerator. The absorbed dose rate was determined with a ferrous sulfate dosimeter. The concentration of surviving dinitramide anions was determined spectrophotometrically from the absorption at 285 nm. The formation of produced nitrite ions was monitored colorimetrically by the Griess diazo dye method. In the presence of added ethanol or *tert*-butyl alcohol, the decomposition rate increased remarkably, whereas the saturation with N_2O gas stabilized the anion. In diluted aqueous solutions, water radiolysis products reduced the dinitramide anion to nitrite ions, with the radiation chemical yield depending on the absorbed dose rate. In concentrated KDN solutions, the radiation chemical yield of nitrite ions was considerably higher, which was explained by a mechanism of direct action of irradiation on the dinitramide anion.

9.3.3 Strand Burning Rates of Alkali Metal Dinitramide Salts

Since KDN does not include any combustible species such as NH_4 , one can study the decomposition of the $-\text{N}(\text{NO}_2)$ anion by itself. If a binder is used, one would expect that most active radicals will react with an external fuel, resulting in an increase in the temperature of the rate-controlling zone. Two reaction pathways were proposed for KDN decomposition: a solid-state decomposition with formation of KNO_3 and N_2O and a liquid-phase decomposition with formation of $\text{KNO}_3/\text{KNO}_2$ and $\text{N}_2\text{O}/\text{NO}$:



However, data of both DSC and TGA suggest that the decomposition of KDN can not be satisfactorily described by this equation alone. An approximate overall equation for the decomposition of KDN would be



Burning rates of KDN and its mixtures with a nitrate ester binder were measured in a window constant-pressure bomb of 1.5-L volume in the 0.1–15 MPa pressure interval [522]. Samples to test were prepared by pressing fine particles of KDN into transparent acrylic tubes of 4-mm internal diameter. KDN by itself in the form of pressed cylinders with an average density of 2.1 g/cm^3 (i.e., 95% of crystal density 2.209 g/cm^3) confined into acrylic tubes 4 mm in diameter started burning at a pressure of 0.2 MPa with a burning rate of 5 mm/s. The log burn rate versus log pressure diagram of KDN showed a kink (break point, a sudden change of slope) at 5 MPa and 8 mm/s. The adi-

abatic combustion temperature of KDN is low: 1410 K at 10 MPa. KDN burned without a luminous flame, leaving a white residue in the form of small solidified drops.

9.3.4 Safety Properties of Alkali Metal Dinitramide Salts

A hazard assessment of Li, Na, K, Rb, and Cs dinitramides showed that the metal dinitramides were insensitive to impact and friction and moderately insensitive to electric discharge, but they were relatively unstable when heated under vacuum stability testing conditions [501]. The drop weight sensitivity of both KDN and CsDN was above 20 J, the friction sensitivity was above 360 N, and the ESD sensitivity was above 5.6 mJ [499].

The metal dinitramide salts showed varied responses to electrostatic discharge. LiDN proved to be the most sensitive, with initiation occurring above the 0.045 J level. CsDN displayed intermediate sensitivity, while NaDN, KDN, and RbDN could not be initiated at a 4.5-J discharge. Table 34 gives a summary of the safety properties of alkali metal dinitramides.

Table 34: Safety properties of alkali metal dinitramides and ADN.

	Density	Gas evolved	BAM friction	Electro-static discharge	Temperature of ignition		Vacuum stability (80 °C/40 h)
	g/cm ³	mL	N	J	K	°C	mL/5g
LiN(NO ₂) ₂	2.15–2.19	140 (1.6)	>360	0.045	>673	>400	Excess gas
NaN(NO ₂) ₂	2.09	>145	>360	4.5	396	123	Excess gas
KN(NO ₂) ₂	2.25	>145	>360	4.5	413	140	22.9
RbN(NO ₂) ₂	2.63	130 (1.1)	>360	4.5	431	158	4.75
CsN(NO ₂) ₂	3.07	>145	>360	0.45	428	155	25.5
For comparison: NH ₄ N(NO ₂) ₂	1.81	30 (2.3)	360	0.45	415	142	0.73

Data source: [501]

9.3.5 Applications of Alkali Metal Dinitramide Salts

The primary application for alkali metal dinitramides, in particular KDN, would be in pyrotechnic formulations as a replacement for KClO₄ or KNO₃. NaDN would not be suitable for any such application because it is very hygroscopic. The need to replace KClO₄ or KNO₃ in pyrotechnic formulations is not as urgent or driven by environmental concerns as the reasoning for replacement of AP by ADN because the quantities of pyrotechnic igniters involved are so much smaller than the amount of perchlorates used in launch vehicle boosters and military intercontinental ballistic missiles.

KDN was used as an oxidizer for pyrotechnic compositions containing boron or magnesium [523] and for boron-based flare compositions [524].

The thermal stability and safety properties of mixtures of KDN with Ti metal were examined as another example for pyrotechnic applications of KDN [499]. Researchers conducted a systematic investigation of the pyrotechnic redox systems KDN/titanium and cesium dinitramide/titanium for a wide range of O/F ratios. The heats of reaction as well as the burning rates of KDN/titanium are higher than those of cesium dinitramide/titanium. Both systems have a moderate sensitivity to friction and electrostatic discharges. However, both mixtures suffer from a very high sensitivity to impact. These sensitivities are in the same range as pure HMX or PETN. KDN can be used as the oxidizer in red flare compositions that would not leave perchlorate residues [525].

Another potential application of KDN would be as a stabilizer for AN [72]. While KNO_3 has been used for decades as a stabilizer for AN in solid propellant and gas generant formulations, the disadvantage of KNO_3 is that it reduces the performance of AN as a rocket propellant. KDN, however, more than compensates for the performance loss due to the introduction of the potassium [513, 526].

With the addition of only 5% KDN, AN can be phase-stabilized, and an increase in the percentage addition of KDN in AN crystals will boost the energy capacity of AN [58, 527, 528]. The phase transition of AN at 330.79 K (57.64 °C) was completely removed in the presence of 3% of KDN. For AN/KDN propellant systems, a maximum of 30% KDN can be added to AN. The reason lies in the decomposition mechanism of KDN.

10 Dinitramide Salts of Other Metals

Dinitramide salts of other metals have been prepared and characterized, but they are of no interest as rocket propellants and have only limited potential as ingredients in pyrotechnic formulations. Transition metal dinitramides may be useful as burning-rate catalysts in ADN-based solid propellants. They would be added only in small percentages.

Salts described in the literature include $\text{AgN}(\text{NO}_2)_2$, $[\text{Ag}(\text{CH}_3\text{CN})][\text{N}(\text{NO}_2)_2]$, $[\text{Ag}(\text{py})_2][\text{N}(\text{NO}_2)_2]$, $[\text{Cu}(\text{NH}_3)_4][\text{N}(\text{NO}_2)_2]$, and $[\text{Pd}(\text{NH}_3)_4][\text{N}(\text{NO}_2)_2]_2$ [529]. Silver dinitramide is useful in the synthesis of other dinitramide salts when the other cation is introduced as the chloride or bromide. When crystallizing from acetonitrile or dioxane solution, it will retain part of the solvent as a solvate.

Electronic and vibrational spectra of mercury(II) dinitramide $\text{Hg}(\text{N}_3\text{O}_4)_2$ show that in the crystalline state and in solutions in non-polar solvents, it is a covalent compound, the mercury atom being bound to the oxygen atoms [530]. In polar solvents, it dissociates to give mercury(II) cation and dinitramide anion N_3O_4^- . This salt can be used as a reagent for mercuration, an addition reaction where mercury is added to the double carbon-carbon bonds, for alkylation, and for complexation in organic chemistry [531].

The crystal structures of the hexaaquomagnesium, hexaaquomanganese, and hexaaquozinc dihydrate salts of dinitramide have been determined [532]. The properties are listed in Table 35.

Table 35: Crystal structures of magnesium, manganese, and zinc dinitramides.

Compound	Space group	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	β , °
Hexaaquomagnesium dinitramide	$P2_1/m$	9.589(2)	7.420(1)	11.116(2)	108.25(3)
Hexaaquomanganese(II) dinitramide	$P2_1/m$	9.623(4)	7.477(2)	11.274(3)	108.38(3)
Hexaaquozinc dinitramide dihydrate	$P2_1/m$	9.513(1)	7.4270(8)	11.164(1)	108.806(6)

Data source: [532]

The three structures are isostructural, consisting of hexaaquo cations, dinitramide anions, and water molecules interlinked by extensive 3D hydrogen-bonding interactions. All oxygen atoms as well as the central nitrogen atom of the dinitramide anion are involved in acceptor hydrogen bonds with neighboring water protons.

Attempts to obtain the dinitramide salts of Cu(I), Al(III), Cr(III), or Fe(III) have failed. The melting points of other metal dinitramides are summarized in Table 36.

Table 36: Melting points of metal dinitramides.

Compound	Melting point		References
	K	°C	
Ag N(NO ₂) ₂	398–404	125–131	[78]
Ag N(NO ₂) ₂	398–404	125–131	[16]
Pb N(NO ₂) ₂	375–379	102–106	[16]
Ba(N ₃ O ₄) ₂ •H ₂ O	347–349	74–76	[16]
Ni(N ₃ O ₄) ₂ •2H ₂ O	366–370	93–97	[16]
Ni(N ₃ O ₄) ₂ •6H ₂ O	353–356	80–83	[16]
Mg(N ₃ O ₄) ₂ •3H ₂ O	333–338	60–65	[16]
Mg(N ₃ O ₄) ₂ •6H ₂ O	362–366	89–93	[16, 532]
Cu(N ₃ O ₄) ₂ •3H ₂ O	324–329	51–56	[16]
Fe(N ₃ O ₄) ₂ •7H ₂ O	358	85	[16]
Co(N ₃ O ₄) ₂ •6H ₂ O	355–359	82–86	[16]
Mn(N ₃ O ₄) ₂ •8H ₂ O	314–336	41–63	[16, 532]
Hg(N ₃ O ₄) ₂	366–376	93–103	[530]

The thermal decomposition of silver dinitramide, $\text{AgN}(\text{NO}_2)_2$, was investigated using DSC, TGA, FT-IR, Raman spectra, and XRD [533]. The results showed that the degradation process of $\text{AgN}(\text{NO}_2)_2$ could be divided into two stages. The first stage, with a mass loss of 21.9%, took place in the 408–483 K range, during which N_2O was released and the intermediate product of thermal decomposition was AgNO_3 . The second stage, with a mass loss of 28.2%, occurred at 483–800 K, with evolution of NO_2 and O_2 and Ag metal as the final product of thermal decomposition.

11 Dinitramide Salts of Nitrogen-Containing Bases

The dinitramide salts of organic nitrogen-rich bases are particularly useful as rocket propellants and gas generants. The alkylammonium dinitramides were studied as additives to change the crystal habits of ADN and allow the production of more compact crystals with lower length/diameter ratios that would pack better in a solid propellant (Section 2.5.2). These salts are discussed under their parent base along with the nitrates and perchlorates, most of them in *Encyclopedia of Liquid Fuels*, chapter “Aliphatic Amines.” In this chapter we only provide a comparison of physical properties of the dinitramide salts of a wide range of nitrogen-containing bases, mostly alkyl amines and heterocyclic amines. Following the summary overview, a few selected amine dinitramide salts are discussed in detail. There is some duplication between the following section and *Encyclopedia of Liquid Fuels*, where the amines that form the cation are discussed in detail, along with their salts.

Hydrazinium(1+) dinitramide, $[\text{N}_2\text{H}_5][\text{N}(\text{NO}_2)_2]$, $\text{N}_5\text{H}_5\text{O}_4$, HDN, CAS RN [165603-97-4], is discussed in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salts.”

Hydroxylammonium dinitramide is described in *Encyclopedia of Oxidizers*, chapter “Hydroxylammonium Salts.”

11.1 Melting Points of Dinitramide Salts of Nitrogen-Containing Bases

Table 37 is a summary of the melting points of the dinitramide salts of organic bases. There is a similar table with enthalpies of formation of these compounds in Section 11.3.2.

The simplest method for preparation of alkylammonium dinitramides is the neutralization of the amine with dinitraminic acid in solution. This is used for the weak amines with basicity constants less basic than ammonia. Stronger base amines can be reacted with ADN, and the liberated ammonia is driven off. These two methods were used for preparation of the salts listed in Table 38 [537].

Table 37: Melting points of dinitramide salts of organic bases.

Compound	Melting point		References
	K	°C	
5-Aminotetrazole dinitramide	356–359	83–86	[449]
Aniline dinitramide	368–370	95–97	[449]
Benzylamine dinitramide	332–334	59–61	[449]
Diethanolamine dinitramide	348–351	75–78	[449]
Ethanolamine dinitramide	310–312	37–39	[449]
Methylamine dinitramide	316–318	43–45	[449]
Morpholine dinitramide	355–357	82–84	[449]
<i>m</i> -Nitroaniline dinitramide	374–376	101–103	[449]
Piperazine bis-dinitramide	485–487	212–214	[449]
Tetramethylammonium dinitramide	507–511	234–238	[449]
<i>o</i> -Toluidine dinitramide	343–344	70–71	[449]
3,5-Dimethylpyridine dinitramide	343–345	70–73	[449]
Hexamethylenediamine bisdinitramide	362–363	89–90	[449]
Cubane 1,4-bis (ammonium dinitramide)	No melting	No melting	[164, 534]
Cubane 1,2,4,7-tetrakis (ammonium dinitramide)	No melting	No melting	[164, 534]
3,3-dinitroazetidinium dinitramide	412	139	[535]
Butane diammonium dinitramide	340–346	67–73	[97]
Ethane diammonium bis(dinitramide)	398	125	[536, 537]
Urea dinitramide	371–373	98–100	[520]
H ₂ NC(=NH)NH ₂ •HN ₃ O ₄ Guanidinium dinitramide	421	148	[449, 537]
	417	144	[506]
H ₂ NC(=NH)NHNH ₂ •HN ₃ O ₄	367	94	[449, 506, 537]
Urotropinium dinitramide		121–124	[529]
Inorganic dinitramide salts			
NH ₂ NH ₂ •HN ₃ O ₄	356	83	[520]
H ₂ NOH•HN ₃ O ₄	291–296	18–23	[520]

Data source: Data gathered from several sources, including [9, 449]

Table 38: Properties of selected alkylammonium dinitramide salts.

Compound	Recrystallized from	Melting point, °C	Decomposition temperature, °C	Friction sensitivity, BAM, kg	Oxygen balance, %
$[\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{N}^+\text{H}_3][\text{N}(\text{NO}_2)_2]_2^-$	i-C ₃ H ₇ OH	125	136	11.8	-5.8
Triethylenetetramine tetrakis(dinitramide)	CH ₃ OH	159	163	4.4	-19.5
$[\text{H}_3\text{N}^+(\text{CH}_2\text{CH}_2\text{NH}_2^+)_2\text{CH}_2\text{CH}_2\text{N}^+\text{H}_3][\text{N}(\text{NO}_2)_2]_4^-$					
Triethylenetetramine trisdinitramide	CH ₃ OH	No crystals	173.5	7.8	-36
$[\text{H}_3\text{N}^+(\text{CH}_2\text{CH}_2\text{NH}_2^+)_2\text{CH}_2\text{CH}_2\text{NH}_2][\text{N}(\text{NO}_2)_2]_3^-$					
$[(\text{O}_2\text{NO}-\text{CH}_2\text{CH}_2)_2\text{NH}_2^+][\text{N}(\text{NO}_2)_2]^-$	CH ₃ OH	114	135	18.4	-15.9
Guanidine $[(\text{H}_2\text{N})_3\text{C}^+][\text{N}(\text{NO}_2)_2]^-$	CH ₃ OH	148	176	>23.5	-9.6
Aminoguanidine $[(\text{H}_2\text{N})\text{C}^+\text{NHNH}_2][\text{N}(\text{NO}_2)_2]^-$	CH ₃ OH	94	180	18.4	-13.3

Data source: [537]

11.2 Thermal Stability of Dinitramide Salts of Nitrogen-Containing Bases

Thermograms of two of the dinitramide salts from organic bases are shown in Figures 76 and 77. The thermal stability of the guanidinium dinitramide is remarkable, but the cause of the first endotherm at 380.2 K (107.1°C) prior to melting has not been explained (an impurity or a phase transition?). See also [538, 539].

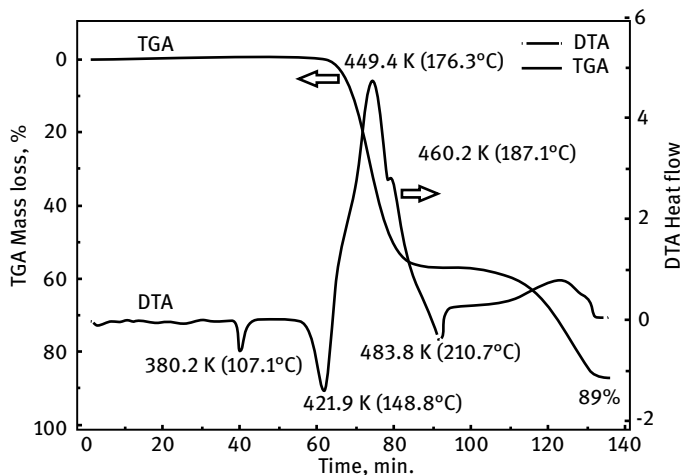


Figure 76: DSC and TGA thermogram of guanidinium dinitramide. (Reproduced and modified from [537].)

Unlike alkali metal dinitramide salts, the guanidinium salt does not exhibit abnormal solid-phase decomposition rates. The rates in vacuum and in air are equal, and no increase in the rate is observed at the point of the eutectic melting with guanidinium nitrate, which is 401 K (128 °C). The rate in the solid state is 400 times slower than in the liquid phase.

The thermal stability of ADN/GUDN mixtures was discussed in Section 4.10. GUDN has excellent thermal stability and is not hygroscopic. The thermal decomposition of GUDN has been studied by non-isothermal TGA and TGA combined with mass spectrometry (TGA-MS) [540]. Additional information on GUDN will be provided in *Encyclopedia of Liquid Fuels*, chapter “Amides and Imides.”

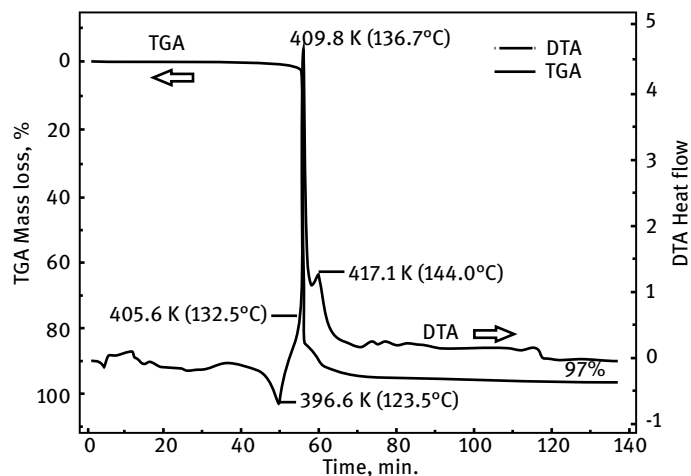


Figure 77: DSC and TGA thermogram of ethylenediammonium bis-dinitramide. (Reproduced and modified from [537].)

Guanidinium dinitramide, GuDN, $[\text{NH}_2\text{C}(\text{NH}_2)\text{NH}_2][\text{N}(\text{NO}_2)_2]$, can be synthesized from guanidinium carbonate and ADN. Two different crystalline forms (α -type and β -type) were obtained depending on the applied solvents and synthesis conditions [541]. Water might become trapped in a crystal lattice between the inner molecules during crystallization. Despite having the same chemical composition, Raman-IR and TGA-DSC revealed different physical characteristics of the two modifications. Peaks of Raman shift near 1000 cm^{-1} implied different chemical structures. Thermal analysis revealed an exothermic temperature of 428.8 K (155.7°C) for α -type but one of 464.7 K (191.6°C) for β -type. The caloric value of the exotherm of α -type was 536.4 J/g and that of the β -type was 1310 J/g . While the synthesized GDN of α -type showed a steep exothermic decomposition, the β -type decomposed slowly after melting through an endothermic process. This implied that despite the same molecular formula, some different molecular-structure thermal properties were formed depending on synthesis conditions.

11.3 Thermodynamic Properties of Dinitramide Salts of Nitrogen-Containing Bases

11.3.1 Heat of Solution of Dinitramide Salts of Nitrogen-Containing Bases

The heats of solution of dinitramide salts of nitrogen-containing organic and inorganic bases in water at infinite dilution were measured in comparison to the corresponding nitrate salts. The results are summarized in Table 39. Some of these salts are useful intermediates in the production of ADN, or they can be used as propellant ingredients in their own right.

Table 39: Enthalpies of solution of amine salts of dinitramidic acid and nitric acid.

Compound	ΔH solution	
	kJ/mol	kcal/mol
Dinitramide salt		
$\text{NH}_4\text{N}(\text{NO}_2)_2$	36.4 ± 0.04	8.71 ± 0.01
$\text{N}_2\text{H}_5\text{N}(\text{NO}_2)_2$	47.3 ± 0.08	11.31 ± 0.02
$(\text{NH}_2)_2\text{C}=\text{NH}_2\text{N}(\text{NO}_2)_2$	53.9 ± 0.08	12.88 ± 0.02
$(\text{NH}_2\text{NH})(\text{NH}_2)\text{C}=\text{NH}_2\text{N}(\text{NO}_2)_2$	56.5 ± 0.04	13.50 ± 0.01
$(\text{NH}_2\text{NH})_2\text{C}=\text{NNH}_3\text{N}(\text{NO}_2)_2$	61.5 ± 0.04	14.69 ± 0.01
For comparison:		
$\text{NaN}(\text{NO}_2)_2$	24.8 ± 0.04	5.93 ± 0.01
$\text{KN}(\text{NO}_2)_2$	47.2 ± 0.04	11.28 ± 0.01
$\text{CsN}(\text{NO}_2)_2$	50.7 ± 0.08	12.12 ± 0.02
Nitrate salt		
$\text{N}_2\text{H}_5\text{NO}_3$	37.9 ± 0.08	9.07 ± 0.02
$(\text{NH}_2)_2\text{C}=\text{NH}_2\text{NO}_3$	41.0 ± 0.08	9.80 ± 0.02
$(\text{NH}_2\text{NH})(\text{NH}_2)\text{C}=\text{NH}_2(\text{NO}_3)$	49.0 ± 0.04	11.71 ± 0.01
$(\text{NH}_2\text{NH})_2\text{C}=\text{NNH}_3(\text{NO}_3)$	52.9 ± 1.25	12.65 ± 0.03

Data source: [201]

11.3.2 Enthalpy of Formation of Dinitramide Salts of Nitrogen-Containing Bases

A summary of the enthalpies of formation of dinitramides of nitrogen-containing bases in comparison to a few alkali metal dinitramides is given in Table 40. These enthalpies of formation were derived from calorimeter measurements in a combustion bomb and from measurements of the heats of solution in water. In addition, the enthalpies of formation of individual ions dissolved in water in infinite dilution were calculated from heat-of-solution measurements and tabulated for comparison.

For the same cation, the difference in the enthalpy of formation of the dinitramide salt and the nitrate salts is typically of the order of 230 kJ/mol (55 kcal/mol).

Table 40: Recommended values of the enthalpies of formation (ΔH°_f) of cations and amine salts of dinitramidic acid and nitric acid.

Compound	Enthalpy of formation ΔH°_f		Enthalpy of formation ΔH°_f		Enthalpy of formation ΔH°_f	
	kJ/mol	kcal/mol	kJ/mol	kcal/mol	kJ/mol	kcal/mol
	Cation in solution		Dinitramide salt		Nitrate salt	
$\text{NH}_4\text{N}(\text{NO}_2)_2$	-133.3 ± 0.25	-31.85 ± 0.06	-134.6 ± 0.46	-32.16 ± 0.11		
$\text{N}_2\text{H}_5\text{N}(\text{NO}_2)_2$	-1.46 ± 1.05	-0.35 ± 0.25	-13.64 ± 1.2	-3.26 ± 0.28	$\text{N}_2\text{H}_5\text{NO}_3$	-246.3 ± 0.96
$(\text{NH}_2)_2\text{C}=\text{NH}_2\text{N}(\text{NO}_2)_2$	-139 ± 0.71	-33.24 ± 0.17	-157.8 ± 0.88	-37.72 ± 0.21	$(\text{NH}_2)_2\text{C}=\text{NH}_2\text{NO}_3$	-92.48 ± 0.13
$(\text{NH}_2\text{NH})(\text{NH}_2)\text{C}=\text{NH}_2\text{N}(\text{NO}_2)_2$	-22.9 ± 0.80	-5.47 ± 0.19	-44.2 ± 0.96	-10.57 ± 0.23	$(\text{NH}_2\text{NH})(\text{NH}_2)\text{C}=\text{NH}_2(\text{NO}_3)$	-66.62 ± 0.16
$(\text{NH}_2\text{NH})_2\text{C}=\text{NNH}_3\text{N}(\text{NO}_2)_2$	$+209.5 \pm 0.92$	$+50.08 \pm 0.22$	$+183.2 \pm 1.09$	$+43.79 \pm 0.26$	$(\text{NH}_2\text{NH})_2\text{C}=\text{NNH}_3(\text{NO}_3)$	-12.01 ± 0.19
$(\text{H}_3\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_3)[\text{N}(\text{NO}_2)_2]_2^a$	-187.7 ± 1.7	-44.87 ± 0.41	-194.6 ± 1.8	-46.52 ± 0.43		-50.25 ± 0.79
$(\text{CH}_3)_4\text{NN}(\text{NO}_2)_2^a$	-114.2 ± 0.92	-27.29 ± 0.22	-103.3 ± 1.09	-24.70 ± 0.26		
For comparison: Alkali metal dinitramides						
$\text{NaN}(\text{NO}_2)_2$	-240.3 ± 0.04	-57.44 ± 0.01	-229.9 ± 0.54	-54.94 ± 0.13		
$\text{KN}(\text{NO}_2)_2$	-252.1 ± 0.08	-60.26 ± 0.02	-264.2 ± 0.54	-63.14 ± 0.13		
$\text{CsN}(\text{NO}_2)_2$	-258.8 ± 0.5	-61.85 ± 0.12	-273.5 ± 0.75	-65.38 ± 0.18		

^a From [206]
Data source: [201]

11.4 Other Properties of Dinitramide Salts of Nitrogen-Containing Bases

A series of long-chain alkyl diamines, amino acids, and aromatic diamines was tested as additives to modify the crystallization habits of ADN [97]. The strategy was unsuccessful, but in the process butanediammonium bis(dinitramide) (BDDN) was isolated and characterized. BDDN has a similar space group to ADN, and its habit is sensitive to growth conditions, crystallizing in short prisms and two types of blades. For these reasons, the growth behavior and surface and packing structure of BDDN was analyzed in the hope that these might give some clues to ADN habit modification.

A large number of dinitramide salts of organic amines were synthesized and their physical properties measured [520]. This included properties of dinitramide salts with ammonia, hydrazine, hydroxylamine, and formamidine and their alkylated and aminated derivatives. In addition, strand burning rates were measured [449]. Table 41 gives a summary of melting points, ignition temperatures, pressed densities, and calculated enthalpies of formation of a group of dinitramide salts of organic amines. The Roman numeral in the “preparation method” column designates salts that were prepared from ADN and the free amine by elimination of ammonia (**I**), boiling of carbonates of the amine with ADN in alcoholic solution (**II**), or precipitation of barium sulfate from solutions of amine sulfates and barium dinitramide (**III**). The burning rates of strands pressed into tubes 4–7 mm in diameter and burned at 150–200 MPa were measured as a function of pressure, and the pressure coefficients were derived from logarithmic graphs. The substitution of an organic amine for ammonium in the dinitramide salt will result in different flame temperature, temperature at the surface, and reactivity of the fuel. The surface temperature can be assumed by analogy with other salts to be determined by the salt dissociation reaction, and thus it will depend on the amine basicity. It was attempted to obtain a correlation between the basicity constant of the amine and the burning rate of its dinitramide salt, but not all data fit into the same scheme. Looking at the burning rate data, the salts could be divided into three main groups according to their burning characteristics:

- (1) dinitramide salts like ADN, the burning rate-pressure dependence of which includes a region of combustion instability;
- (2) salts that show a transition region characterized by a reduced pressure exponent on the $r_b = f(p)$ curve in the medium pressure range; this group includes dinitramide salts of amines of both high and low basicity;
- (3) salts that demonstrate stable combustion, showing invariant pressure exponent throughout the entire pressure range; these include salts of amines of low basicity, e.g., 5-aminotetrazole or *m*-nitroaniline.

The heat of formation measured for guanidinium dinitramide at Los Alamos National Laboratory (LANL) is -40.7 ± 1.5 kcal/mol. Thus, the guanidinium derivative has a fairly high heat of formation as compared to the perchlorate (-74.1 kcal/mol) or nitrate salts (-93 kcal/mol) of guanidine. The DSC of guanidinium dinitramide shows

Table 41: Summary of physical properties of dinitramide salts of organic amines.

Compound	Preparation method	Density of pressed strand g/cm ³	Melting point °C	Ignition point °C	Enthalpy of formation		References
					kJ/mol	kcal/mol	
Aminoguanidine dinitramide	II	1.63	87–88	205	–48	–11.5	[520]
5-Aminotetrazole dinitramide	III	1.87	83–86	170	+201 (calc.)	+48 (calc.)	[449]
Aniline dinitramide	III	1.52	95–97	182	+39 (calc.)	+9.3 (calc.)	[520]
Benzylamine dinitramide	I	1.44	59–61	—	–19 (calc.)	–4.54 (calc.)	[449]
Diethanolamine dinitramide	I	1.55	75–78	198	–598 (calc.)	–143 (calc.)	[449]
3,5-Dimethylpyridine dinitramide	III	1.41	70–73	—	19 (calc.)	4.54 (calc.)	[449]
Ethanolamine dinitramide	I	1.53	37–39	175	–335 (calc.)	–80 (calc.)	[449]
Ethylenediamine bisdinitramide	I	1.78	129–131	174	–209	–49.9	[520]
Guanidinium dinitramide	II	1.53 (pressed)	133–136	—	–168	–40.1	[520]
Guanidinium dinitramide		1.67 (X-ray)			–169	–40.7 ± 1.5 (meas.)	[164]
Hexamethylenediamine bisdinitramide	I	1.40	89–90	192	–154 (calc.)	–36.8 (calc.)	[449]
Methylamine dinitramide	I	1.53	43–45	177	–121	–28.9	[520]
Morpholine dinitramide	I	1.49	82–84	180	–226	–54	[449]
Piperazine bisdinitramide	I	1.50	212–214	215	–236 (calc.)	–56.4 (calc.)	[449]
Tetramethylammonium dinitramide	0	1.22	234–238	—	–191	–45.6	[520]
<i>o</i> -Toluidine dinitramide	III	1.43	70–71	178	+6 (calc.)	+1.4 (calc.)	[449]
Cubane 1,4-bis (ammonium dinitramide)		1.77 (X-ray)	No melting				[164]
Cubane 1,2,4,7-tetrakis (ammonium dinitramide)		1.85 (X-ray)	No melting				[164]
Butane diammonium dinitramide	I	1.548	67–73				[97]
Urotropinium dinitramide			121–124				[529]

what appears to be a phase change at around 373 K (100 °C), with the melting point onset near 413 K (140 °C). This melting point is surprisingly high for a dinitramide salt and is only matched or exceeded in the cubane amine derivatives.

11.5 Individual Dinitramide Salts of Nitrogen-Containing Bases

There is a large group of energetic material salts synthesized by combining an energetic amine (e.g., the amine of a strained-ring caged or heterocyclic compound) cation with an energetic anion such as dinitramide. Several examples are shown in the following paragraphs, including cubane-1,4-diammonium dinitramide and cubane-1,2,4,7-tetraammonium dinitramide [164, 534].

11.5.1 Dinitramide Salts of C₁ Nitrogen-Containing Bases

In the preparation of ADN, instead of trying to isolate the product as the very soluble ADN, it is easier to isolate the dinitramide salt in the form of the poorly soluble guanidinium dinitramide, which precipitates, filtered, washed, and dried; and can later be converted to ADN [41]. Guanidinium dinitramide is described in detail in *Encyclopedia of Liquid Fuels*, chapter “Amides and Imides.”

11.5.2 Dinitramide Salts of C₂ Through C₃ Nitrogen-Containing Bases

Ethylenediamine (1,2-diaminoethane) forms a diprotonated salt, ethylenediammonium(2+) bisdinitramide, C₂H₁₀N₈O₈, with dinitramidic acid, which is of interest as an energetic additive to propellants and gas generants [536]. The salt crystallizes in the triclinic space group *P*1 with cell dimensions $a = 5.614(1)$, $b = 6.867(2)$, $c = 7.371(2)$ Å, $\alpha = 68.89(2)$, $\beta = 89.00(2)$, $\gamma = 78.90(2)^\circ$, $Z = 1$, and $\rho_c = 1.753$ g/cm³. Atomic coordinates, bond lengths, and angles and equivalent isotropic displacement parameters for the salt were calculated and tabulated. These cations provide a constrained local environment for the dinitramide anions because of extensive hydrogen bonding.

Ethylenediamine as a ligand in transition metal complexes forms complex dinitramide salts [542]. Complexes of nickel(II), cobalt(III), copper(II), zinc(II), and cadmium(II) with ethylenediamine containing the dinitramide anion were synthesized and characterized by NMR, ESP, and DTA.

11.5.2.1 N-Guanyllurea Dinitramide

N-guanyllurea dinitramide, also known as GUDN, [H₂NC(=N⁺H₂)NHCONH₂][−] [N[−](NO₂)₂], C₂H₇N₇O₅, FOX-12, CAS RN [217464-38-5], an energetic material developed in Sweden by FOI, has low sensitivity and good potential for use as a propellant ingredient, gas generant, or insensitive explosive. It is already being used in gas generators for automotive airbags, which was the first full-scale application of any

dinitramide outside of Russia. Properties of *N*-guanylurea dinitramide are described in more detail in *Encyclopedia of Liquid Fuels*, chapter “Amides and Imides,” under the cation of this compound, rather than here under the anion of this compound. (We are used to naming salts with the cation first, so that is where these salts are listed.) *N*-guanylurea dinitramide is underoxidized with an oxygen balance of -19.1% , so it should not be discussed here under solid propellant oxidizers.

11.5.3 Other Dinitramide Salts of Organic Bases

11.5.3.1 Biguanidinium Dinitramides

Three different biguanidinium salts of dinitramidic acid were prepared and structurally characterized based on X-ray diffraction data [543]. Details about these salts are presented in *Encyclopedia of Liquid Fuels*, chapter “Amides and Imides.” See also [544].

11.5.3.2 3,3-Dinitroazetidine Dinitramide

3,3-dinitroazetidine is an explosive in its own right. Its explosive power and oxygen balance can be improved by forming the dinitramide salt of the amine, called dinitroazetidinium dinitramide [535].

11.5.3.3 Dinitramide Salts of 3,4,5-Triamino-1,2,4-triazole

The dinitramide salts of 3,4,5-triamino-1,2,4-triazole and similar heterocyclic amines are of interest as ionic liquids since they melt below 373 K and can be used as monopropellants. The thermal decomposition of 3,4,5-triamino-1,2,4-triazole dinitramide was measured using a microcalorimeter at four different temperatures under atmospheric pressure [545]. The apparent activation energy and pre-exponential factor of the exothermic decomposition reaction are 165.57 kJ/mol and $10^{18.04} \text{ s}^{-1}$, respectively. The critical temperature of thermal explosion is 432 K. The entropy of activation (ΔS), enthalpy of activation (ΔH), and free energy of activation (ΔG) are $97.19 \text{ J mol}^{-1} \text{ K}^{-1}$, $161.90 \text{ kJ mol}^{-1}$, and $118.98 \text{ kJ mol}^{-1}$, respectively. The self-accelerating decomposition temperature (T_{SADT}) is 422 K. The specific heat capacity as a function of temperature of 3,4,5-triamino-1,2,4-triazole dinitramide was determined by a micro-DSC method and a theoretical calculation method:

$$C_p = 0.252 + 3.131 \times 10^{-3} T \quad (\text{for the range } 283.1 \text{ K} < T < 353.2 \text{ K})$$

where C_p is the heat capacity in $\text{J g}^{-1} \text{ K}^{-1}$ and T is the temperature in kelvin. The molar heat capacity of 3,4,5-triamino-1,2,4-triazole dinitramide is $264.52 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298 K. See also [546].

11.5.3.4 Dinitramide Salts of Higher ($C_{n>3}$) Nitrogen-Containing Bases

Hexamethylene tetramine (“hexamine,” urotropine) forms monoprotonated salt crystals with different structures with dinitraminic acid, depending on the solvent

from which they are crystallized [536]. Recrystallizing the dinitramide salt of hexamine from polar organic solvents led to the triclinic polymorph, while recrystallizing it from water gave the monoclinic polymorph. The unit cell dimensions of the triclinic space group $P1$ polymorph are $a = 6.391(2)$, $b = 7.5826(9)$, $c = 10.828(1)$ Å, $\alpha = 77.58(1)$, $\beta = 88.18(2)$, $\gamma = 87.54(2)^\circ$, $Z = 2$, and $\rho_c = 1.604$ g/cm³, while the other polymorph crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions $a = 6.4893(3)$, $b = 14.5149(8)$, $c = 10.6557(4)$ Å, $\beta = 94.300(4)^\circ$, $Z = 4$, and $\rho_c = 1.641$ g/cm³. Atomic coordinates, bond lengths, and angles and equivalent isotropic displacement parameters for the salts were calculated and tabulated. These cations provide a constrained local environment for the dinitramide anions because of extensive hydrogen bonding. The amount by which the nitro group has rotated out of the N2–N1–N3 plane varies substantially between these salts and ethylenediammonium(2+) bisdinitramide, which was analyzed for comparison.

Other isocyclic organic amine salts include cubane-1,4-diammonium dinitramide and cubane-1,2,4,7-tetraammonium dinitramide [164, 534].

A series of new energetic salts based on the polyamino-1-guanyl-triazole cation with three to five amino groups and the dinitramide anion were synthesized and characterized [547]. These new nitrogen-rich salts tend to have extensive hydrogen bonding, and they have high densities and good thermal stabilities. The impact of multiple amino groups in the cation of the dinitramide salts was then systematically investigated. Their properties were modified by varying the guanyl substituents and/or the amino substituents on the triazole ring. On the basis of theoretical calculations, 3,5-diamino-1-guanyl-1,2,4-triazole dinitramide has higher detonation pressure and velocity values than the dinitramide energetic materials such as ADN and *N*-GUDN (FOX-12). The structures of other salts (3-amino-1-guanyl-1,2,4-triazole dinitramide, 3,5-diamino-1-guanyl-1,2,4-triazole dinitramide, 5-amino-*N*-amidino-1-guanyl-1,2,4-triazole dinitramide, and 3,5-diamino-*N*-amidino-1-guanyl-1,2,4-triazole dinitramide) were investigated using single-crystal XRD analysis.

The dinitramide and the nitrate salts of the 2,4,6-triamino-1,3,5-triazinium(1+) (“melaminium”) cation were prepared, and the crystal structures were identified based on X-ray single-crystal diffraction data [548]. 2,4,6-triamino-1,3,5-triazinium (melaminium) dinitramide crystallizes in triclinic crystals, space group $P\bar{1}$, $a = 6.6861(11)$, $b = 6.9638(16)$, $c = 10.447(2)$ Å, $\alpha = 99.07(3)$, $\beta = 98.30(3)$, $\gamma = 108.50(3)^\circ$, $V = 445.6(2)$ Å³, and $Z = 2$. For comparison, melaminium nitrate crystallizes in monoclinic crystals, space group $P2_1/c$, $a = 3.5789(7)$, $b = 20.466(4)$, $c = 10.060(2)$ Å, $\beta = 94.01(2)^\circ$, $V = 735.0(3)$ Å³, and $Z = 4$. The crystal structures of both salts showed distinct monoprotonated melaminium cations and dinitramide or nitrate anions, respectively. Efficient packing in the solid state and decent thermal stability are achieved by extensive hydrogen bonding between two-dimensional zigzag ribbons of the melaminium cations and the respective anions. This results in high densities of the solid-state structures of 1.74 and 1.71 g/cm³, respectively.

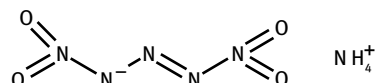
3-Amino-1,2,4-triazolium dinitramide was synthesized through the combination of 3-amino-1,2,4-triazole cation and oxygen-rich dinitramide anion, and its structure was confirmed using single-crystal XRD, elemental analysis, FTIR, UV-Vis spectrometry, and NMR [549]. The thermal stability was studied using DSC, TGA, and TGA tandem IR. Results indicated that this salt was thermally stable up to 439 K. The activation energy of the decomposition reaction was $E_a = 281.9 \text{ kJ/mol}$.

A polymeric polyethylene with intermittent amino groups is a polymeric base that can form dinitramide salts that can be used as solid propellants [550].

11.6 Other Inorganic Nitramine Compounds

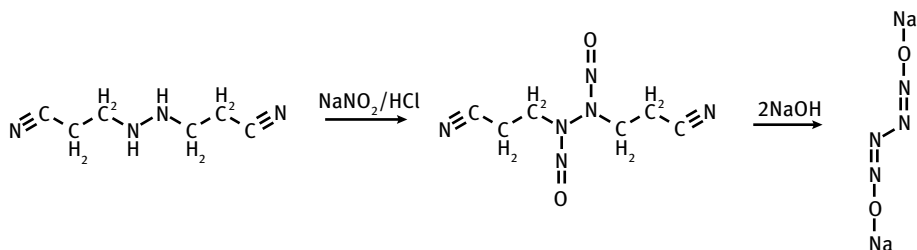
While dinitramine and its salts are already quite powerful oxidizers, one is left to wonder whether the oxidizing power of nitramine could possibly be increased by replacing one of the hydrogens on the amino group with fluorine. The fluoronitramide anion, $\text{O}_2\text{N}-\text{N}^-\text{F}$, in the form of its potassium, tetraisopropyl-*p*-phenylenediguanidinium, and tetraphenylphosphonium salts, has been synthesized [551]. The tetraphenylphosphonium fluoronitramide was characterized in detail as it was by far the most stable. The free acid $\text{HFN}-\text{NO}_2$ was found to be unstable, as was the ammonium salt of fluoronitramide. The fluorine atom was shown to be easily replaced by nucleophiles. In contrast to dinitramide, which at room temperature is unreactive toward aqueous alkali, fluoronitramide reacts instantly with aqueous hydroxide.

Another potential high-energy oxidizer is ammonium di (nitramido) amine (ADNA)



Di(nitramido)amine is a hypothetical compound, but this has not prevented imaginative chemists from including it in an environmental-fate evaluation of high-energy oxidizers [478, 552]. The predicted density is $\rho = 1.76 \text{ g/mL}$, and the predicted enthalpy of formation is $\Delta H_f = +180 \text{ kJ/mol}$ (+43 kcal/mol). The results suggest that ADNA is hydrophilic and highly water soluble (115600 mg/L) and not likely to bioaccumulate.

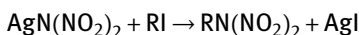
Another unusual nitrogen–oxygen compound and potential rocket propellant is dinitrosohydrazine, which so far is known only in the form of its salts. Dinitrosohydrazine salts were synthesized for the first time by dealkylation of 1,2-dinitroso-1,2-bis(2-cyanoethyl)hydrazine. Nitrosation of 1,2-bis(2-cyanoethyl)hydrazine yields 1-nitroso- and 1,2-dinitroso-1,2-bis(2-cyanoethyl) hydrazines. Decyanoethylation of 1-nitroso-1,2-bis(2-cyanoethyl)hydrazine results in the formation of sodium azide and disodium dinitrosohydrazinate [553].



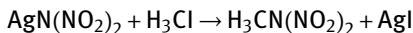
It remains to be seen whether an ammonium salt of this acid can be synthesized. The dinitramide salt of hydrazine is described in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salts.” The dinitramide salt of hydroxylamine is described in *Encyclopedia of Oxidizers*, chapter “Hydroxylammonium Salts.”

11.7 Other Organic Nitramine Compounds

A classical metathetical reaction for the synthesis of alkyl dinitramines would be the reaction of silver dinitramide with an alkyl iodide, precipitating the insoluble silver iodide. Silver dinitramide reacts with alkyl iodides to form *N*-alkyl-*N,N*-dinitroamines [554, 555]:



Methyliodide does not react with $\text{KN}(\text{NO}_2)_2$ in acetonitrile at 253 K, but $\text{AgN}(\text{NO}_2)_2$ reacts with CH_3I within several days to form methyldinitroamine:



Reaction with $\text{C}_2\text{H}_5\text{I}$ gave a mixture of *N*-alkylated and *O*-alkylated products.

The synthesis of monoalkyl-*N,N*-dinitramines from isocyanates as a step for preparation of dinitramide salts was described in Section 2.2.

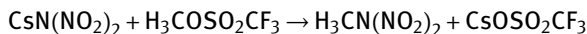
11.8 Alkyl Dinitramides as Intermediates in the Synthesis of Inorganic Dinitramides

The C—N bond in alkyl dinitramides is easily split by hydrolysis with strong alkali hydroxide, yielding the corresponding alkali dinitramide salts. The alkyl dinitramides can be isolated as intermediates, can be purified, or can be hydrolyzed without intermediate purification if dinitramide salts are the desired product. In addition to being useful as intermediates in the production of ADN or KDN, alkyl dinitramides would make good monopropellants similar to nitroalkanes.

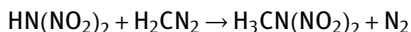
11.8.1 Synthesis of Alkyl Dinitramides (=Alkyl *N,N*-Dinitramines)

Alkyl *N,N*-dinitramines do not belong in this section on inorganic dinitramides, but there is some information here because of their role as intermediates in the synthesis of inorganic dinitramide salts. The main section on alkyl *N,N*-dinitramines is in *Encyclopedia of Liquid Fuels*, chapter “Nitramines.” Alkyl *N,N*-dinitramines were being synthesized long before their potential use as intermediates in the production of ADN became known [69].

Alkyl *N,N*-dinitramines can be obtained by the direct nitration of the corresponding alkyl isocyanates with $\text{NO}_2\text{BF}_4/\text{HNO}_3$. If alkali metal dinitramide salts are already available by synthesis via a different route, they can be converted into alkyl dinitramines by alkylation methods. For instance, cesium dinitramide can be converted into the alkyl dinitramine by reaction with the corresponding alkyl triflates. The product yield is 40%.



Alkylation of dinitramidic acid with diazomethane in ether gives methyl dinitramine in a 30% yield.



12 Other Oxidizing Ammonium Salts

12.1 Ammonium Nitroformate

Ammonium nitroformate, $\text{NH}_4\text{C}(\text{NO}_2)_3$, ANF, CAS RN [17181-40-7] is a potential rocket propellant oxidizer, but it has received only a fraction of the attention devoted to its hydronitrogen analog, hydrazinium nitroformate. The section on hydrazinium nitroformate in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salts,” would have also been a good location for discussion of ammonium nitroformate, but for now, ammonium nitroformate, although it has some commonalities with HNF, is discussed here, immediately following sections on ADN and other dinitramide salts. This was done in order to keep the ammonium salts together, giving sorting by cations priority over sorting by anions. Ammonium nitroformate is an intermediate product of HNF decomposition and may accumulate on the surface of burning HNF pellets. Ammonium nitroformate contains the nitro groups in the anion attached to nitrogen instead of carbon, so the two salts, ADN and ANF, have some similarity. There is a potential for confusion because the name “ammonium nitroformate” has also been used for the ammonium salt of nitroformic acid, O_2NCOOH [556]. The salt $\text{O}_2\text{NCOONH}_4$ should have been called “ammonium nitroformiate”.

12.1.1 Preparation of Ammonium Nitroformate

Similar to methods used for preparation of HNF, ammonium nitroformate can be prepared by direct neutralization of nitroform with ammonia, preferably in non-aqueous solvents where the salt will precipitate and can be separated from unreacted nitroform and solvents.

12.1.2 Physical Properties of Ammonium Nitroformate

Ammonium nitroformate melts at 389 K (116 °C) with incipient decomposition.

12.1.2.1 IR and Raman Spectra of Ammonium Nitroformate

The wave numbers of absorption and fluorescence peaks in IR and Raman spectra of solid ammonium nitroformate are summarized in Table 42.

Table 42: IR and Raman spectra of solid ammonium nitroformate.

IR spectra Wavenumber ν , cm^{-1}	Raman spectra Wavenumber ν , cm^{-1}
3222 (m), 1681 (w), 1533 (m), 1460 (m), 1415 (s), 1375 (s), 1247 (s), 1147 (s), 1006 (m), 926 (m), 869 (m), 823 (w), 788 (s), 735 (s), 689 (m)	3172 (4), 2986 (7), 1610 (7), 1535 (6), 1515 (6), 1475 (10), 1380 (43), 1349 (19), 1310 (28), 1273 (72), 1225 (39), 1156 (36), 1138 (25), 871 (100), 859 (35), 791 (12), 727 (10), 466 (24), 443 (18), 415 (20), 396 (16), 375 (21), 275 (23)

Data source: [557]

12.1.2.2 Molecular Structure of Ammonium Nitroformate

The molecular structure of ammonium nitroformate is illustrated in Figure 78.

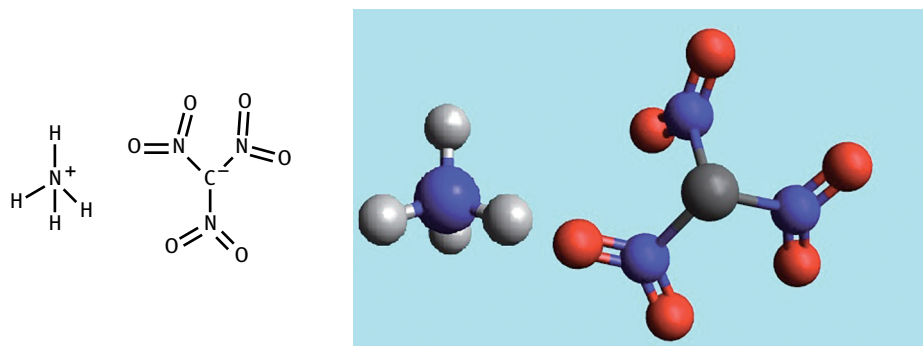


Figure 78: Molecular structure of ammonium nitroformate

12.1.2.3 Crystal Structure of Ammonium Nitroformate

Ammonium nitroformate crystallizes in the chiral tetragonal space group $P4_12_12$ (No. 92) with four formula units per unit cell [557]. The X-ray density of the crystals is 1.910 g/cm^3 .

12.1.2.4 Thermodynamic Properties of Ammonium Nitroformate

The heats of combustion of the ammonium salt of trinitromethane (**I**) (ammonium nitroformate) and the ammonium salt of 1,1-dinitropropane (**II**) were determined in a semi-microcalorimeter [558]. The heats of combustion were 1108.6 ± 1.3 and $3434.2 \pm 2.2\text{ cal/g}$ for **I** and **II**, respectively. From these values one can derive the standard enthalpies of formation (at 101 kPa and 298 K): $\Delta H^\circ_f = -47.3 \pm 0.2\text{ kcal/mol}$ and $\Delta H^\circ_f = +71.7 \pm 0.3\text{ kcal/mol}$ for **I** and **II**, respectively. On the basis of these values of ΔH°_f and data on the enthalpies of formation of $\text{HC(NO}_2)_3$, $\text{EtCH(NO}_2)_2$, and NH_3 taken from the literature, the energy of the salt bond between the nitro compound and NH_3 was estimated as 24.8 ± 0.7 and $19.9 \pm 0.6\text{ kcal/mol}$ for **I** and **II**, respectively.

Koroban et al. [559] and Williams and Brill [560] identified ANF as a product of HNF decomposition. The enthalpy of ANF dissociation, 164.77 kJ/mol (39.38 kcal/mol), is less than that of HNF and agreed closely with the experimental value.

The energies and heats of formation for ANF, HNF, and several organic nitroformate salts were calculated at the Møller-Plesset 2 (MP2) level of theory using an aug-cc-pVDZ basis set (Table 43; [557]). The values for the heat of formation obtained from these calculations were similar to, but different from, the previously reported experimental values for ANF ($-47.3 \pm 0.2\text{ kcal/mol}$) [558] and HNF ($-18.4 \pm 0.3\text{ kcal/mol}$).

Table 43: Calculated energies and heats of formation of solid ANF and solid HNF.

Compound	<i>M</i>	ρ , g/cm ³ , XRD	ΔH_L	ΔU_L	ΔH°_f	ΔU_f^0
ANF	168.10	1.910	132.4	131.2	-35.9	-792
HNF	183.09	1.938	130.0	128.8	+0.8	+125.7
		1.930	129.8	128.6	+1.0	
		1.890	129.1	127.9	+1.7	
		1.860	128.5	127.3	+2.3	

Data source: [557]

M molar mass, g/mol

ρ density obtained from single crystal X-ray diffraction studies, g/cm³

ΔH_L lattice enthalpy, kcal/mol

ΔU_L lattice energy, kcal/mol

ΔH°_f enthalpy of formation at 298 K, kcal/mol

ΔU_f^0 energy of formation, kcal/mol

12.1.3 Thermal Stability and Decomposition of Ammonium Nitroformate

Ammonium nitroformate, ANF, CAS RN [17181-40-7], is an intermediate product of HNF decomposition and may accumulate on the surface of burning HNF pellets [561]. The kinetics of thermal decomposition of ANF and HNF share some common intermediates and pathways and are very similar. The primary reactions of the thermal decomposition of HNF as well as ANF were investigated theoretically using the G3 multilevel procedure [562]. Calculations were done for the reactions in the gas phase and in the melt and showed that the influence of the melt on the reaction barriers involves the solvation free energies. The most energetically favorable structures of HNF and ANF free molecules in the gas phase are H-bonded complexes. In the melt, the ionic structure is lowest in free energy because of solvation effects. The primary dissociation reactions of ANF resemble those of HNF.

DSC was used to determine the thermal stability of ANF. Whereas ANF shows only one decomposition signal at 389 K (116 °C) coincident with its melting, other nitroformates showed separate melting points as well as subsequent decomposition points [557].

12.1.4 Safety Properties of Ammonium Nitroformate

The impact sensitivity of ANF is 3 J, and the friction sensitivity is 96 N, compared with 15 J and 25 N, respectively, for HNF. In the same publication, the detonation velocity and detonation pressure of ADN and several other nitroform salts were calculated [557]. The theoretical detonation velocity of ANF at its maximum density is 8532 m/s.

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Dinitrogen Pentoxide

Nitrogen commonly forms several different oxides with oxygen, depending on the state of oxidation of the central atom, nitrogen. The state of oxidation of nitrogen can be +1, +2, +3, +4, +5, or +6. The correct names of the six oxides are nitrous oxide (N_2O), nitric oxide (NO), dinitrogen trioxide (N_2O_3), nitrogen dioxide (NO_2), dinitrogen tetroxide (N_2O_4), dinitrogen pentoxide (N_2O_5), and nitrogen trioxide (NO_3). This chapter deals with dinitrogen pentoxide, which is also the anhydride of nitric acid. The state of oxidation of nitrogen in dinitrogen pentoxide is the highest that can be achieved without including peroxide bonds in the molecule. Because the valency of nitrogen in covalent bonds with oxygen is at most four, the structure of dinitrogen pentoxide must be formulated with semi-polar bonds, similar to those observed in nitric acid. Nitrogen trioxide NO_3 and its dimer N_2O_6 contain peroxide $-\text{O}-\text{O}-$ linkages, but those are unstable molecules observed only as short-lived transients in reactions of other nitrogen oxides.

Nitrogen oxides had to be covered in seven chapters because a single chapter devoted to the topic would have been unwieldy and made it more difficult for readers to find information on a specific compound; in addition, such an approach would have made it difficult to arrange 30 chapters among 5 subvolumes in such a way that each subvolume was about the same size. Briefer chapters made our task much easier. The other six chapters in this series are titled "Nitrogen Oxides," "Nitrous Oxide," "Nitric Oxide," "Dinitrogen Trioxide," "Nitrogen Dioxide," and "Dinitrogen Tetroxide."

Dinitrogen pentoxide is intrinsically unstable, and its exothermic decomposition has been the subject of some fundamental kinetic studies of first-order reactions.

Dinitrogen pentoxide (which is also known as N_2O_5 , dinitrogen pentaoxide, dinitrogen(V) oxide, nitrogen pentoxide, nitric acid anhydride, nitric anhydride, nitryl nitrate, nitronium nitrate, CAS RN [10102-03-1]) forms colorless crystals that sublime readily at room temperature without melting first. It is not possible to determine a melting point at normal atmospheric sea level pressure. If dinitrogen pentoxide is heated to near the anticipated melting point, it begins to decompose and liquefies, not because it melts, but because it forms a mixture of N_2O_5 and N_2O_4 . A sample of pure N_2O_5 heated in a sealed ampule to 307 K (34 °C) will decompose within 9 min and will contain 6% N_2O_4 . The decomposition may be explosive.

Dinitrogen pentoxide has been considered as a rocket propellant in the form of an additive to N_2O_4 or HNO_3 . Dinitrogen pentoxide is widely used for organic and inorganic nitration reactions in the production of nitramine explosives and ammonium dinitramide oxidizers. This avoids the use of mixed acid ($\text{HNO}_3/\text{H}_2\text{SO}_4$) and one does not have to worry about disposal of the used nitration acid with all the sulfuric acid in it. Using dinitrogen pentoxide instead of nitrating acid is thus an environmentally friendly way of performing nitration reactions [1, 2]. Because dinitrogen pentoxide

cannot be transported commercially and cannot be stored in bulk, it must be prepared immediately prior to use at the location where the nitrations are to be performed.

Dinitrogen pentoxide is a nitrogen reservoir in polar stratospheric clouds found in Antarctica and involved with ozone depletion, creating an ozone hole. It actively interconverts with the other nitrogen oxides under the influence of intense UV irradiation. The atmospheric chemistry of N_2O_5 has been extensively investigated, and this work has contributed many publications on the properties of N_2O_5 , which may also be useful for us in evaluating it as a rocket propellant. That is the main reason that, despite its thermal instability, the properties of N_2O_5 are summarized here in sufficient detail to either reconsider it or eliminate it from further consideration as a rocket propellant. With the advent of cryogenic solid propellants, frozen N_2O_5 could be a useful oxidizer as long as it is kept cold and prevented from decomposing. Because it is difficult to characterize N_2O_5 by spectroscopic methods at room temperature, freezing N_2O_5 or trapping it in a matrix of frozen argon has been standard practice for safe handling of this material. Similarly, frozen N_2O_5 could be used as a rocket propellant. It may be asserted that, at the very least, the elements that go into making N_2O_5 are in ample supply from ambient air.

1 Production of Dinitrogen Pentoxide

Dinitrogen pentoxide was first prepared by the action of dry chlorine on silver nitrate, but it is more easily made by the action of phosphoric acid anhydride (phosphorus pentoxide) on nitric acid [3, 4]. Dinitrogen pentoxide can also be produced by the ozonization of dinitrogen tetroxide or by electrochemical oxidation of N_2O_4 or HNO_3 [5].

Dinitrogen pentoxide is thermally unstable, and even at 273 K (0°C) its half-life time with respect to decomposition is only 245 h. Because of its thermal instability and high melting point, it cannot be used as a rocket propellant at room temperature. However, attempts have been made to mix dinitrogen pentoxide with other oxidizers with the aim of lowering the melting point or to improve the oxygen content of other oxidizers.

1.1 Production of Dinitrogen Pentoxide by Reaction with Ozone

Methods for N_2O_5 preparation on a laboratory scale by gas phase oxidation of N_2O_4 by ozone have been described in the literature [6, 7]. The apparatus consisted of a reaction chamber, where $\text{NO}_2/\text{N}_2\text{O}_4$ in a stream of oxygen was mixed with a stream of ozone (ca. 10%) in oxygen and the product, N_2O_5 , was trapped out as a solid in a chilled receptacle (P_2O_5 desiccant tubes were optional and for larger-scale synthesis were not found to be necessary). Also, trapping efficiency may be improved by adding extra traps. The N_2O_5 thus prepared must be stored in weighed tubes or flasks in the dark

at or below 213 K (-60°C) before use. Amounts of N_2O_5 in excess of 100 g/day may be prepared using this apparatus. Another method describes a process yielding 50 g N_2O_5 per batch [8].

The reaction of gaseous N_2O_4 with ozonized oxygen in a 1:2 molar ratio gave a 99.3% yield of N_2O_5 [9]. In reaction with ozone of solid N_2O_5 at 195 K (-78°C) or N_2O_5 dissolved in CCl_4 at 263 K (-10°C), the composition of N_2O_5 remained unaltered. The solubility of N_2O_5 in CCl_4 in the range 263 to 292 K (-10 to $+19^{\circ}\text{C}$) increased with temperature and reached 45.5% at 292 K (19°C).

Ab initio calculations using several different quantum chemical models have been made on all four reactions in which mononitrogen oxides react with ozone to generate higher oxidation states of nitrogen, culminating in N_2O_5 [10]. The relative reaction energies were determined, and all four reactions were found to be exothermic. Potential energy surfaces of the $\text{O}_3\text{-NO}$ and $\text{O}_3\text{-NO}_2$ reactant pairs were modeled using several methods, and the presence of a transition state was indicated in most of the models. For the $\text{O}_3\text{-NO}$ reaction there was reasonably good correlation with the experimental Arrhenius activation energy of 5 kJ/mol (1.2 kcal/mol). However, for the $\text{O}_3\text{-NO}_2$ reaction the calculated activation energy was four times higher than the experimental Arrhenius activation energy of 9.2 kJ/mol (2.2 kcal/mol). It does not appear to be a safe process to conduct the reaction of N_2O_4 with O_3 in an organic solvent, as suggested by some patents [11].

1.1.1 Production of Dinitrogen Pentoxide by Electrolysis

Dinitrogen pentoxide can be prepared by the electrolysis of concentrated nitric acid [12, 13]. The N_2O_5 thus prepared can be separated from its solution in nitric acid by cooling the acid solution to less than 265 K (8°C) until an N_2O_5 solvate precipitates from the solution [14].

Dinitrogen pentoxide can also be prepared by an electro-oxidation method using N_2O_4 and HNO_3 (RFNA) as raw materials [15]. The two electrochemical synthesis methods for the production of N_2O_5 by the oxidation of N_2O_4 and by the dehydration of HNO_3 were compared in terms of the current efficiency, specific energy, current density, and chemical yield of the electrolytic process [16]. The type of cell membrane and the electrode affect the current efficiency and the specific energy of the electrolysis.

Different porous polytetrafluoroethylene (PTFE) membranes were tested as the separators in the electrochemical synthesis of N_2O_5 by the oxidation of N_2O_4 in nitric acid and the effects of hydrophilicity and of hydrophobicity of the membrane on the electrolysis were studied [17]. The transport of N_2O_4 and water from catholyte to anolyte through a membrane occurred in the electrolysis, especially at the end of the electrolytic process. The water transport had much more of an effect on the electrolysis than the N_2O_4 transport. The hydrophobic PTFE membranes gave better performance with respect to the control of water transport from catholyte to anolyte than the hydrophilic ones gave. Hydrophobicity can increase the chemical yield of N_2O_5 . All the hydrophobic PTFE membranes with low resistance operated with a specific energy of

1.1–1.5 kWh/kg N_2O_5 . A current efficiency of 67–80% and chemical yield of 59–61% were achieved in the production of N_2O_5 .

The effects of electrolysis reaction time, current density, and reaction temperature on the preparation process were investigated [18]. The optimum anolyte with a higher mass fraction of N_2O_5 can be obtained using a reaction time of 4–5 h, a current density of 0.09–0.10 A/cm², and a reaction temperature of 273–283 K (5–10 °C).

Dinitrogen pentoxide can be prepared by the action of bromine pentafluoride or nitryl fluoride on an excess of lithium nitrate [19].

2 Physical Properties of Dinitrogen Pentoxide

The molecular mass of N_2O_5 is 108.0104 g/mol [20].

2.1 Melting Point of Dinitrogen Pentoxide

Dinitrogen pentoxide decomposes at the melting point. There are contradictory data in the literature about the melting point of dinitrogen pentoxide.

It was observed that a 5-g sample of dinitrogen pentoxide, resublimed in a current of ozone, condensed in a glass apparatus, then evacuated and sealed, showed signs of melting after 45 min at 303 K (30 °C), but it was concluded that “It is not a true melting, but a phenomenon complicated by the dissolving of dinitrogen tetroxide in the surface of the crystals.”

The most trustworthy results would be obtained by determining the melting point under an atmosphere of ozonized oxygen that retards some of the decomposition. Using this method, a melting point of 314 K (41 °C) was reported [21].

2.2 Density of Dinitrogen Pentoxide

The density of dinitrogen pentoxide is given in Table 1.

Table 1: Density of dinitrogen pentoxide.

Physical state	Temperature		Density	Literature
	°C	K	g/cm ³	
solid	–195	78	2.18	[22]
solid	–195	78	2.175	[23]
solid	16	289	1.99	—
solid	0	273	2.05	[24]
solid	20	293	1.786 ± 0.06	calculated

2.3 Vapor Pressure of Dinitrogen Pentoxide

The vapor pressure of dinitrogen pentoxide is listed in Table 2.

Table 2: Vapor pressure of dinitrogen pentoxide.

Temperature K	Vapor Pressure	
	mm Hg	kPa
243.2	2.3	0.31
246.7	3.3	0.44
252.2	6.3	0.84
262.5	18.6	2.47
273.1	50.9	6.76
273.2	51.5	6.8
281.9	111.2	14.8
283.7	132.2	17.6
285.45	157.7	21.0
288.2	196.8	26.2
290.7	240.9	32.0

Data source: [22]

The vapor pressure of dinitrogen pentoxide can be calculated from the following equation:

$$\log p_V = -\frac{3161.2}{T} + 1.75 \log T - 0.00606T + 10.771$$

where p_V is the vapor pressure (mm Hg) and T is the temperature (K).

2.4 Thermodynamic Properties of Dinitrogen Pentoxide

The thermodynamic properties of dinitrogen pentoxide are listed in Table 3.

2.4.1 Heat Capacity of Dinitrogen Pentoxide

The heat capacity of gaseous dinitrogen pentoxide as a function of temperature can be calculated from the following polynomial equation:

$$C_p^\circ = A + B \times t + C \times t^2 + D \times t^3 + \frac{E}{t^2}$$

where C_p is the heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$), t is the temperature in kelvin divided by 1000, and A, B, C, D, and E are constants listed in Table 4 for two different temperature ranges. Note that N_2O_5 is unstable at temperatures above 298 K and the column for

Table 3: Thermodynamic properties of dinitrogen pentoxide.

Property	Temperature, K	Physical state	SI Units	Other units	References
Standard enthalpy of formation	298.15	gaseous	$+11.3 \pm 1.2$ kJ/mol	$+2.7 \pm 0.3$ kcal/mol	[25]
Standard enthalpy of formation	298.15	gaseous	$+11.30$ kJ/mol	$+2.7$ kcal/mol	[20]
Heat of fusion	—	solid	34.6 kJ/mol	8.280 kcal/mol	[22]
Heat of vaporization	281	liquid	56.5 kJ/mol	13.5 kcal/mol	[22]
Entropy	298	gaseous	346 ± 4 J mol ⁻¹ K ⁻¹	82.8 ± 1.0 cal mol ⁻¹ °C ⁻¹	[25]

the higher temperature range 1100–6000 K is only of academic interest. It is not very meaningful to list thermodynamic data for a compound that is unstable in the temperature range listed. It would be much more important to have accurate thermodynamic data for the liquid mixtures of dinitrogen pentoxide with dinitrogen tetroxide.

The JANAF tables give the heat capacity of gaseous N₂O₅ at 298 K as 96.303 J mol⁻¹ K⁻¹ [25].

2.4.2 Enthalpy of Formation of Dinitrogen Pentoxide

The standard enthalpy of formation of gaseous dinitrogen pentoxide at 298 K is +11.30 kJ/mol (+2.7 kcal/mol) [20]. The JANAF tables give $\Delta H_f^{298} = +11.297$ kJ/mol [25]. The enthalpy of formation of gaseous dinitrogen pentoxide as a function of temperature can be calculated from the following polynomial equation:

$$H^\circ - H^\circ_{298.15} = At + \frac{B \times t^2}{2} + \frac{C \times t^3}{3} + \frac{D \times t^4}{4} - \frac{E}{t} + F - H$$

where H is the enthalpy (kJ/mol), t is the temperature in kelvin divided by 1000, and A , B , C , D , E , and F are constants listed in Table 4 for two different temperature ranges.

The enthalpy of formation for solid N₂O₅ was determined via the reaction with H₂O(L) and was found to be -54.0 ± 2.5 kJ/mol = -12.91 ± 0.61 kcal/mol [26]. The enthalpy of sublimation was determined from the vapor pressure of N₂O₅ measured as a function of temperature at 211–273 K and was found to be 59.01 ± 0.31 kJ/mol = 14.104 ± 0.075 kcal/mol. From these data and the enthalpy of the reaction

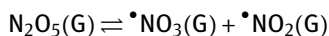


Table 4: Thermodynamic property polynomial equation coefficients for dinitrogen pentoxide vapor.

Temperature range, K	298–800	800–6000
A	23.85152	149.4818
B	337.9894	0.154807
C	−353.4530	−0.038263
D	134.8407	0.003074
E	−0.042447	−8.093070
F	−8.123279	−57.10198
G	288.9203	490.8418
H	11.29701	11.29701

Data source: [20]

(determined from the temperature dependence of the equilibrium constant), the enthalpies of formation for $\text{N}_2\text{O}_5(\text{G})$ and $\cdot\text{NO}_3(\text{G})$ were determined as $+4.98 \pm 2.55 \text{ kJ/mol}$ ($+1.19 \pm 0.61 \text{ kcal/mol}$) and $+64.4 \pm 3.1 \text{ kJ/mol}$ ($+15.39 \pm 0.75 \text{ kcal/mol}$), respectively. The enthalpy of formation of the $\cdot\text{NO}_3$ radical was therefore found to be significantly less than the commonly accepted value.

2.4.2.1 Entropy of Dinitrogen Pentoxide

The standard entropy of formation of gaseous dinitrogen pentoxide at 298 K and 101 kPa is $346.55 \text{ J mol}^{-1} \text{ K}^{-1}$ [20]. The entropy of gaseous dinitrogen pentoxide as a function of temperature can be calculated from the following polynomial equation

$$S^\circ = A \times \ln(t) + B \times t + \frac{C \times t^2}{2} + \frac{D \times t^3}{3} - \frac{E}{2 \times t^2} + G$$

where S° is the enthalpy in $\text{J mol}^{-1} \text{ K}^{-1}$, t is the temperature in kelvin divided by 1000, and A, B, C, D, E, and G are constants listed in Table 4 for two different temperature ranges.

2.5 Molecular Structure of Dinitrogen Pentoxide

It is unfortunate that dinitrogen pentoxide is so unstable that it cannot be used as a rocket propellant. Its oxygen content and energy content would be superior to that of the widely used dinitrogen tetroxide. We are exploring the molecular structure of dinitrogen pentoxide here in the hope of better understanding the causes of its instability and in the hope of finding other nitrogen oxides that may be useful as oxidizers. After all, cryogenic rocket propellants open up avenues to rocket propellants that had previously been rejected from further consideration because they are unstable at room temperature.

Gaseous N_2O_5 consists of two $-\text{NO}_2$ groups bonded to a bridging O atom to form a non-linear $\text{N}-\text{O}-\text{N}$ moiety. The $-\text{NO}_2$ groups undergo slightly hindered internal rotation around the bonds to the bridge so that instantaneous composition of the gaseous system at any time is characterized by molecules with all combinations of torsion angles.

The dinitrogen pentoxide molecule should consist of two nitro groups attached to a central oxygen. If this were a linear, symmetrical molecule with a 180° valence angle for the central oxygen, this structure would have zero dipole moment. In contrast to that, the considerable moment of 1.39 D obtained from microwave measurements showed this to be impossible. Evidently, the molecule is bent and a very rough value of the oxygen valence angle (approx. 140°) may be calculated from the group and bond moments involved [27].

The structure of dinitrogen pentoxide has been investigated in the gas phase at a temperature of 262 K (-11°C) [28]. This study assumed that the structure of the $\text{O}-\text{NO}_2$ groups was invariant to torsion angle and that these groups had C_{2v} symmetry. The molecule consists of two $-\text{NO}_2$ groups joined to a fifth oxygen atom by non-collinear bonds (Figure 1). On each side of the molecule, one of the $\text{N}=\text{O}$ bonds is actually a semipolar bond, but the drawing software does not have the ability to display semipolar bonds.

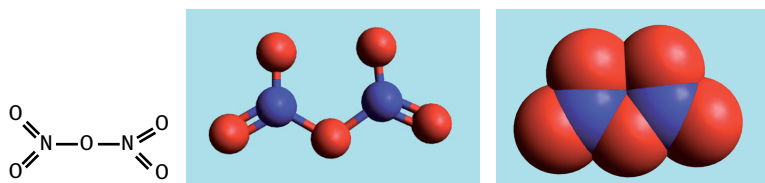


Figure 1: Molecular structure of dinitrogen pentoxide.

The $-\text{NO}_2$ groups are undergoing large-amplitude torsional motion about a point of minimum energy corresponding to C_2 symmetry for molecules at dihedral angles τ_1 and τ_2 between these groups and an $\text{N}-\text{O}-\text{N}$ plane of about 30° each. The torsional motion was modeled by a potential representing a competition between bonding forces tending to stabilize the planar conformation and repulsive forces between oxygen atoms on different $-\text{NO}_2$ groups tending to destabilize it. The results suggested the motions of the $-\text{NO}_2$ groups are loosely coupled in such a way that one torsion angle tends to increase from the minimum energy point as the other decreases. The bond distances and angles with estimated 2σ uncertainties are $r(\text{N}=\text{O})$ 1.188(2) Å, $r(\text{N}-\text{O})$ 1.498(4) Å, $\angle\text{O}=\text{N}=\text{O}$ $133.2(6)^\circ$, $\angle\text{N}-\text{O}-\text{N}$ $111.8(16)^\circ$, and $\langle\tau_1 = \tau_2$ 30° at potential energy minimum.

In the solid phase, N_2O_5 has the ionic structure $[\text{NO}_2^+][\text{NO}_3^-]$. Based on X-ray diffraction (XRD) analysis, the crystal structure of solid N_2O_5 at 105 K (-168°C) is pseu-

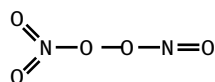
dohexagonal, space group $P6_3/mmc$, with $a = 5.4019(9)$ and $c = 6.5268(13)$ Å; $d_c = 2.175 \text{ g/cm}^3$ for $Z = 2$. The structures were solved by direct methods and refined by least-squares to $R = 0.028$ [29]. An earlier XRD structural analysis of crystalline N_2O_5 at 213 K had resulted in $a = 5.41$ Å, $c = 6.57$ Å [30]. See also [31, 32].

2.5.1 Computational Chemistry of Molecular Structure of Dinitrogen Pentoxide

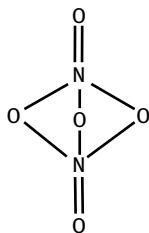
Ab initio MO calculations to determine the minimum-energy structure of N_2O_5 showed that N_2O_5 had an anhydride-type structure with its nitro groups rotated $\sim 42^\circ$ out of the central N—O—N plane in a conrotatory fashion [33].

Several conformers have been considered for N_2O_5 , and *ab initio* calculations on these conformers identified three minimum-energy structures, namely, planar, perpendicular, and fully optimized structure [34]. The global minimum energy was characterized by vibrational frequency analysis. The calculations indicated that the fully optimized structure had a C_2 symmetry with its nitro groups rotated $\sim 35^\circ$ from the central N—O—N plane in a conrotatory manner. The *ab initio* frequencies of N_2O_5 were compared to those determined by experiment or density functional theory (DFT) methods.

Other potential, speculative isomer structures for N_2O_5 are shown in the following graphs (note that some of the N=O bonds are semipolar bonds):



Nitro nitroso peroxide
CAS RN [919401-11-9]



2,4,5-Trioxo-1,3-diazabicyclo[1.1.1]pentane, 1,3-dioxide
CAS RN [224950-19-0]

The N_2O_5 molecule has been investigated in terms of a more realistic model in which the symmetry restriction was relaxed, account was taken of structural changes in the $-\text{NO}_2$ groups with torsion angle as predicted by *ab initio* theory, and a more convenient form of the torsional potential was assumed [35]. The most stable conformation has C_2 symmetry with torsion angles τ_1 , defined as $\angle(\text{N}-\text{O}-\text{N}=\text{O}_4)$, equal to τ_2 , defined as $\angle(\text{N}-\text{O}-\text{N}=\text{O}_6)$, equal to 33.7° ; because of the broad potential minimum in this region, the uncertainty in these angles was difficult to estimate, but it was esti-

mated at 3–4°. The revised results for the bond lengths and bond angles for the most stable conformation were $r_g(\text{N}-\text{O}) = 1.505(4) \text{ \AA}$, $r_g(\text{N}=\text{O}) = 1.188(2) \text{ \AA}$, $\angle(\text{N}-\text{O}-\text{N}) = 112.3(17)^\circ$, $\angle(\text{O}=\text{N}=\text{O}) = 134.2(4)^\circ$, and $\angle(\text{O}-\text{N}=\text{O}) = 112.8(2)^\circ$. The difference between the symmetry-non-equivalent $\text{O}-\text{N}=\text{O}$ angles was estimated to be ca. 6.7°, with the larger angle positioning the two $\text{N}=\text{O}$ bonds on different $-\text{NO}_2$ groups nearest each other.

DFT quantum-chemical calculations have shown that the molecular structures of N_2O_5 with C_s and C_2 symmetries are energetically equivalent [36]. It follows from calculations of the vibrational frequencies that both structures are characterized by potential energy minima and correspond to stationary states of the N_2O_5 molecule. It has been proposed, on the basis of a comparison of the calculated and experimental vibrational spectra of N_2O_5 , that dinitrogen pentoxide exists in the gas phase as an equimolecular mixture of N_2O_5 molecules with C_s and C_2 symmetry, while in the solid phase it is characterized by the C_2 molecular structure. See also [37].

2.6 Optical Properties of Dinitrogen Pentoxide

Because of the involvement of dinitrogen pentoxide in atmospheric chemistry, in particular chemistry taking place in the ozone layer high above the breathable atmosphere, its absorption spectra have been thoroughly investigated. Having accurate spectra of N_2O_5 by itself should help in the identification of other nitrogen oxides potentially formed at the same time that could be used as rocket propellants.

2.6.1 Ultraviolet Spectra of Dinitrogen Pentoxide

Because reactions with N_2O_5 play a role in atmospheric chemistry, UV absorption cross sections for N_2O_5 vapor were measured at wavelengths between 200 and 380 nm and temperatures between 223 and 300 K [38]. The absorption spectrum above 290 nm showed a pronounced temperature dependence.

The spectrum and photoabsorption cross sections of N_2O_5 at 195 K between 150 and 240 nm consisted of a broad intense band with a maximum at 160 nm [39]. The lack of sharp features indicated that excitation of N_2O_5 resulted in dissociation over the entire spectral range studied. At wavelengths >200 nm, the measured absorptions were up to 30% smaller than older data reported in the literature but were in generally good agreement with more recent measurements. Below 200 nm, there were no reported data in the literature.

Dinitrogen pentoxide has UV absorptions at 204, 213, 258 nm ($\pi \rightarrow \pi^*$) 378 and 384 nm ($n \rightarrow \pi^*$) [8]. See also [40].

2.6.2 Infrared Spectra of Dinitrogen Pentoxide

2.6.2.1 Infrared Spectra of Gaseous Dinitrogen Pentoxide

The IR spectrum of N_2O_5 in the gas phase is remarkably similar to that of the equilibrium mixture of $\text{NO}_2/\text{N}_2\text{O}_4$. Like planar N_2O_4 , covalent N_2O_5 showed all the bands characteristic of the nitro group, namely, an asymmetric stretch (at 1720 cm^{-1}), a symmetric stretch (at 1240 cm^{-1}), and an ONO bend (at 730 cm^{-1}), in full agreement with the structure usually postulated for this molecule of two nitro groups linked (non-linearly) through an oxygen atom.

Because N_2O_5 has been detected in the upper atmosphere, where it plays a role in air pollution and ozone layer depletion, its spectral properties have been extensively investigated and methods for the remote analysis of traces of N_2O_5 in the atmosphere have been developed. Daily, seasonal, and vertical profiles of changes in the N_2O_5 concentration in the atmosphere have been developed using a variety of remote sensing techniques.

In the mid-IR region, absorptions were observed at 1720 , 1246 , 743 , and 557 cm^{-1} [41]. These absorptions can be used for the stratospheric detection of N_2O_5 .

The absorption of gaseous dinitrogen pentoxide in the 8.1 - and $5.7\text{-}\mu\text{m}$ spectral regions was measured with a fast-scanning Fourier transform infrared (FTIR) spectrometer with a flow-through system in order to maintain pure, fresh N_2O_5 samples in the absorption cell [42]. The amount of inevitable impurities, such as NO_2 and HNO_3 , in the cell was evaluated from the measurement of their individual absorptions, and the results were used to determine the partial pressure of N_2O_5 . The total intensities of the N_2O_5 bands located at 8.1 and $5.7\text{ }\mu\text{m}$ were as follows: $I_{\text{N}_2\text{O}_5}(8.1\text{ }\mu\text{m}) = 1508 \pm 100\text{ cm}^{-1}\text{ atm}^{-1}\text{ cm}^{-1}$ and $I_{\text{N}_2\text{O}_5}(5.7\text{ }\mu\text{m}) = 3580 \pm 167\text{ cm}^{-1}\text{ atm}^{-1}\text{ cm}^{-1}$ at 296 K .

Absorption cross sections for three strong IR bands of N_2O_5 were measured as a function of temperature at 233 – 350 K [43]. The Beer-Lambert linearity of signal strength vs. concentration was confirmed.

The far-IR spectrum of N_2O_5 at room temperature in the gas phase showed a broad, weak feature with its maximum near 50 cm^{-1} , and its intensity was 1.20 (10%) of that of the band at 350 cm^{-1} [44]. The latter band, in turn, had a band intensity of around 0.33 of that of the band at 1250 cm^{-1} .

Laboratory measurements of the $\nu_{1,2}$ absorption band of gaseous N_2O_5 were made using FTIR spectroscopy at seven different temperatures between 233 and 293 K [45]. Integrated band strengths and absorbance cross sections per molecule showed no significant temperature dependence. The average values were $S_{\text{int}} = (4.09 \pm 0.17) \times 10^{-17}\text{ cm}^2/\text{mol}$ and $\sigma_{\text{peak}} = (1.90 \pm 0.08) \times 10^{-18}\text{ cm}^2/\text{mol}$.

IR absorptions of dinitrogen pentoxide vapor reported at 1428 , 1266 , 1249 , 1206 , 1044 , 822 , 750 , 546 , and 454 cm^{-1} from reference [8] do not agree with absorptions listed at the NIST Chemistry WebBook site [46]. See also [47, 48].

2.6.2.2 Infrared Spectra of Frozen or Matrix-Isolated Dinitrogen Pentoxide

At liquid nitrogen temperatures, pure dinitrogen pentoxide forms an ionic $\text{NO}_2^+\text{NO}_3^-$ lattice, as indicated by its IR spectra, but at liquid helium temperatures, deposition was only in the easily recognized covalent form [49].

FTIR spectra of the covalent dinitrogen pentoxide molecule isolated in a solid Ar matrix at 10 K showed that frequencies in the $200\text{--}4000\text{ cm}^{-1}$ region were in close agreement with previously reported gas phase values [50]. An accurate and sophisticated *ab initio* study showed that the stable equilibrium structure, C_2 symmetry, was in agreement with the structure previously determined by electron diffraction data.

2.6.3 Raman Spectra of Dinitrogen Pentoxide

A Raman spectral study of solutions of N_2O_4 and N_2O_5 in anhydrous and aqueous HNO_3 provided a more detailed knowledge of the species present in these solutions and assessed the applicability of Raman spectroscopy as an analytical measurement technique [51]. The nitronium cation, NO_2^+ , is the dominant species in solutions of N_2O_5 in anhydrous HNO_3 . A new band was discovered in the spectra of concentrated solutions of N_2O_5 . This weak band, which may be the same as a band found in the spectra of solids containing the nitronium cation, was attributed to a second vibrational mode of the molecule. This indicated a non-linear conformation of the NO_2^+ ion and suggested that it is strongly associated with other species in the solution. The Raman data indicated that N_2O_5 in HNO_3 is completely ionized at concentrations up to at least 3.0 mol/L (21 mass-%).

Nitrosonium nitrate, NO^+NO_3^- , and dinitrogen pentoxide (nitronium nitrate), $\text{NO}_2^+\text{NO}_3^-$, ionic crystals were synthesized by laser heating of a condensed oxygen-rich O_2/N_2 mixture compressed to extremely high pressures, up to 40 GPa, in a diamond anvil cell [52]. High-pressure/high-temperature Raman and XRD studies of high-pressure samples revealed a transformation of NO^+NO_3^- to $\text{NO}_2^+\text{NO}_3^-$ crystals at temperatures above ambient and pressures below 9 GPa. High-pressure experiments revealed previously unreported bands in the Raman spectra of NO^+NO_3^- and $\text{NO}_2^+\text{NO}_3^-$ ionic crystals. There may be a rotational disorder in solid NO^+NO_3^- and $\text{NO}_2^+\text{NO}_3^-$. See also [19].

2.6.4 Microwave Spectra of Dinitrogen Pentoxide

Nine molecular constants were determined from the preliminary assignments of microwave absorptions of N_2O_5 , but they did not allow for reproducing all the observed microwave transitions to their experimental accuracy [53].

The rotational spectrum of expanding N_2O_5 gas jets was studied between 8 and 25 GHz at a rotational temperature of around 2.5 K using a pulsed-molecular-beam Fourier-transform microwave spectrometer [54]. Two weak b-dipole spectra were observed for two internal-rotor states of the molecule, with each spectrum poorly characterized by an asymmetrical-rotor Hamiltonian. Analysis of the ^{14}N nuclear hyperfine

structure demonstrated that the two N nuclei occupy either structurally equivalent positions or are interchanging non-equivalent structural positions via tunneling or internal rotation at a rate larger than around 1 MHz. The spectrum was assigned to the symmetrical and anti-symmetrical tunneling states of a C_2 symmetry N_2O_5 with internal-rotation tunneling of the two NO_2 groups via a geared rotation about their respective C_2 axes. Model dynamical calculations suggested that the internal-rotation potential was significantly more isotropic than implied by electron-diffraction analysis.

Rotational spectra of b-type subbands of N_2O_5 for both internal-rotor states were recorded using a pulsed-nozzle Fourier-transform microwave spectrometer [55]. The measurements extended previous results on N_2O_5 , which were confined to the rR0, rR1, rQ1, and rP1 b-type subbands due to limitations in the frequency coverage of the instrument. The measurements provided new energy-level differences, which gave a nearly complete picture of the $K = 0, 1$, and 2 energy levels. The measurements also supported N_2O_5 as a C_2 symmetry molecule with facile geared internal rotation of two equivalent NO_2 groups. The IR spectra of the 1246 cm^{-1} , $\nu_{1,2}$, N—O stretching fundamental band of N_2O_5 were also recorded and revealed a complex resolved rotational structure, which remained unanalyzed.

2.6.5 Photoelectron (XPS) Spectroscopic Studies of Dinitrogen Pentoxide

He I photoelectron spectra for dinitrogen tetroxide and dinitrogen pentoxide obtained by rapid expansion of the vapor were compared with Gaussian *ab initio* molecular orbital calculations and with the spectra of the dissociated species, also in relation to nitric acid [56]. Several possible geometrical structures were considered in the case of dinitrogen pentoxide. It was shown that a planar form with an N—O—N angle on the order of 120° is most consistent with the photoelectron spectra results.

3 Chemical Properties of Dinitrogen Pentoxide

Dinitrogen pentoxide is soluble in bromine, dinitrogen tetroxide, tetrachloromethane, chloroform, ethylene chloride, ethylidene chloride, pentachloroethane, or nitromethane without chemical reaction. Nitric acid at room temperature dissolves up to 90 mass-% N_2O_5 , which makes it a powerful nitrating agent for the synthesis of organic high-energy compounds. Nitromethane at 288 K (15°C) dissolves 4.38 Mol N_2O_5 /L. See also [57].

3.1 Reactions of Dinitrogen Pentoxide

3.1.1 Reactions of Dinitrogen Pentoxide with Inorganic Substances

Dinitrogen pentoxide reacts with water under strong heat evolution to form nitric acid. In spite of this reactivity, it is surprising to learn that frozen N_2O_5 and ice crystals co-exist in the high atmosphere, where they do not immediately react with each other. Dry ammonia will not ignite spontaneously with N_2O_5 .

3.1.2 Reactions of Dinitrogen Pentoxide with Organic Substances

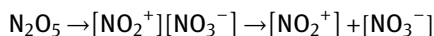
Most organic compounds undergo nitration, and not all ignite spontaneously when they first come in contact with N_2O_5 . Some inert organic solvents have been patented as solvent media for the production of N_2O_5 from N_2O_4 and ozone. Reactions of N_2O_5 with alkanes lead to mixtures of nitroalkanes. Nitroalkanes can be prepared by the direct nitration of aliphatic or alicyclic hydrocarbons with nitric acid, nitrogen dioxide, or dinitrogen pentoxide. Two complementary but essentially different reaction systems are available, namely, N_2O_5 in nitric acid and N_2O_5 in organic inert solvents. The former system possesses strength similar to that of mixed acid (nitric/sulfuric acid) systems but has advantages such as ease of generation of the nitration reagent by electrolysis and more easily recyclable reaction media. The latter system permits the generation of polynitrated species directly without the formation of acidic byproducts, notably by a new type of nitration reaction, addition nitration, where reactions with strained-ring heterocyclic compounds yield a wide variety of products [58–61] in the vapor phase at elevated temperatures, but this is a very hazardous operation since one is essentially feeding rocket propellants into a reactor just short of ignition or explosion conditions. N_2O_5 produced *in situ* by the electrolysis of HNO_3 has become an important nitration agent in the production of explosives such as HMX and RDX. For this application, N_2O_5 does not have to be isolated in the pure state, but it can be used as a solution in nitric acid, the same nitric acid used as the electrolyte in electrosynthesis apparatus. The use of dinitrogen pentoxide instead of a mixture of nitric acid and concentrated sulfuric acid as a nitrating agent results in an environmentally more friendly production process because it is not necessary to dispose of the spent nitrating acid that contains sulfuric acid. Cyclotetramethylenehexamine can be converted to RDX in a one-step reaction with N_2O_5 as the nitrating agent [62]. Nitrations with N_2O_5 give clean products with fewer byproducts [63].

Both N_2O_5 and HNO_3 are soluble in liquid CO_2 (not necessarily under supercritical conditions because supercritical CO_2 dissolves just about everything) and can be used in this inert solvent to safely nitrate many organic compounds in the preparation of energetic materials [64].

3.2 Thermal Stability of Dinitrogen Pentoxide

3.2.1 Dissociation of Dinitrogen Pentoxide

Dinitrogen pentoxide can dissociate and convert to the ionic form of nitryl nitrate, which then dissociates in a heterolytic reaction into nitronium and nitrate ions [65]:



A third-law method was used to assess the authenticity and accuracy of the available equilibrium constants and thermodynamic properties of the thermal dissociation of N_2O_5 in accordance with

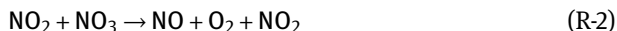


Recommendations were made for the heats of formation and dissociation and for identifying the need for further determination of the basic property values of this compound [66].

Equilibrium geometries and transition states for the equilibrium



and for the reaction



have been predicted using DFT methods and *ab initio* calculations [67]. The optimized geometries for N_2O_5 were in good agreement with experiments and previous calculations reported in the literature. A transition state for the decomposition of N_2O_5 has been located. Reaction (R-2) proceeds via a complex mechanism. The first step is the formation of a peroxy intermediate $\text{ONO}\cdots\text{ONO}_2$ that can rearrange via a high lying intermediate to $\text{ON}(\text{O}_2)\cdots\text{ONO}$, which can then yield $\text{NO}_2 + \text{NO} + \text{O}_2$.

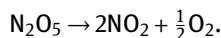
3.2.2 Thermal Decomposition of Dinitrogen Pentoxide

The decomposition of N_2O_5 was studied by measuring the pressure rise in an all-glass apparatus in the temperature range from 298 to 328 K (25 to 55 °C), and it was then that it was first recognized that the decomposition reaction is a monomolecular reaction [68–70]. The experiments were conducted in a blackened apparatus to exclude any light since it was known that N_2O_5 will decompose faster through photolysis. The surface: volume ratio of several different apparatus used had no effect on the rate of decomposition. The pressure measurements were corrected for the equilibrium dissociation of N_2O_4 , which resulted in additional pressure that was subtracted from the total pressure.

The thermal decomposition of N_2O_5 can be retarded somewhat in the presence of ozone [71, 72], but not in the presence of excess oxygen or dinitrogen tetroxide [73].

3.2.2.1 Kinetics of Dinitrogen Pentoxide Decomposition

The decomposition of dinitrogen pentoxide is a first-order reaction and has served as a model substance in the derivation of kinetic equations to characterize such reactions. Dinitrogen pentoxide decomposes irreversibly similar to radioactive decay in a monomolecular first-order reaction that has often been used as a model reaction for fundamental kinetic studies [74]:



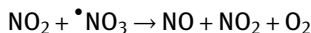
The half-life at 273 K (0 °C) is 244.8 h, at 288 K (15 °C) it is 18.5 h, and at 293 K (20 °C) it is only 9.9 h. The rate of decomposition cannot be influenced by lowering the pressure, by dilution with inert gases, or by dissolving it in inert solvents [75]. The decomposition of N_2O_5 proceeds at the same rate down to pressures of 0.06 mm Hg [76–79]. This rapid decomposition makes it very improbable that dinitrogen pentoxide can be stored long enough to be used as a rocket propellant.

In some solvents, the rates of decomposition and their temperature coefficients behave quite abnormally [80]. The rate of decomposition is greatly accelerated by illumination, so thermal decomposition becomes photolysis. In the presence of ozone, N_2O_5 decomposes more slowly. On the other hand, the addition of N_2O_4 shortens the half-life. The decomposition of N_2O_5 in N_2O_4 solution proceeded twice as fast as in the gas phase. Some reports have stated that samples of N_2O_5 stored at room temperature explode randomly without an identifiable cause. Most construction materials that are resistant to N_2O_4 can also be used for handling N_2O_5 .

The equilibrium constant for $\text{N}_2\text{O}_5 \rightleftharpoons \bullet\text{NO}_2 + \bullet\text{NO}_3$ has been determined through direct concentration measurements of N_2O_5 , NO_2 , and $\bullet\text{NO}_3$ in a temperature-controlled long path cell using absorption spectroscopy in the infrared and visible regions from 243 to 397 K [81]. The equilibrium constant was found to be

$$k_{1C} = 1.30 \times 10^{26} \exp(-21490/RT) \text{ molecules cm}^{-3}$$

with an estimated overall uncertainty of 30% at the 95% confidence level. This equilibrium constant at near room temperature was approximately half that of previously accepted values. Using the temperature dependence of the equilibrium constant and new data for the enthalpy of formation of gaseous N_2O_5 yielded an enthalpy of formation for $\bullet\text{NO}_3$ of $+64.4 \pm 3.1 \text{ kJ/mol}$ ($+15.39 \pm 0.75 \text{ kcal/mol}$). The temperature-dependent first-order decay rates of N_2O_5 were determined, from which a value for the product of the equilibrium constant k_{1C} and the rate constant for



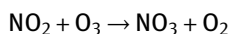
was obtained for temperatures from 298 to 396 K:

$$k_1 k_2 = 1.23 \times 10^{13} \exp(-24300/RT) \text{ s}^{-1}.$$

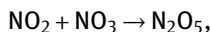
When this was combined with the equilibrium constant, the following expression was obtained for k_2 :

$$k_2 = 9.5 \times 10^{-14} \exp(-2810/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

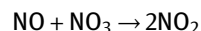
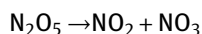
Qualitative valence bond considerations were used to explain how electronic reorganization could proceed for (a) the formation of N_2O_5 via the reactions



and



and (b) the thermal decomposition of N_2O_5 via the following sets of reactions:



Increased-valence structures, which possess one-electron bonds and fractional electron-pair bonds as well as so-called normal electron-pair bonds, were used to represent the electronic structures of molecules [82].

The thermal decomposition rate of the tropospheric component N_2O_5 at 101 kPa of air as a function of temperature between 314 and 348 K was investigated using pulsed laser cavity ring-down spectroscopy (CRDS) for the detection of NO_3 radicals at 662 nm [83]. The Arrhenius expression of the thermal decomposition rates determined by CRDS over the temperature range 263–348 K is

$$k = 1.36 \times 10^{15} \exp\{(-11300 \pm 200)/T\} \text{ s}^{-1}.$$

3.3 Photolysis of Dinitrogen Pentoxide

Because small amounts of dinitrogen pentoxide form in the stratosphere under the influence of ozone and ultraviolet light, the same conditions that bring about its formation are also conducive to its decomposition, most of all by photolysis [84].

Pulsed laser photolysis of N_2O_5 near 290 nm coupled with fluorescence detection (calibrated by NO_2 photolysis) showed that the $\text{O}(^3\text{P})$ quantum yield is ≤ 0.1 [85]. A pulsed laser optoacoustic technique in a flow tube was tested by the photolysis of NO_2 and then applied to the photolysis of N_2O_5 . Nitric oxide was added to react with $\bullet\text{NO}_3$ free radicals, and the resulting increase in the optoacoustic signal confirmed the presence of $\bullet\text{NO}_3$ free radicals. Based on the relative optoacoustic signals observed for NO_2 and N_2O_5 , the quantum yield for $\bullet\text{NO}_3$ production was 0.8 ± 0.2 .

The quantum yield for the production of $\bullet\text{NO}_3$ free radicals in N_2O_5 photolysis at 248 nm was measured to be near unity [86]. The concentration of $\bullet\text{NO}_3$ produced upon photolysis was measured using 662-nm laser absorption. The quantum yields for $\text{O}(^3\text{P})$ production in the photolysis of N_2O_5 at 248, 266, 287, and 289 nm were also measured using resonance fluorescence detection of $\text{O}(^3\text{P})$. The quantum yield for $\text{O}(^3\text{P})$ decreased from 0.7 at 248 nm to 0.15 at 289 nm.

A combination of matrix isolation and FTIR spectroscopy was used to investigate the low-temperature photochemistry (4.2 K) of dinitrogen pentoxide [87]. UV photolysis of the matrix isolated precursor at $\lambda > 230$ nm resulted in the photoreduction of N_2O_5 to N_2O via N_2O_3 as an intermediate. Both *asym*- and *sym*- N_2O_3 were formed in argon matrices, whereas in solid nitrogen only *asym*- N_2O_3 was produced. Little or no evidence was found for the potential formation of isomeric forms of N_2O_4 .

3.4 Analysis of Dinitrogen Pentoxide

Solutions of N_2O_5 , N_2O_4 , and HNO_3 in methylene chloride can be analyzed by IR spectroscopy [88].

4 Hazardous Properties of Dinitrogen Pentoxide

According to some reports, samples of pure N_2O_5 stored at room temperature have exploded spontaneously without an identifiable cause. The material should therefore be stored separate from all other chemicals and only in non-fragmenting, vented containers. N_2O_5 solutions in inert solvents can be stored at low temperatures in vented containers with pressure relief valves.

The vapors of subliming N_2O_5 are very toxic. They hydrolyze in the nostrils, trachea, and lungs, forming nitric acid. The vapor pressure of N_2O_5 crystals at room temperature is sufficiently high to cause serious poisoning accidents [89]. Dinitrogen pentoxide is much more poisonous than N_2O_4 . Test rats exposed to various constant concentrations in a range of 1 to 4 ppm N_2O_5 for a few hours died at any concentration higher than 2 ppm within a few hours. In a parallel test, other animals survived 8 to 20 ppm N_2O_4 without undue effects. The toxicity of N_2O_5 has been compared to that of phosgene. Dinitrogen pentoxide may form as a byproduct during the ozonization of air. Ozone made by ozonization of air is much more toxic than ozone made from a glow discharge in or UV illumination of pure oxygen.

5 Dinitrogen Pentoxide Mixtures with Other Oxidizers

It would be ideal to be able to mix N_2O_5 with other compatible oxidizers to stabilize it and widen the liquid range. The most likely candidates for such mixtures would be dinitrogen tetroxide, N_2O_4 , and the acid for which N_2O_5 is the anhydride, nitric acid HNO_3 . Unfortunately, N_2O_4 accelerates the decomposition of N_2O_5 and cannot be used as a solvent.

If one accepts the need to keep these propellants cool as a necessary evil, one can consider oxidizer mixtures containing dinitrogen pentoxide and evaluate them as rocket propellant oxidizers. What makes them attractive is the high oxygen content, high enthalpy of formation, ready availability of the constituent elements nitrogen and oxygen from ambient air, and clean combustion products (as opposed to fluorinated high-energy oxidizers). However, most experienced rocket propellant chemists scoff at the idea of using dinitrogen pentoxide and regard it as pure speculation. There have been no known applications of dinitrogen pentoxide in rocket engines. On the other hand, future use of cryopropellants where all ingredients are solid at the temperature of liquid nitrogen will enable us to use propellant ingredients previously thought to be too unstable for practical applications.

5.1 Dinitrogen Pentoxide/Nitric Acid Mixtures

Solutions of dinitrogen pentoxide in nitric acid are very useful nitrating agents and cleaner than traditional nitrating acid (a mixture of nitric acid and sulfuric acid). Electrochemical methods for the preparation of $\text{N}_2\text{O}_5/\text{HNO}_3$ mixtures have been thoroughly investigated [90–93]. Therefore, knowledge of the electrical conductivity of such mixtures is useful information (Section 5.1.5). A nitration method using an N_2O_5 /organic solvent system is a much milder and more selective nitration method, which is well suited for cases where the substrates or products are sensitive to acid or water and for regioselective O-nitration [94].

Mixtures of N_2O_5 and HNO_3 would be easier to use as a rocket propellant oxidizer than N_2O_5 by itself. They would be hypergolic with many fuels that are not reactive or less reactive with White Fuming Nitric Acid (WFNA) or Red Fuming Nitric Acid (RFNA). There are no known uses of such mixtures as rocket propellants.

5.1.1 Freezing Point of Dinitrogen Pentoxide/Nitric Acid Mixtures

The freezing point of dinitrogen pentoxide/nitric acid mixtures goes through a minimum near 23% N_2O_4 at 204 K (−69 °C) (Table 5).

The liquid-liquid and solid-liquid equilibrium phase boundaries and liquid-liquid and solid-liquid equilibrium data for the ternary $\text{N}_2\text{O}_4/\text{N}_2\text{O}_5/\text{HNO}_3$ system were measured by a cloud point method at 258.2, 265.2, 273.2, and 281.2 K [95, 96]. The criti-

Table 5: Freezing point of dinitrogen pentoxide/nitric acid mixtures.

Concentration of free N_2O_5	Total amount of N_2O_5 (free and in the form of HNO_3 chemically bound)	Concentration of N_2O_4 (a contaminant)	Freezing point	
Mass-%	Mass-%	Mass-%	K	°C
8.35	86.89	<0.01	230	-43
13.60	87.64	<0.01	225	-48
17.45	88.17	0.03	218.6	-54.5
20.46	88.60	0.03	212	-61
23.46	89.03	0.03	204	-69
26.75	89.51	0.02	217	-56
33.05	90.10	0.33	231	-42

Data source: [24]

cal points and the solubility of dinitrogen pentoxide in dinitrogen tetroxide and nitric acid, the solubility of dinitrogen tetroxide in nitric acid, and the solubility of nitric acid in dinitrogen tetroxide were also obtained separately. With an increase in temperature, the two-phase area shrank and the solubilities of dinitrogen pentoxide in dinitrogen tetroxide and nitric acid, dinitrogen tetroxide in nitric acid, and nitric acid in dinitrogen tetroxide increased, as expected. A versatile method for analyzing ternary $\text{N}_2\text{O}_4/\text{N}_2\text{O}_5/\text{HNO}_3$ mixtures was developed for the study of $\text{N}_2\text{O}_4/\text{N}_2\text{O}_5/\text{HNO}_3$ systems [97].

5.1.2 Vapor Pressure of Dinitrogen Pentoxide/Nitric Acid Mixtures

The physical properties of $\text{N}_2\text{O}_5/\text{HNO}_3$ mixtures have been well characterized. The boiling point of $\text{N}_2\text{O}_5/\text{HNO}_3$ mixtures decreased with increasing N_2O_5 concentration (Table 6). The vapor pressure of $\text{N}_2\text{O}_5/\text{HNO}_3$ mixtures at 273 K follows an additive behavior of the partial pressures [98] (Table 7).

Table 6: Boiling point of dinitrogen pentoxide/nitric acid mixtures.

Concentration of free N_2O_5	Total amount of N_2O_5 (free and in the form of HNO_3 chemically bound)	Concentration of N_2O_4 (a contaminant)	Boiling point	
Mass-%	Mass-%	Mass-%	K	°C
9.47	87.05	<0.01	338	65
14.51	87.77	0.01	333.6	60.5
19.27	88.44	0.02	325.6	52.5
24.58	89.19	0.03	318.6	45.5
27.87	89.67	0.02	310.6	37.5
33.05	90.10	0.03	308.6	35.5

Data source: [24]

Table 7: Vapor pressure of dinitrogen pentoxide/nitric acid mixtures.

Concentration of free N_2O_5	Total amount of N_2O_5 (Free and in the form of HNO_3 chemically bound)	Concentration of N_2O_4 (a contaminant)	Temperature					
Mass-%	Mass-%	Mass-%	°C					
			0	5	10	15	20	25
Vapor pressure, mm Hg								
9.47	87.05	0.01	—	—	—	—	55.5	71.0
17.66	88.22	0.01	17.9	24.2	31.8	45.1	64.4	79.8
20.39	88.61	0.01	18.1	26.2	36.8	—	—	—
24.93	89.24	0.03	22.9	—	—	67.2	96.0	142.0
27.87	89.67	0.02	—	49.8	71.0	102.0	156.7	226.0
33.05	90.10	0.33	50.0	72.0	103.8	157.0	241.0	323.0

Data source: [24]

Evaluation of published data led to the conclusion that a heteroazeotropic equilibrium exists in the nitric acid-dinitrogen pentoxide system, and a phase diagram was constructed [99]. The heteroazeotrope contained 1–2 mass-% HNO_3 at 101 kPa (760 mm Hg) and approximately 303 K (30 °C).

5.1.3 Density of Dinitrogen Pentoxide/Nitric Acid Mixtures

The density of $\text{N}_2\text{O}_5/\text{HNO}_3$ mixtures increased steadily with an increasing concentration of N_2O_5 (Table 8) (Figure 2). The densities of $\text{N}_2\text{O}_5/\text{HNO}_3$ mixtures at 253 and 263 K (–20 and –10 °C) were measured by Taylor, Lyne, and Follows [100] as part of an electrical conductivity study experiment.

Table 8: Density of dinitrogen pentoxide/nitric acid mixtures.

Free N_2O_5 , mass-%	Total mass% N_2O_5 (free and in the form of HNO_3 chemically bound)	Mass-% N_2O_4 (a contaminant)	Density at 288 K (15 °C), g/cm ³
1.92	85.98	—	1.530
9.40	87.05	—	1.553
13.53	87.64	0.003	1.572
16.47	88.04	0.02	1.588
19.27	88.04	0.02	1.605
24.93	89.24	0.03	1.630
30.53	89.98	0.09	1.643
33.05	90.10	0.33	1.645

Data source: [24]

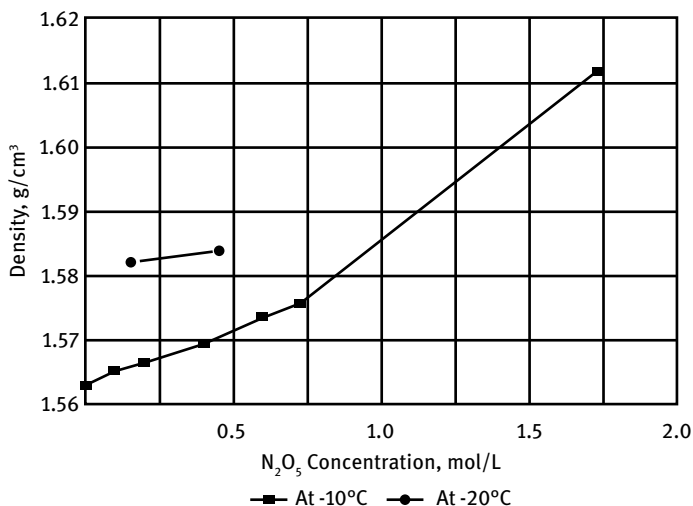


Figure 2: Density of dinitrogen pentoxide/nitric acid mixtures (chart created by Schmidt 2021, based on data from [101])

It was shown that the addition of ammonium nitrate confers a considerable degree of thermal stability on anhydrous HNO_3 . The densities and viscosities of a few ternary $\text{N}_2\text{O}_5/\text{HNO}_3/\text{NH}_4\text{NO}_3$ mixtures at 298 K are listed in Table 9.

Table 9: Density and viscosity of ternary $\text{N}_2\text{O}_5/\text{HNO}_3/\text{NH}_4\text{NO}_3$ mixtures.

Mol-% N_2O_5	Mol-% NH_4NO_3	Density, g/cm ³	Dynamic viscosity, cPs
53.68	0.00	1.558	1.060
53.68	20.72	1.580	4.27
53.00	0.00	1.620	1.553
58.00	17.08	1.594	3.88

Data source: [100]

Solutions of N_2O_5 in HNO_3 are stable only at very low temperatures. Above 0 °C one observes rapid discoloration (brown fumes of NO_2) and effervescence (oxygen bubbles), but only in solutions containing more than 20 mass-% free N_2O_5 . These are mixtures of an oxidizer acid with its anhydride. The physical properties of such binary mixtures are summarized in Table 5–8, also with small percentages of N_2O_4 as an inevitable contaminant. Nitric acid dissolves up to 90 mass-% N_2O_5 .

5.1.4 Viscosity of Dinitrogen Pentoxide/Nitric Acid Mixtures

Viscosity measurements of the $\text{N}_2\text{O}_5/\text{HNO}_3$ system by Taylor, Lyne, and Follows [100] showed a minimum viscosity at 50 mol-% N_2O_5 . Viscosities and surface tensions of solutions of N_2O_4 or N_2O_5 in nitric acid were determined at 278–293 K (5–20 °C), 0–10 mass-% N_2O_4 , or 0–20 mass-% N_2O_5 [102]. The data were fitted to empirical equations as functions of composition and temperature.

5.1.5 Electrical Conductivity of Dinitrogen Pentoxide/Nitric Acid Mixtures

Conductance measurements in the $\text{H}_2\text{O}/\text{N}_2\text{O}_5/\text{HNO}_3$ system over a range of temperatures revealed the presence of a minimum specific conductance at about 96 mass-% HNO_3 and the existence of a negative temperature coefficient of specific conductance for solutions rich in nitric acid [100], see *Encyclopedia of Oxidizers*, chapter “White Fuming Nitric Acid.” The addition of dinitrogen pentoxide to nitric acid increased the conductivity; the addition of water to nitric acid decreased it. According to Taylor, Lyne, and Follows [100], the specific conductance of solutions of N_2O_5 in HNO_3 at room temperature initially increased with increasing concentration of N_2O_5 , attained a maximum near 5 mol-% N_2O_5 , and then decreased with further increase in the N_2O_5 content. This is in contrast to later measurements by Lee and Millen [101], which measured only lower concentrations up to 12 mass-% N_2O_5 and showed a steady increase of electrical conductivity (Figure 3).

Conductance measurements in $\text{H}_2\text{O}/\text{N}_2\text{O}_5/\text{HNO}_3/\text{NH}_4\text{NO}_3$ mixtures at various temperatures and over a wide range of concentrations showed that for all solutions, except those rich in N_2O_5 , the variation of the specific conductance with the con-

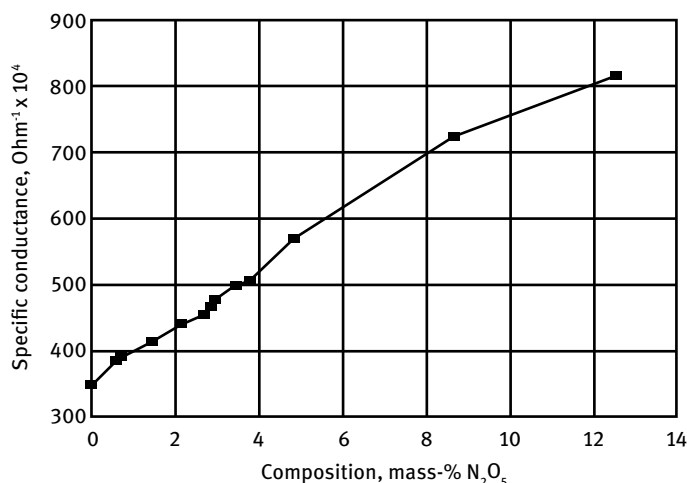


Figure 3: Specific conductance of dinitrogen pentoxide/nitric acid mixtures (chart created by Schmidt 2021, based on data from [101])

centration of ammonium nitrate was similar to that observed for many electrolytes in a variety of solvents [103]. With N_2O_5 -rich solvents the specific conductance of ammonium nitrate was observed to decrease with increasing salt concentration. It is difficult to explain why the conductance of a solution containing 61.4 mol-% N_2O_5 falls almost continuously as ammonium nitrate is added. This was regarded as being indicative of an interaction between the salt and one or more of the components of the $\text{HNO}_3/\text{N}_2\text{O}_5$ system. The variation of conductance with temperature was normal in all cases.

5.1.6 Thermodynamic Properties of Dinitrogen Pentoxide/Nitric Acid Mixtures

Heats of mixing and ^1H , ^{14}N , and ^{17}O NMR spectra of $\text{N}_2\text{O}_5\text{-HNO}_3$ mixtures were determined experimentally [104]. The heats of solution increased as the N_2O_5 concentration increased; a sharp peak was observed at an $\text{N}_2\text{O}_5:\text{HNO}_3$ mol ratio of 1:32, and a less pronounced peak was observed at 1:12. These peaks indicated the formation of intermolecular adducts.

The equilibrium properties of the $\text{H}_2\text{O}/\text{HNO}_3/\text{N}_2\text{O}_5$ system were represented using an electrolyte activity model to obtain a representation of both vapor-liquid equilibrium data and the liquid phase composition [105]. Real species concentrations were deduced from Raman spectroscopy measurements. The accuracy of the electrolyte activity model representation compared well with the experimental deviations.

5.1.7 Corrosive Activity of Dinitrogen Pentoxide/Nitric Acid Mixtures

Corrosive attack on wrought iron, cast iron, and stainless steel in white fuming nitric acid is accelerated by the addition of N_2O_5 .

5.2 Dinitrogen Pentoxide/Dinitrogen Tetroxide Mixtures

Mixtures of dinitrogen pentoxide and dinitrogen tetroxide have already been discussed in the chapter "Dinitrogen Tetroxide." Such mixtures would have the advantage that even if a small percentage of N_2O_5 decomposes, because N_2O_4 is both the solvent and the decomposition product, the resulting mixture will still be a mixture of N_2O_4 and N_2O_5 , albeit with a somewhat lowered N_2O_5 content. If N_2O_5 was dissolved in other solvents (e.g., tetranitromethane), the changes in chemical composition would be less tolerable.

The use of a rapid method to measure the N_2O_5 content of $\text{N}_2\text{O}_4/\text{N}_2\text{O}_5$ mixtures allows for adjustments in the N_2O_5 content to the desired nominal level just prior to use. Of course, the storage container may not be hermetically closed, but it needs to have a pressure relief valve to allow the escape of oxygen gas that forms during storage.

5.3 Other Dinitrogen Pentoxide Mixtures

Mixtures of dinitrogen pentoxide with organic nitro compounds, such as nitromethane or tetranitromethane (TNM), have been considered, but very little is known about their stability. One must assume that such mixtures are potentially detonable.

A mixture of 80% dinitrogen pentoxide and 20% TNM freezes at 267 K (-7°C) and is supposedly stable enough to be used as a hypergolic oxidizer with many different fuels [106].

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Dinitrogen Tetroxide

Nitrogen commonly forms several different oxides with oxygen, depending on the state of oxidation of the central atom, nitrogen. The state of oxidation of nitrogen can be +1, +2, +3, +4, +5, or +6. The correct names of the six oxides are nitrous oxide, N_2O , nitric oxide, NO , dinitrogen trioxide, N_2O_3 , nitrogen dioxide, NO_2 , dinitrogen tetroxide N_2O_4 , dinitrogen pentoxide N_2O_5 , and nitrogen trioxide NO_3 . Nitrogen dioxide, NO_2 , is used mostly in its dimeric form, dinitrogen tetroxide, N_2O_4 , which can be stored as a liquid at room temperature. The state of oxidation of nitrogen in dinitrogen tetroxide is the same as that in nitrogen dioxide.

The topic of nitrogen oxides had to be distributed over seven chapters because it would have been a very large single chapter that would have made it more difficult for readers to find information on a specific compound. In addition, it would have been difficult to arrange thirty chapters among five subvolumes so that each subvolume would be about the same size. That arrangement was made easier by dealing with smaller-increment chapters. The other six chapters in this series are titled “Nitrogen Oxides,” “Nitrous Oxide,” “Nitric Oxide,” “Dinitrogen Trioxide,” “Nitrogen Dioxide,” and “Dinitrogen Pentoxide.”

Nitrogen forms at least six covalently bound oxides, N_2O , NO , N_2O_3 , NO_2 , N_2O_5 , and NO_3 , which are all thermodynamically unstable with regard to their tendency to decompose to dinitrogen and dioxygen. Dinitrogen tetroxide is the result of dimerization of nitrogen dioxide by way of $\pi^*-\pi^*$ -interactions. As far as rocket propellants are concerned, the first two oxides in this family of nitrogen oxides, nitric oxide and nitrous oxide, have not found the same widespread application as dinitrogen tetroxide and its mixtures with dinitrogen trioxide or nitric acid.

Dinitrogen tetroxide, dinitrogen tetraoxide, N_2O_4 , CAS RN [10544-72-6] (also CAS RN [64476-91-1] or [15969-55-8]) is the dimer of nitrogen dioxide and exists only in equilibrium with its decomposition products. Pure dinitrogen tetroxide free of nitrogen dioxide exists only in the frozen state. Between its freezing point and boiling point, dinitrogen tetroxide is a colorless liquid, but it is often contaminated by traces of dinitrogen trioxide, which may stain it blue. The liquid darkens as the temperature is raised. At temperatures near its boiling point, the vapor space is filled with nitrogen dioxide, which stains it red. At the normal boiling point, the vapor contains 16.1% of NO_2 monomer and is reddish-brown. As the temperature is increased, the proportion of NO_2 monomer increases, and at 423 K (150 °C) the vapor is dark black. Dinitrogen tetroxide has often erroneously also been called “nitrogen tetroxide,” abbreviated NTO, or “nitrogen peroxide.” (Because the NTO abbreviation is common, however, it will be used here.) In the older French literature, the name for N_2O_4 is sometimes *peroxyde d'azote*, which may lead to confusion with real peroxides containing O–O bonds.

Dinitrogen tetroxide has the advantage over liquid oxygen as a rocket propellant oxidizer in that it can be stored as a liquid at room temperature, and it has an advantage over nitric acid in that it is less corrosive and does not decompose during storage. On the other hand, it does not have the same specific-impulse rocket performance as liquid oxygen. In many cases, a compromise between the advantages and disadvantages of dinitrogen tetroxide and nitric acid resulted in a mixture called red fuming nitric acid (RFNA), which has found widespread use as an oxidizer in ballistic missiles and other military applications that require instant readiness and storability.

1 General Information on Dinitrogen Tetroxide

1.1 History of Dinitrogen Tetroxide Use as a Rocket Propellant

Dinitrogen tetroxide had already been considered as a rocket propellant oxidizer during the 1930s in Germany, but it found more widespread use only after World War II [1]. Development work with dinitrogen tetroxide was carried out in the 1950s at the Jet Propulsion Laboratory (JPL) in the United States (at that time administered by the California Institute of Technology in Pasadena) and in the Laboratoire de Recherches Balistiques et Aerodynamiques in Vernon, France.

Next to liquid oxygen, dinitrogen tetroxide is one of the most important rocket propellant oxidizers, and it is certainly the most important storable oxidizer. As such it has been used in many prepackaged rocket propulsion systems that have to be stored in the field under sometimes very challenging environmental conditions until they are put to use. Dinitrogen tetroxide began to replace nitric acid(s) in the late 1950s and early 1960s because it gave higher performance and presented less of a corrosion problem.

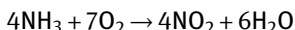
Dinitrogen tetroxide is rarely used in the pure form. Most often it is used with small amounts of dinitrogen trioxide added in the form of nitric oxide as a stabilizer and additive to alleviate stress-corrosion cracking (refer to Section 4.1 on mixed oxides of nitrogen).

1.1.1 Summary Publications on Dinitrogen Tetroxide

A good source of physical properties and materials compatibility information is the *USAF Propellant Handbook*, Volume 2: “Nitric Acid/Nitrogen Tetroxide Oxidizers” [2].

2 Production of Dinitrogen Tetroxide

The production of dinitrogen tetroxide is essentially the same as what is described in the chapter on nitrogen dioxide. The conversion of nitrogen dioxide gas to dinitrogen tetroxide liquid occurs as it condenses. Dinitrogen tetroxide is produced in the form of nitrogen dioxide and dimerizes during condensation from the vapor phase. Nitrogen dioxide is produced by catalytic combustion of ammonia in air over a platinum gauze



and in most cases is immediately processed into nitric acid and ammonium nitrate as fertilizer. Because there are no other commercial uses for dinitrogen tetroxide, the U.S. government on several occasions had to negotiate with large-scale nitric acid producers to entice them to divert a small part of the production stream and sell it in the form of high-purity N_2O_4 for use as a rocket propellant. For large-scale nitric acid producers, the N_2O_4 business was not a very profitable operation, and the U.S. government was the main customer. Vicksburg Chemical of Vicksburg, Mississippi, manufactured NTO from 1960 to 2002. Vicksburg filed for bankruptcy and discontinued operations in 2002. After being awarded a \$24 million five-year requirements contract in August 2002, and producing a successful first article sample in January 2003, Mississippi Chemical Corporation (MissChem) filed for Chapter 11 bankruptcy protection in May 2003. DESC Missile Fuels CBU immediately developed and executed a plan to place orders for all known requirements for the duration of the five-year contract and arranged for storage and distribution support to shield customers from the impact should MissChem not be able to meet the full five-year term of its contract. Approximately 1 million pounds of N_2O_4 (\$1.2 million) was ordered from MissChem. MissChem was sold to Terra Industries in 2004. CF Industries Holdings acquired Terra Industries in 2010.

Prior to the invention of the Haber-Bosch process for making ammonia and fixing nitrogen from the air, a large share of nitric acid and nitrogen oxides was made by electrical discharges in air. Because this process required large amounts of electricity, this process (the Birkeland process) was practiced mostly in Scandinavian countries where there was an abundance of cheap hydroelectric power.

Prior to 1958, the Nitrogen Division of Allied Chemical was the sole commercial producer of liquid dinitrogen tetroxide. Other producers entered the market when the demand by the U.S. Air Force (USAF) rose substantially when the design of TITAN intercontinental ballistic missiles (ICBMs) was changed from liquid oxygen/kerosene to NTO/Aerozine-50 to become the next generation, TITAN-II, and the missiles were placed in bomb-proof silos.

Pure NTO is rarely used as rocket propellant. Most NTO is used in mixtures with dinitrogen trioxide. Food Machinery and Chemical Corporation investigated the direct production of mixed oxides of nitrogen (MON)-30 from a commercial nitrogen fixation reactor by chilling the hot reaction products by passing them through a MON-30

bath at temperatures below 222 K (-60°F) and thus quenching the further oxidation of NO to NO_2 [3]. Unfortunately, the commercial process gases contained several percent CO_2 , which also dissolved in the MON liquid and lowered its freezing point. In a separate experiment, CO_2 was bubbled into a MON liquid containing 27% nitric oxide until saturated. By weighing the sample before and after bubbling, it was found that CO_2 was soluble to the extent of about 5% at 222 K (-60°F). This amount of carbon dioxide lowered the freezing point of the mixture by 2 K (3.5°F), from 204.5 to 202.6 K (-91.5 to -95°F). An alternative (but more expensive) method of producing MON starting with NTO would vaporize the N_2O_4 to NO_2 and heat it to 922 K (1200°F), where NO_2 partially dissociates into NO and O_2 , and then quench and condense the mixture at a fast rate that would prevent the reoxidation of NO.

Instead of relying on commercial supplies of NTO of dubious purity that would require elaborate purification at the point of end use, it is possible to manufacture high-purity NTO at the launch site by catalytic oxidation of ammonia with air, followed by cleanup by passing the products through a filter with molecular sieves [4]. This process may be suitable for skid-mounted on-site production of N_2O_4 in locations where local transportation regulations prohibit shipping of N_2O_4 in tank cars through populated areas.

2.1 Purification of Dinitrogen Tetroxide

Because commercial grades of dinitrogen tetroxide are very corrosive and may have been stored in tank cars or other shipping containers for quite some time before it is used, it may contain varying amounts of contaminants, mostly due to absorption of water and leached metals, which would interfere with the intended application as a rocket propellant. In almost all cases, as-received NTO is purified at the point of use before it is loaded into a rocket or a satellite.

Distillation and filtration have been shown by radioisotope tracer techniques to be effective methods of removing iron from brown N_2O_4 [5]. Radioactive ^{59}Fe was added to samples of N_2O_4 , which were then distilled or filtered. Following these operations, the distilled N_2O_4 was checked in a multi-channel analyzer for the presence of radioactivity. Within the measurement limits of the instrumentation, distillation appeared nearly 100% effective in removing iron. Filtration through sintered glass filters and through screen-type stainless steel filters was only of limited effectiveness and pointed to adsorption as the primary filtering mechanism. Passing the N_2O_4 through a column packed with molecular sieve material was shown to be the most effective iron-removal method [6]. Two different molecular sieve materials, Linde LMS-4A and Linde LMS-5A, were evaluated for this purpose, giving similar results (Figure 1). The materials were vacuum-dried at 473 K (200°C) and 0.2 mm Hg prior to use. At the same time, it was shown that passing the NTO through a molecular sieve did not result in any soluble contaminants being leached from the molecular sieve material. In addition to 4A and

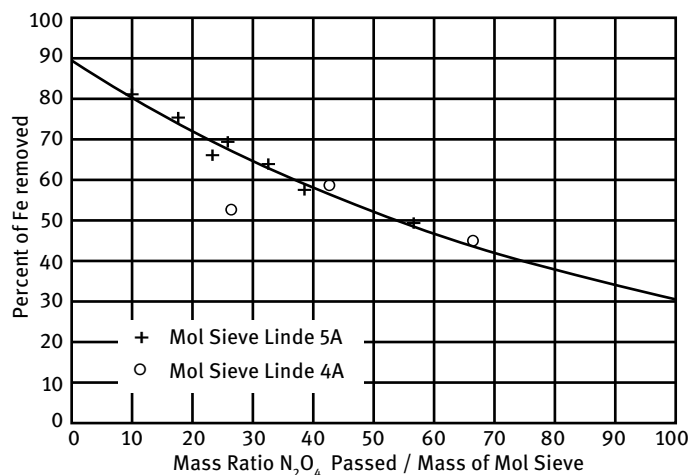


Figure 1: Efficiency of iron removal as a function of N_2O_4 /molecular sieve mass ratio. (Reproduced and modified from [6].)

5A type molecular sieves, a type LZ-Y82 was also evaluated as the adsorbent and was a very effective iron adsorber.

Commercial-grade nitrogen tetroxide, before it can be used as rocket propellant, must be upgraded to prevent flow decay problems and to increase the shelf life of the product, thereby providing for longer-duration trouble-free rocket engine performance. In one version of this purification process, the green raw MON material is initially converted (if necessary) to the “red” type by adding an excess of oxygen [7, 8]. Iron salts are less soluble in NTO than in MON and precipitate once all N_2O_3 is oxidized and cooled. Dissolved iron salts and other dirt particulates are then removed by cooling and repeated filtering while cold. The propellant is filtered at each subsequent transfer operation. The stress-corrosion-cracking inhibiting quality of the filtered propellant is then restored by bubbling nitric oxide through the filtered propellant until the desired NO content is achieved. Researchers at the JPL also evaluated molecular sieves as a means of purifying MON [9].

An electrostatic filtration distillation apparatus can be used to significantly reduce contaminants in N_2O_4 vapor and liquid [10]. It operates at ambient temperatures, thus avoiding the need to chill the propellant as in the other, older iron contaminant removal methods. The apparatus described in a patent used an electret vapor filter with a stack of layers of electret material through which the N_2O_4 vapor had to pass. The electret material can be polypropylene or Teflon. The electret vapor filter removed iron contaminants as well as NOCl and volatile iron contaminants. A flow-retarding filter downstream of the electret liquid filter regulated sufficient dwell time for removal of contaminants. The filter was constructed of chemically inert materials to prevent

additional contamination. In a series of tests with different filter materials, initial Fe contents of 0.4–2.6 ppm were effectively reduced to 0.01–0.03 ppm.

The U.S. National Aeronautics and Space Administration (NASA) White Sands Test Facility (WSTF) initially had installed an NTO purification facility based on the chill-and-filter technique, but the method proved to be too time-consuming and ineffective [11]. The problem was that the flow-decay adduct precipitated on the coils of the heat exchanger and was not collected on the membrane filter. The membrane filter with a halfway-tolerable pressure drop still had a pore size of 5 μm , which allowed excessive numbers of smaller particles to pass. Subsequently, NASA started evaluating molecular sieves in 1982 and designed, constructed, and tested a full-scale system for purification of MON [12–14]. Initially, the researchers evaluated 13X, 4A, and 5A, but eventually they selected Linde LZ-Y82 as the best-performing molecular sieve. Both 13X and 5A showed signs of exothermicity during most of the flow periods. The iron concentration in the starting product was 3.6 ppm. With LZ-Y82, a load of 195 g of molecular sieve packed to a bed depth of 27 cm (10.6 in.) was able to treat 108 L (30 gallons) of NTO with average flow rates of 0.15 L/min (0.04 gallon/min) before the column was exhausted and the breakthrough point was reached. The capacity for iron removal was 59×10^{-4} g Fe/g molecular sieve. A filter sized at 0.2 μm was placed downstream of the molecular-sieve column to retain dust that might have been shed from the molecular-sieve pellets. An additional benefit was that this column material not only removed most of the iron but also absorbed water (nitric acid). A large batch (1500 gallons) of NTO had become accidentally contaminated with water, but the propellant was able to be salvaged and brought back into specification limits by passing it through a column packed with 68 kg (150 lb) of LZ-Y82 that had been previously activated by drying at 477–533 K (400–500 °F).

If NTO is to be purified by passing it through molecular-sieve columns, the molecular sieve has to be activated before use to drive off all trapped moisture [15, 16]. Spent molecular sieve can also be reactivated by heating in vacuum. The design of molecular-sieve purification columns can be facilitated by a computer program that takes the initial iron concentration, the desired flow rate, and the desired level of purification as input variables [17].

It is known that distillation will remove iron but not all of the water (nitric acid). Molecular-sieve treatment by passing liquid NTO through a bed of molecular sieves will remove most of the iron but not all. Thus, if one distilled NTO vapors through a packed column with molecular sieves, one would expect to obtain NTO of superior purity, but this process is more time-consuming than either the distillation or the liquid NTO percolation treatment by itself.

Molecular sieve type 3A testing was performed at NASA's WSTF to evaluate the effectiveness of 3A molecular-sieve material to remove water and iron from MON-3 [18]. The overall testing consisted of three test phases. The first phase involved recycled tests performed using an existing molecular sieve unit. This series consisted of eight tests at various pressures, temperatures, and flow rates to determine the rate of wa-

ter removal with contact time and the effect of different operating parameters on the system. The second test phase consisted of two high-iron tests to evaluate the ability of the molecular-sieve material to remove iron from MON-3. The final test phase was a single-pass high-water test that was designed to (1) evaluate the amount of water removed in a single pass and (2) evaluate the effect of water saturation on the ability of the molecular sieve to absorb water. The tests showed that the type 3A molecular-sieve material will remove from 50 to 96% of the water in MON-3, depending on the initial water concentration and on the quantity of water the molecular sieve had previously adsorbed. The tests also demonstrated that the type 3A molecular-sieve material is more effective at removing iron than LZ-Y82, a molecular-sieve material already in use at WSTF for iron removal. Based on the test results, the type 3A material was recommended to replace the LZ-Y82 material in existing molecular-sieve units.

2.1.1 Small-scale Purification of Dinitrogen Tetroxide in the Laboratory

After several small-scale N_2O_4 purification methods were tested in preparation for compatibility testing, a purification system employing BaO treatment and distillation through activated type 3A molecular sieve was close to optimum performance [19].

When N_2O_4 was purified by distillation in glass apparatus in the laboratory, the use of BaO in the distilling flask appeared to aid in the removal of HNO_3 .

Instead of passing the vapor through an absorbent bed of molecular sieve 3A, the absorbent can be combined in direct contact with liquid N_2O_4 in a flask and stirred. This essentially removes all protonated species, mostly HNO_3 . In one experiment, when 1300 mL of red N_2O_4 was combined with 330 g of molecular sieve in a stainless steel cylinder under oxygen pressure and stored for 20 d, the HNO_3 concentration determined by NMR was near the detection limit of the apparatus. At a ratio of 200 g molecular sieve per liter of N_2O_4 , complete deprotonation of 1–2-L batches usually required 2–3 weeks. When this process was scaled up to 34 L (9 gallons), HNO_3 concentration decreased from 5146 to 67 ppm in 45 d. There were no metals leached from the molecular sieve.

In a critical review at the JPL, it was concluded that although distillation was clearly the most effective method, the absorbent-bed approach was considered to be far more practicable. The development of large-scale MON purifiers was subsequently reported at both the JPL and NASA WSTF. In Europe, however, distillation had been preferred, and propellant users expressed concerns about the possibility that absorption beds might introduce silicon and aluminum into the propellant from the molecular sieve. Concern was also expressed about particulate contamination. After detailed consideration, it was decided that the purification efficiency of distillation, together with unreserved acceptance of the technique, established this method as the basis for the Royal Ordnance and Edotek production facilities in the United Kingdom [20].

3 Physical Properties of Dinitrogen Tetroxide

The physical properties of pure dinitrogen tetroxide are summarized here only as a baseline for comparison. Dinitrogen tetroxide is rarely used in the pure form because it contains either unwanted contaminants or additives that were deliberately added to improve its storage and corrosion properties.

The molecular mass of NO_2 is 46.0055 g/mol, and the molecular mass of its dimer N_2O_4 is 92.0110 (1983 IUPAC ^{12}C values).

Due to the dissociation of N_2O_4 into NO_2 , the liquid (under pressure) is a mixture in which the expansion coefficient, specific heat, and thermal conductivity all pass through maxima at temperatures ranging from 313 to 338 K (40 to 65 °C).

3.1 Freezing Point and Phase Behavior of Dinitrogen Tetroxide

Table 1 is a summary of freezing points of pure dinitrogen tetroxide reported in the literature by various investigators. The values differ depending on the purity of the sample and the temperature calibration. Looking at some of the freezing-point and boiling-point data gathered for comparison by Giauque and Kemp [21], it is surprising to see that the earliest data on the freezing point and boiling point of dinitrogen tetroxide date back to 1816 and 1841.

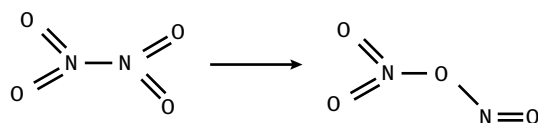
Table 1: Literature summary of freezing points of pure dinitrogen tetroxide.

Temperature		Author	Year	References
K	°C			
262.6	−10.5	Egerton	1914	[22]
261.90	−11.25	Giauque and Kemp	1938	[21]
261.92	−11.23	Whittaker et al.	1952	[23]
261.86	−11.29	Beattie, Bell, and Vosper	1960	[24]

Dinitrogen tetroxide is widely used as the oxidizer in hypergolic bipropellant systems. One of the disadvantages of dinitrogen tetroxide is its high freezing point. In a rocket engine operating in vacuum, propellant evaporating in the injector hold-up volume may cool by evaporation and freeze. Injector clogging by frozen propellants has been a concern for bipropellant engines operating on NTO and Aerozine-50 [25–28]. The freezing point of NTO is only slightly lowered by adding NO, so injector clogging by freezing may be less of a concern with MON-3 or even MON-10.

3.1.1 Phase Behavior at Very High Pressures

Dinitrogen tetroxide and other nitrogen oxides have been subjected to very high pressures in the hope of coercing it into forming a new oxide of nitrogen that might make a better rocket propellant oxidizer. Significantly, Raman spectra of N_2O_4 compressed in a diamond anvil cell showed two new peaks at 1104 and 2208 cm^{-1} , indicating the formation of a new phase when the pressure is increased from 8.8 to 12.3 GPa [29]. It is possible that this new γ -phase is an isomerization from



which has a lower symmetry and may be an intermediate in the transition to the ionic isomer $[\text{NO}^+][\text{NO}_3^-]$ called nitrosonium nitrate. At even higher pressures and temperature, dinitrogen tetroxide and many other nitrogen oxides (most notably nitrous oxide) convert to its ionic isomer nitrosonium nitrate [29]:



The mechanisms governing the transformation between the two forms were studied extensively, but the answers were not unequivocal. Nitrosonium nitrate can be isolated at atmospheric pressure from freshly oxidized NO or dissociated N_2O_4 trapped in a matrix of solid neon. It can be characterized by its IR, Raman, and XRD spectra. Characteristic peaks in the Raman spectra appear at $740\text{ cm}^{-1}(\nu_4)$, $827\text{ cm}^{-1}(\nu_2)$, $1096\text{ cm}^{-1}(\nu_1)$, and $2253\text{ cm}^{-1}(\nu_{\text{NO}^+})$, but they disappear when the pressure is lowered. X-ray diffraction (XRD) at 21 GPa indicates an orthorhombic structure with $a = 5.66\text{ \AA}$, $b = 6.47\text{ \AA}$, and $c = 5.39\text{ \AA}$. Nitrosonium nitrate $[\text{NO}^+][\text{NO}_3^-]$ is denser than mixtures of $\text{N}_2 + \text{O}_2$ or $\text{N}_2\text{O} + \text{O}_2$ under the same pressure. Below 1 GPa , $[\text{NO}^+][\text{NO}_3^-]$ transforms back to molecular N_2O_4 .

At very high pressures (higher than normally encountered in rocket engines), N_2O_4 undergoes transformations into other phases involving nitrosonium nitrate NO^+NO_3^- and dinitrogen pentoxide NO_2NO_3^- ionic crystals [30]. High-pressure/high-temperature Raman and XRD studies of synthesized samples disclosed a transformation of NO^+NO_3^- compound to NO_2NO_3^- crystal at temperatures above ambient and pressures below 9 GPa . High-pressure experiments revealed previously unreported bands in Raman spectra of NO^+NO_3^- and NO_2NO_3^- ionic crystals.

There is evidence for three crystalline modifications, two of which have not previously been observed [31]. The α -phase appeared to be identical with the known low-temperature form, cubic $Im\bar{3}$. Laser irradiation of $\alpha\text{-N}_2\text{O}_4$ caused the formation of a second phase, $\beta\text{-N}_2\text{O}_4$, which was also composed of planar nitro- N_2O_4 molecules and was non-cubic. While the crystal structure of $\beta\text{-N}_2\text{O}_4$ was as yet unknown, polarized Raman spectra gave evidence for the alignment of the N—N bond axis

as opposed to the cubic α -form, which showed no molecular alignment. Both α -N₂O₄ and β -N₂O₄ are molecular crystals. At pressures in the range 15–30 kbar, however, β -N₂O₄ exhibited a reversible phase transition with a large hysteresis to a third structure ionic NO⁺NO₃[−]. In contrast, α -N₂O₄ is stable to at least 76 kbar.

3.2 Boiling Point and Vapor-Phase Composition of Dinitrogen Tetroxide

The boiling point of dinitrogen tetroxide is difficult to determine directly because N₂O₄ at that point has already begun to dissociate into nitrogen dioxide. One does not deal with a pure compound but rather with an equilibrium mixture of two compounds. The boiling points summarized in Table 2 were derived from vapor pressure measurements extrapolated to atmospheric pressure.

Table 2: Literature summary of boiling points of pure dinitrogen tetroxide.

Temperature		Author	Year	References
K	°C			
294.25	21.10	Giauque and Kemp	1938	[31]
294.3	21.15	Gray and Rathbone	1958	[32]
294.3	21.15	Addison and Smith	1960	[33]

3.3 Density of Dinitrogen Tetroxide

3.3.1 Density of Liquid Dinitrogen Tetroxide

Density data for liquid dinitrogen tetroxide are tabulated in Table 3 and illustrated in Figure 2.

The density of liquid N₂O₄ between 273 K (0°C) and 294 K (21 °C) follows the equation

$$\rho = 1.490 - 0.00215 \times t$$

where ρ is the density in g/cm³ and t is the temperature in °C.

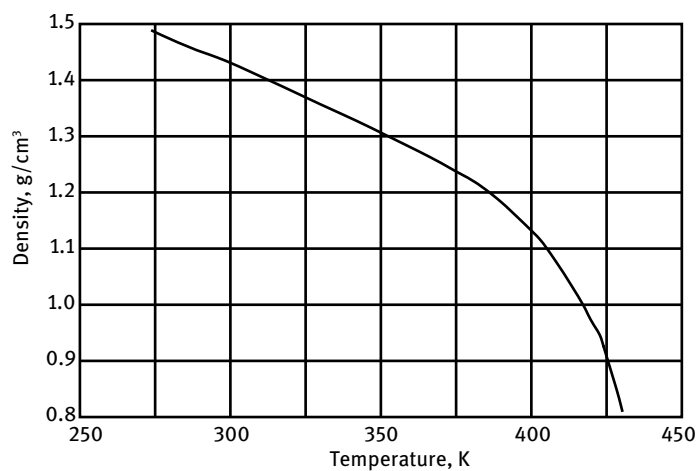
The density of a sample of “reddish-brown” dinitrogen tetroxide with a water content of less than 0.01% (equivalent, it could have been HNO₃) was measured over the temperature range 279.3–351.3 K (6.2–78.2 °C; 43.1–172.8 °F) and curve-fitted by a least-squares method. The polynomial equation fitting these data was [35]

$$\rho = 1.4903 - 2.0517 \times 10^{-3}t - 6.0813 \times 10^{-6}t^2$$

Table 3: Density of liquid dinitrogen tetroxide.

Temperature		Density
°C	K	g/cm ³
0	273.2	1.4906
3.2	276.4	1.4838
6.0	279.2	1.4780
10.3	283.5	1.4688
15.2	288.4	1.4571
19.9	293.1	1.4461
20	293.2	1.4468
25	298.21	1.4342
30	303.2	1.4246
40	313.2	1.3990
50	323.2	1.3746
60	333.2	1.3495
70	343.2	1.3245
80	353.2	1.2990
90	363.2	1.2725
100	373.2	1.2440
110	383.2	1.2120
120	393.2	1.1688
130	403.2	1.1128
140	413.2	1.0395
150	423.2	0.9410
157	430.2	0.8120

Data source: [34]

**Figure 2:** Density of liquid dinitrogen tetroxide. (Based on [34] data)

where ρ is the density in g/cm^3 and t is the temperature in $^\circ\text{C}$, with a standard error of estimate of $\pm 0.0014 \text{ g/cm}^3$. A similar equation was derived for N_2O_4 that contained small amounts (up to 1.07%) NO; see Section 4.1.4 for MON density data. See also [36].

3.3.2 Density of Solid Dinitrogen Tetroxide

Dinitrogen tetroxide may inadvertently freeze unless some dinitrogen trioxide is added as an anti-freeze. Unlike water, dinitrogen tetroxide does not expand on freezing, so there should be no immediate rupturing danger for the hardware; it will just become non-functional. Literature data of the density of frozen dinitrogen tetroxide are summarized in Table 4. The coefficient of thermal expansion of solid N_2O_4 between 78 and 194 K (-195 and -79 $^\circ\text{C}$) is $3.6 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$.

Table 4: Density of frozen dinitrogen tetroxide.

Temperature		Density	Author	Year	References
K	$^\circ\text{C}$	g/cm^3			
194	-79	1.899	Biltz, Fischer, and Wuennenberg	1930	[37]
78	-195	1.979	Biltz, Fischer, and Wuennenberg	1930	[37]
20	-253	2.0	Gray and Yoffe	1955	[38, 39]
78	-195	1.981	Gray and Yoffe	1955	[38, 39]
194	-79	1.902	Gray and Yoffe	1955	[38, 39]
233	-40	1.95	Gray and Yoffe	1955	[38, 39]

3.4 Critical Point Properties and Equation of State of Dinitrogen Tetroxide

Based on experimental data published by other authors, pressure-volume-temperature (PVT) relationships of dissociating N_2O_4 were computed and graphed [40]. An equation of state (EOS) of the Wohl type (similar to van der Waals EOS) for dissociating N_2O_4 was derived, which contained an additional term that accounts for attraction and repulsion between molecules. Figure 3 gives the specific PVT diagram of dinitrogen tetroxide vapor. The critical constants used for creating this chart were $T_c = 431.7 \text{ K} = 777 \text{ }^\circ\text{R}$; $p_c = 10.13 \text{ MPa} = 1469 \text{ psia}$; and $V_c = 1.8166 \text{ cm}^3/\text{g} = 0.02910 \text{ ft}^3/\text{lb}$.

Figure 4 gives the specific volume of saturated dinitrogen tetroxide over a wide range of temperatures, from below freezing to near the critical point.

Critical point properties as referenced in other sources are as follows:

$$\begin{aligned}t_{\text{crit.}} & 431.35 \text{ K} = 158.2 \text{ }^\circ\text{C} \\P_{\text{crit.}} & 99 \text{ atm} \\\rho_{\text{crit.}} & 0.56 \text{ g/cm}^3\end{aligned}$$

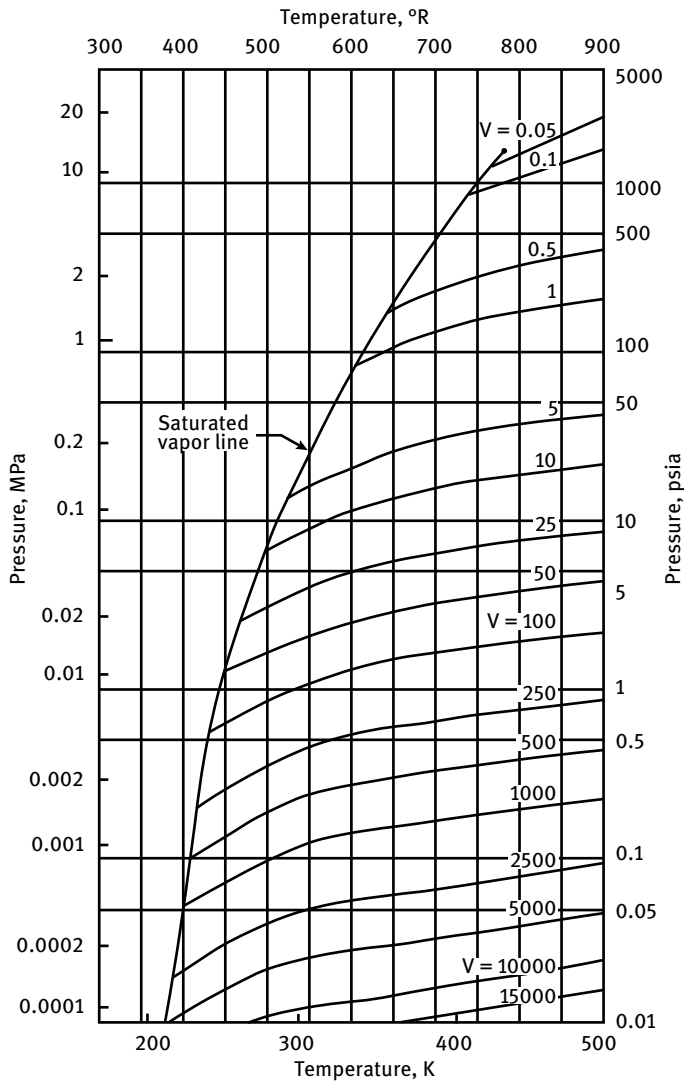


Figure 3: Specific pressure-volume-temperature diagram of dinitrogen tetroxide vapor. (Republished and modified from [40], with permission of © 1965 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

The EOSs for pure N_2O_4 and pure NO_2 are not available because neither fluid exists in a pure state over the global P - T range. Because of this, ideal assumptions are usually made that allow the composition calculation to be performed. This procedure works reasonably well at low and even moderate densities but is grossly in error in the liquid region. The National Bureau of Standards derived a mathematical model of the EOS

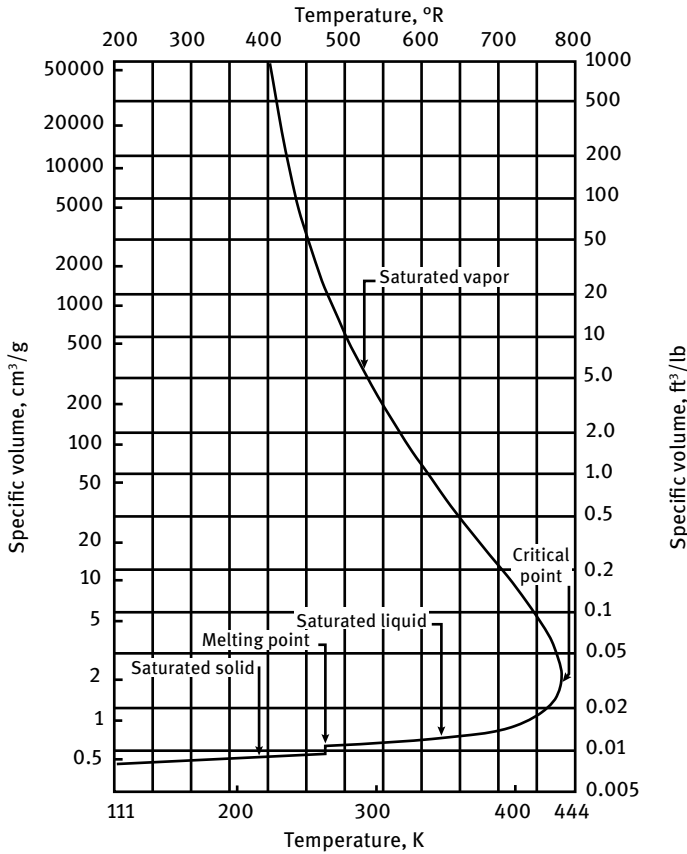


Figure 4: Specific volume of saturated dinitrogen tetroxide. (Republished and modified from [40], with permission of © 1965 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

of dinitrogen tetroxide from literature data and isobaric tables of P – ρ – T and composition for temperatures from the triple point (261.95 K) to 600 K with pressures up to 40 MPa. In doing so, the National Bureau of Standards, in a study of the thermodynamic properties of equilibrium N₂O₄, used the following critical data:

$$\begin{aligned} T_{\text{crit.}} & 431.373 \text{ K} \\ P_{\text{crit.}} & 10.1578 \text{ MPa} \\ \rho_{\text{crit.}} & 550.463 \text{ kg/m}^3 \end{aligned}$$

The pseudo-critical parameters of the hypothetical pure N_2O_4 and the parameters of the hypothetical pure N_2O_4 and NO_2 were taken as adjustable parameters. The least-squares fit gave the following pseudo-critical parameters:

$$\begin{aligned}\text{N}_2\text{O}_4: \quad T_c &= 547.4567 \text{ K} \\ P_c &= 22.0951 \text{ MPa}\end{aligned}$$

$$\begin{aligned}\text{NO}_2: \quad T_c &= 239.3036 \text{ K} \\ P_c &= 10.325 \text{ MPa}\end{aligned}$$

The mathematical model of the equation of state was a 32-term modified Benedict-Webb-Rubin equation for the equilibrium mixture [41]. See also [42–47].

3.5 Velocity of Sound and Compressibility of Dinitrogen Tetroxide

3.5.1 Velocity of Sound and Compressibility of Liquid Dinitrogen Tetroxide

The velocity of sound (also called sonic velocity) of any rocket propellant oxidizer or fuel is an important criterion in trying to understand combustion instabilities that arise from pressure oscillations propagating upstream from the combustion chamber through the injector and into the feed systems. Some launch vehicles have exhibited “pogo” problems due to the compressibility of tall columns of liquids and hidden gas pockets in the system. Some engines started chugging because of insufficient hardness in the feed and injector system, somewhat related to the compressibility of the liquid. The velocity of sound in liquid N_2O_4 is illustrated in Figure 5.

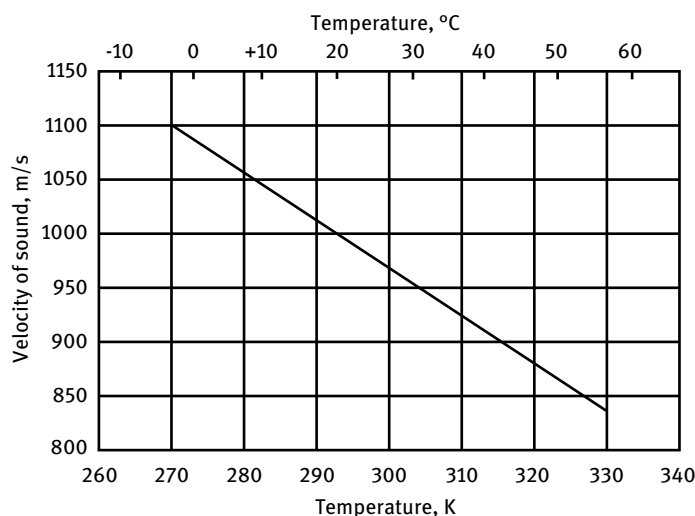


Figure 5: Velocity of sound in liquid dinitrogen tetroxide. (Based on data from [48].)

The data in Figure 5 were curve-fitted from the equation

$$c = 2296 - 4.425T$$

where c is the velocity of sound in m/s and T is the temperature in kelvin.

Not only thermal conductivity but also sound absorption in liquid dinitrogen tetroxide show unusual behavior due to dissociation of N_2O_4 . Sound absorption in liquid N_2O_4 due to relaxation of the dissociation equilibrium exhibits two sound-absorption maxima resulting from relaxation of the dissociation equilibrium [49]. See also [50].

3.5.1.1 Adiabatic Compressibility of Liquid Dinitrogen Tetroxide

The adiabatic compressibility of liquid N_2O_4 was derived from the velocity of sound measurements. The dependence of adiabatic compressibility on temperature is illustrated in Figure 6.

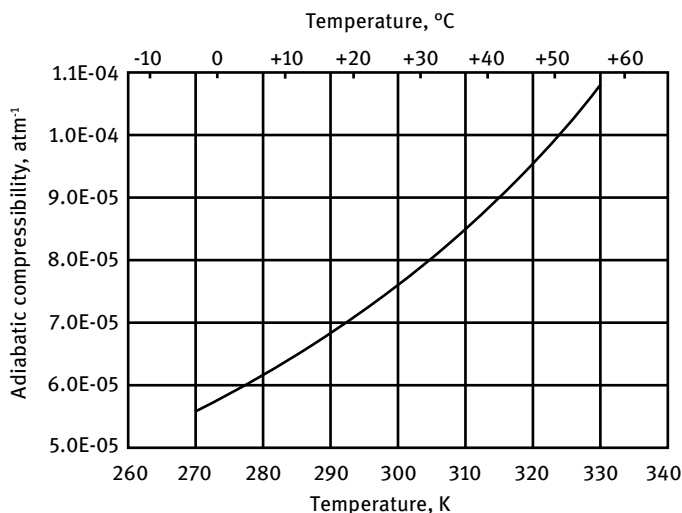


Figure 6: Adiabatic compressibility of N_2O_4 . (Reproduced and modified from [48].)

The data in Figure 6 can be represented by the equation

$$\beta = 5.776 \times 10^{-5} + 5.454 \times 10^{-7}t + 5.185 \times 10^{-9}t^2 - 1.659 \times 10^{-11}t^3 + 5.291 \times 10^{-13}t^4$$

where β is the compressibility in atm^{-1} and t is the temperature in $^{\circ}\text{C}$.

3.5.1.2 Velocity of Sound in Dissociating Gaseous Dinitrogen Tetroxide

The velocity of sound in dissociating gaseous $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ was determined at various temperatures and used to calculate equilibrium constants as a function of tempera-

ture and pressure [51, 52]. The velocity of sound in dinitrogen tetroxide vapor was measured between 274 and 303 K (1 and 30 °C), at pressures between 17 and 101 kPa (130 and 760 mm Hg), with sound waves between 9 and 93 kHz [53]. The change of the velocity of sound with frequency allows an estimate of the rate of dissociation of dinitrogen tetroxide into nitrogen dioxide, driven by sound energy and the oscillation of local pressure. It has been attempted to measure the rate of dissociation of N_2O_4 vapor by measuring the attenuation of sound waves as a function of frequency. At sufficiently high frequencies, the velocity of sound is independent of frequency because the N_2O_4 dissociation equilibrium cannot adjust itself fast enough to the local pressure fluctuations as the sound wave moves through [54]. At low frequencies, the intensity and travel velocity of the sound wave is diminished because part of the energy goes toward dissociating N_2O_4 . This dissociating equilibrium gas is a good example for demonstrating the capabilities of photoacoustic resonance spectroscopy [55].

A randomly abbreviated sample list of raw velocity of sound data is presented in Table 5, but the wide spread of the data is still disturbing [56]. It also lists the percentages of NO_2 and K_p derived from the pressure measurements. The trend of the velocity

Table 5: Velocity of sound in gaseous dinitrogen tetroxide equilibrium mixture.

Temperature		Pressure		Velocity	NO_2	K_p
K	°C	mm Hg	atm	m/s	Vol-%	
276	3	168.7	0.2220	181	16	0.0068
296	22.9	464.7	0.6114	191.5	33	0.099
296	22.9	476.8	0.6274	194.2	37	0.14
300	27.0	470.6	0.6192	192.6	32	0.093
300	27.0	483.1	0.6357	195.3	36	0.13
302	29.1	489.7	0.6443	197.3	38	0.15
302	29.1	516.3	0.6793	204.0	47	0.28
304	31.2	496.3	0.6530	199.4	40	0.17
304	31.2	522.8	0.6879	205.8	49	0.32
306	33.3	504.0	0.6632	200.6	41	0.19
306	33.3	529.4	0.6966	207.5	50	0.35
309	35.4	536.0	0.7053	208.9	51	0.37
311	37.6	542.5	0.7138	210.2	51	0.38
311	37.6	574.1	0.755	218.3	61	0.72
313	39.7	561.6	0.7389	215.4	57	0.56
315	41.9	580.1	0.763	219.8	61	0.73
318	45.3	592.0	0.7789	222.4	62	0.79
320	46.4	597.7	0.7864	223.9	63	0.84
320	46.4	603.4	0.7939	224.4	64	0.90
322	48.7	586.0	0.7711	220.8	59	0.65
322	48.7	614.3	0.8083	227.6	66	1.04
326	53.3	608.9	0.8012	226.0	63	0.86

Data source: [56]; sorted by temperature and pressure

of sound seen from these data is that it increases with temperature and pressure. The velocity of sound increased from 181 m/s at 276 K and 22.3 kPa to 226 m/s at 326 K and 81 kPa.

3.6 Vapor Pressure of Dinitrogen Tetroxide

3.6.1 Vapor Pressure of Liquid Dinitrogen Tetroxide

Vapor pressure data for pure dinitrogen tetroxide are listed in Table 6 and illustrated in Figure 7.

Table 6: Vapor pressure of dinitrogen tetroxide equilibrium mixture.

Temperature		Vapor pressure	
°C	K	mm Hg	kPa
−23	250.2	70	9.3
−20	253.2	85	11.3
−15	258.2	115	15.3
−10.8	262.4	146	19.4
−5.3	267.9	198	26.3
+0.8	274.0	276	36.7
7.7	280.9	393	52.2
12.4	285.6	497	66.0
19.2	292.4	690	91.7
24.3	297.5	873	116
29.55	302.71	1108	147
35.65	308.81	1447	192
41.15	314.31	1825	243
45.65	318.81	2189	291
48.7	321.9	2478	329
54.25	327.41	3116	414
64.95	338.11	4636	616
74.7	347.9	6592	876
86.7	359.9	9804	1303
98.15	371.31	14136	1879
		atm	MPa
110.3	383.5	27.0	2.73
120.0	393.2	35.7	3.61
131.1	404.3	48.1	4.86
139.1	412.3	60.5	6.11
151.2	424.4	82.4	8.32
157.4	434.6	97.2	9.82

Data source: Allied ChemicalNT-1

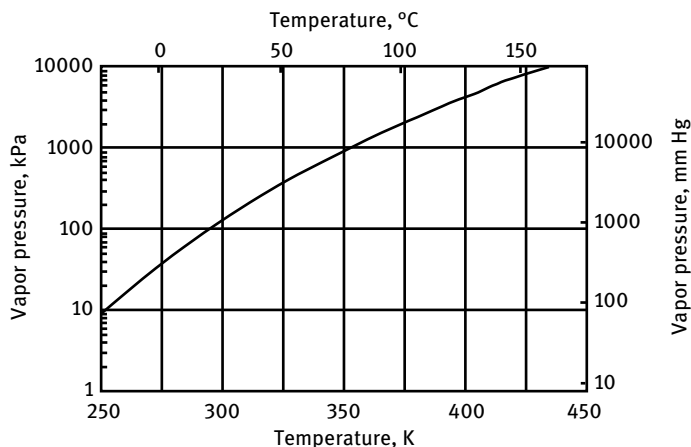


Figure 7: Vapor pressure of dinitrogen tetroxide equilibrium mixture. (Reproduced and modified from Allied Chemical.)

The vapor pressures of solid and liquid dinitrogen tetroxide were measured with a mercury manometer by means of an arrangement in which a purge gas of carbon dioxide protected the mercury surface from reaction with the dinitrogen tetroxide. For the range from 261 to 295 K (−12 to 22°C), the following equation gives more accurate data [22]:

$$\log_{10} p_v = 1753.00/T + 8.00436 - 11.8078 \times 10^{-4} T + 2.0954 \times 10^{-6} T^2$$

where $\log_{10} p_v$ is the decadic logarithm of the pressure in cm Hg (NOT mm Hg!!) and T is the absolute temperature in kelvin.

Another vapor pressure equation for the temperature range from 262 to 431 K (−11 to 158°C) was based on a combination of data from three earlier sources

$$\log_{10} p_v = 6.94291 - 2331.98/T + 84567/T^2$$

where p_v is the vapor pressure in atm and T is the temperature in kelvin. Data from this equation were used to construct the graph in Figure 8.

In a similar data analysis of existing data, the raw vapor pressure data from Giauque and Kemp [22] and Schlinger and Sage [36] were combined and fitted to a polynomial equation [41]:

$$\ln p = N_1 + N_2 \chi + N_3 \chi^2 + N_4 \chi^3 + N_5 \chi^4 + N_6 \chi(1 - \chi)^{1.5}$$

where

$$\chi = (1 - T_{tr}/T)/(1 - T_{crit.}/T)$$

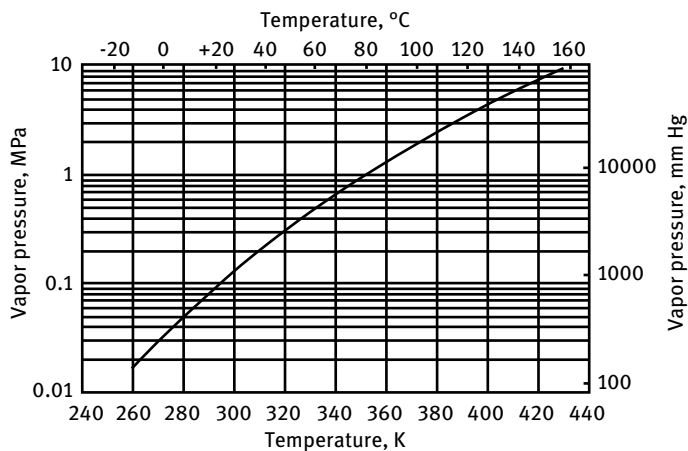


Figure 8: Vapor pressure of liquid dinitrogen tetroxide. (Based on data from [48].)

Table 7: Coefficients for vapor pressure equation.

N_1	-3.98267618
N_2	5.680987615
N_3	$4.725629483 \times 10^{-1}$
N_4	$1.036003737 \times 10^{-1}$
N_5	$4.376388591 \times 10^{-2}$
N_6	$3.6714221706 \times 10^{-1}$

Data source: [41]

and $T_{tr} = 261.95\text{ K}$ (triple-point temperature), $T_{crit.} = 431.372\text{ K}$ (critical-point temperature), T is the temperature in kelvin, and the vapor pressure p is in MPa. The coefficients are given in Table 7.

The vapor phase of MON-3 consists of four constituents: N_2O_4 , N_2O_3 , NO_2 , and NO . The vapor pressure is the sum of the partial pressures of these four constituent gases. A new empirical fit to existing vapor pressure data for NTO and MON-3 was compared to other existing fits while showing the accuracy of each as compared to available data [57].

3.6.2 Vapor Pressure of Solid Dinitrogen Tetroxide

Dinitrogen tetroxide as a solid sublimates quite readily, so we must take the vapor pressure of the solid into account. It may be possible to purify dinitrogen tetroxide by sublimation at low temperatures. The vapor pressure of frozen N_2O_4 between 238 K (-35°C) and 173 K (-100°C) listed in Table 8 was measured by a dynamic transference sublimation method and compared to the vapor pressure of an undercooled liquid [21].

Table 8: Vapor pressure of solid dinitrogen tetroxide.

Temperature		Vapor pressure (interpolated)	
$^\circ\text{C}$	K	mm Hg	kPa
-100	173	0.0023	0.0003
-90	183	0.0093	0.0012
-80	193	0.0360	0.0048
-70	203	0.151	0.0201
-60	213	0.605	0.0804
-50	223	2.44	0.324
-40	233	9.77	1.298
-30	243	39.24	5.21

Data source: [21]

The vapor pressure of solid dinitrogen tetroxide was measured with a mercury manometer by means of an arrangement in which a purge gas of carbon dioxide protected the mercury surface from reaction with the dinitrogen tetroxide. For the range from 240.3 to 261.9 K (-32.85 to -11.25°C), the following equation gives fairly accurate data [22]:

$$\log_{10} p_v = -2460.000/T + 9.58149 + 7.6170 \times 10^{-3} T - 1.51335 \times 10^{-5} T^2$$

where $\log_{10} p_v$ is the decadic logarithm of the pressure in cm Hg (NOT mm Hg!!) and T is the absolute temperature in kelvin.

Another set of vapor pressure data covering both the solid and liquid ranges of N_2O_4 is shown in Figure 9, taken from [58].

Yet another set of data was used to derive the vapor pressure equation for solid dinitrogen tetroxide:

$$\log p_v = 5.05334 + 763.176/T - 399161/T^2$$

where p_v is the vapor pressure in mm Hg and T is the temperature in kelvin. This equation was used to generate the vapor pressure graph shown in Figure 10.

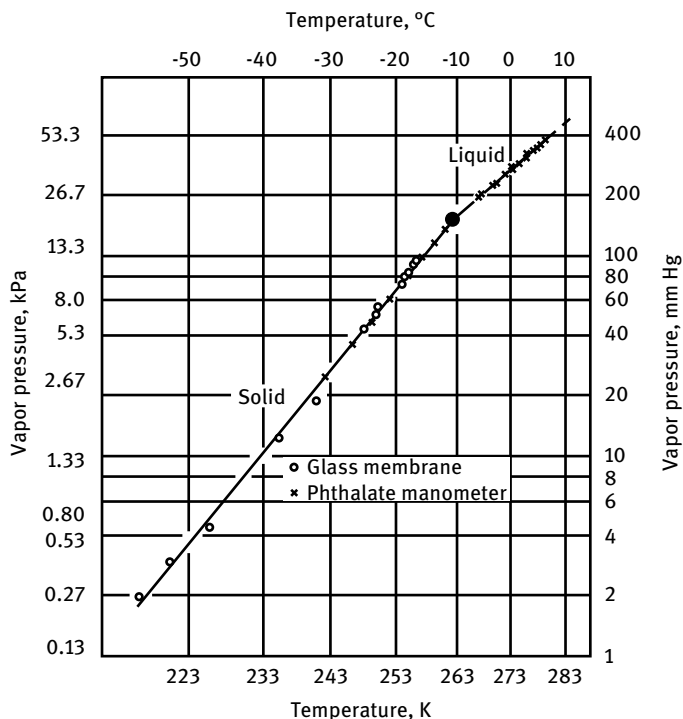


Figure 9: Vapor pressure of solid and liquid N_2O_4 . (Reproduced and modified from [58].)

3.7 Viscosity of Dinitrogen Tetroxide

One must differentiate between dynamic (also called absolute) viscosity and kinematic viscosity. The SI physical unit of *dynamic viscosity* μ is the Pascal-second ($\text{Pa} \cdot \text{s}$), which is equivalent to $(\text{N} \cdot \text{s})/\text{m}^2$, or $\text{kg m}^{-1} \cdot \text{s}^{-1}$. The cgs physical unit for dynamic viscosity is the *poise*, abbreviated as Ps.

$$1 \text{ Ps} = 0.1 \text{ Pa} \cdot \text{s}$$

$$1 \text{ cPs} = 1 \text{ mPa} \cdot \text{s} = 0.001 \text{ Pa} \cdot \text{s}.$$

The SI unit of *kinematic viscosity* ν is m^2/s . The cgs physical unit for *kinematic viscosity* is the *stokes*, abbreviated as St. It is sometimes expressed in terms of centistokes (cSt).

$$1 \text{ St} = 1 \frac{\text{cm}^2}{\text{s}} = 10^{-4} \frac{\text{m}^2}{\text{s}}$$

$$1 \text{ cSt} = 1 \frac{\text{mm}^2}{\text{s}} = 10^{-6} \frac{\text{m}^2}{\text{s}}.$$

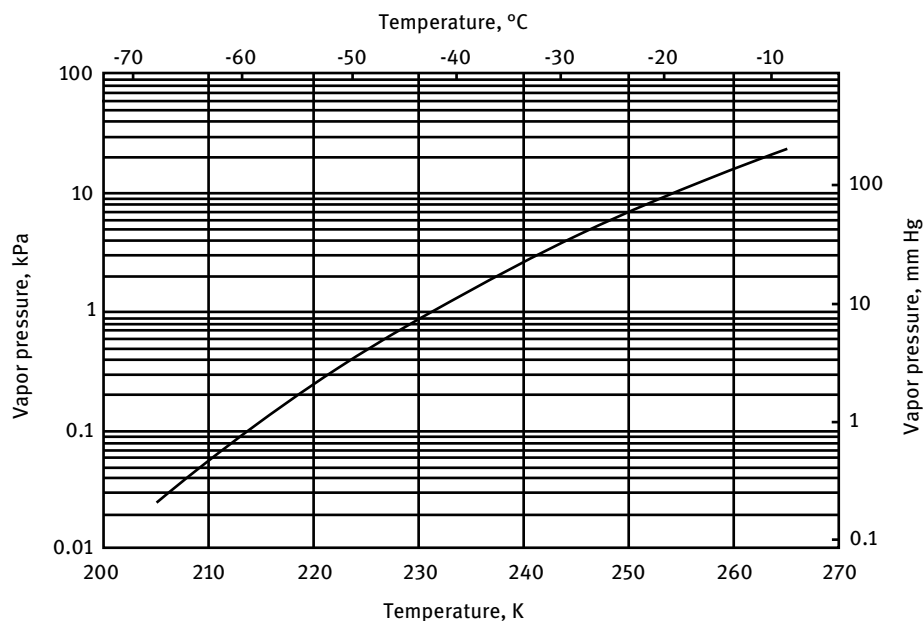


Figure 10: Vapor pressure of solid dinitrogen tetroxide. (Chart created by Schmidt 2016, based on data from [48].)

3.7.1 Viscosity of Liquid Dinitrogen Tetroxide

Table 9 is a summary of single-point dynamic viscosity data for dinitrogen tetroxide reported in the literature.

Table 9: Literature summary of dynamic viscosity data of pure dinitrogen tetroxide.

Dynamic viscosity		At temperature		Author	Year	References
cPs	mPa·s	K	°C			
0.35	0.35	311	38	Richter, Reamer, and Sage	1953	[59]
0.422	0.422	293	20	Suarez-Alfonso, Chambers, and Hatz	1961a	[60]
0.396	0.396	298	25	Wright, <i>USAF Propellant Handbook</i>	1977	[2]
0.394	0.394	298	25	Constantine et al.	1968	[48]

As of 1953, there were only limited viscosity data of liquid N_2O_4 at saturated vapor pressure available in the literature. Most of that came only from foreign sources, and some dated back to 1895. Therefore, the primary interest of renewed and more accurate measurements was focused on the development of an analytical expression to describe the effect of temperature on the viscosity of liquid [59]. These data were needed for the prediction of the characteristics of flow or thermal transfer in rocket engines. The viscos-

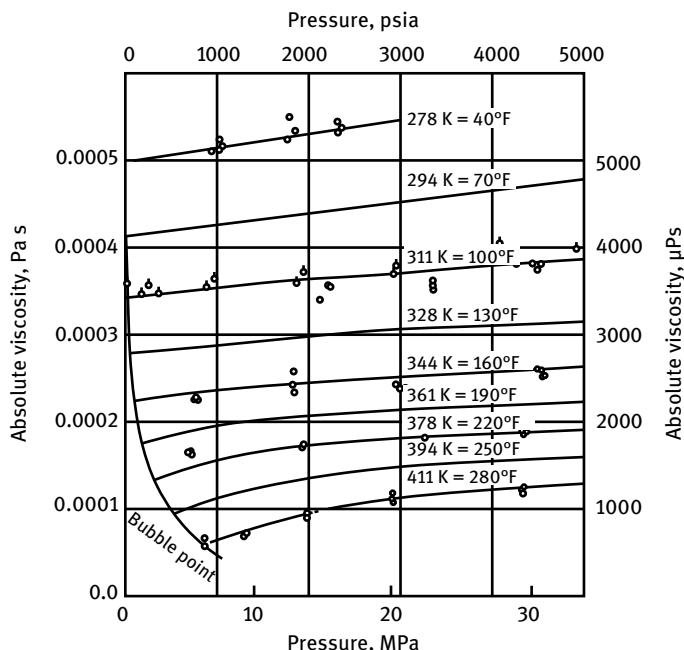


Figure 11: Effect of pressure with temperature as a secondary variable on the dynamic viscosity of liquid N_2O_4 . (Reprinted and modified from [59], with permission from © 1953 American Chemical Society.)

ity of liquid dinitrogen tetroxide was measured at pressures up to 34.4 MPa (5000 psia) in the temperature interval between 278 and 411 K (40 and 280 °F). A rolling-ball viscometer was employed, which is a stainless steel tube inclined at an angle of approximately 15°, down which a closely fitting stainless steel ball was permitted to roll under the influence of gravity. Figure 11 shows the effect of pressure (with temperature as a secondary variable) on the viscosity of liquid N_2O_4 .

Figure 12 shows the same data with the primary and secondary variable reversed, showing the effect of temperature on the dynamic viscosity of liquid N_2O_4 , with pressure as a secondary variable. The original publication contains tabulated raw measured data and smoothed values of the viscosity as a function of pressure for each of the temperatures investigated.

The same data that served as the source for Figure 12 were reevaluated and curve-fitted to an equation for the dynamic viscosity of liquid dinitrogen tetroxide at the bubble point:

$$\eta = -0.2005 - 72.003/T + 74314.6/T^2$$

where η is the dynamic viscosity in cPs and T is the temperature in kelvin. The data derived from this equation were used to generate the bubble-point line in Figure 13, which also contains viscosity data for higher pressures.

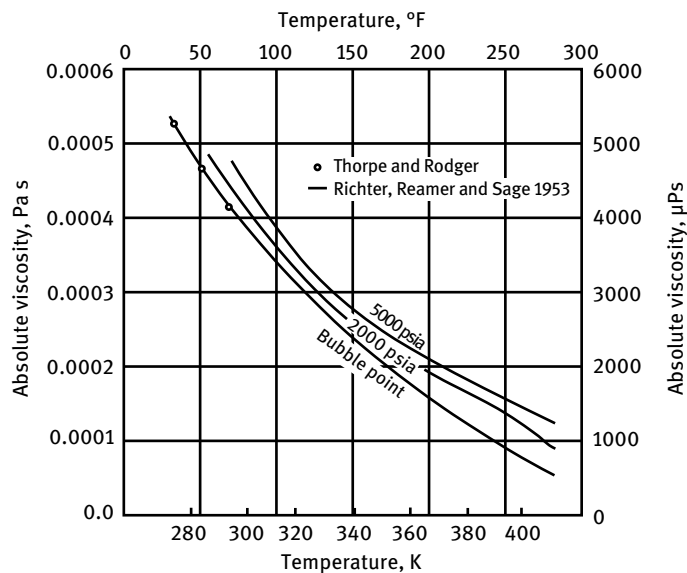


Figure 12: Effect of temperature, with pressure as a secondary variable, on the dynamic viscosity of liquid N_2O_4 . (Reprinted and modified from [59], with permission from © 1953 American Chemical Society.)

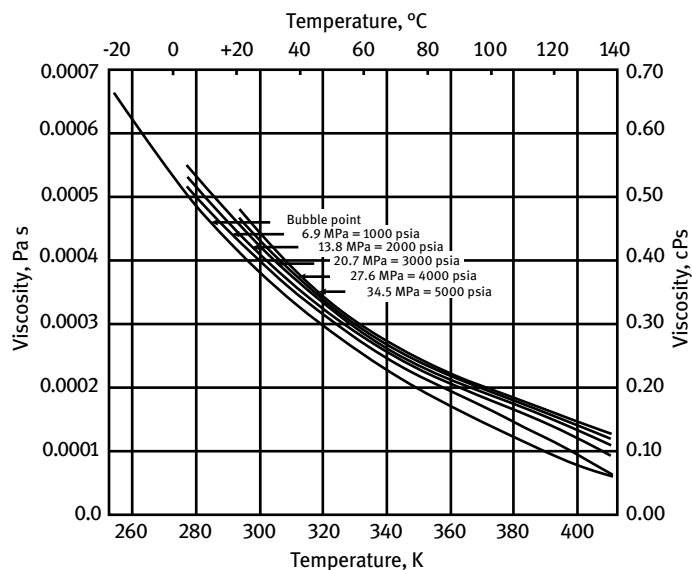


Figure 13: Dynamic viscosity of liquid dinitrogen tetroxide at high pressures. (Reproduced and modified from [48].)

Figure 14 shows the dynamic viscosity of liquid dinitrogen tetroxide under its own vapor pressure for higher temperatures, beyond the range of data shown in Figure 11.

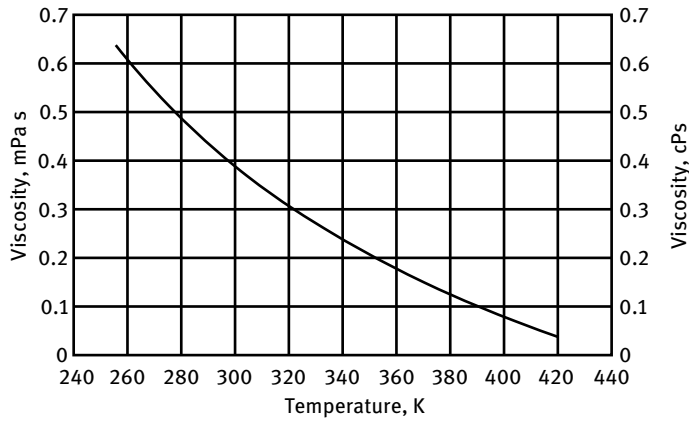


Figure 14: Dynamic viscosity of liquid dinitrogen tetroxide under its own saturation vapor pressure. (Chart created by Schmidt 2016, based on data from [2].)

The bubble-point data in Figure 14 can be expressed by the following polynomial equation:

$$\eta = 7.533 - 6.167 \times 10^{-2}T + 2.055 \times 10^{-4}T^2 - 3.234 \times 10^{-7}T^3 + 1.966 \times 10^{-10}T^4$$

where η is the dynamic viscosity in cPs and T is the temperature in kelvin. Table 10 gives the dynamic viscosity of liquid N_2O_4 at 311 K = 37.8 °C at very high pressures.

Gelling of dinitrogen tetroxide will reduce the spill hazard but will substantially increase the viscosity of the oxidizer. The effort to make gelled N_2O_4 often goes hand in hand with efforts to make gelled RFNA. The applications would be very similar. For gelled N_2O_4 properties and gelling agents tested, see Section 8.11.

Table 10: Dynamic viscosity of liquid dinitrogen tetroxide as a function of pressure.

Pressure, atm	Dynamic viscosity, cPs ^a
13.6	0.3441
40.8	0.3495
68.0	0.3544
102.1	0.3587
136.1	0.3628
170.1	0.3670
204.1	0.3713

^aat 311 K = 37.8 °C

Data source: [34]

The values of dynamic viscosity below 284.2 K (11.2 °C) of N_2O_4 were described by a straight line fitting the equation

$$\log \eta = \frac{400}{T} - 1.742$$

where η is the dynamic viscosity in cPs and T is the temperature in kelvin [33]. No discontinuity was apparent.

Viscosity data for MON are in Section 4.1.5.

3.7.2 Viscosity of Gaseous Dinitrogen Tetroxide

Data on the viscosity of equilibrium dissociating dinitrogen tetroxide in the vapor state are insufficient. This difficulty is partially due to the dissociation equilibrium. The viscosity of the equilibrium gaseous system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ (for brevity, called NO_2) was measured in the temperature range of 298–443 K (25–170 °C) at pressures from 55 to 505 kPa (0.5–5 atm) employing a rolling-ball viscometer [61]. The viscosity of the equilibrium gaseous system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ is shown in Figure 15 in comparison to some literature data. The fact that the viscosity decreases with increases in pressure below 373 K (100 °C) can be explained by the fact that the equilibrium $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ shifts to the left with an increase in pressure, at the same time increasing the concentration of the less viscous species N_2O_4 .

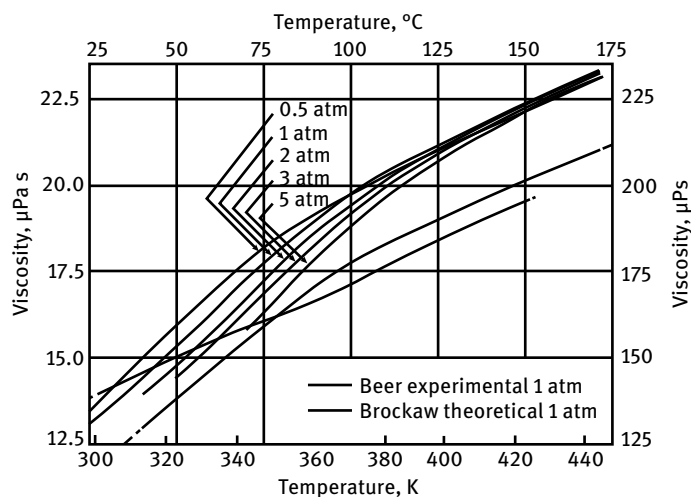


Figure 15: Dynamic viscosity of dissociating gaseous N_2O_4 . (Reprinted and modified from [61] with permission from © 1964 American Chemical Society.)

By analyzing the experimental viscosity of the dissociating system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, the force constants of N_2O_4 and NO_2 have been obtained for the Lennard-Jones (12:6) potential [62]. Calculations made with these force constants have suggested that, in agreement with theory, chemical reaction has no significant effect on the viscosity of a chemically reacting gas mixture.

Dinitrogen tetroxide will rarely be used in the gaseous form as a rocket propellant, but viscosity data for the gas are available as shown in Figure 16. At the higher temperatures, most of the vapor will consist of NO_2 instead of N_2O_4 . Of course, all of the N_2O_4 has to evaporate before it can react with a rocket fuel; therefore, viscosity in the gas phase becomes important. The viscosity of $\text{NO}_2/\text{N}_2\text{O}_4$ vapor in the range of 298–443 K (25–170 °C) can be expressed by the polynomial equation

$$\eta = 123.66 - 7.04 \times 10^{-2}t + 2.0996 \times 10^{-2}t^2 - 1.72 \times 10^{-4}t^3 + 4.290 \times 10^{-7}t^4$$

where η is the dynamic viscosity in μPs and t is the temperature in °C.

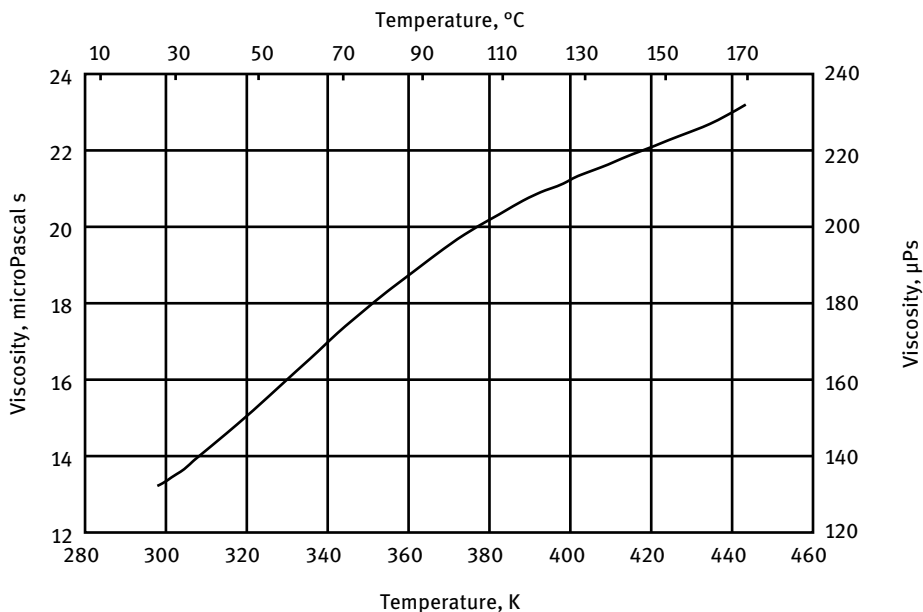


Figure 16: Viscosity of dinitrogen tetroxide/nitrogen dioxide vapor at 101 kPa. (Chart created by Schmidt 2016, based on data from [48].)

The pressure dependence at a constant temperature of the dynamic viscosity of a reacting mixture ($\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$) was calculated at 300–1000 K and 1–300 bar by using a pseudo-critical constant method and from semi-empirical mixing rules for the Lennard-Jones potential force [63, 64]. The two methods gave almost identical results, which differed by approximately 5–8% from experimental values.

The viscosity of dinitrogen tetroxide vapor expanding to supersonic velocities in a Laval nozzle will depend on the rate at which the $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2$ equilibrium can adjust to the rapidly changing pressure and temperature environment as it expands. Calculations were made for shifting and frozen equilibrium during expansion [65].

3.8 Surface Tension of Dinitrogen Tetroxide

Table 11 is a summary of single-surface tension data for dinitrogen tetroxide as reported in the literature.

Table 11: Literature summary of surface tension data of pure dinitrogen tetroxide.

Surface tension			At temperature		Author	Year	References
N/m	dyn/cm	lb _f /ft	K	°C			
0.02648	26.48	0.001815	298	25	Suarez-Alfonso, Chambers, and Hatz	1961	[66]
0.0251	25.1		298	25	<i>USAF Propellant Handbook</i>	1987	[2]
0.0306	30.6 ± 1.0		274.7	1.6	Kit and Evered	1960	[67]
0.0275	27.5 ± 1.0		292.9	19.8	Kit and Evered	1960	[67]

1 lb_f/ft = 14.5939 N/m

The surface tension of dinitrogen tetroxide as a function of temperature is illustrated in Figure 17.

The surface tension data in Figure 17 can be expressed by the equation

$$\sigma = 109.00 - 0.3709T + 3.0 \times 10^{-4}T^2$$

where σ is the surface tension in dyn/cm and T is the temperature in kelvin. Surface tension data for MON are in Section 4.1.6.

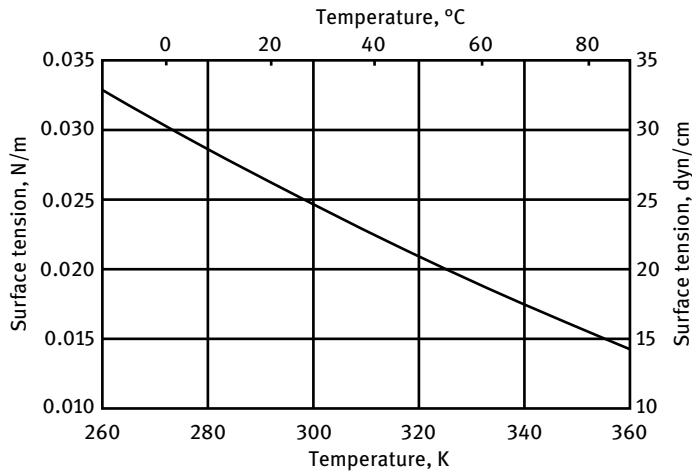


Figure 17: Surface tension of dinitrogen tetroxide. (Chart created by Schmidt 2016, based on data from [2])

3.9 Thermal Conductivity of Dinitrogen Tetroxide

Table 12 is a short summary of thermal conductivity data for dinitrogen tetroxide as found in the literature.

Table 12: Thermal conductivity of NO₂ and N₂O₄ equilibrium mixture

Physical state	Temperature		Thermal conductivity	
	°C	K	cal cm ⁻¹ s ⁻¹ °C ⁻¹	W m ⁻¹ K ⁻¹
Gaseous	55	328	9.6 × 10 ⁻⁵	0.0402
Liquid	4.4	277.6	3.35 × 10 ⁻⁴	0.140
Saturated liquid	37.8	310.9	2.98 × 10 ⁻⁴	0.125
Saturated liquid	71	344	2.31 × 10 ⁻⁴	0.097

Data sources: Various literature citations
1 mW m⁻¹ · K⁻¹ = 10⁻³ W m⁻¹ · K⁻¹ = 10⁻⁵ W cm⁻¹ · K⁻¹ = 0.000002388 cal s⁻¹ cm⁻¹ °C⁻¹ = 2.388 × 10⁻⁶ cal s⁻¹ cm⁻¹ °C⁻¹; 1 cal s⁻¹ cm⁻¹ °C⁻¹ = 418.68 W m⁻¹ K⁻¹

3.9.1 Thermal Conductivity of Liquid Dinitrogen Tetroxide

The thermal conductivity of liquid dinitrogen tetroxide was determined in an apparatus that consisted of two concentric spherical shells whose temperatures were measured while a known outward-bound radial thermal flux passed between them [68]. The results are illustrated in Figure 18 and tabulated in Table 13.

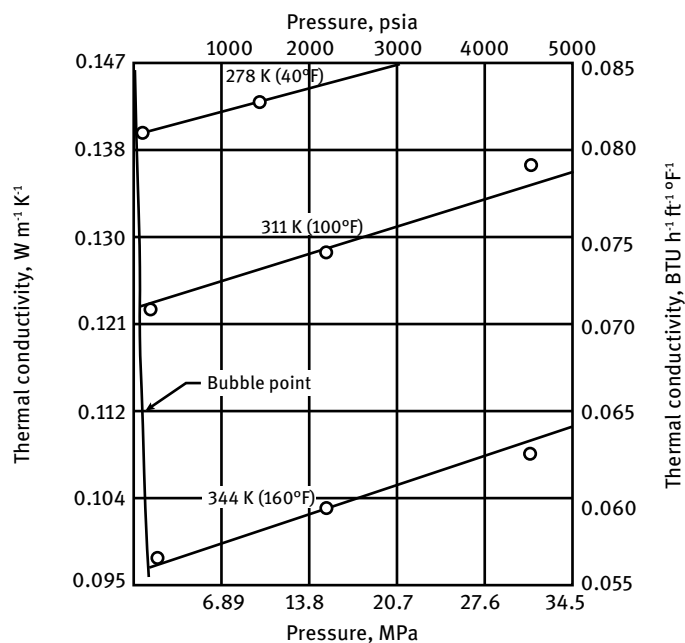


Figure 18: Thermal conductivity of liquid N_2O_4 . (Reprinted and modified from [68], with permission from © 1956 American Chemical Society.)

Table 13: Experimental values of thermal conductivity of liquid dinitrogen tetroxide.

Temperature		Pressure		Thermal conductivity	
K	°F	MPa	psia	$\text{W m}^{-1} \text{K}^{-1}$	Absolute $\text{BTU h}^{-1} \text{ft}^{-1} \text{°F}^{-1}$
277.6	40	0.45	65	0.140	0.0811
277.6	40	9.76	1418	0.143	0.0827
310.9	100	1.09	157.9	0.123	0.071
310.9	100	15.00	2179.8	0.128	0.0742
310.9	100	31.11	4522	0.137	0.0791
344.3	160	1.51	219.3	0.098	0.0566
344.3	160	14.91	2167.7	0.103	0.0596
344.3	160	31.08	4517.5	0.108	0.0626

Data source: [68]

It is assumed that thermal conductivity graphs presented in the *USAF Propellant Handbook* on N_2O_4 [2] are actually based on measurements of Richter and Sage 1957 [68], just represented in a different format (Figure 19 for several elevated pressures and Figure 20 for the bubble-point pressure).

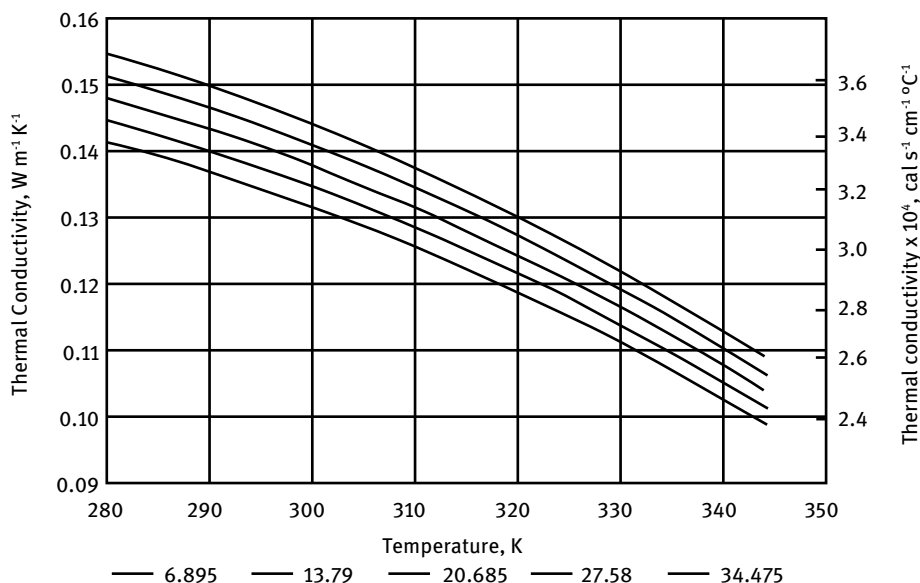


Figure 19: Thermal conductivity of liquid N₂O₄ at elevated pressures. (Based on data from [48].)

The thermal conductivity of liquid dinitrogen tetroxide from Figure 19 for the ranges of 277–344 K (4–71 °C) and 0.45–31 MPa (65–4500 psia) can be represented by the following equation:

$$\kappa = 3.363 \times 10^{-4} - 7.955 \times 10^{-7}t + 8.231 \times 10^{-9}p - 3.04 \times 10^{-11}pt - 9.36 \times 10^{-9}t^2$$

where κ is the thermal conductivity in cal cm⁻¹ s⁻¹ K⁻¹, p is the pressure in psia, and t is the temperature in °C. To convert from cal cm⁻¹ s⁻¹ K⁻¹ to W m⁻¹ K⁻¹, the conversion factor is 1 cal cm⁻¹ s⁻¹ K⁻¹ = 418.4 W m⁻¹ K⁻¹.

The thermal conductivity of liquid dinitrogen tetroxide from Figure 20 can be represented by the following equation:

$$\kappa = -3.294 \times 10^{-4} + 5.566 \times 10^{-6}T - 1.144 \times 10^{-8}T^2$$

where κ is the thermal conductivity in cal cm⁻¹ s⁻¹ K⁻¹ and T is the temperature in kelvin. See also [69].

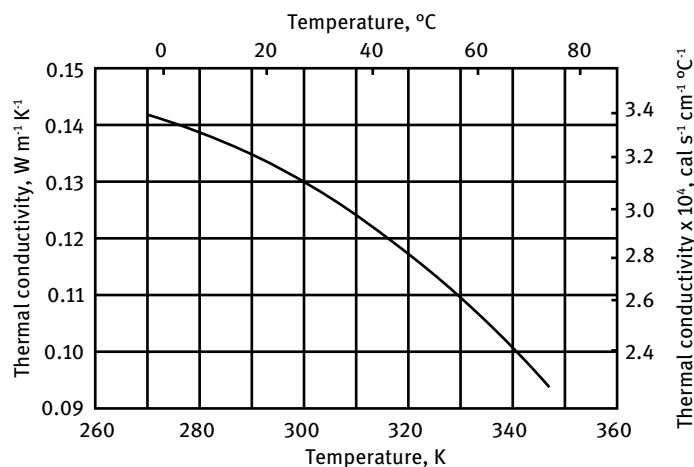


Figure 20: Thermal conductivity of liquid N_2O_4 at the bubble point. (Chart created by Schmidt 2016, based on data from [2, 48].)

3.9.2 Thermal Conductivity of and Heat Transfer to Dissociating Gaseous Dinitrogen Tetroxide

For a non-dissociating system with the same physical properties as non-dissociating gaseous N_2O_4 , theoretical calculations would only predict one-ninth of the rate of heat transfer and thermal conductivity as for a dissociating system. Because of the high rate of heat transfer and good thermal conductivity, dinitrogen tetroxide has been considered as a working fluid in chemical heat pipes and as a working fluid in nuclear reactors [70, 71]. Table 14 gives a comparison of predicted thermal conductivity of N_2O_4 with and without equilibrium dissociation. See also [72].

Table 14: Calculated thermal conductivity of the gaseous system $\text{NO}_2/\text{N}_2\text{O}_4$ at 1 atm.

Temperature K	Thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$		Thermal conductivity, $\text{cal cm}^{-1} \text{s}^{-1} \text{K}^{-1}$	
	With shifting equilibrium	With frozen equilibrium	With shifting equilibrium	With frozen equilibrium
290	0.084	0.013	20.083×10^{-5}	3.110×10^{-5}
300	0.107	0.014	25.668×10^{-5}	3.337×10^{-5}
320	0.147	0.016	35.233×10^{-5}	3.860×10^{-5}
340	0.142	0.018	33.977×10^{-5}	4.427×10^{-5}

Data source: [73]

The thermal conductivity of gaseous dinitrogen tetroxide is higher than one would expect from theoretical considerations. This discrepancy is the result of the fact that in addition to heat transfer by conduction, convection, and radiation (purely physical transport of energy), a portion of the heat is transported as chemical energy. This is a chemical heat pipe where the energy is transported as heat of dissociation. Dinitrogen tetroxide dissociates at the hot end of the heat pipe into NO_2 . NO_2 diffuses to the cold end and recombines there to N_2O_4 , releasing heat. This theory has been confirmed in the course of several experimental investigations.

Heat transfer rates of both heating and cooling for dissociating N_2O_4 gas were experimentally measured under turbulent pipe-flow conditions [74]. The range of the average Reynolds numbers for which these measurements were made was from 6700 to 22000. Thermal flux at the inside surfaces of the tubes ranged from 946 to 26480 W/m^2 (300–8400 $\text{BTU h}^{-1} \text{ft}^{-2}$) for heating and cooling. Wall temperatures of the heater section were varied from 294 to 333 K (70 to 140 °F). Mixed-mean bulk gas temperatures for both heating and cooling were in the range of 295–361 K (72–190 °F). Radial velocity and temperature profiles were measured at various longitudinal positions in the heater section. For this equilibrium gas mixture, heat-transfer coefficients as high as 12 times those for the gas under frozen equilibrium conditions were obtained.

An all-glass apparatus has been used to measure the thermal conductivity of the system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ by a thick-wire variant of the hot-wire method in a temperature range of 305–363 K (32–90 °C) and up to a pressure of about 67 kPa (500 mm Hg), measuring the equilibrium constant and the thermal conductivity of the system simultaneously [75]. The discrepancy between the experimental and the calculated values of the heat conductivity, which is particularly large at the lower pressures, showed the necessity of applying non-equilibrium heat-transfer theory to interpret the data. A correlation between dissociation constants and thermal conductivity is presented in Section 5.2 for N_2O_4 .

The kinetics of dissociation, recombination, and relaxation of chemical energy play an important role in the thermal conductivity of the dissociating system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, where a chemical accommodation coefficient must be considered [76].

The thermal conductivity of doubly dissociating N_2O_4 involving both the reactions $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ and $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ has been measured between 373 K (100 °C) and 473 K (200 °C) at pressures below 101 kPa (1 atm) using both the absolute hot-wire method and an all-glass apparatus with a glass diaphragm manometer [77]. The results were, however, not in good agreement with the values calculated on the assumption of local chemical equilibrium for both the reactions.

It has been found by conducting measurements at varying pressures that the theoretical estimate of relaxation effects in the heat conductivity of a chemically reacting gas mixture holds only up to a certain upper limit of pressure, beyond which the observed effect becomes insignificant compared with the theoretical predictions [78].

The thermal conductivity of dissociating dinitrogen tetroxide was measured by the hot-wire method with a platinum wire in the temperature range of 290–870 K and

at four pressures (27, 53, 80, and 100 kPa) [79]. The predicted thermal conductivity as a function of temperature at 100 kPa showed two maxima, the first one at 350 K ($143 \text{ mW m}^{-1} \text{ K}^{-1}$) due to $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ and a second one ($\sim 200 \text{ mW m}^{-1} \text{ K}^{-1}$) at 700 K due to $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$. See also [80].

Thermal transport properties such as heat capacity, thermal conductivity, and coefficient of thermal expansion of equilibrium-type reacting systems are usually large, non-monotonic functions of temperature. Accordingly, in convective heat transfer to such systems, large heat transfer coefficients dominate. In correlating heat transfer data in reacting systems, it is necessary to have information on the pertinent physical properties of the equilibrium system. Properties such as molecular weight, density, diffusion coefficient, viscosity, thermal conductivity, isobaric specific heat capacity, specific enthalpy, and coefficient of thermal expansion were calculated for the systems



and



Reaction (1) is much more likely to be at equilibrium for most processes than reaction (2) is, since kinetic measurements indicated reaction times for reaction (1) of the order of a microsecond at 298 K (25 °C), whereas reaction (2) is relatively slow [62, 81].

The balanced equations for the intensity of turbulent pulsations of temperature and composition of chemically reacting binary mixtures were used to investigate the effect of chemical non-equilibrium on the characteristics of turbulent heat and mass transfer in turbulent flows in or near the boundary layer [82]. It was shown that in a flow of dissociating dinitrogen tetroxide at subcritical pressure gradients, representations with the usual relations for the turbulent transfer coefficients can be used for the description of the turbulent heat and mass flows, including the effect of pulsations of temperature and composition on the averaged rate of chemical transformations in turbulent flows. The results of numerical calculations of the heat transfer and friction resistance in a flow of dinitrogen tetroxide, with due allowance for the variation of the physicochemical properties of the coolant and the mutual effect of dissociation and turbulence, showed that heat transfer to a dissociating fluid is higher than heat transfer to a non-dissociating fluid.

For predicting the heat exchange of dissociating dinitrogen tetroxide in fully developed turbulent flow used as a working fluid in fast breeder nuclear reactors, it was assumed that in the first stage the medium is a homogeneous gas [83]. Results of calculations and experiments in the range between $\text{Re} = 2 \times 10^4$ and $\text{Re} = 8 \times 10^4$ agreed satisfactorily with each other.

3.10 Heat-Transfer Coefficient of Liquid N_2O_4

With regard to the regenerative cooling of rocket engines using liquid N_2O_4 , it is important to know the heat-transfer properties of the coolant fluid. Dinitrogen tetroxide is well suited for regenerative cooling, but it is not used very often in that capacity [84]. The heat-transfer coefficient at the upper limit to nucleate boiling of dinitrogen tetroxide is low in comparison to other rocket propellants that might also be used as coolants in regenerative rocket engines (Table 15). See also [85, 86].

Table 15: Heat-transfer coefficient of dinitrogen tetroxide in comparison to other rocket propellants.

Coolant liquid	Heat-transfer coefficient q_{ul} at 2.07 MPa = 20.4 atm, 9.1 m/s and 310.9 K = 37.8 °C inlet temperature		Heat capacity at 310.9 K = 37.8 °C	
	kW/cm ²	BTU in. ⁻² s ⁻¹	J g ⁻¹ K ⁻¹	cal g ⁻¹ °C ⁻¹
N_2O_4	29.38	179.8	1.64	0.393
NH_3	15.95	97.6	4.89	1.17
JP-3	28.73	175.8	1.82	0.435
RFNA	43.39	265.5	1.76	0.42
Corporal-Fuel ^a	51.64	316	2.09	0.50
N_2H_4	79.10	484		

^aThe fuel used in the Corporal ballistic missile consisted of 80 mass-% aniline and 20 mass-% furfuryl alcohol

Data source: [84]

Local heat-transfer coefficients were measured for the liquid nitrogen dioxide/dinitrogen tetroxide system in well-developed turbulent flow in an electrically heated tube of inner diameter 4.9 mm (0.194 in) [87]. The average probable error determined from reproducibility tests was less than 2%. A modification of the Deissler analogy presented earlier was found to predict coefficients that agreed well (0–19% deviation) with the observed results. Some of this deviation may be due to uncertainties in the viscosity data.

Local turbulent heat-transfer coefficients were obtained for the dissociating system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ flowing through an electrically heated tube with a length-to-diameter ratio of 40 [88]. Experimental test conditions covered heat flux up to 44000 BTU h⁻¹ ft⁻² = 138.7 kW/m² and mass flow rates up to 130000 lb_m h⁻¹ ft⁻² = 176 kg m⁻² s⁻¹. The maximum tube wall temperature reached from 359 to 572 K.

Heat-transfer coefficients were measured in the boiling $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ system at ≤ 157 MPa (≤ 1550 atm absolute) and heat fluxes of 34.9 to 872 kW/m² (3×10^4 to 7.5×10^5 kcal m⁻² h⁻¹) [89]. At 0.1–1 MPa (1–10 atm), there was a marked increase in the heat-transfer coefficient with an increase in pressure. There was only an insignificant increase in the intermediate range at 1.8–5.1 MPa (18–50 atm). At 1–2 MPa (10–20 atm),

the heat-transfer coefficient exhibited hysteresis, i.e., the values obtained on increasing the pressure were noticeably higher than those obtained on reducing the pressure.

At a high level of superheating, the thermal transfer properties of N_2O_4 lag behind the flow [90]. See also [91, 92].

The heat-exchange coefficients during the flow of a two-phase vapor-liquid stream of dissociating N_2O_4 in vertical pipes heated by a nuclear reactor were analyzed, and functions were derived for calculating the heat flux under different flow conditions [93].

Dinitrogen tetroxide has been evaluated as the working fluid in nuclear power plants driving a turbine. The condensation of NTO after expansion through the turbine occurs in the return loop of the power plant in vertical pipes [94]. The results of a calculation of the heat exchange and hydraulic resistance during film condensation of NTO in a vertical pipe were compared with experimental data on the condensation of water steam.

Pressure-drop and heat-transfer measurements in a dinitrogen tetroxide closed-loop turbulent flow system indicated that after 3000 h of operation at 35–80 bar, 650–840 K, flow velocities between 30 and 50 m/s, and Reynolds numbers between 6×10^3 and 70×10^3 , the friction losses were increased by 14–19% because of roughening of the surface, but the heat-transfer coefficient had not changed significantly [95].

Experimental heat-transfer data obtained with N_2O_4 boiling and dissociating in a vertical tube were correlated in a set of empirical equations that will allow one to predict heat flux and temperature gradient as a function of boiling condition (undercooled or saturated condition boiling), pressure, flow velocity, and fluid-stream quality [96].

In tests with measuring the boiling heat transfer to flowing MON-3, the critical heat-transfer point was reached when the superheat temperature was about 50 K (50°C) under different flow conditions [97]. Pressure oscillations with 8–22 Hz frequency were observed when MON-3 was boiling. This frequency was similar to the frequency observed with combustion instabilities in a test injector that simulated the actual rocket engine combustion chamber.

3.11 Solubility of Pressurant Gases in Dinitrogen Tetroxide

There are several general science publications that provide the basics of gas solubility and list some solubility numbers in NTO as examples [98–100].

3.11.1 Equilibrium State of Gas Solubility in Dinitrogen Tetroxide

Henry's law describes the maximum amount of pressurant gas that can dissolve in a liquid under equilibrium conditions. Henry's law states that at a constant temper-

ature, the concentration of the gas in the liquid phase is proportional to the partial pressure of the dissolving gas in the gas phase:

$$P_g = X_g \cdot k_{\text{Hp},c} = N_{\text{gas}}/N_{\text{solvent}} \cdot k_{\text{Hp},c}$$

where P_g is the partial pressure of the dissolving gas in the gas phase, X_g is the mol fraction of dissolved gas, $k_{\text{Hp},c}$ is Henry's constant in the dimension of atm L/mol, and N_{gas} and N_{solvent} are the number of mols in the saturated solution.

In reality, the variation of the partial pressure of a gas is never completely linear with variation of mol fraction X_g of gas in the liquid phase, especially when it is considered over the whole of the concentration range from $X_g = 0$ to $X_g = 1$. Nevertheless, for low concentration of gas in liquid phase, when $X_g < 0.01$, the variation of mol fractions usually fit a linear relation within experimental error.

Because there are several forms of equations used to express Henry's law, and all k_{H} may be referred to as Henry's law constants, readers of the technical literature must be quite careful to verify which version of the equation is being used because the constant will have different numbers and different units.

Henry's constant varies with temperature, which is why it would be better to call it Henry's coefficient instead of Henry's constant. Depending on the gas and the solvent, solubility can increase or decrease with increasing temperature. In a closed vessel with liquid at the bottom and gas in the ullage, when the temperature increases, **(1)** the density of the liquid propellant decreases, which leads to a smaller ullage volume and compression of the ullage volume gases. In addition, **(2)** the vapor pressure of the propellant increases, and in some cases **(3)** the gas solubility increases. In tanks with a small ullage volume fraction, the effects of **(1)** and **(3)** are accentuated.

The most common pressurant gases for N_2O_4 and MON are helium and nitrogen, and the solubility of these gases in N_2O_4 and MON has been thoroughly investigated. The solubility data for helium or nitrogen in N_2O_4 available prior to 1964 were inaccurate, and more accurate measurements needed to be made. The solubilities of He, N_2 , O_2 , and Ar in liquid N_2O_4 were measured at moderate pressures (0.5–1.9 atm) and temperatures between 262 and 303 K [101–103]. In all cases Henry's law was obeyed; i.e., the solubility was proportional to the partial pressure of gas dissolved by N_2O_4 . The logarithms of the Henry's constant $K = X/P$ were plotted against reciprocal absolute temperature and gave straight lines, as shown in Figure 21. This illustration is unusual because it shows only three segments of a chart with an uninterrupted ordinate scale. To save space, the three areas of interest were extracted from a complete chart, and each segment has its own ordinate scale. If the data for the solubility of four different gases were combined in one chart, its vertical expanse might occupy an entire page, as would three individual, rectangular charts. This type of graph saves space, but we have rarely seen it done this way. These gases are more soluble in N_2O_4 than in H_2O or other solvents. It would be difficult to extrapolate from the data obtained at 0.5–1.9 atm to higher pressures at which rockets operate. Data for higher pressures would be of more practical interest.

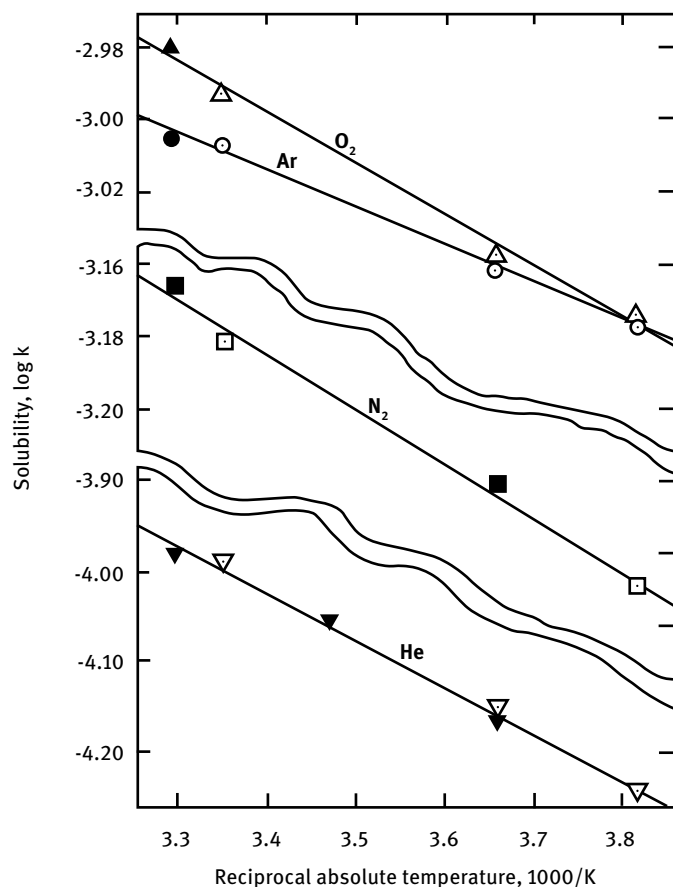
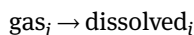


Figure 21: Solubilities of He, N₂, O₂, and Ar in liquid N₂O₄. (Reproduced and modified from [104].)

Although dissolving a gas (here identified by the subscript i) in a liquid solvent (identified by the subscript j) is a physical process in which no chemical changes are involved, the process



can be expressed by an equilibrium constant similar to those used for chemical reactions:

$$K = \frac{\text{ppm}_i}{P} = 10^6 M_i \frac{X_i}{M_j} P_i$$

where M_i and M_j are the molecular masses of the gas and the solvent, respectively; X_i is the mol fraction of the gas in the solution; and P_i is the pressure above the solution

(in units of atmospheres). K is temperature dependent, and a plot of $\log K$ versus $1/T$ gives a linear correlation similar to an Arrhenius curve:

$$\log K_i = \frac{A}{T} + B$$

where A and B are dimensionless constants tabulated in Table 16.

Table 16: Gas solubility equation constants for gases dissolving in NTO.

Gas	A	B	Solubility at 1 atm, in units of ppm	
			at 273 K	at 298 K
He	-521	2.3874	3.0	4.3
N ₂	-153	2.8194	182	203
O ₂	-145	3.0367	320	355
Ar	-104	2.9757	394	424

Data source: [103]

The solubilities of O₂, NO, and N₂O₃ in liquid N₂O₄ were measured over a modest pressure range between 0.3 and 1.9 atm at 262, 273, and 298 K (-11, 0, and +25 °C) [105]. The results showed that Henry's law was obeyed for all pressures at each temperature for O₂ and at low pressures for NO and N₂O₃. The standard free energy, enthalpy, and entropy of solution for each gas were computed [106]. Oxygen solubility data indicated that no formation of other nitrogen oxides occurred in the oxygen-saturated N₂O₄ under the conditions of this test.

During the Apollo program for the testing of the lunar module ascent and descent propulsion systems at NASA WSTF, large quantities (up to 4.5 m³ [1200 gallons]) of Aerozine-50 and N₂O₄ were saturated with gaseous helium at pressures ranging from 344 to 1690 kPa (50–245 psia). To promote rapid absorption of the helium by the propellant, equipment was designed to expose a large surface area of the propellant to a helium atmosphere [107]. Before the as-received propellant was loaded into an auxiliary conditioning unit, it was vented at atmospheric pressure in the ready storage units for 3 h to allow any gaseous nitrogen (normally used for the tank or vessel pressure maintained in the ullage during shipping and storage) dissolved in the propellants to come out of solution. The dinitrogen tetroxide bubble-point pressure as a function of calculated 100% helium saturation pressure was then graphed for six different temperatures. For the measurement ranges encountered, the relationship between temperature or pressure and helium content for a given constant pressure or temperature was linear. The dissolved helium can be calculated from the equation

Helium content of N₂O₄ = -0.1771 + (0.001568 × pressure) + (0.001656 × temperature)

where helium content is in cubic centimeters STP per gram N_2O_4 , pressure is in pounds per square inch gauge, and temperature is in °F. Similar data were obtained for Aerozine-50. In a later program, similar helium solubility data were obtained for MON-1 and MMH (see *Encyclopedia of Liquid Fuels*, chapter “Methylhydrazine”).

Pressure conditions for a MON-3 propellant tank in Eurostar satellites with the intention of being launched on the Space Transportation System (Space Shuttle) but (for unforeseen reasons) returning to Earth after a failed launch attempt while in orbit were calculated, taking into consideration the out-of-spec heating of the spacecraft sitting in the payload bay during re-entry and the heat soaking back if the shuttle had to land in hot desert climate conditions at White Sands or Edwards Air Force Base [108]. The maximum soak-back temperature was predicted to be 318 K (45 °C). The increased temperature has several effects on the tank pressure, which were considered in the model:

- Thermal expansion of the propellant
- Partial pressure of pressurant gas released on heating
- Propellant vapor pressure
- Solubility and release of pressurant gas
- Tank volume expansion

The Eurostar oxidizer tank has to stay within the 17.7 bar MEOP. Experiments with 94.4% fill level were made with a 1-L bomb with 35-bar operating pressure and 70-bar proof test pressure, and the experimental results were compared to predictions from the computer model. Because dissolution of He in MON is a slow process, or only the top layer becomes saturated, zero helium solubility was assumed as the worst case in the computer model.

Experience gained with NTO and MMH tank pressurization during launch preparations for Galileo and Mars Observer space probes was compared with literature data (Table 17) on helium solubility in these propellants [109].

Techniques were developed for achieving the required levels of helium saturation in monomethylhydrazine (MMH) and NTO during launch preparations, and the measured values were evaluated for equilibrium solubilities of He in liquid propellants as known to the industry at that time. At that time (1990), there were still enough uncertainties in the published He saturation values to warrant further basic experimental studies. From the several possible methods for measurement, the manometric measurement of gas volume from a frozen sample of propellant was the recommended method for gas analysis.

Dissolved pressurant gases and the degree of gas saturation may affect the performance (ignition delay, injector boiling, dribble volume expulsion) of bipropellant rocket engines [110].

Table 17: Comparison of literature data for solubility of helium in dinitrogen tetroxide.

Helium solubility, cm ³ He STP/g N ₂ O ₄ at 298 K and 1723 kPa gauge (250 psig)	Source
Literature data	
0.41	Aerospace (extrapolated value)
0.39	Marquardt
0.34	JPL Viking tests
0.33	NASA WSTF
0.32	<i>Air Force Handbook</i> AFRPL-TR-76-76
0.32	TRW
JPL/MBB measured data	
0.26–0.40	MBB Galileo ^a
0.31	JPL Galileo alternate thruster
0.27–0.28	JPL Mars Observer large tank
0.29–0.40	JPL Mars Observer small-run tank

Data source: [109]

^aMBB data normalized to 25 °C and 250 psig.

3.11.2 Rate of Pressurant Gas Absorption into Dinitrogen Tetroxide

The rate of solution of a gas in a liquid is highly dependent upon the extent of agitation and mixing. Gas diffusion through an immobile liquid can take months to equilibrate. The configuration of the propellant supply tanks at a launch or test facility will determine the most efficient saturation technique for its system. Gas saturation of liquids can be accelerated by aeration, bubbling, and stirring. In a tank without an expulsion diaphragm, immediately after pressurizing a stagnant unsaturated propellant in a satellite or upper-stage propellant tank with pressurant gas and locking up the system, the pressure in the ullage starts decaying because a fraction of the gas from the ullage goes into solution. The rate at which the pressure decays depends on a large number of variables and has been the subject of several analytical modeling studies. There is little published data against which to test the validity of those models. In a stagnant tank containing NTO or MON in direct contact with the pressurant gas (e.g., in a surface-tension propellant management device [PMD] tank, not a bladder or diaphragm tank), it may take 20–30 d to achieve a fully saturated propellant. Because it is not desirable to keep the pressurized satellite on the launch pad for so long, and the feed pressure will drop as soon as the system is being used anyway, most satellites are launched with only partially saturated propellant and saturation changes during the mission. The amount of propellant saturation affects the performance of cavitating venturi used as flow limiters in some feed systems.

The aerospace industry has developed several methods to minimize the adverse effects of gas solubility variations on propulsion subsystem performance reproducibility. Temperature variability and effect of the rate at which pressurant gas flows into

the ullage, causing a limited amount of turbulence in the liquid, make this a source of uncertainty. In trying to achieve a nominal design pressure at the time of launch, one can either

- pre-saturate the propellant with pressurant gas in the ground support equipment (GSE) propellant cart before loading
- initially pressurize to above the specified launch pressure and wait for the equilibrium to establish itself at the nominal pressure
- pressurize once, wait several days, and then top the propellant tank off just before launch

All three methods have shortcomings. In method **(1)**, some of the pressurant gas is lost during transfer from the GSE into the satellite; in method **(2)**, the tank may not be designed for the higher pressure required to hold all the gas that will eventually dissolve; and method **(3)** requires the propellant loading crew to suit up and enter the hazardous area twice. The rate of gas absorption depends on whether the tanks are first pressurized at a satellite processing facility and then moved, which may agitate the propellant and enhance mixing, or whether the satellite is attached to the payload adaptor and remains still, with the tanks then being pressurized. In the latter case, the pressurant gas would have to diffuse through the liquid from the top layer of the liquid to the bottom of the tank to achieve complete saturation. It has been observed that diffusion varies with the density of the liquid. The higher the density, the slower the diffusion. It seems that for low-density propellants, less time is required to reach the saturation level.

Some satellite designers have added a dip tube and a dispersing element to feed the pressurant to the bottom of the liquid instead of to the top, but that adds weight and introduces an additional failure mode. Others have recirculated the propellant for several hours before launch to achieve equilibrium. Even if an elastomer-bladder positive expulsion device is used to separate pressurant gas and propellant, sufficient pressurant gas may diffuse through the bladder and saturate the propellant.

The rate of solution of N_2 in liquid N_2O_4 was measured in terms of the change of pressure with time at 5.1 and 7.6% ullage at 293 K (20 °C) and at 6.6% ullage at 273 K (0 °C) [104]. In preparation for the test, the N_2O_4 was distilled into a cylindrical container with a capacity of 97 mL, 40-mm diameter, and 95-mm height, which approximated the scaled-down dimensions of a typical propellant tank. After pressurization, pressure readings were taken every 10–15 min for the first hour and every 30 min for the subsequent 3 or 4 h. At the end of a run, the N_2O_4 was stirred vigorously for about 10 min, and then the final pressure reading was taken. The pressure decay was slower with increasing ullage and increasing temperature because of the relative masses of gas and liquid and the diffusional barrier near the interphase both in the gas and the liquid (Figure 22). The pressure decay did not fit a reasonable reaction rate, although it appeared to follow a first-order reversible reaction rate after 40 min.

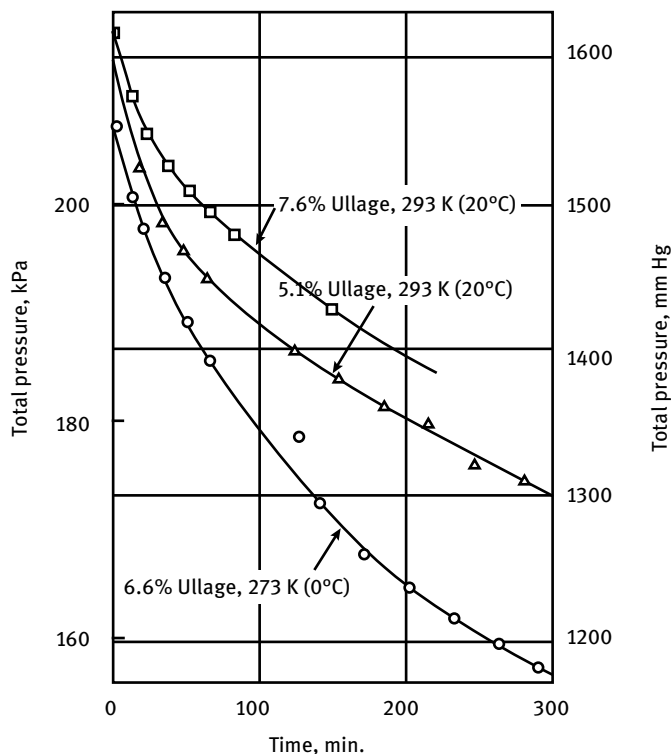


Figure 22: Pressure decay of nitrogen pressurant in a N_2O_4 tank. (Reproduced and modified from [104].)

The absorption rate of helium into NTO can be expressed by the equation

$$N_i = 3.27 \times 10^{-5} (P - P_s) A$$

where N_i is the mass convection rate of He into the propellant in mol/h, P is the total pressure of the ullage gas, P_s is the pressure when the propellant is totally saturated with helium, and A is the liquid-gas interface area in m^2 [111]. The pressure decay of a freshly pressurized tank can be predicted by the equation

$$(P - P_s)/(P_0 - P_s) = \exp\left(3.27 \times 10^{-5} \frac{ART}{V}\right)\theta$$

where P is the total pressure of the ullage gas, P_0 is the initial pressure, P_s is the pressure when the propellant is totally saturated with helium (all pressures in atm), T is the temperature in kelvin, A is the liquid-gas interface area in m^2 , V is the total volume of the ullage in m^3 , and θ is the time in h.

A very detailed treatise of the effect of the rate of gas absorption on spacecraft operations, as well as an attempt to model the process in sufficient detail so that pressure in the ullage of a propellant tanks can be predicted as a function of the time elapsed since locking up of the system, are provided in [112]. By knowing the speed of the pressure decay, it would be possible to compute the necessary initial elevated filling pressures that would then drop to the desired pressure at launch time. Measured pressure-decay data from the European Space Agency (ESA) Cluster spacecraft and a number of American satellites were used to predict the pressure decay in liquid MON-propellant and MMH-propellant tanks of the ESA Meteosat Second Generation (MSG) and Rosetta spacecraft [113]. That study was based on measured data of pressure histories from several different spacecraft, including some that were referenced in [114]. See also [115–117].

The Japanese H-II Transfer Vehicle (HTV) has four main thrusters (500N) used for orbit control and 28 reaction control system (RCS) thrusters (110N) used for reaction control. The HTV has multiple engine and long propellant supply lines, which makes its operation and surge-pressure spikes dependent on the saturation level of the propellant pressurant gas. A visual bubble-point technique and gas chromatography were used to determine the helium saturation level prior to ground-level testing of the propulsion system [118].

Because of the solubility of helium in propellants (MMH and NTO), tank pressure may decrease for several days after initial tank pressurization on the ground prior to launch. A model is necessary to predict the pressure loss. Conventional models had assumed that the tank was static. However, in the case of the Japanese HTV, propellant sloshing occurred by movement of the HTV between buildings on the ground prior to launch. Tank pressure loss in HTV tanks could not be predicted by the conventional model because of the sloshing. An improved numerical solubility model expresses the influence of sloshing on helium solubility by solving the vertical distribution of helium concentration in the stratified tank contents [119]. Not only does the pressurant gas dissolve in and diffuse through liquid dinitrogen tetroxide, but dinitrogen tetroxide and nitrogen dioxide vapors will also diffuse in the opposite direction through the gas atmosphere in the ullage volume. The diffusivity of nitrogen tetroxide evaporating into a nitrogen or a helium atmosphere has been determined by theoretical calculations and two experimental test methods [120]. The first method used the rate of evaporation in an open cylindrical vessel. The second method studied the evaporation kinetics in a closed vessel. The measured diffusivity of dinitrogen tetroxide in nitrogen was $0.098\text{--}0.101\text{ cm}^3/\text{s}$, and the diffusivity of dinitrogen tetroxide in helium was $0.398\text{--}0.415\text{ cm}^3/\text{s}$.

3.11.3 Rate of Pressurant Gas Release from Dinitrogen Tetroxide

Helium evolution during the transfer of helium-saturated propellant under zero-gravity conditions in space causes two-phase gas/liquid flow from the supply tank, gas injection into the receiving tank, and potential liquid discharge and propellant loss from the vented receiving tank if the PMD fails to keep the liquid puddle in place. An engineering study was made of propellant transfer taking place between two similar surface-tension PMD tanks whose maximum storage capacity was approximately 2.55 m^3 , each transferring a maximum on-orbit propellants of 4082 kg (9000 lb_m) (fuel and oxidizer). The transfer line was approximately 1.27 cm in diameter and 6096 cm in length. This system was supposed to serve the International Space Station propulsion module (ISSPM) if the Russian propulsion module had been further delayed [121, 122]. Work on ISSPM in the United States was discontinued after the Russian propulsion module Zvezda was launched after an extended delay. The propellant transfer rate was assumed to begin at approximately 11 L/min and would subsequently drop to approximately 0.5 L/min. The tank nominal operating pressure was approximately 1827 kPa (absolute). The line pressure drops for NTO at 11 L/min were approximately 302 kPa, assuming single-phase flow, but would have been higher for two-phase flow. These pressure-drop scenarios caused the helium-saturated propellants to release excess helium. For tank ullage venting, the maximum volumes of helium evolved at tank pressure were approximately 57 L (2 ft³) for NTO. In addition to releasing pressurant gas helium, MON may also have lost some NO during transfer.

The rate of bubble formation in pressurized dinitrogen tetroxide upon sudden pressure release determines the quality of flow of the discharging liquid, resulting in non-steady two-phase gas-liquid flow in channels [123]. A study was made of the effect of non-equilibrium phase transformations in NTO on the dynamics of vapor bubbles in the case of sudden occurrence of a pressure drop.

3.11.4 Analysis of Propellant for Dissolved Gases

Samples of propellant for gas analysis should be obtained at the pressure and temperature of the holding tanks. The best technique places the sampling cylinder as part of a pressurized, recirculating loop, but most test systems cannot accommodate such a loop. A simpler and less accurate technique is the filling of an evacuated sampling cylinder. However, such a filled cylinder will have no ullage and must not be allowed to warm up on its way to the laboratory for analysis; otherwise, it would over-pressurize and rupture due to thermal expansion. The dissolved gases can then be analyzed by gas chromatography.

3.12 Thermodynamic Properties of Dinitrogen Tetroxide

Based on experimental data published by other authors, temperature-entropy relations, enthalpy-temperature relations, and PVT relations of dissociating N_2O_4 were computed and graphed [40].

Further study was undertaken because of the lack of experimental data on the enthalpy of dissociating nitrogen tetroxide [124]. A calculation of the entropy (S) and enthalpy (H) of dissociating N_2O_4 was performed in the temperature range 300–1500 K and pressure range 1–140 atm, taking into account the deviation of reacting N_2O_4 from ideal gas behavior. The calculation was carried out on the basis of general thermodynamic functions of the thermodynamic theory of empirical corrections and was based on generalized tables. The calculated S and H values were then used for plotting H – S and T – S diagrams.

Thermodynamic properties of the chemically reactive system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ have been evaluated over a pressure range of 0.005–200.0 atm and a temperature range of 200–900 K based on computations for the Lennard-Jones potential [125]. In these calculations, the dissociation of dinitrogen tetroxide to nitrogen dioxide, nitric oxide, and oxygen, and the effect of pressure on the equilibrium constants for the system of reactions $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ and $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ had to be taken into account.

The ideal gas chemical thermodynamic properties for NO , NO_2 , N_2O_3 , and N_2O_4 for the temperature range of 50–5000 K were evaluated by a statistical thermodynamic method using an updated set of molecular parameters [126].

Researchers at the National Bureau of Standards conducted a thorough literature survey and compiled all thermodynamic data for the N_2O_4 equilibrium mixture on a uniform basis [41]. A search of the world's literature revealed a substantial experimental data base but few correlations of those data, and the correlations that did exist either covered only portions of the P – ρ – T surface or involved ideal gas assumptions that, for a wide range of pressures and temperatures, resulted in substantial inaccuracies. A computerized search of the literature produced 172 titles concerned with N_2O_4 . On the basis of the titles alone, 98 of the 172 appeared to be of possible use in the study. A mathematical model of the EOS of nitrogen tetroxide was derived from the literature data. Isobaric tables of P – ρ – T and composition for temperatures from the triple point (261.95 K) to 600 K with pressures to 40 MPa were compiled. The thermodynamic data of the equilibrium mixture were affected by the chemical equilibrium for the system. The mathematical model of the equation of state was a 32-term modified Benedict-Webb-Rubin equation. The EOS for N_2O_4 did not perform well for derived thermodynamic properties such as specific heat capacity, and the correlation of N_2O_4 thermodynamic properties was only partially complete. See also [127].

3.12.1 Heat Capacity of Gaseous Dinitrogen Tetroxide

Most heat capacity data are derived from infrared (IR) spectra and molecular structure quantum mechanical calculations; few data are actually obtained by calorimetry. The calculations derived from IR spectra are extended to high temperatures at which the molecule may no longer be able to exist. Such tabulations have only limited practical use, but we list them here for the sake of completeness.

The most detailed thermodynamic data can be downloaded from the NIST Chemistry WebBook site [128]. The heat capacity of undissociated gaseous dinitrogen tetroxide as a function of temperature can be calculated from the following polynomial equation

$$C_p^\circ = A + B \times \tau + C \times \tau^2 + D \times \tau^3 + \frac{E}{\tau^2}$$

where C_p is the molar heat capacity in $\text{J mol}^{-1} \text{K}^{-1}$, τ is the temperature in kelvin divided by 1000, and A, B, C, D, and E are constants listed in Table 18 for two different temperature ranges. One must note that N_2O_4 is unstable at temperatures above 298 K, and the column for the higher temperature range of 1100–6000 K is only of academic value. It is not very practical to list thermodynamic data for a compound that is unstable at the temperature range listed. It would be much more important to have more accurate thermodynamic data for liquid dinitrogen tetroxide.

Table 18: Thermodynamic property polynomial equation coefficients for dinitrogen tetroxide gas.

Temperature range, K	500–1000	1000–6000
A	34.05274	128.6220
B	191.9845	2.524345
C	−151.0575	−0.520883
D	44.39350	0.036630
E	−0.158949	−11.55704
F	−8.893428	−59.22619
G	293.7724	417.0444
H	9.078988	9.078988

Data source: [128]

3.12.2 Heat Capacity of Liquid Dinitrogen Tetroxide

The heat capacity of the equilibrium $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ mixture consists of two components: **(1)** a frozen contribution, corresponding to an inert, non-reacting mixture of NO_2 and N_2O_4 , and **(2)** a reaction contribution to take into account the heat of dissociation. The reaction contribution to C_p , is approximately 5–10 times the inert contribution.

The isobaric specific heats, refractive indices, and viscosities at 1 atm of dinitrogen tetroxide were determined at bubble-point pressures for a number of temperatures in the range of 305–378 K (90–220 °F) [129].

Figure 43 (in Section 5.2) shows that the change in degree of dissociation α with temperature is greatest (steepest) at temperatures from 327 to 344 K. Therefore, the contribution of the heat of reaction to the equilibrium heat capacity is greatest in this temperature range, and the curves in Figure 23 show a maximum of C_p at each pressure [130].

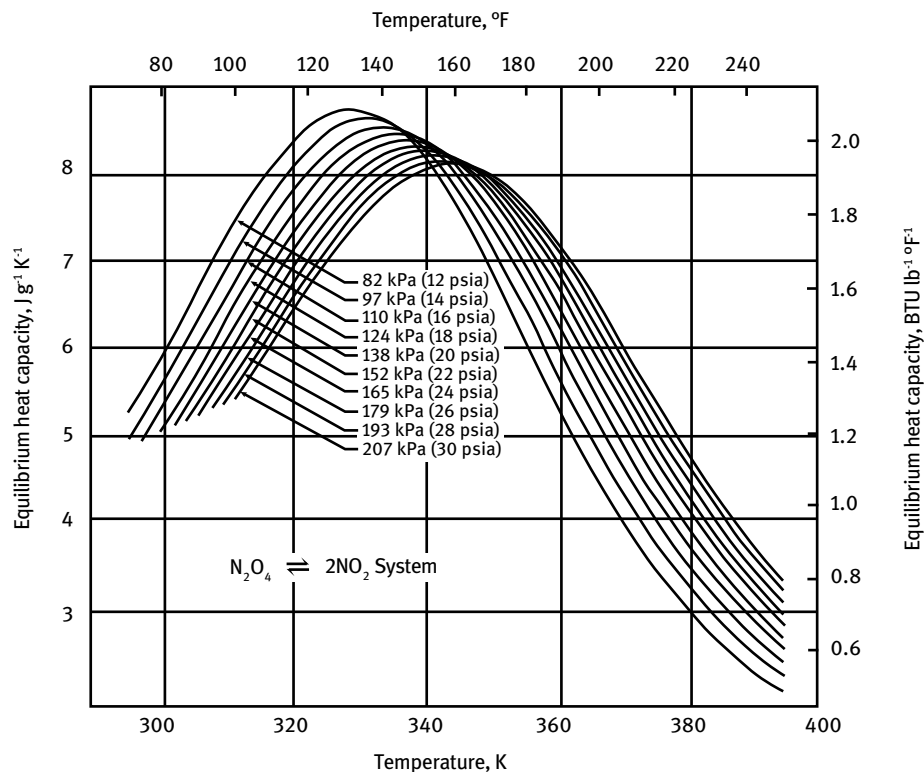


Figure 23: Heat capacity of dinitrogen tetroxide equilibrium mixture as a function of temperature and pressure. (Reprinted and modified from [130] with permission from © 1962 American Chemical Society.)

The heat capacity of liquid dinitrogen tetroxide as a function of temperature can be calculated from the following polynomial equation

$$C_p^\circ = A + B \times \tau + C \times \tau^2 + D \times \tau^3 + \frac{E}{\tau^2}$$

where C_p is the molar heat capacity in $\text{J mol}^{-1} \text{K}^{-1}$, τ is the temperature in kelvin divided by 1000, and A, B, C, D, and E are constants listed in Table 19.

Table 19: Thermodynamic property polynomial equation coefficients for liquid dinitrogen tetroxide.

Temperature range, K	298–500
A	89.16313
B	178.9141
C	0.929459
D	0.000000
E	−0.007107
F	−54.13217
G	263.6757
H	−19.56401

Data source: [128]

The NIST data are partially based on measurements by Giauque and Kemp, who measured the heat capacity of solid and liquid dinitrogen tetroxide from 15 K to the boiling point, 294.25 K [22]. The raw data are summarized in Table 20.

Table 20: Experimental heat capacity at constant pressure values for liquid N_2O_4 .

Temperature		Molar heat capacity, c_p		Heat capacity, c_p	
°C	K	$\text{cal mol}^{-1} \text{°C}^{-1}$	$\text{J mol}^{-1} \text{K}^{-1}$	$\text{cal g}^{-1} \text{°C}^{-1}$	$\text{J g}^{-1} \text{K}^{-1}$
−7.71	265.44	32.79	137.2	0.356	1.491
−3.24	269.91	32.92	137.7	0.358	1.497
2.23	275.38	33.10	138.5	0.360	1.505
8.04	281.19	33.34	139.5	0.362	1.516
13.71	286.86	33.60	140.6	0.365	1.528
18.13	291.28	33.74	141.2	0.367	1.534

Data source: Giauque and Kemp [21]

Heat-capacity data calculated with above equation were tabulated in Table 21.

Most heat-capacity data are for isobaric conditions at constant pressure, but a few isochoric specific heat-capacity data at constant volume were recorded (liquid at 288 K [15 °C] and 101 kPa [1 atm]) $27.9 \text{ J mol}^{-1} \text{K}^{-1} = 6.67 \text{ cal mol}^{-1} \text{°C}^{-1}$. From the ratio of the heat capacity at constant pressure to heat capacity at constant volume, one derives the adiabatic coefficient $\gamma C_p/C_v$, which is 1.303 for the liquid at 288 K = 15 °C and 101 kPa = 1 atm [131].

The heat capacity of dinitrogen tetroxide was measured in the temperature range of 410–484 K at densities between 2.0121 and 9.8039 g/cm³ and for pressures up to

Table 21: Heat capacity of liquid dinitrogen tetroxide.

Temperature, K	C_p , $\text{J mol}^{-1} \text{K}^{-1}$	C_p , $\text{cal mol}^{-1} \text{K}^{-1}$	c_p , $\text{J g}^{-1} \text{K}^{-1}$	c_p , $\text{cal g}^{-1} \text{K}^{-1}$	Remarks
273.15	138.0	32.98	1.500	0.358	Ice point of water
294.25	141.8	33.89	1.541	0.368	Normal boiling point of N_2O_4
298.15	142.5	34.06	1.549	0.370	Standard reference temperature
300	142.8	34.14	1.552	0.371	
310	144.6	34.57	1.572	0.376	
320	146.4	35.00	1.592	0.380	
330	148.2	35.43	1.611	0.385	
340	150.0	35.86	1.631	0.390	
344	150.8	36.03	1.638	0.392	65 °F is upper specification limit for storable propellants
350	151.8	36.29	1.650	0.394	
360	153.6	36.72	1.670	0.399	
370	155.4	37.15	1.689	0.404	
373	156.0	37.28	1.695	0.405	Boiling point of water
380	157.2	37.58	1.709	0.408	

Data source: [128]

Molecular mass: 92.0110 g/mol

35 MPa using a high-temperature and high-pressure adiabatic calorimeter [132, 133]. The measurements were performed in the one-phase region at 17 isochores (11 liquid and 6 vapor densities), including coexistence curve and critical region. The liquid and vapor one-phase isochoric heat capacities, temperatures, and densities at saturation were extracted from experimental data for each measured isochore. Some of the experimental data (TS , ρS) and C_v along isochores and at saturation are compared with values derived from isobaric heat capacity C_p , sound velocity, and PVT measurements. The critical parameters for N_2O_4 ($T_c = 431.072 \text{ K}$) were measured using a quasi-static thermogram method. See also [134–136].

The heat capacity of dinitrogen tetroxide was measured in the temperature range of 410–484 K at densities between 201.21 and 980.39 kg/m and for pressures up to 35 MPa using a high-temperature and high-pressure adiabatic calorimeter [132]. The measurements were performed in the single-phase region at 17 isochores (11 liquid and 6 vapor densities), including data points along the coexistence curve and into the critical region. The liquid and vapor one-phase isochoric heat capacities, temperatures, and densities at saturation were extracted from experimental data for each measured isochore. Some of the experimental data along isochores and at saturation were compared with values previously derived from isobaric heat capacity C_p , sound velocity, and PVT measurements. The critical parameters for N_2O_4 were measured using a quasi-static thermogram method.

3.12.3 Heat Capacity of Solid Dinitrogen Tetroxide

Smoothed heat-capacity data for solid dinitrogen tetroxide, taken from a curve-fitted formula based on measurements between 16.8 and 291.28 K, are tabulated in Table 22.

Table 22: Smoothed molar heat capacity at constant pressure values for solid N_2O_4 .

Temperature		Molar heat capacity		Temperature		Molar heat capacity	
K	°C	cal °C ⁻¹ mol ⁻¹	J K ⁻¹ mol ⁻¹	K	°C	cal °C ⁻¹ mol ⁻¹	J K ⁻¹ mol ⁻¹
20	-253	2.03	8.49	160	-113	19.07	79.79
30	-243	4.5	18.83	170	-103	19.76	82.68
40	-233	6.86	28.70	180	-93	20.46	85.60
50	-223	8.7	36.40	190	-83	21.18	88.62
60	-213	10.2	42.68	200	-73	21.92	91.71
70	-203	11.46	47.95	210	-63	22.66	94.81
80	-193	12.56	52.55	220	-53	23.41	97.95
90	-183	13.58	56.82	230	-43	24.15	101.0
100	-173	14.51	60.71	240	-33	24.89	104.1
110	-163	15.34	64.18	250	-23	25.63	107.2
120	-153	16.15	67.57	260	-13	26.36	110.3
130	-143	16.9	70.71	261.9	Melting point		
140	-133	17.63	73.76	270	-3	32.93	137.8
150	-123	18.36	76.82	280	7	33.28	139.2
				290	17	33.71	141.0

Data source: [21]

3.12.4 Enthalpy of Formation of Dinitrogen Tetroxide

3.12.4.1 Enthalpy of Formation of Gaseous Dinitrogen Tetroxide

The standard enthalpy of formation of N_2O_4 gas is $\Delta H_f^\circ \text{gas} = 9.079 \text{ kJ/mol} = 2.17 \text{ kcal/mol}$ [128]. The enthalpy of formation of gaseous dinitrogen tetroxide as a function of temperature can be calculated from the following polynomial equation

$$H^\circ - H^\circ_{298.15} = A\tau + \frac{B \times \tau^2}{2} + \frac{C \times \tau^3}{3} + \frac{D \times \tau^4}{4} - \frac{E}{\tau} + F - H$$

where H is the enthalpy in kJ/mol, τ is the temperature in kelvin divided by 1000, and A , B , C , D , E , F , and H are constants listed in Table 18 for two different temperature ranges. Other sources report N_2O_4 (gaseous) +9.828 kJ/mol (+2.349 kcal/mol) [22].

3.12.4.2 Enthalpy of Formation of Liquid Dinitrogen Tetroxide

The enthalpy of formation of liquid N_2O_4 is listed in [128] as $\Delta H_f^\circ \text{liquid} = -19.56 \text{ kJ/mol} = -4.675 \text{ kcal/mol}$. The enthalpy of formation of liquid N_2O_4 as a function of temperature can be calculated from the following polynomial equation

$$H^\circ - H^\circ_{298.15} = A\tau + \frac{B \times \tau^2}{2} + \frac{C \times \tau^3}{3} + \frac{D \times \tau^4}{4} - \frac{E}{\tau} + F - H$$

where H is the enthalpy in kJ/mol, τ is the temperature in kelvin divided by 1000, and A, B, C, D, E, F, and H are constants listed in Table 19.

Other sources list the enthalpy of formation of liquid N_2O_4 as

$$\text{N}_2\text{O}_4 \text{ (liquid)} - 19.56 \pm 1.7 \text{ kJ/mol} = -4.676 \pm 0.4 \text{ kcal/mol} \quad (\text{JANNAF})$$

3.12.4.3 Enthalpy of Formation of Solid Dinitrogen Tetroxide

The enthalpy of formation of solid N_2O_4 is listed in [128] as $\Delta H_f^\circ \text{solid} = -35.05 \text{ kJ/mol} = -8.377 \text{ kcal/mol}$.

3.12.5 Heat of Fusion of Dinitrogen Tetroxide

From the difference of the enthalpies of formation for solid and liquid N_2O_4 as listed in [128], one can calculate the heat of fusion at 298 K as $15.49 \text{ kJ/mol} = 3.702 \text{ kcal/mol}$.

Other sources list the heat of fusion (ΔH)_{fusion} (at 261.9 K = -11.2°C) as $14.652 \text{ kJ/mol} = 3.502 \text{ kcal/mol}$ [22].

3.12.6 Heat of Evaporation of Dinitrogen Tetroxide

From the difference of the standard enthalpies of formation for liquid and gaseous N_2O_4 as listed in [128], one can calculate the heat of evaporation at 298 K as $28.64 \text{ kJ/mol} = 6.845 \text{ kcal/mol}$.

Other sources give the heat of vaporization (leading to an equilibrium mixture of $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$) (ΔH)_{evap}, (at 294.3 K = 21.15°C) as $38.11 \text{ kJ/mol} = 9.110 \text{ kcal/mol}$ [22].

3.12.7 Heat of Dissociation of Dinitrogen Tetroxide

The dissociation equilibrium of dinitrogen tetroxide is discussed in Section 5.2 under thermal stability and chemical reactions. From the dissociation equilibrium measurements at different temperatures, one can calculate the heat of dissociation: $\Delta H^\circ_0 = 12873 \text{ cal/mol} = 12.873 \text{ kcal/mol}$ and $\Delta H^\circ_{298} = 13873 \text{ cal/mol} = 13.873 \text{ kcal/mol}$ as confirmed by accurate measurements by [22]. See also [32].

3.12.8 Entropy of Gaseous Dinitrogen Tetroxide

The standard entropy of formation of gaseous dinitrogen tetroxide at 298 K and 101 kPa is 308.54 J mol⁻¹ K⁻¹ [128]. The entropy of gaseous dinitrogen tetroxide as a function of temperature can be calculated from the following polynomial equation

$$S^\circ = A \times \ln(\tau) + B \times \tau + \frac{C \times \tau^2}{2} + \frac{D \times \tau^3}{3} - E/(2 \times \tau^2) + G$$

where S° is the enthalpy in J mol⁻¹ K⁻¹, τ is the temperature in kelvin divided by 1000, and A, B, C, D, E, and G are constants listed in Table 18 for two different temperature ranges.

Other sources [21] list the following entropy data:

$$S_{298}\text{NO}_2 \text{ (gaseous) } 57.47 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$$

$$S_{298}\text{N}_2\text{O}_4 \text{ (gaseous) } 72.73 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$$

3.12.9 Entropy of Liquid Dinitrogen Tetroxide

The standard entropy of formation of liquid dinitrogen tetroxide at 298 K and 101 kPa is 209.20 J mol⁻¹ K⁻¹ [128]. The entropy of liquid dinitrogen tetroxide as a function of temperature can be calculated from the following polynomial equation

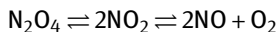
$$S^\circ = A \times \ln(t) + B \times t + \frac{C \times t^2}{2} + \frac{D \times t^3}{3} - E/(2 \times t^2) + G$$

where S° is the enthalpy in J mol⁻¹ K⁻¹, t is the temperature in kelvin divided by 1000, and A, B, C, D, E, and G are constants listed in Table 19.

Other sources [137] give the entropy of liquid N₂O₄ as

$$S_{298}\text{N}_2\text{O}_4 \text{ (liquid) } 50.00 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$$

By application of the third law of thermodynamics to the calorimetric measurements, the entropy of the gas, which is dissociated to the extent of 16.1% into nitrogen dioxide at the boiling point, was found to be 80.62 cal mol⁻¹ °C⁻¹ of gas as N₂O₄ [21]. From a consideration of the available data on the equilibria

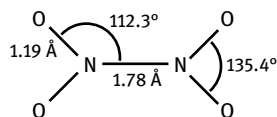
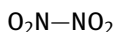


in combination with spectroscopic data for the several substances and the experimental entropy value given above, a number of quantities of thermodynamic interest have been evaluated for N₂O₄(G), $S_{298.1}^0 = 72.73 \text{ cal }^\circ\text{C}^{-1} \text{ mol}^{-1}$ and for NO₂(G), $S_{298.1}^0 = 57.47 \text{ cal }^\circ\text{C}^{-1} \text{ mol}^{-1}$. These values, which are the ones that should be used in ordinary thermodynamic calculations, do not include the nuclear spin entropy, $R \ln 3 = 2.183$, for each nitrogen atom. The absolute entropies are N₂O₄(G), $S_{298.1}^0 = 77.10$; NO₂(G), $S_{298.1}^0 = 59.65 \text{ cal }^\circ\text{C}^{-1} \text{ mol}^{-1}$ and for the reactions: $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$, $\Delta F_{298.1}^0 = -1110 \text{ cal}$, $\Delta H_{298.1}^0 = -13693 \text{ cal}$; $\text{N}_2 + 2\text{O}_2 \rightleftharpoons \text{N}_2\text{O}_4$, $\Delta F_{298.1}^0 = 23440 \text{ cal}$, $\Delta H_{298.1}^0 = 2239 \text{ cal}$; $\text{NO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{NO}_2$, $\Delta F_{298.1}^0 = -8375 \text{ cal}$, $\Delta H_{298.1}^0 = -13562 \text{ cal}$; $\frac{1}{2}\text{N}_2 + \text{O}_2 \rightleftharpoons \text{NO}_2$,

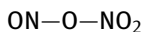
$\Delta F^0_{298.1} = 12275 \text{ cal}$, $\Delta H^0_{298.1} = 7964 \text{ cal}$. The experimental entropy value obtained in this investigation, together with band spectrum data, has made possible a much better correlation of the various measurements on the above equilibria than was previously possible. Accepting the band spectrum evidence that NO_2 is a symmetrical non-linear molecule, it was possible to show from the equilibrium measurements that the statistical weight of the normal electronic state is 2. The calculations did not permit an estimate of the potential barrier concerned in the rotational oscillations of these groups.

3.13 Molecular Structure of Dinitrogen Tetroxide

It would be useful to fully understand the molecular structure of dinitrogen tetroxide and all of its isomers and high-pressure phase variants if it would lead us to a more energetic form of this molecule that would push the specific impulse beyond 300 s. Isomers of N_2O_4 have been identified but not yet tested as rocket propellants. Dinitrogen tetroxide can exist in two isomeric forms, the more common symmetrical structure



and an unsymmetrical structure



The unsymmetrical isomer can exist in a *cis* and a *trans* stereoisomeric form.

Experimental results, such as NO_2 hydrolysis and the hypergolicity of hydrazine/dinitrogen tetroxide pair, have been interpreted in terms of NO_2 dimers. Such interpretations are complicated by the possibility of several forms for the dimer: symmetric N_2O_4 , *cis*- $\text{ONO}-\text{NO}_2$, and *trans*- $\text{ONO}-\text{NO}_2$. Quantum mechanical studies of these systems are complicated by the large resonance energy in NO_2 , which changes differently for each dimer and changes dramatically as bonds are formed and broken. As a result, none of the standard methods for quantum mechanical orbital calculations is uniformly reliable. Using density functional theory (B3LYP) and several *ab initio* methods (MP2, CCSD[T], and GVB-RCI), the enthalpy barrier to form *cis*- $\text{ONO}-\text{NO}_2$ was calculated as 7.9 kJ/mol (1.9 kcal/mol), whereas the enthalpy barrier to form *trans*- $\text{ONO}-\text{NO}_2$ was calculated as 55.2 kJ/mol (13.2 kcal/mol) [138]. The enthalpy barrier for N_2O_4 isomerizing to *trans*- $\text{ONO}-\text{NO}_2$ was calculated as 183.7 kJ/mol (43.9 kcal/mol), ruling out the possibility of such an isomerization playing a significant role in the gas-phase hydrolysis of NO_2 . A much more favored path

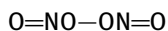
is to form *cis*-ONO—NO₂ first and then convert to *trans*-ONO—NO₂ with a 10.0 kJ/mol (2.4 kcal/mol) enthalpy barrier.

An unstable isomer of dinitrogen tetroxide, ONO—NO₂ (*asym*-N₂O₄), was photolyzed in an Ar matrix at 11 K at 436 and 510 nm [139]. *Asym*- to *sym*-N₂O₄ (O₂NNO₂) isomerization was the major process at 436 nm, and other products observed were NO, *cis*-(NO)₂, *asym*-N₂O₃ (O₂NNO), and N₂O₅. Irradiation of *asym*-N₂O₄ above 510 nm induced no reaction.

The N₂O₄ isomerization in the gas phase has an energy barrier of 129.7 kJ/mol (31 kcal/mol) at 298 K. This energy barrier may be reduced due to the interaction of the N₂O₄ isomers with water or nitric acid clusters adsorbed on surfaces. Calculations using the *ab initio* and the polarizable continuum model (PCM) methods indicated that the Gibbs free-energy barrier for this reaction in an aqueous medium is reduced to 88.3 kJ/mol (21.1 kcal/mol) [140]. Other calculations using the transition state theory (TST) model estimated that the N₂O₄ isomerization may be as fast as $2.0 \times 10^{-3} \text{ s}^{-1}$ in aqueous phase at room temperature. The activation energy of the N₂O₄ isomerization is about 87.9 kJ/mol (21 kcal/mol). The rate coefficient for this reaction is considerably fast, $1.2 \times 10^{-2} \text{ s}^{-1}$, in aqueous phase at $T = 373 \text{ K}$.

3.13.1 Molecular Structure of Gaseous Dinitrogen Tetroxide

Another possible isomer of N₂O₄ that might form as an intermediate during NO oxidation in the gas phase would be a peroxide structure:



This structure is very unlikely and has not yet been confirmed. Nevertheless, its energy surface has been calculated [141].

Dinitrogen tetroxide vapor that is vented to vacuum at the end of a launch phase may directly cool to frozen NTO. The residual vapor of N₂O₄ at the venting stage may develop an aerodynamic problem that is linked with the vapor-phase nucleation phenomena of the propellant. A study based entirely on computational molecular treatment examined the problem by considering the thermodynamic free energies of N₂O₄ clusters, leading to the evaluation of nucleation flux rates of critical nuclei at incipient nucleation from a molecular perspective [142].

3.13.2 Molecular Structure of Liquid Dinitrogen Tetroxide

A computational study of the microdynamics of translational, orientational, and vibrational motions in liquid N₂O₄ based on molecular dynamics simulations, including all degrees of freedom of vibrating N₂O₄ molecules and atom-atom Lennard-Jones (LJ) potentials with and without Coulomb potentials (LJ + C and LJ, respectively), showed that the velocity and angular momentum correlation functions decayed faster to more evident negative parts and that both the translational and orientational diffusion slowed down [143]. Simulated rotational correlation functions

for LJ + C agreed reasonably with those derived from Raman spectroscopy, while those for LJ were found to decay too fast. Vibrational correlation functions for the N–N stretching ν_3 mode were calculated, and the vibrational spectra were obtained from their Fourier transforms. Results of the simulation were compared with the isotropic Raman band shapes in liquid N_2O_4 measured earlier [144].

3.13.3 Molecular Structure of Solid Dinitrogen Tetroxide

Single-crystal neutron diffraction measurements of frozen dinitrogen tetroxide showed that it crystallized in cubic crystals, space group I_{m3} ; $Z = 6$ [145]. The crystal lattice is a body-centered cubic with six N_2O_4 molecules in the unit cell. The lattice parameter, measured at seven temperatures, increased from 7.6937(6) Å at 20 K to 7.7925(6) Å at 140 K. The observed N–N bond length and $\angle\text{O–N–O}$ angle were invariant between 20 and 100 K at values 1.7562(± 4) Å and 134.46(± 6)°. The observed N–O bond length increased linearly from 1.1855(9) Å at 100 K to 1.1893(5) Å at 20 K. *Ab initio* calculations gave a reasonable value for the N–N bond length: 1.80 Å and a corrected value of 1.74 Å.

The structure of the metastable monoclinic modification of N_2O_4 was redetermined from XRD diffractometer data [146]. The temperature range in which it is possible to study this modification depends on the amount of impurity. At 228 K (–45°C) the structure was refined in space group $P2_1/n$ (no. 14), with lattice constants $a = 591.7(1)$, $b = 475.8(1)$, $c = 644.1(1)$ pm, $\beta = 116.34(2)^\circ$, and $R = 0.032$. The structure contained planar N_2O_4 molecules.

The atomic and molecular interactions in a crystal of $\alpha\text{-N}_2\text{O}_4$ have been studied by quantum topological theory of molecular structure using high-resolution, low-temperature XRD data [147]. The experimental electron density and electrostatic potential were then reconstructed with the Hansen-Coppens multipole model. The application of the quantum theory of atoms in molecules and crystals (QTAIMC) indicated two types of intermolecular bond paths between O atoms in crystalline $\alpha\text{-N}_2\text{O}_4$, one measuring 3.094 Å and the other measuring 3.116 Å. It was found that the intermolecular interactions in $\alpha\text{-N}_2\text{O}_4$ are accompanied by the correlation of energy-density “bridges,” lowering the local potential energy along the intermolecular $\text{O}\cdots\text{O}$ bond paths in the electron density, while the exchange energy density governs the shape of associated molecules.

3.13.4 Bond Lengths and Bond Strengths in Dinitrogen Tetroxide

A reinvestigation of the structure of N_2O_4 in the gas phase at 252 K (–21°C) by electron diffraction has given results in good agreement with earlier studies so far as the molecular shape is concerned, but the size of the molecule appears to be about 0.9% larger than originally thought [148]. The results for the coplanar (D_{2h} symmetry) model were as follows: $r \text{ N–N} = 1.782 \text{ Å}(0.0083)$, $r \text{ N–O} = 1.190 \text{ Å}(0.0018)$, $\angle\text{ONO} = 135.4^\circ(0.58)$, $l \text{ N–N} = 0.0816 \text{ Å}(0.0178)$, $l \text{ N–O} = 0.0381 \text{ Å}(0.0019)$, $l \text{ O}_1\text{O}_2 =$

0.0493 Å(0.0040), $1 \text{ N} \cdots \text{O} = 0.0729 \text{ Å}(0.0061)$, $1 \text{ O}_1\text{O}'_1 = 0.0970 \text{ Å}(0.0167)$, and $1 \text{ O}_1\text{O}'_2 = 0.0730 \text{ Å}(0.0114)$. These distances and root-mean-square amplitudes are r_a and l_a values; the parenthesized values are 2σ and include estimates of systematic error. The $-\text{NO}_2$ groups have a structure very similar to that of NO_2 itself. The very long N—N bond and its large amplitude of vibration imply a weak link and are in accord with the low dissociation energy.

Dinitrogen tetroxide is a weakly bound dimer of NO_2 . The molecule is characterized by two NO_2 groups whose geometrical parameters are virtually identical with those found in free NO_2 gas. The most prominent geometrical feature found in N_2O_4 is the exceptionally long N—N bond as well as its planar structure [149]. This geometry is based on a series of both gas-phase electron diffraction and solid-state neutron diffraction measurements indicating that the N—N bond length lies between 1.756 and 1.782 Å. This is in stark contrast to the N—N bond length found in hydrazine, whose N—N bond length is known to be 1.47 Å, and tetrafluorohydrazine, whose N—N bond is $1.489 \pm 0.007 \text{ Å}$. This unusual geometry has prompted a number of explanations and discussions in the literature. It was suggested that the molecule was held together by a π -only bond, while Pauling pointed out the need for an N—N—O bond that would accommodate the two open-shell electrons centered on the nitrogen atoms from the two NO_2 fragments.

3.13.5 Torsional and Rotational Barriers in Dinitrogen Tetroxide Molecule

The rotation of two halves of the molecule around the long axis of the N_2O_4 molecule is not unhindered but is similar to the situations in N_2O_3 or N_2H_4 , in which the rotation has barriers where the orbitals of the outer atoms overlap and repel each other. Torsional energy potentials for N_2O_4 and N_2O_3 were calculated based on optimized geometries of the respective 90° -twisted saddle points [150]. These potentials were refined by obtaining potential energies of points along the intrinsic reaction coordinate. A comparison was made between these *ab initio* potentials and an analytical form based on a two-term cosine expansion in terms of the N—N dihedral angle. The shapes of these two potential curves were in close agreement. The torsional barriers in N_2O_4 and N_2O_3 obtained from the calculations were 2333 and 1704 cm^{-1} , respectively. For N_2O_4 the torsion fundamental frequency from the intrinsic reaction coordinate potential was 87.06 cm^{-1} , which was in good agreement with the experimentally reported value of 81.73 cm^{-1} . N_2O_4 and N_2O_3 exhibit strong hyperconjugative interactions of in-plane O lone pairs with the central N—Ns* anti-bond. The torsional barriers in these molecules arise principally from a combination of 1,4 interactions and hyperconjugation.

The shape of the potential energy function governing internal rotation about the N—N bond has been determined [151]. Based on the infrared spectrum in the region of $200\text{--}650 \text{ cm}^{-1}$ and analysis of the sequence of weak bands near 540 cm^{-1} involving a combination of the ν_6 (NO_2 rocking) and ν_4 (torsion) modes, it was concluded that

in the ground vibrational state, the height of the barrier at the staggered conformation is $1900 \pm 200 \text{ cm}^{-1}$.

3.14 Dipole Moment of Dinitrogen Tetroxide

The dipole moment of N_2O_4 gas is 0.55 Debye. The dipole moment of NO_2 gas is 0.39 Debye.

3.15 Molecular Orbital Calculations of Dinitrogen Tetroxide

With the advancement of computational chemistry and the continued interest in the unusual molecular structure of dinitrogen tetroxide with its labile N—N bond, there have been numerous molecular orbital theoretical chemistry calculations with the intent to predict the dissociation energy of the N—N bond and the energy levels of the infrared and Raman active vibrations in the molecule.

While other people theorized that the labile N—N bond in N_2O_4 is a π -only bond, Hartree-Fock linear combination of atomic orbitals molecular orbital (LCAO-MO) calculations performed on a basis of symmetry orbitals formed from a minimal Slater basis set predicted that there is only a small amount of N—N π -bonding [152]. A bond energy analysis showed that the lowest state is markedly stabilized by N—N—O three-center interactions.

Localized molecular orbitals were derived from the molecular orbitals calculated by a complete neglect of differential overlap (CNDO) method for N_2O_2 , N_2O_3 , and N_2O_4 , and the theoretical Lewis structures were given with bond angles and bond lengths [153]. The molecules have σ -type nitrogen-nitrogen bonds of high p -orbital character, but no π bonds. Oxygen lone electron pair delocalization to both nitrogen atoms is anti-bonding, reducing the strength of the nitrogen-nitrogen bond.

A redetermination of the barrier to rotation around the N—N bond of N_2O_4 focused attention on the primary valence bond explanation of the “*cis*-O—O overlap” contribution to this barrier [154]. The explanation involved *cis*-O—O overlap-dependent resonance between covalent (NO_2NO_2) structures with “long” or formal N—O bonds, as well as resonance of these structures with the ionic ($\text{NO}_2^-\text{NO}_2^+$, $\text{NO}_2^+\text{NO}_2^-$) structures that can be obtained from them via *cis*-O—O electron transfer in the planar conformer. The results of some *ab initio* valence bond calculations for both N_2O_2 and N_2O_4 were used to illustrate this phenomenon.

A non-empirical valence bond method investigating the conformation of N_2O_4 showed that the π resonance energy of the planar conformer between the two NO_2 fragments was only 3.60 kJ/mol, so the planarity cannot result primarily from the presence of N—N π bonding [155]. A study of the origin of the rotation barrier for N_2O_4 indicated that the variations of the one-electron orbital energies of the $\text{N}_2\text{P}\pi$ and $\text{O}_2\text{P}\pi$ atomic

orbitals as well as their electron populations were responsible for the stability of the planar conformer compared with the skew conformer.

The molecular parameters of N_2O_4 were determined by large-scale *ab initio* calculations using a multi-configurational second-order perturbation method and basis sets of double-zeta to quadruple-zeta quality [156]. With the largest basis set employed, the structural equilibrium parameters were determined to be $r_{\text{N-N}} = 1.7040 \text{ \AA}$, $r_{\text{N-O}} = 1.1906 \text{ \AA}$, and $\angle \text{N-N-O} = 112.55^\circ$. The potential energy barrier at the staggered conformation of the molecule was found to be 2313 cm^{-1} ($23 \text{ kJ/mol} = 6.6 \text{ kcal/mol}$), and the binding energy of the N—N bond was calculated to be 4616 cm^{-1} ($55 \text{ kJ/mol} = 13.2 \text{ kcal/mol}$).

Ab initio studies of dinitrogen tetroxide were performed to predict the equilibrium geometry, harmonic vibrational frequencies, and dissociation energy ($\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$) [157]. The structure was optimized at the self-consistent field, configuration interaction, and coupled-cluster levels of theory with large basis sets. At the highest level of theory, the N—N bond distance was $1.752 \text{ \AA}$, in excellent agreement with the experimental value of $1.756 \pm 0.01 \text{ \AA}$. In addition, the harmonic vibrational frequencies were predicted with an average absolute error of 51 cm^{-1} relative to experimental fundamental values, with differences largely attributed to anharmonic effects. The predicted dissociation energy was 30.1 kJ/mol (7.2 kcal/mol), in fair agreement with the experimental value of 53.1 kJ/mol (12.7 kcal/mol).

3.16 Optical Properties of Dinitrogen Tetroxide

3.16.1 Infrared Spectra of Dinitrogen Tetroxide

Infrared spectra of dinitrogen tetroxide (and nitrogen dioxide) are of importance for analytical methods for the quality control of NTO and MON and for leak detection and surveillance in propellant storage areas. When the literature was studied in search of information on IR absorption of nitrogen oxides, most of the publications were found to deal with N_2O_4 or NO_2 as atmospheric pollutants. Most of the work was done with nitrogen oxides with their natural isotope composition, but additional work was done with isotope-labeled nitrogen oxides in order to identify the atoms and mode of vibrations of the molecule responsible for specific absorption bands. Isotope labeling facilitates the assignment of absorption bands to specific rotations and vibrations and their harmonics, for IR as well as for Raman and microwave spectra.

The IR spectrum of dinitrogen tetroxide has been obtained between 5500 and 320 cm^{-1} for the gaseous, liquid, and solid states of this substance [158]. In general, the spectrum of N_2O_4 remained practically unaltered in going from one phase to another. The same four intense absorptions, presumably fundamentals, always appeared within 15 cm^{-1} of 1735 , 1255 , 745 , and 4404 cm^{-1} . It was very difficult to purify the N_2O_4 and obtain samples that were free of N_2O_3 . The wide-range, low-resolution scans shown in Figure 24, 25, and 26 were obtained with a model 21 Perkin-Elmer

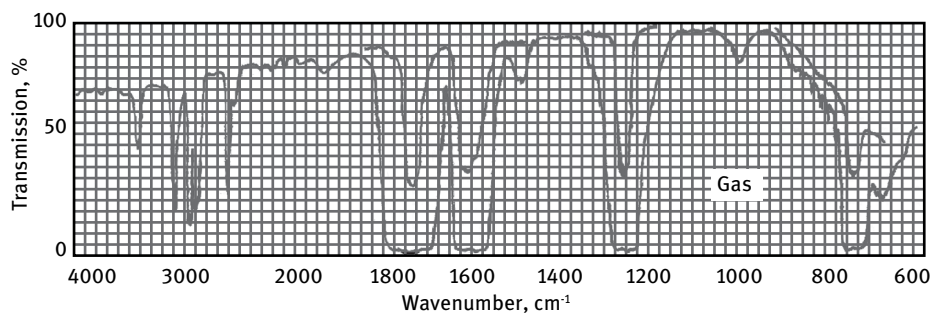


Figure 24: Infrared spectrum of gaseous N_2O_4 at approximately 40 and 2 cm Hg pressure at 296 K (23°C) in a 10-cm path length Pyrex cell. (Republished and modified from [158], with permission of © 1957 Elsevier Science Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

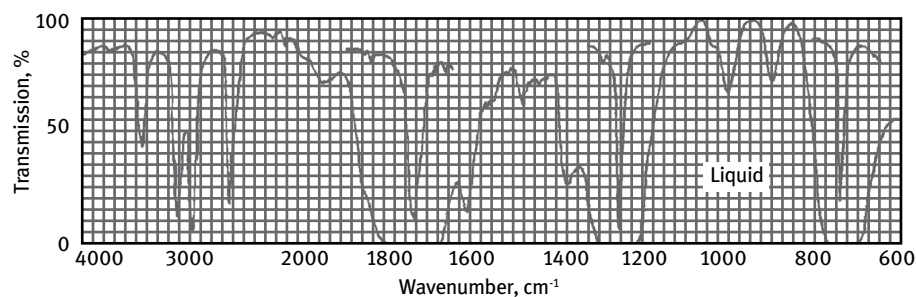


Figure 25: Infrared spectrum of liquid N_2O_4 0.1-mm path length cell at 283 K (+10°C). (Republished and modified from [158], with permission of © 1957 Elsevier Science Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

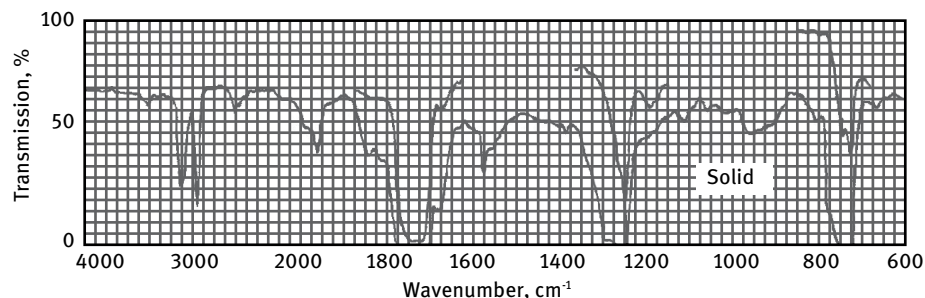


Figure 26: Infrared spectrum of solid N_2O_4 at approximately 93 K (−180°C). (Republished and modified from [158], with permission of © 1957 Elsevier Science Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

spectrometer equipped with a NaCl prism. This is a historic instrument similar to one the author of this book once worked with, which was a model 21 Perkin-Elmer spectrometer that carried the very low serial number 0030.

Table 23 gives a comparison of the four fundamentals in the infrared absorption and Raman fluorescence spectra. The assignments are only preliminary and may have to be revised based on more recent and more accurate data. Comparing the infrared and Raman frequencies for the solid, it is seen that there are no real coincidences except between 1728 and 1724 cm^{-1} . The latter is not surprising because these have both been assigned to characteristic N—O anti-symmetric stretching modes. Thus, the data strongly support the center of symmetry of the structure that was indicated by XRD. The consistency of the IR and Raman spectra in going from the solid to the liquid and gaseous states is remarkable. The spectra support the planar structure of the molecule in all three states. From these and other data, it was speculated that the internal barrier of rotation is about 12.1 kJ/mol (2.9 kcal/mol).

Table 23: Comparison of the four fundamentals in the infrared and Raman spectra of dinitrogen tetroxide.

Spectrum	Infrared			Raman		Assignment
Physical state	Gas	Liquid	Solid	Liquid ^b	Solid ^c	
Temperature, K	296	283	93	263	83	
Temperature, °C	23	+10	−180	−10	−190	
	1748 s ^a	1737 s	1728 s			V ₉
				1724 ms	1724 m	V ₅
		1379 vw		1382 s	1382 m	V ₁ , 2V ₈ , 2V ₂
				1325 mw	1336 m	
	1261 s	1253 s	1255 s			V ₁₁
			815 vw	811 s	812 s	V ₆ , V ₂
	750 s	743 s	737 s			V ₁₂
	~689 m		~678 vw			V ₂ , V ₈
			512?	500 m	500 m	V ₈ , V ₆
	430 m		442 s			V ₁₀ , V ₇
	~385 w		346 m			V ₇ , V ₁₀
				265 vs	283 vs	V ₂
		(49?)				V ₄

^as = strong, m = medium, w = weak, and vw = very weak

^bJ. D. S. Goulden and D. J. Millen, J. Chem. Soc. **1950**, 2620–2627 [159].

^cG. B. B. M. Sutherland, Proc. Roy. Soc. **AA141**, 535 (1933) [160]

Data source: [158]

Infrared studies have been made of several oxides of nitrogen, including NO₂ and N₂O₄, trapped at liquid-helium temperatures in matrices of Ar, N₂, O₂, CO₂, H₂, or N₂O [161]. NO₂ was found as the monomer, the known stable dimer of planar struc-

ture, and two new dimers. One of these had the $\text{ONO}-\text{NO}_2$ structure, and the other may be the twisted V_d form of the stable dimer.

Isotope labeling helps to identify IR absorption bands and assign them to specific vibrations and rotations. The IR spectra of gaseous and liquid $^{15}\text{N}_2\text{O}_4$ have been observed from 340 to 5500 cm^{-1} , and the Raman spectra of liquid and solid $^{15}\text{N}_2\text{O}_4$ have been recorded as well [162]. The corresponding spectra of $^{14}\text{N}_2\text{O}_4$ were observed as a baseline to provide an accurate measure of the isotope shifts. Assignments of all 11 active fundamental frequencies could be made. These assignments fit the product rule within experimental error and accounted for all observed overtones.

The temperature dependence of the IR spectra of N_2O_4 and N_2O_3 in the solid phase at liquid-nitrogen temperatures has been investigated [163]. From these spectra of both ^{14}N and ^{15}N isotope-labeled molecules, absorption bands that may be assigned to unstable isomers of these nitrogen oxides could be identified. A speculative interpretation of these absorption bands was made by assuming the existence of two unstable forms of N_2O_4 and one unstable form of N_2O_3 . Their existence was later proven by other techniques.

The integrated IR absorption intensities as a function of temperature have been measured for one NO_2 band and for four N_2O_4 combination bands in the spectral region from 1 to $5\text{ }\mu\text{m}$ [164]. The temperature was varied from 323 to 373 K ($50\text{--}100^\circ\text{C}$) for the gas-phase studies and from 298 to 373 K ($25\text{--}100^\circ\text{C}$) for the liquid-phase experiments. Saturated vapors were used in all experiments. The optical depth was varied by using a series of spacers in a specially designed IR absorption cell capable of handling both liquid and gas. Measured intensities for N_2O_4 combination bands in the liquid and gas phases were compared and found to differ by less than 16% for three out of four combination bands studied; for the fourth band, the observed difference was about 50%. Results for all of the combination bands investigated indicated that the integrated intensities varied approximately as a function of $1/T$ in the temperature range under consideration.

Infrared spectra of gaseous $\text{NO}_2/\text{N}_2\text{O}_4$ were obtained under conditions that allowed study of both strongly and weakly absorbing features [165]. These spectral features were then assigned with the aid of vibration-rotation band shape theory. Weakly absorbing sequence bands were identified that contained torsional vibrations. The rocking frequency of the $-\text{NO}_2$ group, the only mode that had not been observed directly, was estimated from a third-law entropy calculation. The frequencies provided for the first time a reliable determination of all the vibrational frequencies of N_2O_4 . The observation of the torsional mode frequencies allowed an internal rotation potential function to be estimated which has a barrier height of $2\text{--}3\text{ kcal/mol}$. It was suggested that in addition to the $\text{N}-\text{N}$ bond, weak σ bonds formed between the *cis* oxygens stabilize the eclipsed oxygen configurations and tend to lock the N_2O_4 molecule into a planar configuration. The planarity of N_2O_3 and the stability of *cis* $(\text{NO})_2$ can also be explained by these weak oxygen σ bonds.

Infrared absorptions of N_2O_4 in the ν_9 band at CO laser frequencies were monitored while an $\text{NO}_2/\text{N}_2\text{O}_4$ sample was subjected to visible radiation from an argon laser to dissociate it [166]. Double resonance signals corresponding to a two-molecule scheme involving the $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ chemical equilibrium were observed and interpreted.

The question of whether the formation of the NO^+NO_3^- (nitrosonium nitrate), the ionic form of nitrogen dioxide, via the decomposition of the $\text{ON}-\text{O}-\text{NO}_2$, is an intermolecular or intramolecular process was addressed via temperature-dependent and concentration-dependent Fourier-transform infrared spectroscopy (FTIR) studies of mixed films of N_2O_4 with CCl_4 [167, 168]. It was concluded that the process of nitrosonium nitrate production, both during deposition of disordered solid films of nitrogen dioxide and during their subsequent warming, is intermolecular but not order dependent, and a mechanism was tentatively suggested.

A complete set of band identifications was derived from a Fourier transform absorption spectrum of N_2O_4 in the gas phase at medium resolution between 650 and 7000 cm^{-1} under various temperature conditions [169].

Based on the IR spectrum in the region $200\text{--}650\text{ cm}^{-1}$ and analysis of the sequence of weak bands near 540 cm^{-1} involving a combination of the ν_6 (NO_2 rocking) and ν_4 (torsion) modes, it was concluded that in the ground vibrational state, the height of the barrier at the staggered conformation is $1900 \pm 200\text{ cm}^{-1}$ [151].

The integrated band intensities of the ν_9 and ν_{11} bands of N_2O_4 around 1757 and 1261 cm^{-1} were measured by varying temperature and pressure and found to be as follows: S-band (ν_9) = 9.60, 9.10, 8.80 and S-band (ν_{11}) = 5.93×10^{-17} , 5.70×10^{-17} , and $5.33 \times 10^{-17}\text{ cm/molecule}$ at 293.15, 277.25, and 261.65 K, respectively [170].

The rotationally resolved jet-cooled IR spectra of the b-type ν_9 (b2u) fundamental band at 1757 cm^{-1} and the a-type ν_{11} (b3u) fundamental band at 1261 cm^{-1} of the N—O stretches of N_2O_4 have been recorded with a diode laser [171]. The ν_9 band was found to be unperturbed, and it was possible to assign nearly 100% of the observed lines with a signal-to-noise ratio greater than 2. In contrast, most of the K_a states of the ν_{11} band were found to be strongly perturbed. A large number of strong lines (more than 20%) remained unassigned and presumably arose from the perturbing state as well as torsional hot band transitions. The rotational analysis yielded precise spectroscopic constants for the ground vibrational state, which were interpreted in terms of a planar centrosymmetric dimer with a N—N bond length of $1.756(10)\text{ \AA}$.

It is possible that some payloads (satellites or space probes) may become contaminated if bipropellant thrusters used for orbit insertion, midcourse correction, or attitude control have a dribble volume of unreacted NTO. NTO vapors might condense on cold parts of the spacecraft, where they change the albedo, fog up camera lenses, or put a curtain on solar cells. Infrared spectra of frozen NTO and other propellants were measured to better understand the hazards of frozen NTO contamination [172].

The spectrum of a molecular beam of N_2O_4 has been obtained in the 3.2, 5.7, 7.9, and 13.3- μm regions, using a supersonic slit jet system coupled to a Fourier transform spectrometer with a spectral resolution of 0.005 cm^{-1} [173]. Analysis of the spectra obtained indicated that the temperature of the expanding molecular beam is close to 30 K. In the three lowest-frequency spectral regions, not only were the ν_9 , ν_{11} , and ν_{12} fundamental bands observed, but each fundamental was accompanied by an intense combination band that appeared because of a strong anharmonic resonance leading to a transfer of intensity from the fundamental band to the combination band. In the 13.3- μm region, two a-type bands with nearly equal intensities were seen. All of the bands were successfully analyzed, leading to ground-state combination differences that were combined with those obtained in a previous diode laser study and fitted to obtain ground-state rotational constants. The upper-state energy levels were fitted using a Hamiltonian, which explicitly took into account the anharmonic resonances.

FTIR spectra of NO and NO_2 are used for the analysis of NO in MON [174].

3.16.2 Raman Spectra of Dinitrogen Tetroxide

3.16.2.1 Raman Spectra of Liquid Dinitrogen Tetroxide

The Raman spectra of liquid N_2O_4 have been measured at 262, 279, and 297 K [144]. The rotational relaxation rate was found to increase with increasing temperature, and spectra were analyzed qualitatively in terms of two models of vibrational dephasing that took into account the effect of vibrational anharmonicity.

Isotope substitution enables one to assign some of the Raman bands to specific molecular vibrations [162].

3.16.2.2 Raman Spectra of Frozen Dinitrogen Tetroxide

Raman and IR spectra of polycrystalline samples of N_2O_4 at low temperatures were recorded, and the number and activities of the fundamentals were compared with the predictions of group theory, based on known molecular and crystal geometries [175]. Several additional peaks were observed and attributed to Fermi resonances of combinations with fundamentals. A new low-frequency internal mode and five lattice modes were found that are unique to the solid and were not seen in the liquid.

In Raman spectra of frozen N_2O_4 in a matrix of frozen Ne at 9 K, most lines could be assigned to different configurations of N_2O_4 . However, the most intense line was caused by NO^+ ions of the species NO^+NO_3^- , a surprising result explainable by a special aggregation of NO_2 molecules during condensation, followed by trapping of the dimer at adjacent vacancies [176].

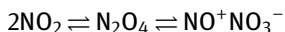
Raman spectra of solid N_2O_4 condensed from gaseous $\text{NO}_2/\text{N}_2\text{O}_4$ showed that the $\text{O}_2\text{N}-\text{NO}_2$ dimer was formed at 80 K [177]. Deposition at 15 K additionally produced bands of the NO_2 monomer and the O_2NONO isomers. Warming to 180 K induced autoionization to NO^+NO_3^- , which remained stable over the 15–180 K range. It was sug-

gested that the transition is probably an intermolecular process invoked through the low-energy lattice modes or ν_4 twist vibration of the dimer.

For nitrosonium nitrate, produced by slow NO_2 deposition, three solid modifications (two crystalline, one amorphous) could be characterized spectroscopically by Raman spectra [178]. In the amorphous phase, a light-induced, temperature-dependent, reversible transition between molecular and ionic nitrogen tetroxide is observed below 150 K.

3.16.2.3 Raman Spectra of Dinitrogen Tetroxide Solutions

When the Raman spectra of solutions of dinitrogen tetroxide in nitric acid were recorded, it was noted that the spectrum of the dinitrogen tetroxide molecule was completely absent [159]. The strongest appearances, apart from solvent lines, were a line at 2240 cm^{-1} , which could belong only to the nitrosonium ion in some form, and one at 1050 cm^{-1} , which was identified as the main nitrate ion frequency. The latter constitutes an intensification of one of the self-ionization frequencies of the nitric acid solvent; consistently, its development is accompanied by a disappearance of the other self-ionization line, 1400 cm^{-1} , belonging to the nitronium ion. The solute spectrum also contained a somewhat weak frequency 1380 cm^{-1} , which was assumed to be the totally symmetric fundamental of the nitrogen dioxide molecule, a frequency usually observed only as a weak band in the infrared. It was concluded that the dinitrogen tetroxide molecule, in dilute solution in nitric acid, is almost completely disassociated, partly homolytically, but chiefly heterolytically, as follows:



The frequency of the nitrosonium ion is usually found at about 2300 cm^{-1} , though the value can vary a little with the conditions of solvation. The line at 2240 cm^{-1} , obtained in nitric acid, is, however, outside the usual range of variation, and it was shown to arise from a modification of the nitrosonium ion by some specific molecular interaction. The modifying agent was identified as the nitrogen dioxide molecule. It is assumed to form a molecular compound $\text{NO}^+\bullet\text{NO}_2$, held together by a partly homopolar, but mainly electrostatic, one-electron bond.

3.16.3 Ultraviolet-Visible Spectra of Dinitrogen Tetroxide

Pure liquid dinitrogen tetroxide is a colorless liquid that does not absorb light in the visible range. However, its dissociation product nitrogen dioxide, being a free radical, has an intense reddish-brown color in the gaseous state, which is what gives the distinctive brown color to smog and haze hanging over densely populated cities when the wind is not blowing it away. The absorption spectra of nitrogen dioxide will be discussed in *Encyclopedia of Oxidizers*, chapter "Nitrogen Dioxide."

The individual absorption coefficient curves of NO_2 and N_2O_4 were separated by means of a mechanical analog differential analyzer in the range of 2400–5000 Å, showing the apparently continuous nature of the N_2O_4 absorption [179].

A study of the temperature dependence of the ultraviolet (UV)-visible absorption cross sections for NO_2 has been made in the temperature range of 213–298 K and between 310 and 570 nm using a diode array spectrometer [180]. Analysis of the experimental data allowed the simultaneous measurement of the NO_2 and N_2O_4 cross-sections and the equilibrium constant for the dimerization of NO_2 . Values of cross-sections for N_2O_4 and equilibrium constant for the association of NO_2 were presented in the range of 213–263 K. No temperature effect was observed on the overall shape of the NO_2 absorption spectrum or on the averaged cross-section values used for calculating atmospheric photolysis rates. Changes in the fine structure of the NO_2 spectrum with temperature were observed, and this has important implications for measurements of atmospheric NO_2 made by UV-visible absorption techniques.

3.17 Electron Spin Resonance and Electron Paramagnetic Resonance Studies of Dinitrogen Tetroxide

The homolytic dissociation constants K_{diss} of dinitrogen tetroxide in organic solvents were determined by electron paramagnetic resonance (EPR) measurements [181]. The values are the highest in non-donor and the lowest in n-donor solvents. The variations of K_{diss} with the type of solvent were interpreted in terms of electron donor-acceptor interactions between dinitrogen tetroxide and electron donor solvent molecules.

3.18 Photoelectron Spectroscopic Studies of Dinitrogen Tetroxide

Rapid expansion of vapor through a nozzle inlet system has been used for the study of X-ray photoelectron spectroscopy (XPS) spectra of some molecular species normally only present at pressures much above those usually obtained at the ionization region of a photoelectron spectrometer [182]. The He I photoelectron spectra for dinitrogen tetroxide and dinitrogen pentoxide obtained in this way were compared to Gaussian *ab initio* molecular orbital calculations and the spectra of the dissociated species, also in relation to nitric acid.

Photoelectron spectra excited with a He I line source were measured for a mixture of NO_2 and N_2O_4 in the gas phase at a temperature of about 213 K (–60 °C) [183]. Some photoelectron bands attributable to N_2O_4 were observed below about 16 eV.

3.19 Index of Refraction of Dinitrogen Tetroxide

The index of refraction of liquid dinitrogen tetroxide at 293 K (20 °C) was measured at four different wavelengths, as shown in Table 24.

Table 24: Index of refraction of liquid dinitrogen tetroxide.

Wavelength, Å	Spectral line source	Index of refraction
6893	Sodium	1.420
4916.4	Hg blue-green	1.431
5460.7	Hg green	1.424
4358.3	Hg blue	1.442

Data source: [184]

The refractive index of a thin layer of frozen dinitrogen tetroxide on a silicon substrate at 16 K at 543 nm is 1.316 [185]. At 60 K, the refractive index of frozen dinitrogen tetroxide at 543 nm is 1.548, and its density is 1.90 g/cm³. The refractive index of liquid N₂O₄ at 300 K at 543 nm is 1.40. This work also contains infrared spectra of NO₂/N₂O₄ equilibrium mixtures flash-frozen on a sample holder at 16 or 60 K.

3.20 Electrical Properties of Dinitrogen Tetroxide

3.20.1 Dielectric Constant of Dinitrogen Tetroxide

The relative permittivity of a material for a frequency of zero is known as its *static relative permittivity* or *specific inductance capacity* or *dielectric constant*. The dielectric constant ϵ is a dimensionless quantity but is definable in terms of capacitance:

$$\epsilon = \frac{C}{C_0}$$

where ϵ = dielectric constant, C = capacitance of a capacitor when the spaces between the plates are occupied by a given dielectric, and C_0 = capacitance of same capacitor *in vacuo*.

The dielectric constant of N₂O₄ was determined by comparing the capacity of a specially prepared capacitor at 1000 Hz in air and in liquid N₂O₄. The dielectric constant of liquid N₂O₄ has been found to be 2.42 at 18 °C [184]. When the temperature of the sample was reduced from 291 K (18 °C) to 268 K (−5 °C), the dielectric constant did not change much. Earlier investigators had reported 2.56 (at 15 °C) and 2.6 (at −40 °C) for the dielectric constant of N₂O₄.

The relative permittivity and electrolytic conductivity of N₂O₃, N₂O₄, and their mixtures have been measured over a range of temperatures limited by the freezing

point of the system on the one hand and its vapor pressure on the other [186]. The results for N_2O_4 are presented in Table 25. The values of relative permittivity ϵ N_2O_4 are typical for a non-polar liquid and showed little variation with temperature.

Table 25: Electrical physical properties of dinitrogen tetroxide.

Temperature, K	293	283	273	263	253
Temperature, °C	+20	+10	0	−10	−20
Relative permittivity ϵ N_2O_4	2.44	2.45	2.47	2.48	2.49
Molar polarization P , $\text{cm}^3 \text{mol}^{-1}$	20.6	20.4	20.3	20.1	19.9
Electrolytic conductivity $\lambda \times 10^{12}$, $\Omega^{-1} \text{cm}^{-1}$	5.03	3.32	2.18	1.38	0.84

Data source: [186]

Since N_2O_4 has a symmetric structure in the gas and solid, it is unlikely to possess a permanent dipole moment in the liquid. Although NO_2 is a polar molecule, its concentration in the N_2O_4 liquid is far too low to account for such a large temperature variation. The same applies to other possible species such as NO^+ and NO_3^- in the form of ion-pairs or solvated ions.

Liquid propellant-level gauging in a rotating spacecraft can be achieved by capacitance measurements of the liquid-filled space between two concentric tubes serving as the electrodes of a capacitor. Dielectric properties (permittivity and specific conductivity) of MON-1 and MMH were measured as a function of temperature because these numbers were needed for calibrating the sensors [187, 188]. The relative permittivity of MON-1 between 283 and 323 K can be expressed by the following equation:

$$\epsilon = 2.833 - 0.0052 \times (T - 273)$$

where ϵ is the relative permittivity (a dimensionless number) and T is the temperature in kelvin.

3.20.2 Electrical Conductivity of Dinitrogen Tetroxide

When the electrical conductivity of several batches of N_2O_4 prepared by decomposition of lead(IV) nitrate was compared, it was noted that there was a slight variation in conductivity from one preparation to another, which, in view of the extremely low order of conductivity, was unavoidable. The drying system employed in the preparation of the dinitrogen tetroxide was efficient, since further redistillation through phosphoric oxide desiccant did not decrease the conductivity any further. The most reliable value of the electrical conductivity of liquid dinitrogen tetroxide was $1.3 \times 10^{-12} \text{ ohm}^{-1} \text{cm}^{-1}$ at 290 K (17 °C) [189] (Table 26).

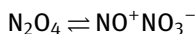
Other sources reported a specific conductivity of $3.0 \times 10^{-13} \text{ ohm}^{-1} \text{cm}^{-1}$ at 297 K (24 °C). These values indicate that the concentration of ionic species in the pure liquid is extremely small. A different sample was measured at several temperatures between

Table 26: Specific electrical conductivity of N_2O_4 as a function of temperature

Temperature		$\lambda \times 10^8$
K	°C	$\text{ohm}^{-1} \text{cm}^{-1}$
263	-10	1.16
273	0	7.83
283	+10	9.75
293	20	14.2
303	30	17.6

Data source: [190, 191]

280.4 K (7.3 °C) and 293.5 K (20.4 °C), and the electrical conductivity increased almost linearly from 1.17×10^{-12} to $2.24 \times 10^{-12} \text{ohm}^{-1} \text{cm}^{-1}$ with a temperature coefficient of $8.5 \times 10^{-14} \text{ohm}^{-1} \text{cm}^{-1} \text{°C}^{-1}$. The low electrical conductivity in liquid dinitrogen tetroxide may arise from either ionic or electronic conduction. If conduction is ionic, the low conductivity value indicates that the number of free ions is extremely small, and this is consistent with the low value observed for the dielectric constant. The positive temperature coefficient may be a result of the increase in homolytic dissociation



with temperature.

The addition of water increased the electrical conductivity of commercial-grade N_2O_4 substantially, from $1.88 \times 10^{-6} \text{ohm}^{-1} \text{cm}^{-1}$ at 1% H_2O addition to $4.52 \times 10^{-2} \text{ohm}^{-1} \text{cm}^{-1}$ at 14% H_2O [192]; see Table 27.

Table 27: Electrical conductivity in the $\text{N}_2\text{O}_4/\text{H}_2\text{O}$ system.

Added H_2O Volume-%	Resistance ohm	Specific conductivity $\text{ohm}^{-1} \text{cm}^{-1}$
1.0	4.20×10^5	1.88×10^{-6}
2.0	3.50×10^5	2.6×10^{-6}
3.0	4.22×10^5	1.86×10^{-6}
5.0	4.16×10^5	1.90×10^{-6}
10.0	5.03×10^5	1.57×10^{-6}
11.0	1.33×10^2	5.95×10^{-3}
12.0	7.37×10^1	1.07×10^{-2}
13.0	1.42×10^1	5.57×10^{-2}
14.0	1.75×10^1	4.52×10^{-2}

Data source: [192]; Cell constant 0.792cm^{-1}

3.21 Magnetic Properties of Dinitrogen Tetroxide

NO_2 gas is paramagnetic, and frozen N_2O_4 is diamagnetic. The molecular susceptibility of frozen N_2O_4 is $\chi = -30 \times 10^{-6}$ cgs units. The paramagnetism of NO_2 was used to determine its concentration in an equilibrium mixture of dissociating pure N_2O_4 . The magnetic susceptibility of pure liquid N_2O_4 was measured by the Gouy method over the temperature range 273–303 K (0–30 °C) [193]. The liquid was found to be diamagnetic throughout this temperature range, although the diamagnetism decreased as the temperature increased. The magnetic measurements were found to be in good agreement with the spectrophotometrically determined equilibrium composition of the liquid, as reported earlier [194].

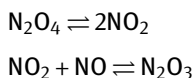
Nuclear magnetic resonance (NMR) can also be used for the rapid quantitative analysis of water (mostly in the form of nitric acid) in dinitrogen tetroxide and MON oxidizers [195].

4 Physical Properties of Oxidizer Blends with Dinitrogen Tetroxide

For some space mission applications, in particular those in the shadow of the Earth or at great distances from the sun, the relatively high freezing point of dinitrogen tetroxide, 262 K (−11 °C), is a disadvantage. Some space missions involve long cruising periods when not much energy is available to heat the tank to prevent the propellants from freezing. There have been numerous attempts to identify additives to N_2O_4 that will lower its freezing point without unduly increasing the vapor pressure or reducing its rocket performance.

4.1 $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ Mixtures

The most successful additive for lowering the freezing point of dinitrogen tetroxide is dinitrogen trioxide, N_2O_3 . Dinitrogen trioxide is not added as such, but instead the pure dinitrogen tetroxide is doped with nitric oxide, NO, which is added as a gas. The reaction taking place in the liquid phase is



and the solution turns from colorless or slightly yellow to blue. This reaction is exo-endo-thermic, depending on the direction in which it proceeds. Little to no NO exists in the liquid phase of the MON system. One can assume that the liquid phase contains only N_2O_3 and N_2O_4 .

The mixtures of N_2O_3 with N_2O_4 could have been discussed at the N_2O_3 chapter (*Encyclopedia of Oxidizers*, chapter “Dinitrogen Trioxide”) or here in the N_2O_4 section. We preferred to describe the mixtures here because the major constituent of the practically used $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures is N_2O_4 and not N_2O_3 .

Dinitrogen trioxide and dinitrogen tetroxide are completely miscible in all proportions over their entire range of mixture ratios.

Blends of N_2O_4 with N_2O_3 are called “**mixed oxides of nitrogen**,” abbreviated as MON. The designation MON is often followed by a number, such as MON-3 or MON-25, which indicates the mass (weight) percent of NO (not the mass-percent of N_2O_3) in the mixture. The MIL-SPEC MIL-PRF-26539F on MON describes this type of oxidizer as having a green color. It is a sort of blue-green. Specification requirements for these different grades of oxidizers are described in Table 41.

Small amounts of MON (50 mL) with NO mass concentrations between 0 and 30% NO can be prepared from $\text{N}_2\text{O}_4(\text{L})$ and $\text{NO}(\text{G})$ feedstocks in a glass apparatus at low pressures [196]. The glass tube was rated to a safe operating pressure of 1.03 MPa (150 psi) gauge, which allowed for synthesis of MON-30 at 273 K without risk of overpressurization. Using a glass vessel for synthesis allows for visual monitoring of reactant loading and mixing, which is a convenient feature considering the significant color change that accompanies the dissolution of NO into N_2O_4 . The contents of the glass tube were weighed before and after the addition of N_2O_4 and NO. The N_2O_4 had to be stirred during NO addition. The measured quantity of NO gas was coming from a buffer tank with known volume and pressure. For higher MON-X mixtures, several buffer tank loads had to be added. Vapor pressure readings on the freshly prepared MON-13 samples ran high because of inert gases introduced with the NO. The final NO composition of samples prepared using this setup could be confirmed by observing the mass (and color) change of the sample following complete oxidation of the NO in the system by pressurizing it with oxygen in the same apparatus.

The U.S. Defense Logistics Agency at its website [197] lists the available grades of NTO and MON as MON-1, MON-3, MON-10, and MON-25 in addition to bulk NTO. The price is the same for all grades. All grades of NTO or MON are substantially more expensive than inhibited red fuming nitric acid (IRFNA).

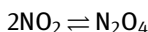
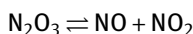
MON-10 is typically used to increase the NO content of MON-1 or MON-3 that has fallen below specification levels (NO is preferentially lost from MON during transfer operations). Occasionally, a program may require the low-temperature freezing point quality of MON-10 versus the other grades, but this requirement is usually limited to tactical missile systems or interplanetary missions.

One of the first flight applications of MON-10 oxidizer was in the MIRA-150A throttleable engine that powered the first unmanned lunar landers Surveyor 1 through 7 [198]. The reason for selecting MON-10 instead of pure NTO was to lower the freezing point of NTO. At the same time, instead of pure MMH, a mixture of MMH

and 28% water was used instead of pure MMH as the fuel to facilitate cooling of the engine.

As explained in the chapter on pure dinitrogen trioxide, N_2O_3 begins to decompose reversibly into nitric oxide and nitrogen dioxide (dinitrogen tetroxide) at temperatures above 173 K (-100°C) [199]. The presence of dinitrogen tetroxide, one of the decomposition products, should retard the decomposition in accordance with the law of mass action, but it does not prevent it altogether.

In the liquid phase there is an equilibrium between nitric oxide and nitrogen dioxide and between nitrogen dioxide and dinitrogen tetroxide:



The addition of nitric oxide (dinitrogen trioxide) to N_2O_4 in quantities exceeding 3% NO has several potential disadvantages, and the amount of additive has to be optimized depending on the intended application:

- increased vapor pressure
- reduced available oxygen content
- reduced enthalpy of formation
- extended ignition delay with hypergolic fuels
- possible change in composition of propellant as the result of repeated transfers or pressurant venting
- decreased density

A mixture consisting of 70 mass-% N_2O_4 and 30 mass-% NO contains only 64.7 mass-% oxygen, whereas pure N_2O_4 contains 69.6% oxygen.

The physical properties of the binary system $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ have been thoroughly measured in view of the various applications as rocket propellants. Temperature gradients in a compartmented system filled with MON-25 might result in composition gradients. An excellent summary of properties of MON and methods for analysis of MON was provided in [200], with emphasis on MON-25.

4.1.1 Freezing Point and Phase Diagram of $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ Mixtures

The freezing points of mixtures of dinitrogen tetroxide and dinitrogen trioxide, as well as those of the pure components, have been accurately determined [23]. Although the phase diagram (Figure 27) has the appearance of a simple binary mixture with one eutectic, it seems probable that, on the nitrogen dioxide-rich side of the composition range, solid solutions crystallize rather than the pure component. A possible misinterpretation of previous results in the region of the eutectic composition would account for the discrepancy between the eutectic temperature and composition compared with

previously accepted values. Dinitrogen trioxide behaves as a pure compound at its freezing point. The following data have been recorded: freezing point of dinitrogen tetroxide, 261.86 K (−11.29 °C); eutectic composition, 33.7 mass-% of nitric oxide; eutectic temperature, 166.95 K (−106.2 °C); and freezing point of dinitrogen trioxide, 172.45 K (−100.7 °C). The Beattie, Bell, and Vosper [24] results are presented in Table 28 and Figure 27.

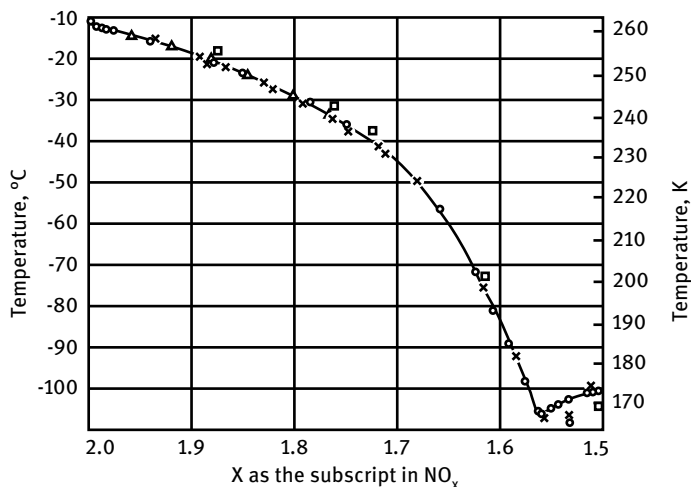


Figure 27: Freezing-point diagram of the $\text{NO}/\text{NO}_2=\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ system. (Reprinted and modified from [24]. Reprinted with permission from © 1960 The Royal Society of Chemistry.)

Additional data on physical properties of $\text{NO}/\text{NO}_2=\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures are available in [23, 201, 202].

As illustrated in Figure 27, the freezing point of the binary system $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ passes through a minimum and then gradually increases to the value for pure N_2O_3 (171 K [−102 °C]) [203]. MON-25 begins to separate into two phases and N_2O_4 crystals precipitate below 233 K (40 °C) [204].

The triple point of MON-2.2 was determined using two different methods [205]. The first method used a glass apparatus in the laboratory. In the second method, the fluid was exposed to a specific pressure in a very large vacuum chamber and was allowed to cool by evaporation to the equilibrium temperature for the fluid at the pressure exerted. This method simulated a space-like environment to allow more proper evaluation of the behavior of propellants when exposed to the near vacuum of space if a leak should occur in the tankage and feed system. Tentative values for the effective freezing point under space-like conditions of MON containing 2.2 mass-% nitric oxide were determined to be 259.4 K (7.2 °F) at 15.444 pascals (2.24 psia). This value differed con-

Table 28: Freezing points in the $\text{NO}/\text{NO}_2=\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ system.

NO_x fraction, $x =$	Freezing point	
	K	°C
2	261.9	-11.29
1.991	261.2	-11.93
1.985	261.0	-12.2
1.982	260.8	-12.38
1.974	260.2	-13
1.936	257.4	-15.72
1.876	252.8	-20.36
1.846	249.7	-23.44
1.816	246.1	-27.06
1.785	242.4	-30.77
1.747	236.6	-36.54
1.656	216.2	-57
1.644	213.9	-59.24
1.606	192.2	-81
1.591	184.2	-89
1.575	174.5	-98.7
1.561	167.3	-105.8
1.56	167.0	-106.2
1.549	168.8	-104.3
1.545	169.3	-103.8
1.516	172.2	-101
1.508	172.5	-100.7
1.504	173.0	-100.2
1.5	172.4	-100.74

Data source: [24]

siderably from the triple-point values of 261.9 K (11.73 °F) at 18.637 pascals (2.703 psia) determined using the 1938 laboratory triple-point technique on NTO containing little or no nitric oxide.

4.1.2 Boiling Point of $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ Mixtures

The graph shown in Figure 28 was composed by Beattie and Vosper ([206], part III), who collected boiling-point data of $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures from several sources and compared them to their own measurements.

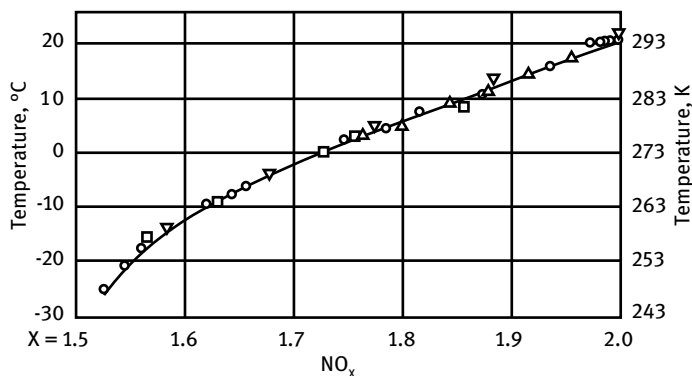


Figure 28: Boiling-point data of $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures from several sources. (Reprinted and modified from [206], part III. Reprinted with permission from © 1960 The Royal Society of Chemistry.)

4.1.3 Vapor Pressure of $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ Mixtures

The vapor pressure of mixtures of nitrogen dioxide and nitric oxide has been measured by several investigators at various temperatures. One set of results can be expressed by

$$\log_{10} p = 8.95 - f \frac{(x)}{T}$$

where p is the pressure in mm Hg, T is the temperature in kelvin, and $f(x)$ is a function dependent only on the composition of the mixture [206]. Extrapolating from those data, the apparent boiling point of dinitrogen trioxide would be at least 40° below the previously accepted value. Low-temperature vapor pressure data indicate that Giauque and Kemp's equation for nitrogen dioxide can be extrapolated down to about 223 K (-50°C). The only more recent work on the vapor pressure of mixtures of nitric oxide and nitrogen dioxide at pressures below 1 atm is that of Whittaker and colleagues [23]. Unfortunately, their results do not extend beyond the region near nitrogen dioxide, where they are in reasonable agreement with those ancient data of Baume and Robert. The data of Baume and Robert cover the whole range of compositions from nitrogen dioxide to dinitrogen trioxide but do not extend below 253 K (-20°C), and in this region agreement with Purcell and Cheesman's results [207] is poor. Further, in the latter paper only "smoothed" results are given, which lie very erratically on a graph of $\log_{10}$ (pressure) against the reciprocal of the absolute temperature.

The vapor pressure isotherms graph (Figure 29) was composed by Beattie and Vosper ([206], part III), in which they collected the vapor pressure of $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures from several sources and compared them to their own measurements.

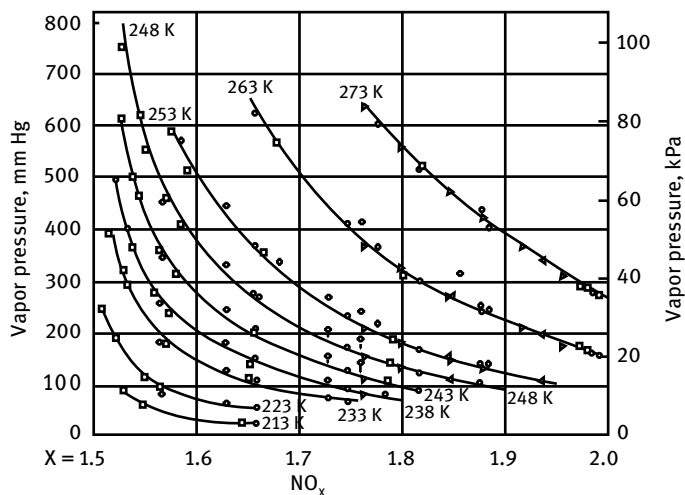


Figure 29: Vapor pressure isotherms of $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures. (Reprinted and modified from [206]. Reprinted with permission from © 1960 The Royal Society of Chemistry.)

Measured vapor pressures of $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures over the range of 0–16.95 mass-% NO at temperatures from 288 to 313 K (15–40 °C) can be curve-fitted and expressed as a set of equations, each valid for a narrow temperature range, as shown in Table 29 [23].

Table 29: Vapor pressure equations of NO/ $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures.

Mass-% NO	Temperature range, °C	P_V equation*, torr	Mean error, ±torr
2.89	+15 to -14.1	$\log P_V = 9.0121 - 1782.2/T$	2.8
5.55	+15 to -17.1	$\log P_V = 8.9700 - 1751.3/T$	2.3
8.30	+15 to -20.4	$\log P_V = 9.0105 - 1745.3/T$	1.4
10.67	+9 to -23.5	$\log P_V = 9.1163 - 1760.46/T$	2.3
14.11	+2 to -28.8	$\log P_V = 8.9847 - 1704.6/T$	2.2
16.85	+5 to -33.6	$\log P_V = 9.0347 - 1702.4/T$	1.8

* P_V is the vapor pressure in mm Hg, and T is the temperature in kelvin

Data source: [23]

Most of the work on MON mixtures has been done with MON-1 and MON-3. Thus, it is very useful to find some older data on the physical properties of MON mixtures with higher NO contents in the range of 20–30 mass-% NO. The raw vapor pressure data

from which the curves in Figure 30 were generated originated in a 1954 report from Food Machinery and Chemical Corporation [3]. The measured vapor pressures of three MON mixtures are tabulated in Table 30 and graphed in Figure 30. The curves for 28.5 and 29.2 mass-% NO overlap.

Table 30: Vapor pressure of mixed oxides of nitrogen.

21.6 mass-% NO				28.5 mass-% NO				29.2 mass-% NO			
T, °F	K	psia	kPa	T, °F	K	psia	kPa	T, °F	K	psia	kPa
-45	230	2.63	18	-91	205	1.07	7	-90	205	1.12	8
-35	236	3.12	21	-70	216	1.49	10	-80	211	1.28	9
-33	237	3.23	22	-61	221	1.88	13	-70	216	1.57	11
-25	241	3.8	26	-49	228	2.71	19	-60	222	1.99	14
-15	247	4.79	33	-37	235	3.53	24	-50	228	2.55	18
-10	250	5.49	38	-23	243	5.85	40	-39	234	3.4	23
0	255	7.19	49	-10	250	9.09	63	-30	239	4.66	32
10	261	9.38	65	2	256	12.7	87	-20	244	6.46	44
19	266	12.1	83	9	260	16.3	112	-10	250	8.88	61
21	267	12.9	89	20	266	21.8	150	3	257	15.5	107
30	272	16.4	113	30	272	28.7	197	15	264	18.8	129
41	278	21.9	151	—	—	—	—	29	271	27.8	191
48	282	27	186	—	—	—	—	—	—	—	—

Data source: [3]

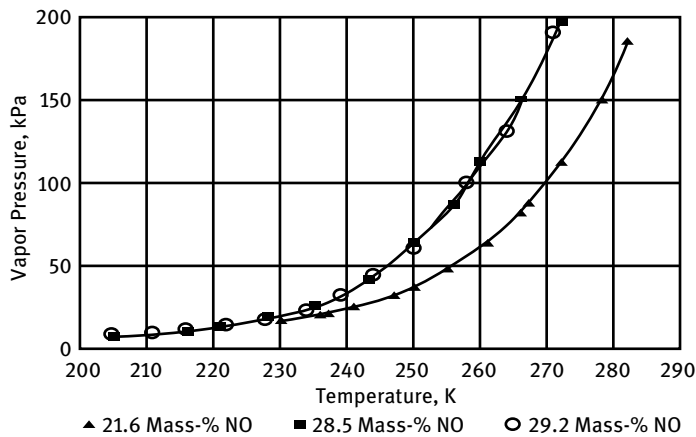


Figure 30: Vapor pressure of mixed oxides of nitrogen. (Chart created by Schmidt 2016, based on data from [3].)

Data in a later publication by the same author giving data for NO concentrations up to 30 mass-% NO are based on the earlier WADC report cited earlier [203] (Figure 31).

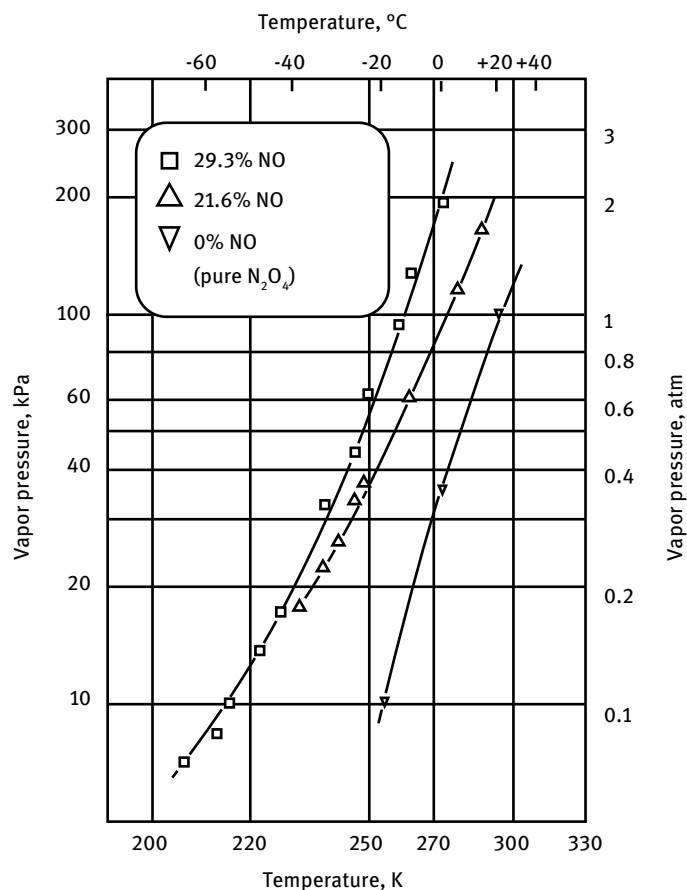


Figure 31: Vapor pressure of the system $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$. (Reproduced and modified from [3].)

Vapor pressure measurements of samples of MON containing 1.69, 2.10, or 2.98 mass-% NO indicated that the actual vapor pressure is 13.8–34 kPa (2–5 psia) higher than that listed in the *Nitric Acid/Nitrogen Tetroxide Oxidizers Handbook* (AFRL-TR-76-76) for any given temperature [208].

The vapor pressures of MON-10, MON-25, and MON-30 can be calculated from the equations listed in Table 31.

Table 31: Equations for vapor pressure of MON-10, MON-25, and MON-30.

MON-	Vapor pressure equation*	Lower <i>T</i>		Upper <i>T</i>	
		K	°F	K	°F
10	$\log_{10}P = 7.4956 - 1352.4/T - 56662/T^2$	250.2	-9.3	405.2	270
25	$\log_{10}P = 7.4956 - 1236.0/T - 56662/T^2$	219.2	-65	405.2	270
30	$\log_{10}P = 7.4956 - 1190.7/T - 56662/T^2$	192.2	-114	405.2	270

**P* is the pressure in kPa, and *T* is the temperature in kelvin

Data source: [209]

4.1.4 Density of N₂O₄/N₂O₃ Mixtures

The density of the N₂O₄/N₂O₃ mixtures decreases with increasing NO content (Figure 32).

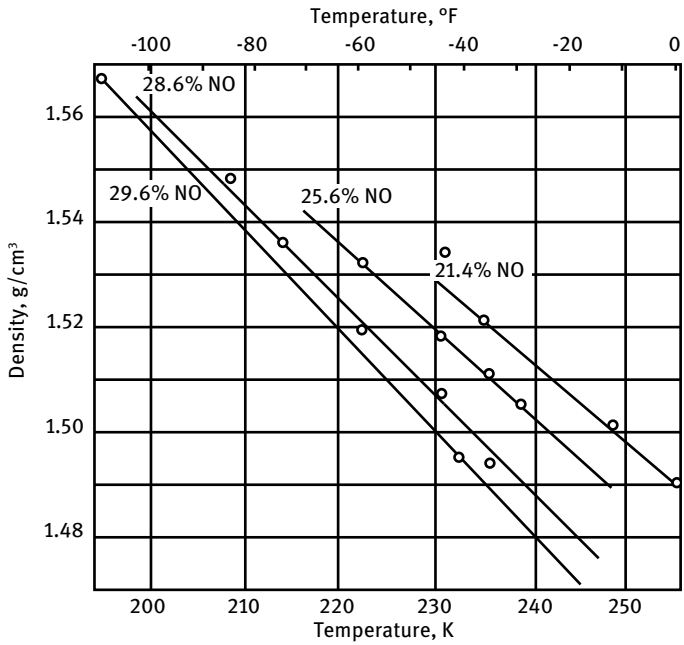


Figure 32: Density of N₂O₃/N₂O₄ mixtures as a function of temperature. (Reproduced and modified from [3].)

Figure 33 presents the same density data in a different format as a function on NO content rather than as a function of temperature.

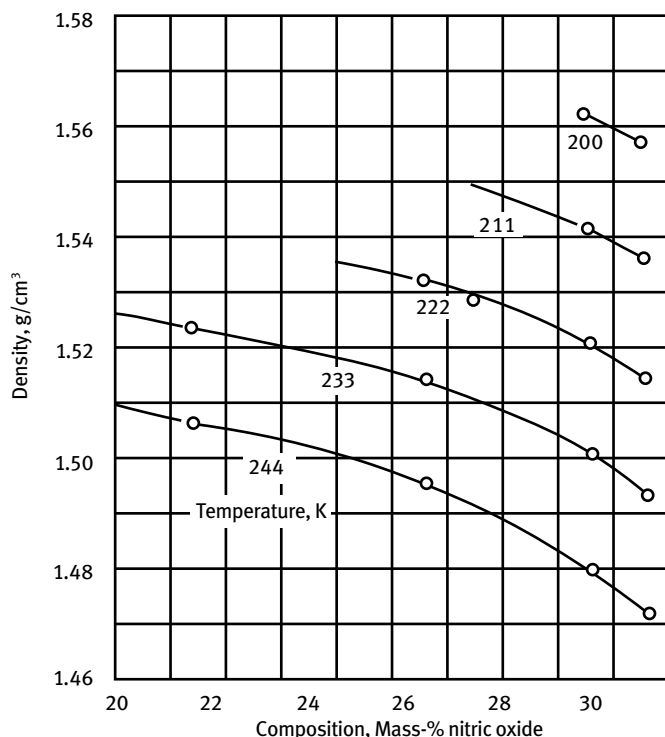


Figure 33: Density of $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures as a function of NO content. (Reproduced and modified from [3].)

Density measurements were conducted on a MON-1 composition containing 1.17 mass-% NO and 0.07 mass-% H_2O over the temperature range 295.4–347.3 K (22.3–74.2°C; 72.1–165.6°F). A total of 16 individual data points were generated from two measurement sets using a Poole-Nyberg densimeter. A least-squares curve-fit of the data resulted in the following expression of density as a function of temperature [35]:

$$\rho = 1.4883 - 2.180 \times 10^{-3}t - 4.109 \times 10^{-6}t^2$$

where ρ is the density in g/cm^3 and t is the temperature in °C. The standard error estimate was $\pm 0.001 \text{ g}/\text{cm}^3$. For mixtures with varying NO content, the density of MON as a function of temperature from 279.3 to 351.3 K (6.2–78.2°C; 43.1–172.8°F) and composition (0–1.17 mass-% NO) can be calculated from

$$\begin{aligned} \rho = & 1.4901 - 1.80169 \times 10^{-3}t - 2.71835 \times 10^{-5}t^2 + 5.093 \times 10^{-7}t^3 - 3.614 \times 10^{-9}t^4 \\ & - 2.9839 \times 10^{-3}N \end{aligned}$$

where ρ is the density in g/cm^3 , t is the temperature in °C, and N is the concentration of NO in mass-%. The effect of a trace of water within the specification range of 0–

0.17 mass-% H_2O was negligible. For higher NO contents, the following equation was derived for temperatures from freezing points to 378 K (105 °C) and NO contents from 0 mass-% NO to 30 mass-% NO:

$$\rho = 1.4905 - 2.124 \times 10^{-3}t - 5.01 \times 10^{-6}t^2 - 3.250 \times 10^{-3}N + 1.804 \times 10^{-5}N^2 \\ + 1.458 \times 10^{-5}Nt + 3.852 \times 10^{-7}N^2t - 2.226 \times 10^{-7}Nt^2$$

where ρ is the density in g/cm^3 , t is the temperature in °C, and N is the concentration of NO in mass-%.

The density of MON-10 as a function of temperature for a temperature range of 250.2–378.2 K (–9.3 to 221 °F) can be calculated from

$$\rho_L = 1.465 - 2.14 \times 10^{-3}(T - 273.2) - 6.26 \times 10^{-6}(T - 273.2)^2$$

where ρ_L is the liquid density of MON-10 in g/cm^3 and T is the temperature in kelvin. The density of MON-25 between 219.2 K (–65 °F) and 378.2 K (221 °F) can be calculated from

$$\rho_L = 1.436 - 2.16 \times 10^{-3}(T - 273.2) - 4.80 \times 10^{-6}(T - 273.2)^2$$

where ρ_L is the liquid density of MON-25 in g/cm^3 and T is the temperature in kelvin. Likewise, the density of MON-30 between 192.2 K (–114 °F) and 378.2 K (221 °F) can be calculated from

$$\rho_L = 1.425 - 2.07 \times 10^{-3}(T - 273.2) - 4.31 \times 10^{-6}(T - 273.2)^2$$

where ρ_L is the liquid density of MON-30 in g/cm^3 and T is the temperature in kelvin.

Results of measurements of the volumetric behavior of $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures under a wide range of different conditions are reported in [210].

A very thorough and critical review of literature data on the density of MON mixtures as a function of NO content, temperature, and pressure was conducted to determine the accuracy of the empirical fit for the liquid density of MON oxidizers [211]. The data of Pascal and Garnier [212] cited therein were found to disagree with data in McGonigle [213] and Brice [3] for MON blends with higher NO content. The data of Pascal and Garnier for NO content of 12, 20, and 30 mass-% were omitted from the data set. Several of the older literature sources cited in that publication are not easily accessible, in particular [212, 213]. The compilation of literature data from numerous sources deemed to be reliable was fitted with a useful polynomial equation for the density of MON:

$$\rho = 1689.3 + 0.61408T - 4.9261 \times 10^{-3}T^2 - 2.4615W$$

where ρ is the density in kg/m^3 , T is the temperature in kelvin, and W is the NO content in mass-%. The density as a function of temperature, pressure, and NO content can be calculated from the equation

$$\rho = 1689.3 + 0.61408T - 4.9261 \times 10^{-3}T^2 - 2.4615W + 1.6 \times 10^{-3} \cdot (P - P_{\text{vap}})$$

where ρ is the density in kg/m^3 , T is the temperature in kelvin, W is the NO content in mass-%, and P is the pressure in kPa.

A Poole-Nyberg densimeter was modified to measure density data for MON over a wider range of NO contents up to 30% NO between 193 K (-80°C) and 323 K (50°C) and higher pressures up to 6.8 MPa [214]. In order to check the apparatus, the density of pure NTO was measured at first from 263 K (-10°C) to 323 K (50°C) for pressures between 207 and 620 kPa (30 and 90 psia, respectively) and compared to literature data. With this measurement technique, the density of NTO at 293 K (20°C) was obtained with an estimated deviation from literature data of less than 0.2%, with larger deviations at higher temperatures. Subsequent measurements for MON-10 did not give the expected results. The density of frozen N_2O_3 at 78 K is 1.782 g/cm^3 [37].

4.1.5 Viscosity of $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ Mixtures

The viscosity of $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures varies only moderately with varying NO content of $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures [203, 215]. Figure 34 gives the dynamic viscosity as a function of temperature for four different $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures.

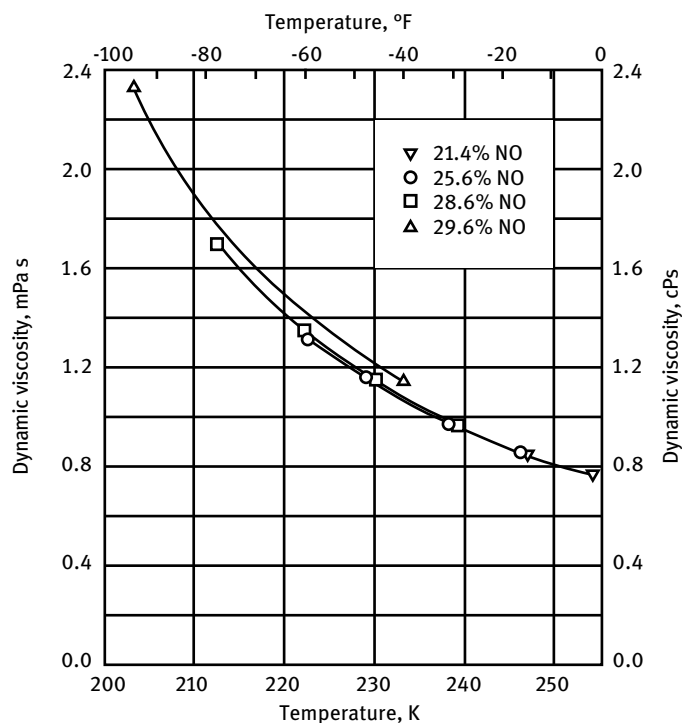


Figure 34: Dynamic viscosity of $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures. (Reproduced and modified from [3].)

The viscosity of a mixture containing 8 mass-% N_2O_3 /92% N_2O_4 is shown in Figure 35 as a function of temperature and pressure.

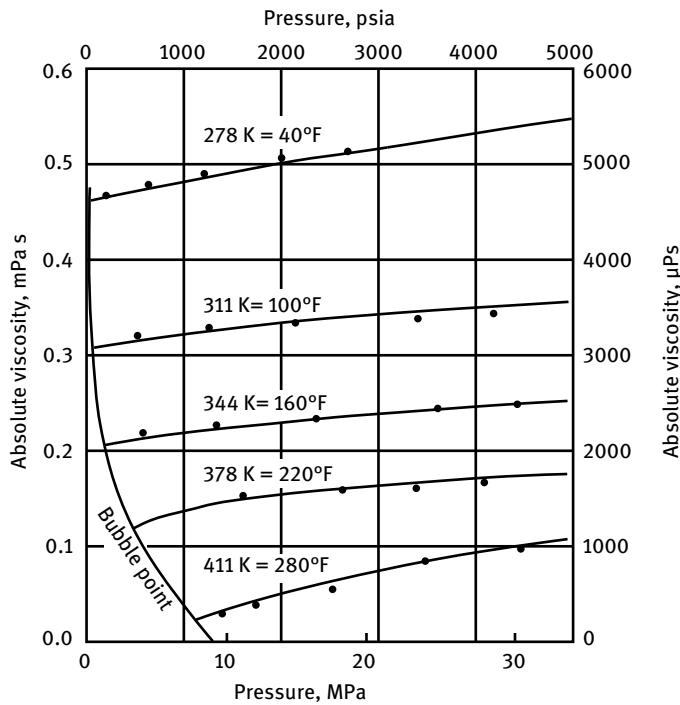


Figure 35: Viscosity of $\text{NO}/\text{N}_2\text{O}_4$ mixture containing 92 mass-% N_2O_4 . (Reprinted and modified from [215], with permission from © 1954 American Chemical Society.)

The viscosities of MON-10, MON-25, and MON-30 can be calculated from the equations listed in Table 32.

Table 32: Equations for viscosity of MON-10, MON-25, and MON-30.

MON- Viscosity ^a		Lower <i>T</i>		Upper <i>T</i>	
		K	°F	K	°F
10	$\mu = -0.03148 + 28.143/T - 8.569 \times 10^3/T^2 + 9.822 \times 10^5/T^3$	277.2	39.3	377.2	219
25	$\mu = -0.0335 + 28.876/T - 8.569 \times 10^3/T^2 + 9.822 \times 10^5/T^3$	277.2	39	377.2	219
30	$\mu = -0.03463 + 29.376/T - 8.569 \times 10^3/T^2 + 9.822 \times 10^5/T^3$	278	40.7	378	221

^a Viscosity equation where μ is the viscosity in N s m^{-2} and T is the temperature in kelvin
Data source: [209]

4.1.6 Surface Tension of $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ Mixtures

Surface tension does not change significantly as the result of adding NO or N_2O_3 to N_2O_4 . For instance, surface tension at 233 K (-40°C) changes only from 37.4 to 39 dyn/cm if the NO concentration is increased from 21 to 28 mass-%, as shown in Figure 36 [3, 203].

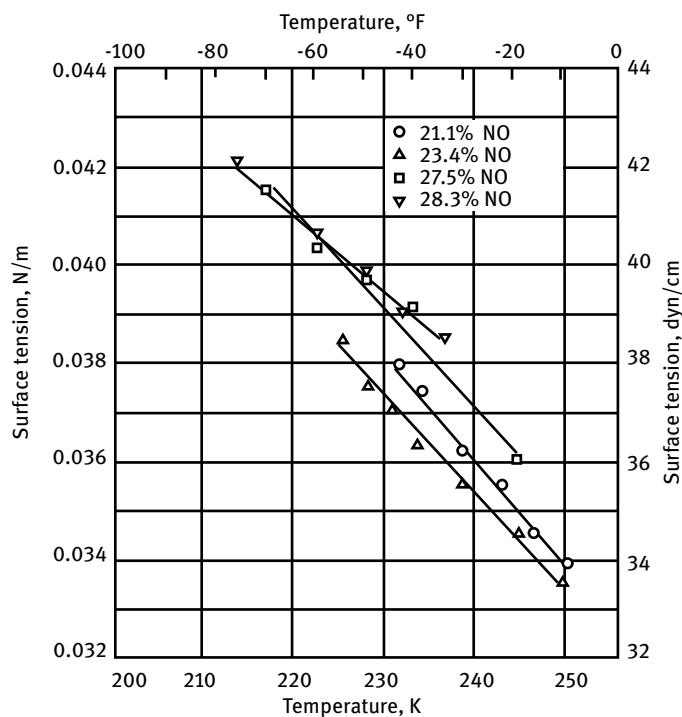


Figure 36: Surface tension of $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures. (Reproduced and modified from [3].)

4.1.7 Electrical Properties of $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ Mixtures

4.1.7.1 Dipole Moment and Relative Permittivity

For $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ mixtures, the relative permittivity increased with the mol fraction of N_2O_3 in a non-linear manner, but the molar polarization increased rapidly at first and then reached an almost constant value (Figure 37) [186]. If one wants to use either of these properties for the analysis of $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ mixtures, it would have been better if they showed a linear relationship, or one must restrict the use to lower N_2O_3 concentrations (0.5).

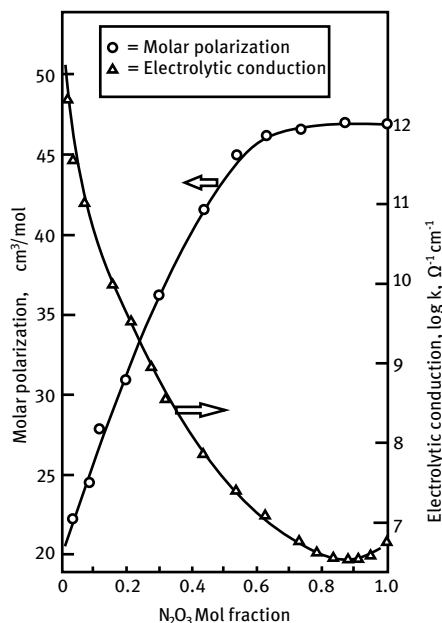


Figure 37: Molar polarization and electrolytic conductivity of $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ mixtures at 253 K. (Republished and modified from [186], with permission of © 1974 Royal Society of Chemistry; permission conveyed through Copyright Clearance Center Inc.)

4.1.7.2 Electrical Conductivity of $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ Mixtures

The addition of small amounts of N_2O_3 caused a rapid increase in the electrolytic conductivity of N_2O_4 . The electrical conductivity of N_2O_4 is substantially increased by the addition of NO (to form N_2O_3) and/or NOCl, with the former exerting the greater effect. It has been shown that the presence of 10 mol-% N_2O_3 increases the conductivity of N_2O_4 by a factor of 1400, while the presence of an equivalent molar concentration of NOCl increases it by a factor of 350. At a given temperature, the electrolytic conductivity increased with the concentration of N_2O_3 , reaching a maximum at about 90 mol-% N_2O_3 and then decreasing until it reached the value for pure N_2O_3 (Figure 37; note that the right-hand scale in Figure 37 is logarithmic!). The maximum conductivity does not necessarily correspond to the greatest concentration of ions since it also depends on the viscosity of the medium and the ionic mobilities of the ions.

4.1.8 Solubility of Pressurant Gases in $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ Mixtures

A bubble-point technique was developed at NASA's WSTF to provide an on-the-spot method for determining when the propellant is saturated with helium [216]. The bubble point, for this application, was defined as the pressure at which gas coming out of solution can be visually detected. For any set of liquid conditions, the bubble point will always occur at some pressure below the pressure at which the liquid is saturated. For MON, the observed bubble point pressures were measured over the pressure range of 689–1930 kPa gauge (100–280 psig). The NO content of the oxidizer was 1.5 mass-%. The average temperature of the oxidizer was 286 K (12.8 °C; 55 °F). These data were ana-

lyzed by a least-squares method to obtain the following equation relating bubble-point pressure as a function of supply tank pressure:

$$P = -8.829432 + 0.933971S$$

where P is the bubble-point pressure in psig and S is the supply tank pressure in psig.

A model was created to simulate the two-phase behavior of MON- x /He mixtures, with x ranging from 0 to 6, and the accuracy of the model predictions was scrutinized by comparison with experimental results [217]. The first tests were performed with pure gas (He and NO) and binary mixtures (N_2O_4 /He, NO_2 /NO, NO/He). Thermodynamic equilibria were studied for the MON-3/He mixture over a temperature range from 273 to 323 K (0–50 °C) at pressures ranging from 0 to 17 bars, with various tank ullage values. Afterward, experimental results were compared with the simulation model predictions. Where deviations were noted, the model was then improved and applied to a bipropellant system of an in-flight satellite in order to calculate the remaining MON mass in the oxidizer from telemetry data.

4.1.9 Thermodynamic Properties of N_2O_4 / N_2O_3 -Mixtures

The heat capacity of N_2O_4 / N_2O_3 mixtures was measured in a calorimeter in comparison to that of well-characterized liquids such as diethyl ether [3]. The heat capacities of four N_2O_4 / N_2O_3 mixtures are listed in Table 33. See also [218].

Table 33: Heat capacities of N_2O_3 / N_2O_4 mixtures.

NO content, mass-%	Heat capacity	
	$\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$	$\text{J g}^{-1} \text{ K}^{-1}$
21.1	0.71	2.97
26.3	0.75	3.14
28.2	0.62	2.59
28.3	0.55	2.30

Data source: [3]

4.1.10 Applications of MON-25 Oxidizers

MON-25/MMH hypergolic combinations are intended for Mars-sample return missions, which have to operate in a very cold environment [200, 219, 220]. Other applications of MON-25 will be discussed in future volumes of this encyclopedia dealing with bipropellant combinations.

4.2 $\text{N}_2\text{O}_4/\text{N}_2\text{O}_5$ Mixtures

At first glance, one would think that mixtures of dinitrogen tetroxide with dinitrogen pentoxide should make even more powerful oxidizers than mixtures of dinitrogen tetroxide with dinitrogen trioxide. For practical and safety reasons, none of these have been examined or even tested.

The oxygen content of N_2O_4 can be improved by the addition of N_2O_5 . Such additions might also lower the freezing point of N_2O_4 in a manner similar to that effected by N_2O_3 . However, dinitrogen pentoxide, the anhydride of nitric acid, is even less stable than nitric acid and slowly decomposes **irreversibly** to lower oxides of nitrogen and free oxygen. If the oxidizer blend is kept cold (close to its freezing point), the storage life could be extended without having to vent the pressure buildup in the tank from oxygen, which dissolves only sparingly in the oxidizer blend.

As illustrated in the melting-point diagram of the $\text{N}_2\text{O}_4/\text{N}_2\text{O}_5$ system in Figure 38, a low-melting eutectic point (257.2 K; -15.8°C) can be achieved with only 10.8 mass-% N_2O_5 , but it is not a significant improvement over the freezing point of pure N_2O_4 [221]. The dashed line indicates areas where the mixtures supercooled without freezing.

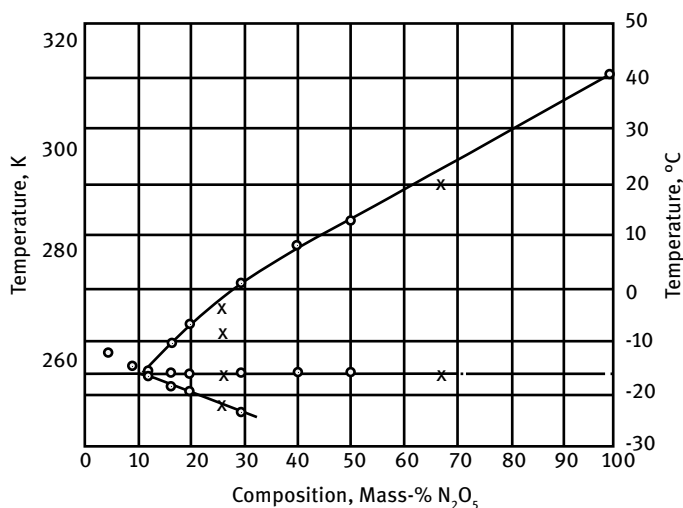


Figure 38: Melting-point diagram of the $\text{N}_2\text{O}_4/\text{N}_2\text{O}_5$ system. (Republished and modified from [221], with permission from © 1935 Royal Society of Chemistry; permission conveyed through Copyright Clearance Center Inc.)

Solutions of N_2O_5 in N_2O_4 had a strong tendency to supercool, such that it was difficult to obtain accurate melting points. Solutions of N_2O_5 in N_2O_4 exhibited such remarkable supercooling that it was possible to determine the freezing point of supercooled mixtures far beyond the eutectic temperature. In this way the (metastable) freezing-

point curve was extended from 11 to 30% N_2O_5 , the supercooling then being a ΔT of 24 °C. It was necessary to initiate crystallization by chilling the liquid either in ice or in carbon dioxide snow and acetone, and then shaking the tube or agitating the liquid with an internal stirrer.

The effective freezing-point suppression of N_2O_4 by the addition of N_2O_5 is only minimal, but it may be possible to achieve even lower melting blends by adding a third ingredient, such as HNO_3 or $\text{C}(\text{NO}_2)_4$. It is a prerequisite that the third ingredient must be fully compatible with N_2O_5 , and only a few chemicals do not react with it. Melting-point data of the $\text{N}_2\text{O}_4/\text{N}_2\text{O}_5$ system are listed in Table 34.

Table 34: Melting points of $\text{N}_2\text{O}_4/\text{N}_2\text{O}_5$ mixtures.

Mass-% N_2O_5	Mass-% N_2O_4	Melting point		Supercooling possible down to	
		K	°C	K	°C
4.29	95.71	261.3	−11.8		
8.76	91.24	258.8	−14.3		
11.86	88.14	256.8	−16.3		
16.12	83.88	263.0	−10.1		
19.46	80.54	266.7	−6.4	254.9	−18.2
29.31	70.69	274.2	+1.1	254.0	−19.1
39.86	60.14	281.1	+8.0	249.9	−23.2
50.05	49.95	286.0	+12.9		

Data source: [221]

There is no indication that N_2O_4 and N_2O_5 might form compounds with stoichiometric molar ratios. As long as the mixture is kept painstakingly anhydrous, N_2O_4 and N_2O_5 are miscible over the entire range of mixture ratios. However, in the presence of only a trace of water, phase separation occurs because of the formation of nitric acid.

4.3 $\text{N}_2\text{O}_4/\text{N}_2\text{O}$ Mixtures

If nitrous oxide is bubbled into a cooled sample of N_2O_4 kept in an ice bath with a salt/ice mixture, a partially saturated solution will contain 9.5% N_2O and will have a freezing point of 255.7 K (−174 °C) and a boiling point of 301 K (28 °C) [222]. In a similar test, where it was observed that N_2O bubbles bubbling through cooled N_2O_4 were completely absorbed before they reached the surface, the saturated solution contained 41.5 mass-% N_2O and had a freezing point of 222 K (−51 °C) and a boiling point of 306 K (33 °C). The absorption of N_2O into N_2O_4 was exothermic, suggesting that some sort of chemical reaction may have taken place in addition to forming a physical solution. Many years later, propellant combinations with mixtures of N_2O and N_2O_4 containing

between 28 and 52 mass-% N_2O_4 were again patented [223], but there was no reference to prior art such as [222].

4.4 Mixtures of Dinitrogen Tetroxide with Nitro Compounds

Dinitrogen tetroxide dissolves readily in many organic nitro compounds, e.g., nitromethane, nitroethane, and nitrobenzene, without reaction. However, such mixtures must be handled with extreme caution because they are shock sensitive and are very powerful explosives, comparable in sensitivity and power to glycerol trinitrate. Binary mixtures of dinitrogen tetroxide and benzene have been used in bombs, in which the components were mixed in mid-air only after the bomb was dropped from the bomber. Under these conditions, N_2O_4 /fuel mixtures are explosives and are not suitable as rocket propellants.

4.4.1 Dinitrogen Tetroxide/Nitromethane Mixtures

Nitromethane is miscible with N_2O_4 over the entire range of mixture ratios. The eutectic temperature is 217 K (-56°C), and the eutectic mix contains 47 mass-% N_2O_4 . The mixture is detonable.

4.4.2 Dinitrogen Tetroxide/Tetranitromethane Mixtures

The formula of nitromethane is H_3CNO_2 , and one can see that it contains hydrogen (a fuel) and combustible carbon as the central atom. Tetranitromethane (TNM), $\text{C}(\text{NO}_2)_4$, on the other hand, is quite different. The carbon and hydrogen balance in tetranitromethane is more than oxidized, and tetranitromethane can no longer act as a fuel but is an oxidizer. Consequently it can be mixed with other oxidizers such as dinitrogen tetroxide without unduly increasing the shock sensitivity of the mixture. In Germany during World War II, experiments were conducted with a mixture containing 62 mass-% TNM (code name X-Stoff) and 38% NTO (code name U-Stoff). The mixture was designated "XU Stoff." Such mixtures were first studied in Peenemünde in Germany during World War II, and the interest was later revived and more in-depth studies of the physical properties were conducted at the German Deutsche Versuchsanstalt für Luft- und Raumfahrt in Stuttgart-Vaihingen in the mid-1960s.

Both oxidizers, N_2O_4 and TNM by themselves have undesirably high freezing points. When mixing them in the appropriate mixture ratios, one can obtain oxidizer blends with favorably low freezing points and other desirable properties. For instance, the oxygen content in a given volume of N_2O_4 oxidizer can be improved by adding TNM.

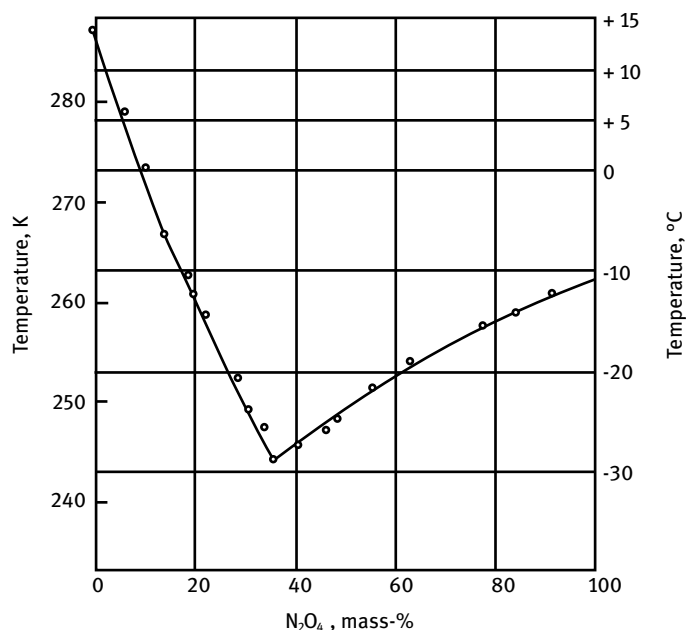


Figure 39: Freezing-point diagram of the dinitrogen tetroxide/tetranitromethane system. (Reproduced and modified from [226].)

The freezing point of TNM can be lowered by the addition of 12.6 mass-% N_2O_4 to 271–269 K (–2 to –4 °C), by the addition of more (20 mass-% N_2O_4) down to 265–263 K (–8 to –10 °C), and finally by the addition of 27.5 mass-% N_2O_4 to 253–251 K (–20 to –22 °C) [224, 225]. It appears that these data were obtained not by using pure N_2O_4 but by oxides contaminated with N_2O_3 because the liquid was described as blue. Subsequent melting-diagram determinations used a better grade of N_2O_4 . The tetranitromethane/dinitrogen tetroxide system is completely miscible over the entire range of mixture ratios [226]. The freezing-point diagram in Figure 39 shows a low-melting eutectic containing 65 mass-% TNM and a melting point of 244 K (–29 °C).

Two additional NTO/TNM data points were determined at Rocketdyne in addition to two dinitrogen tetroxide/fluorotrinitromethane (FTM) freezing points listed in Table 35 [35].

The density of $\text{N}_2\text{O}_4/\text{C}(\text{NO}_2)_4$ mixtures increased linearly with the $\text{C}(\text{NO}_2)_4$ content (Figure 40) and can be expressed by the following equation:

$$\rho = 1.4458 + 0.00191 c \text{ C}(\text{NO}_2)_4$$

where ρ is the density in g/cm^3 at 293 K and $c \text{ C}(\text{NO}_2)_4$ is the TNM concentration in mass percent.

Table 35: Melting points of NTO/TNM and NTO/FTM mixtures.

Mixture	Composition, mass-% TNM	Freezing point		
		K	°C	°F
N ₂ O ₄ -TNM	10.0	260.0	-13.1	8.4
N ₂ O ₄ -TNM	20.0	258.3	-14.8	5.4
N ₂ O ₄ -FTM	10.0	259.6	-13.5	7.7
N ₂ O ₄ -FTM	20.0	257.8	-15.3	4.5
For comparison:				
FTM		231.2	-41.9	-43.4

Data source: [35]

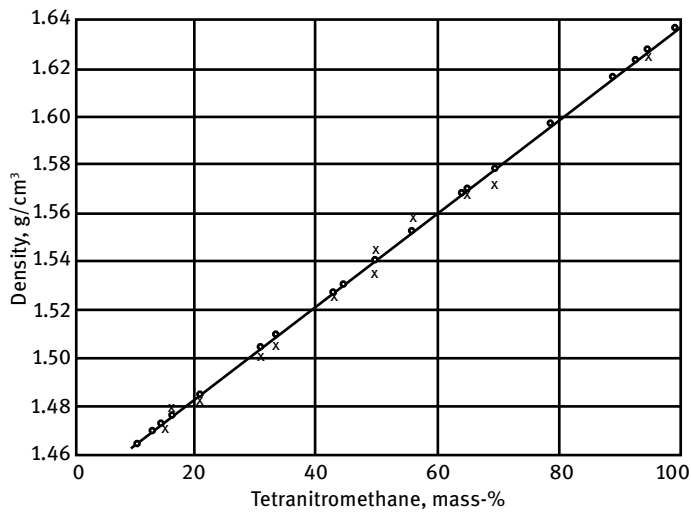


Figure 40: Density of dinitrogen tetroxide/tetranitromethane mixtures. (Reproduced and modified from [226].)

Vapor pressure isotherms illustrated in Figure 41 show that the mixture obeys Raoult's law, i.e., it behaves as an ideal mixture and does not form azeotropes or other associations.

The viscosity of N₂O₄/C(NO₂)₄ mixtures exhibits the behavior that is typical for binary mixtures, as illustrated in Figure 42.

Mixtures of NTO with dinitrotoluene that may form as a by-product of making dinitrotoluene for toluene diisocyanate (TDI) manufacturing or making trinitrotoluene (TNT) are highly detonable [227].

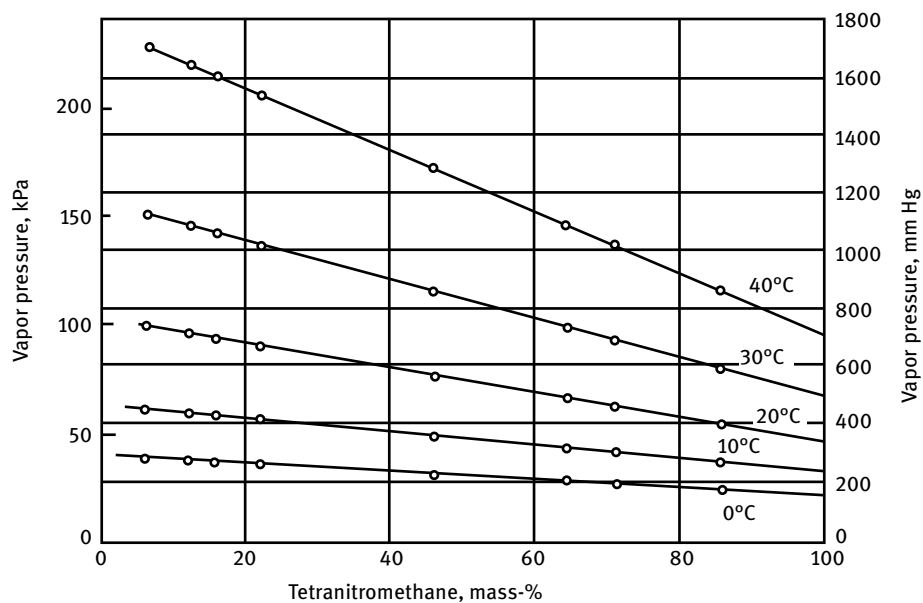


Figure 41: Vapor pressure isotherms of the dinitrogen tetroxide/tetranitromethane system. (Reproduced and modified from [226].)

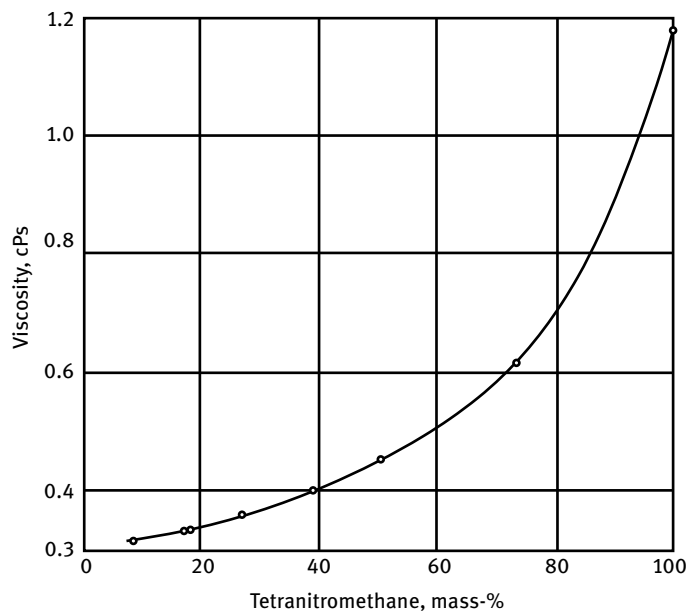


Figure 42: Viscosity of dinitrogen tetroxide/tetranitromethane mixtures at 288.2 K (15.1°C). (Reproduced and modified from [226].)

4.5 Mixtures of Dinitrogen Tetroxide with Fluorine Compounds

One of the many chemicals evaluated as freezing point depressant for N_2O_4 is fluorotrinitromethane $\text{FC}(\text{NO}_2)_3$. The freezing points of these mixtures are listed in Table 35.

5 Chemical Properties of Dinitrogen Tetroxide

5.1 Dinitrogen Tetroxide as a Solvent

Dinitrogen tetroxide is a polar solvent and can dissolve some salts and many organic substances. The ranking of salt solubilities in NTO follows those in non-polar solvents such as diethyl ether. N_2O_4 is often contaminated by materials leached from tank walls, surface-tension PMD screens, and flow control components. Because these salts and their adducts have only limited solubility in N_2O_4 , they precipitate when the saturated solution cools off and cause flow decay problems when small orifices become clogged. The solubility of iron(III) nitrate and other corrosion products in N_2O_4 determines the onset of flow decay.

Among the chemistry in non-aqueous media, reactions in N_2O_4 as a solvent assume a very important role. Dinitrogen tetroxide as a solvent has been thoroughly investigated by Addison in the United Kingdom. A series of publications by Addison [228, 229] summarized the solvent properties of N_2O_4 , but the later publications in this series deal mostly with reactions with sulfur compounds and complex formation with metal salts and are of less interest to rocket propellant chemists. In addition to its use as a solvent, dinitrogen tetroxide and/or nitric acid can also be used as a reactant in numerous reactions with inorganic and organic compounds [230]. Dinitrogen tetroxide is a liquid with unique solvent properties. Because it undergoes autodissociation according to



it is a polar solvent and can dissolve many salts and organic substances. Among the chemistry in nonaqueous media, reactions in N_2O_4 as a solvent assume a very important role [184, 190, 229]. There are also some monographs on non-aqueous solvents that contain sections on dinitrogen tetroxide as a non-aqueous solvent [231].

5.2 Dissociation of Dinitrogen Tetroxide

Dinitrogen tetroxide is the dimer of nitrogen dioxide. The forward dimerization/backward dissociation reactions occur quickly, and the equilibrium concentrations of N_2O_4 are temperature-dependent and pressure-dependent. Dinitrogen tetroxide N_2O_4 vapor is dissociated to the extent of 16.1% into nitrogen dioxide NO_2 at the normal boiling point at atmospheric pressure. From measurements of magnetic susceptibility, it was concluded that the pure liquid N_2O_4 at 273 K contains only 0.7 mass-% NO_2 .

Dinitrogen tetroxide is a hypergolic oxidizer. In order to study the kinetics of hypergolic ignition with N_2O_4 , the extent to which N_2O_4 is dissociated at the time of contact with the fuel needs to be known. This is why this book contains sections on the dissociation of dinitrogen tetroxide. Very rarely is N_2O_4 used as a regenerative coolant in bipropellant rocket engines. If it were, one would have to know whether N_2O_4 dissociates under the conditions in the cooling jacket or not.

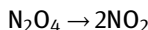
Several detailed summaries of the literature on the kinetics and thermodynamics of the dissociation of N_2O_4 have been published and are referenced here for further study [38, 39].

As stated, dinitrogen tetroxide is rarely used as a regenerative coolant, but if it were, it would change its heat transfer properties while heating up in the cooling jacket before being injected into the rocket engine. This change in properties is due to both chemical changes and changes in temperature-dependent physical properties of the constituents of the mixture. Similar changes take place in a N_2O_4 droplet that is injected into a combustion chamber; it heats up and evaporates before it starts to react with the fuel. Another application of N_2O_4 dissociation is in heat pipes, where the heat transport is much more efficient than with a non-dissociating working fluid. N_2O_4 dissociates at the hot end, flows through the gas passage as gaseous NO_2 , recombines at the cold end, condenses to form liquid N_2O_4 , and wicks through the wick by capillary forces to complete the loop. Dissociating N_2O_4 has also been proposed as a working fluid for turbines in which the heat source is a nuclear reactor. This is another reason we are taking a closer look at the dissociation chemistry of N_2O_4 in this chapter. Because there is a change in the number of mols, the equilibrium is not only temperature dependent but also pressure dependent. The dissociation of one molecule of N_2O_4 into two molecules of NO_2 is due to a homolytic bond fission reaction. Homolytic fission is the chemical bond dissociation of a neutral molecule generating two free radicals. The most efficient method of studying N_2O_4 dissociation kinetics and equilibria is by measuring the absorption spectra, which can also be done by remote sensing methods in the atmosphere. Several papers dealing with these analytic methods were referenced in the previous spectroscopic section.

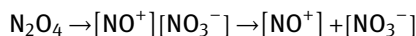
Thermodynamic and transport properties, including enthalpy, entropy, heat capacity, average molecular mass, viscosity, and thermal conductivity, have been calculated for the $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ equilibrium and also for the $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ equi-

librium from 3000 to 1280 K and from 0.01 to 100 atm [232]. An expression for the thermal conductivity due to chemical reaction was also included.

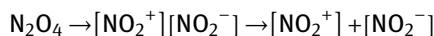
Dinitrogen tetroxide can dissociate as a homolytic reaction into electrically neutral fragments



or it can convert to the ionic form of nitrosyl nitrate, which then dissociates in a heterolytic reaction into nitrosonium and nitrate ions [233]:



A less likely path of dissociation would theoretically go to nitronium and nitrite ions:

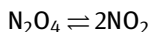


Autodissociation via the heterolytic reaction can be measured by electrical redox potential measurements.

The reversible redox potential of the $\text{NO}_2^+/\text{NO}_2$ couple in liquid N_2O_4 was measured by cyclic voltammetric (CV) examination of the reduction of the nitronium ion as well as the microscopic reverse oxidation of NO_2 [234]. The facile association of NO_2 and dissociation of N_2O_4 were specifically included in the electrode kinetics by a successful computer simulation of the cyclic voltammograms at relatively slow and fast CV scan rates. The kinetics of the N_2O_4 dissociation (k_1) and NO_2 association (k_2) were determined with the aid of single-step chronoamperometry by developing the theoretical working curves based on the CE(mono) mechanism. The strong dependence of the redox potential on the medium is associated with significant NO_2^+ coordination in the solvent. The heterogeneous rate constant (k_s) for electron transfer to NO_2^+ was found to be faster than k_s for NO^+ despite a significantly enhanced value of the intrinsic reorganization energy of NO_2^+ compared to NO^+ for outer-sphere electron transfer.

5.2.1 Experimental Study of Dinitrogen Tetroxide Dissociation

At 263 K (−10 °C), N_2O_4 is a colorless liquid that, upon heating, becomes reddish-brown because of the beginning dissociation leading to nitrogen dioxide [52]



It begins to boil at 294.2 K (21.1 °C). The enthalpy of dissociation in the gas phase at 298 K is 57.3 kJ/mol (13.693 kcal/mol). In the vicinity of the boiling point, the vapor still consists mostly of undissociated N_2O_4 (Figure 43).

The velocity of sound in dinitrogen tetroxide vapor was measured between 274 K (1 °C) and 303 K (30 °C), at pressures between 17 kPa (130 mm Hg) and 101 kPa (760 mm Hg) with sound waves between 9 and 93 kHz [53]. The change of the velocity

of sound with frequency allowed an estimate of the rate of dissociation of dinitrogen tetroxide into nitrogen dioxide, driven by sound energy and the oscillation of local pressure.

It has been attempted to measure the rate of dissociation of N_2O_4 vapor by measuring the attenuation of sound waves as a function of frequency. At sufficiently high frequencies, the velocity of sound is independent of frequency because the N_2O_4 dissociation equilibrium cannot adjust itself fast enough to the local pressure fluctuations as the sound wave moves through [54]. At low frequencies, the intensity and travel velocity of the sound wave are diminished because part of the energy goes toward dissociating N_2O_4 .

Dissociation kinetics can be measured by subjecting N_2O_4 vapor to a shock wave, causing it to be heated very rapidly [235, 236]. As soon as the shock front has passed through the sample, the spectroscopic instrument and photomultiplier record the changing light transmission as it approaches equilibrium at the new temperature and pressure. The rate of dissociation of N_2O_4 in the presence of a large excess of N_2 or CO_2 at pressures from 50 to 707 kPa has been measured by this method. Near 101 kPa, the rate law was

$$-\frac{d[\text{N}_2\text{O}_4]}{dt} = k[\text{N}_2\text{O}_4][\text{N}_2]$$

and the reaction constant was

$$k = 2.0 \times 10^{14} \exp(-11000/RT)$$

See also [237, 238].

Most of the N_2O_4 dissociation studies were done for the vapor phase, and only a few studies were done for the dissociation in the liquid phase. The liquid-phase equilibrium constants for the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ in pure dinitrogen tetroxide were measured over the normal liquid range of the substance [194]. The NO_2 concentration in the liquid was determined by comparing its light absorption in the liquid with the absorption of a known concentration in the vapor. The results gave a linear relation between the logarithm of the equilibrium constant and the reciprocal absolute temperature. From the slope of the curve, an average heat of dissociation of N_2O_4 in the liquid phase of 81.6 kJ/mol (19.5 kcal/mol) was derived. The optical measurements of the dissociation equilibrium constant were later confirmed by magnetic susceptibility measurements [193].

Dissociation of N_2O_4 is much less in the liquid state than in the vapor state. In the liquid state, the equilibrium mixture of N_2O_4 and NO_2 can be considered as a solution of NO_2 in N_2O_4 , and the Henry's law coefficient can be derived from vapor pressure measurements of the mixture. Combining vapor pressure measurements with spectroscopic measurements, it is possible to calculate standard enthalpy, free energy, and entropy of the N_2O_4 dissociation in the liquid phase [32].

Rapid pressure and temperature changes such as those experienced by a gas mixture in a supersonic nozzle flow take place faster than the equilibrium of N_2O_4 dissociation can adjust to, resulting in non-equilibrium conditions [239–241]. The viscosity of dinitrogen tetroxide vapor expanding to supersonic velocities in a Laval nozzle will depend on the rate at which the $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2$ equilibrium can adjust to the rapidly changing pressure and temperature environment as it expands.

The equilibrium constant of the dissociation of dinitrogen tetroxide and the kinetic rate of how fast equilibrium is achieved can be measured by a variety of analytical methods, including spectrophotometry, EPR measurements, velocity-of-sound measurements, and electrical conductivity measurements [199].

An all-glass apparatus has been used to measure the thermal conductivity of the system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ by a thick-wire variant of the hot-wire method in a temperature range of 305–363 K (32–90 °C) and up to a pressure of about 67 kPa (500 mm Hg) [75]. A correlation between equilibrium constant and the thermal conductivity experimental data was discussed in light of theories based on the assumption of local chemical equilibrium. The discrepancy between the experimental and the calculated values of the heat conductivity, which is particularly large at the lower pressures, showed the necessity of applying non-equilibrium heat transfer theory to interpret the data. Table 36 gives the measured thermal conductivity and equilibrium constants for temperatures from 305 to 363 K (32–90 °C) and pressures from 13 to 70 kPa (100–520 mm Hg). The measured equilibrium constant (in column 5 of Table 36) agreed well with literature data from Giaque and Kemp [21] (in column 6 of Table 36). It may be seen from Table 36 that at any particular temperature, K_p is not strictly independent of pressure. At least a part of this variation of K_p with pressure must be ascribed to gas imperfections. To test this, the equilibrium constant K_p was calculated from fugacities.

The gas-phase equilibrium constants for the dissociation of nitrogen tetroxide, $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, have been calculated from experimental data based on IR absorption techniques [242]. The quantitative analysis of NO_2 in the mixture was made at varying pressures and temperatures by observation of the 3.425- μm nitrogen dioxide absorption band to obtain equilibrium constants in the temperature range of 300–370 K. It was also shown that the 3.21- μm band previously assigned to NO_2 should be assigned to N_2O_4 .

NO_2 in the atmosphere can be measured by its absorption in the UV/visible range. Its absorption in the long UV range overlaps with that of its dimer, N_2O_4 . To compensate for the interfering contribution of N_2O_4 from studies of NO_2 profiles in the atmosphere, either the form of the temperature dependence of the equilibrium constant for the equilibrium of N_2O_4 and NO_2 in the gaseous state, $K_p(T)$, must be known, or K_p must be measured at the specific temperature of interest.

At 101 kPa (1 atm) and 294 K (70 °F), the fraction α of N_2O_4 vapor dissociated is 0.163, while at the same pressure and 394 K (250 °F), α is 0.954. Thus, a wide range of dissociation levels can be obtained at conditions easily established in the laboratory. The degree of dissociation is summarized in Table 37. Compare this also to Figure 43.

Table 36: Thermal conductivity and dissociation equilibrium constant of gaseous N_2O_4 .

Column 1	2	3	4	5	6	7	8
Temperature		Pressure		Dissociation constant K_p		Exp. thermal conductivity	
K	°C	kPa	cm Hg	Srivastava and Barua 1961 [75]	Giauque Kemp [21]	$\text{cal cm}^{-1} \text{s}^{-1} \text{°C}^{-1} \times 10^5$	$\text{W m}^{-1} \text{K}^{-1}$
305	32	19.3	14.51	0.235		34.14	0.143
305	32	32.3	24.33	0.25		36.35	0.152
305	32	36.0	27.12	0.245	0.253	37.04	0.155
305	32	69.8	52.5	0.232		31.1	0.130
318	45	13.6	10.22	0.718		26.59	0.111
318	45	22.6	17.03	0.73		32.88	0.137
318	45	37.3	28.06	0.651	0.636	37.21	0.156
318	45	41.4	31.18	0.624		37.36	0.156
333	60	15.1	11.37	1.784		17.95	0.075
333	60	25.5	19.22	1.789		25.77	0.108
333	60	43.0	32.38	1.746	1.852	31.72	0.133
333	60	48.1	36.2	1.744		32.75	0.137
348	75	16.2	12.17	–		12.07	0.050
348	75	28.0	21.08	4.13		16.53	0.069
348	75	47.9	36.08	4.03	4.286	21.58	0.090
348	75	54.0	40.62	4.22		23.21	0.097
363	90	17.1	12.89	–		10.78	0.045
363	90	30.9	23.23	–		12.11	0.051
363	90	51.9	39.07	8.25	8.933	14.71	0.061
363	90	58.6	44.08	8.8		16.65	0.070

$$1 \text{ cal cm}^{-1} \text{ s}^{-1} \text{ °C}^{-1} = 418 \text{ W m}^{-1} \text{ K}^{-1}$$

Data source: [75]

Table 37: Dissociation of dinitrogen tetroxide.

Temperature		Mass-%
K	°C	N_2O_4
273	0	100
300	27	80
323	50	60
373	100	11
408	135	1

The enthalpy of dissociation in the gas phase at 298K is 57.3kJ/mol (13.693kcal/mol). In the vicinity of the boiling point, the vapor still consists mostly of undissociated N_2O_4 (Figure 43).

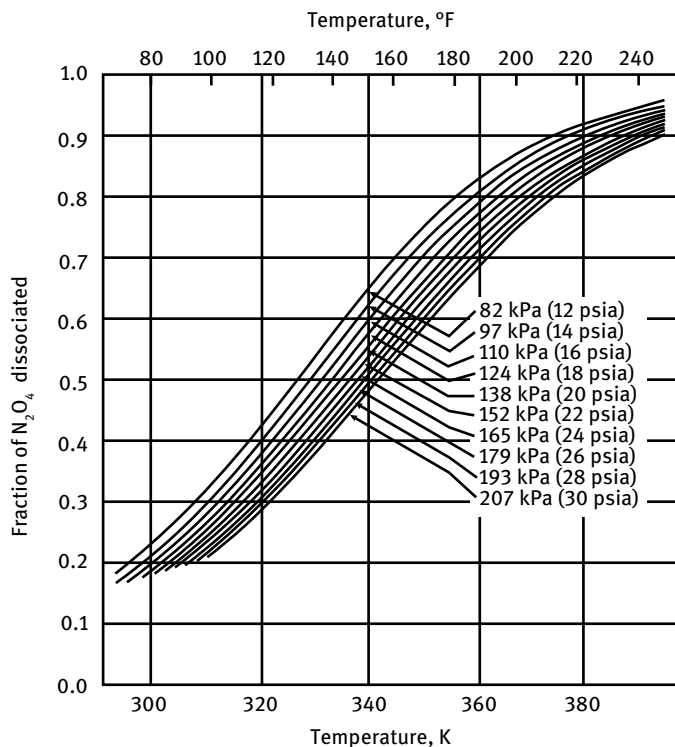
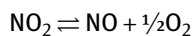


Figure 43: Dissociation of dinitrogen tetroxide as a function of temperature and pressure. (Reprinted and modified from [130] with permission from © 1962 American Chemical Society.)

The equilibrium constant K of N_2O_4 dissociation is related to the dissociation fraction α by the equation

$$K = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{4P\alpha^2}{1 - \alpha^2}$$

In turn, nitrogen dioxide is not thermally stable either, but above 473 K (200 °C) it decomposes reversibly in accordance with



until at 923 K (650 °C) this reaction proceeds to completeness [81, 199]. The decomposition of NO_2 can also be achieved by absorption of UV light (436 nm), a process that is closely related to the formation and dispersal of atmospheric smog. The process is reversible because nitric oxide and oxygen eventually react to restore the NO_2 molecule.

Going one step back to discussing the dissociation of N_2O_4 (not NO_2), the equilibrium constant K_p that gives the mol fraction of thermal N_2O_4 dissociation

$$K_p = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{4P\alpha^2}{1-\alpha^2}$$

is a function of temperature and can be calculated from [243]

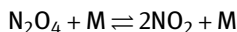
$$\log K_p = -\frac{2692}{T} + 1.75 \log T + 0.00483T - 7.144 \times 10^{-6}T^2 + 3.062$$

where K_p is the equilibrium constant in mm Hg and T is the temperature in kelvin.

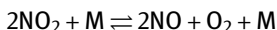
Molecular data of N_2O_4 were derived from natural frequencies of IR-active oscillations and freedom of rotation with assumed data on the electronic levels of N_2O_4 in order to develop a model of the molecule in the ideal gas state and to derive an equilibrium constant for its dissociation [244].

Calculations were made for shifting and frozen equilibrium during expansion [65].

A study of the reactions



and



was carried out in a shock tube [245]. For the first of these two reactions, the rate equation was taken to be

$$d[\text{N}_2\text{O}_4]/dt = -k_{D1}[\text{N}_2\text{O}_4][\text{M}] + k_{R1}[\text{NO}_2]^2[\text{M}]$$

based on previous results. With argon as the inert gas M, with a reactant mol fraction of less than 0.1, the rate constant was found to be

$$k_{D1} = 2.2 \times 10^{14} \exp(-11000/RT) \text{L mol}^{-1} \cdot \text{s}^{-1}.$$

The new application of fully dispersed shock waves was found to produce more accurate results than the conventional use of partly dispersed shock waves. For the second reaction, the rate equation was established as

$$d[\text{NO}_2]/dt = -k_{D2}[\text{NO}_2]^2 - k_{D3}[\text{NO}_2][\text{M}]$$

and with argon as the inert gas, the dissociation rate constants were found to be

$$k_{D2} = 3.0 \times 10^9 \exp(-26900/RT) \text{L mol}^{-1} \cdot \text{s}^{-1}$$

and

$$k_{D3} = 3.6 \times 10^{13} \exp(-65400/RT) \text{L mol}^{-1} \cdot \text{s}^{-1}.$$

An analytical description of the flow fields agreed well with the experimental values, which were determined by a light-absorption technique.

The equilibrium constant for the reaction $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ was determined by FTIR spectroscopy of the ν_2 band of NO_2 near $13.3\mu\text{m}$ [246]. Spectra were recorded alternately through two absorption cells of different path lengths. Working within the validity of the Beer-Lambert law of absorption of radiation, an equation was derived that related the equilibrium constant to pairs of gas pressures that gave the same spectral absorbance of NO_2 in the two unequal cells. No knowledge of the absorption coefficient was needed using this technique. All samples were pressurized to 740 mm Hg with high-purity nitrogen, and measurements were taken at room temperature (296 K). Using this two-cell technique, the equilibrium constant was $K_{\text{eq}} = 0.14 \pm 0.02 \text{ atm}$ at room temperature.

The rate of recombination of shocked and dissociated dinitrogen tetroxide can be measured in the reflected shock wave in a shock tube filled with diluted dinitrogen tetroxide [247]. It was shown that the kinetics has a significant influence on the characteristics of a shock wave and a contact discontinuity, such as a wall, from which the shock wave is reflected.

In a nuclear reactor heat exchanger, the dissociating gas does not behave as an ideal gas, and its properties change with time and location as it passes through a heat exchanger [248]. Relaxation times measured from sudden adiabatic compressions at 0.27 to 1 atm were of the order of 0.7–0.14 μs .

The rate of association of NO_2 to N_2O_4 in very high N_2 dilution was measured at pressures from 1 to 207 bar [249]. The relaxation of $\text{NO}_2/\text{N}_2\text{O}_4$ mixtures was followed after laser flash photolysis of N_2O_4 at 248 nm. The high-pressure and low-pressure rate constants at 298 K were as follows:

$$k_{\text{assoc}} = (8.3 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (at high pressure)}$$

and

$$k_{\text{assoc}} = (1.4 \pm 0.2) \times 10^{-33} [\text{N}_2] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (at low pressure)}$$

In the hydrodynamic calculation of transonic flow of dinitrogen-tetroxide in flow channels, one should avoid the use of the hydrodynamic-drag coefficient, which is a sharply varying quantity [250]. Instead, a more accurate method can be based on the hypothesis of a linear approximation of entropy along the axis of the flow.

The equilibrium between N_2O_4 and NO_2 not only affects its use as a rocket propellant but also affects processes in the polluted atmosphere and the potential deposition of N_2O_4 and NO_2 on the surface of ice crystals and water droplets in the upper atmosphere, particularly in cold regions [251]. Similarly, it would also affect the absorption of NO_x fumes vented from a propellant tank in a water-spray absorption tower.

Measurements of stratospheric NO_2 by ground-based visible spectrometers rely on laboratory measurements of absorption cross-sections. When reviewing low-

temperature laboratory measurements, some investigators claimed that literature data disagreed by significant amounts. A recalculation of errors showed that, in general, these disagreements were not all that significant and that errors in the ratios of cross-sections at low to room temperature were between $\pm 3\%$ and $\pm 8.8\%$ [251]. Of these errors, up to $\pm 3.5\%$ were contributed by errors in the equilibrium constant, K_p , in those measurements where the pressure was above 0.1 mbar. The optimum experiment might therefore simultaneously measure the visible and IR spectra.

The velocity of sound in gaseous $N_2O_4 \rightleftharpoons 2NO_2$ was determined at various temperatures [56]. The velocity-of-sound data obtained were used to calculate the mol fractions of N_2O_4 and NO_2 in the $N_2O_4 \rightleftharpoons 2NO_2$ mixtures. From these data, the equilibrium constants of dimerization were calculated for the system at various temperatures and compared to the literature. That work contains a table summarizing and comparing equilibrium constants measured by six previous investigators using four different methods.

The equilibrium constant of the N_2O_4 dissociation was determined at 283 K and at pressures at and below 1 mm Hg using cavity ring-down spectroscopy (CRDS) [252]. CRDS is a sensitive absorption technique that in this case consisted of a 0.5-m long thermostatted stainless steel tube (diameter 0.75 in) sealed by highly reflective mirrors. A flash of 80 mJ of 532-nm light was injected into a dye laser to provide 694-nm light for the experiment. This light was propagated through several apertures before being gently focused into the CRDS cavity. The light exiting at the opposite end of the cavity was gently focused onto and detected by a photomultiplier tube. The output of the photomultiplier was collected on a digital oscilloscope and then transferred to a computer. N_2O_4 is expected to be relatively transparent at 694 nm. The equilibrium constant of 21 ± 5 mm Hg derived from these measurements was below previously used numbers for this constant. Table 38 gives the proposed constants for the standard form of T -dependence of $K_p(T)$ and the predicted values of K_p (283 K) for the dissociation of dinitrogen tetroxide according to the equation

$$K_p(T) = Ae^{-\left(\frac{B}{T}\right)}$$

and the predicted values of K_p at 283 K.

Table 38: Proposed constants and predicted values for the dissociation of dinitrogen tetroxide.

A $\text{cm}^3 \text{ mol}^{-1}$	B K	K_p at 283 K mm Hg	References
6.62×10^{-30}	7258	32	Estupinan, Wine et al. 2001 [253]
5.9×10^{-29}	6643	32	NASA panel [254]
		21 ± 5	Tuchler, Schmidt, and Morgan [252]

Quantitative measurements of the dimerization of nitrogen dioxide in a gas mixture of NO_2 and N_2O_4 have been made using long-duration pulses from 7.84 and 7.46 μm quantum cascade lasers in an intra-pulse quantum cascade laser spectrometer [255].

5.2.2 Computational Chemistry Treatment of Dinitrogen Tetroxide Dissociation

Molecular dynamics simulations were performed for the thermal dissociation and association reactions $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ in the gas phase and in liquid N_2O_4 [256]. Energy transfer between intra-fragment vibrational modes and the inter-fragment translational mode, which occurs at the inner turning point of the inter-fragment potential, was found to be the dominant prompter of the dissociation and association reactions.

Reacting systems containing N_2O_4 and NO_2 in equilibrium, pure or dissolved in organic solvents, were modeled in two ways: **(1)** assuming that all species in the system are hard spheres with an attractive mean field component (HSA), and **(2)** using a semi-empirical EOS [257]. In both cases, estimates of the relative size of the species, obtained by Monte Carlo simulations, were made to reduce the number of adjustable parameters. As a result, for a pure system, both the HSA model and the semi-empirical EOS required only three adjustable parameters. The agreement between both model predictions and experimental results was good, with higher accuracy for the semi-empirical EOS. The predicted effect of pressure on the equilibrium constant of the gas mixture was underestimated by both models. The predicted dissociation constants of N_2O_4 in the liquid phase were underestimated by about 25% by the HSA model and overestimated by 5% by the semi-empirical EOS.

Classical molecular dynamics simulations of liquid NO_2 and $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2$ and *ab initio* molecular orbital calculations were carried out to elucidate the $\text{NO}_2 \cdots \text{NO}_2$ attraction potential, and an orientation-sensitive pairwise potential (OSPP), which can reproduce highly anisotropic character of covalent bonding between N—N, was formulated [258]. The reactive liquid N_2O_4 was modeled as liquid NO_2 , which interacts with the OSPP potential between N—N atoms and Lennard-Jones potentials between N—O and O—O atoms. The likelihood of more than two NO_2 molecules associating to a trimer or tetramer is extremely small. The equilibrium constant for the dissociation reaction was derived by computing the potential of mean force as a function of the N—N distance reaction coordinate. The OSPP potential reproduced the observed liquid-phase equilibrium properties fairly well.

The $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ dissociation reaction was investigated at a high level of theory using the couple cluster with all single and double excitations and connected triples and complete active-space self-consistent field approaches [259]. Including an estimate for basis set superposition error, ΔH^{298}_0 for the dissociation reaction was predicted to be 53.4 kJ/mol (12.76 kcal/mol). (For comparison, experiments by others measured 54.8–57.3 kJ/mol [13.1–13.7 kcal/mol].)

Transition state dynamics of dissociation and association reactions $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ in the liquid state were studied by classical molecular dynamics simulations of reactive liquid NO_2 at 298 K [260]. One possible path of dissociation is the dissociation via bond transfer from a dimer to a monomer NO_2 through the transition state of a $(\text{NO}_2)_3$ trimer. The reactant experiences the transition state of a $(\text{NO}_2)_3$ trimer for a “long” time (1–10 ps) in NO_2 -mediated bond transfer reactions.

5.3 Isomerization of Dinitrogen Tetroxide

Under certain conditions, dinitrogen tetroxide can react not in its symmetric form of O_2NNO_2 but also in the form of its isomer nitrosyl nitrate NO^+NO_3^- . The kinetics of the reaction of dinitrogen tetroxide/nitrogen dioxide with hydrazoic acid in the gas phase were examined between 293 and 323 K [261]. The reaction proceeded as a reaction of second order with respect to NO_2 and first order with respect to HN_3 . The negative temperature coefficient of the reaction rate indicated an exothermic pre-dissociation equilibrium. The stoichiometry of the reaction and the abnormal Arrhenius factor indicated that N_2O_4 does not react as symmetric O_2NNO_2 but rather in the form of its isomer nitrosyl nitrate NO^+NO_3^- . This may also be the reactive species in hypergolic reactions of N_2O_4 with amines and hydrazines.

5.4 Photolysis of Dinitrogen Tetroxide

Unwanted photolysis of N_2O_4 takes place in a UV-visible spectrophotometer that is used to measure the concentration of NO_2 . Photolysis of N_2O_4 and NO_2 takes place in the upper atmosphere as a key step in the formation and decay of smog. Photolysis of N_2O_4 in the presence of oxygen or ozone was attempted as a method to synthesize higher oxides of nitrogen.

A molecular beam of N_2O_4 molecules was photodissociated by an excimer laser at 193 and 248 nm [262]. The time-of-flight distribution of NO_2 photofragments was consistent with the formation of two electronically excited NO_2^* molecules in the $\bar{\text{A}}(^2\text{B}_2)$ or $\bar{\text{B}}(^2\text{B}_1)$ state. Visible emission from NO_2^* was observed in the photolysis at both 193 and 248 nm excitation. The parallel angular distribution of the NO_2 photofragments showed that at 193 nm N_2O_4 has a transition dipole along the N–N axis, and the dissociative lifetime was estimated to be less than 1 ps.

Velocity and angular distribution of the products of N_2O_4 photodissociated at 193 nm showed evidence for only N–N bond fission, with no significant branching to N–O bond fission or NO elimination products [263]. The translational energy distribution of the N–N bond fission products was bimodal, indicating that at least

two different $\text{NO}_2 + \text{NO}_2$ product channels contributed significantly to the observed products. Both product channels had an anisotropy parameter of $\beta = 1.7 \pm 0.2$.

Nitrogen dioxide was photolyzed at room temperature in a long-path infrared cell [264]. The concentrations of NO_2 and N_2O_5 were followed as a function of time, and the molecular modulation spectrum of nitrogen dioxide was obtained in a steady-flow experiment with 1 atm of nitrogen. The rate constant ratios and standard deviations were as follows:

$$\begin{aligned}k_1 \frac{[\text{M}]}{k_2} &= 0.18 \pm 0.01 \\k_3 \frac{[\text{M}]}{k_2} &= 0.22 \pm 0.01 \\ \frac{k_4}{K} &= 0.71 \pm 0.05 \text{ s}^{-1}\end{aligned}$$

where

- (1) $\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}$
- (2) $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$
- (3) $\text{NO}_2 + \text{O} + \text{M} \rightarrow \text{NO}_3 + \text{M}$
- (4) $\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$

$$K = ([\text{N}_2\text{O}_5]/[\text{NO}_2][\text{NO}_3])_{\text{eq.}}$$

By using literature values for k_1 ($6.9 \times 10^{-32} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and for K ($1.24 \times 10^{-11} \text{ cm}^{-3}$), the values of the elementary rate constants were

$$\begin{aligned}k_2 &= 9.2 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\k_3 &= 8.2 \times 10^{-32} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1} \\k_4 &= 8.7 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-2} \text{ s}^{-1}\end{aligned}$$

Multi-reference configuration interaction calculations were performed for vertical excitation energies and potential curves of N_2O_4 in D_{2h} symmetry [265]. The strong absorption of N_2O_4 around 185 nm was assigned to the transition from the ground state to $1^1B_{1u}(\sigma\text{O} \rightarrow \sigma^*\text{N}-\text{N})$ rather than $1^1B_{2u}(\pi\text{O} \rightarrow \pi^*\text{NO}_2, n \rightarrow \sigma^*\text{N}-\text{N})$, as previously assumed. N_2O_4 is placed in the yz -plane, with $\text{N}-\text{N}$ axis along z . The weak absorption around 340 nm was assigned to $11B_{3u}$. Excitation to 1^1B_{2u} was calculated at 227 nm. Multi-reference configuration interaction (MRCI) singlet and triplet potential curves for the dissociation $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$, combined with a table of NO_2 states correlating with those of N_2O_4 , indicated possible products of photodissociation at various wavelengths. The extensive literature on the photodissociation of N_2O_4 was reviewed and updated. Density functional theory geometry optimizations were performed on low-lying singlet and triplet states.

5.5 Radiolysis of Dinitrogen Tetroxide

The radiolysis of dinitrogen tetroxide has been studied because N_2O_4 may decompose under the influence of cosmic radiation during long-duration space missions. Solar cosmic rays have a high-energy proton component. Satellites in the van Allen belt around Earth and in the radiation belt around Jupiter are subjected to intense radiation that may cause propellants to decompose. On long-term deep-space missions, radioisotope thermal generators (RTGs) provide electric power from the heat generated by the decomposition of radioactive isotopes. Although RTGs are shielded and placed on extendable booms away from the spacecraft core, some radiation penetrates the shielding. Propellant tanks in vicinity to RTGs are still subjected to nuclear radiation. Because oxidizers are less sensitive to radiation damage than fuels, it would be best to design the spacecraft such that the oxidizer tank is between the radiation source and the fuel tank. Both the United States and the former USSR have flown satellites with nuclear fission reactors such as SNAP-8 as powerplants. Some of these satellites may have used NTO/MMH thrusters for attitude control, orbit adjustment and controlled de-orbit.

Radiolysis of N_2O_4 opens up new paths of chemistry, and another reason radiolysis has been studied is to look for the formation of higher, more energetic oxides of nitrogen that may also be useful as rocket propellants (if they are stable enough to be stored).

The ^{60}Co γ -radiolysis of liquid dinitrogen tetroxide $\text{N}_2\text{O}_4(\text{L})$ as a function of temperature, gas-to-liquid volume ratio, dose rates, and method of $\text{N}_2\text{O}_4(\text{L})$ purification showed that the radiolytic products were N_2 , N_2O , and N_2O_5 [266–268]. The material balance of the O_2 released at post-irradiation thermal equilibrium as compared with the calculated O_2 derived from the production of N_2 and N_2O from N_2O_4 was accurate to within 10%. $\text{N}_2\text{O}_4(\text{L})$ was relatively radiation resistant, having a G value of only 0.075, the ratio of N_2 and N_2O product formation being 2:1. The addition of O_2 , over the partial pressure range of 26.7–46.7 kPa (200–350 mm Hg), resulted in an elevated G value for N_2O_5 formation.

Radiolysis experiments with liquid dinitrogen tetroxide (inhibited and uninhibited) were conducted in stainless steel vessels of approximately 15 mL under γ -irradiations by ^{60}Co at a dose rate of 5.76×10^5 rad/h and a temperature of 294 K (21°C) [269]. Sample vessels were evacuated prior to being filled with N_2O_4 . After filling, the liquid N_2O_4 was frozen, and any non-condensable gases were removed by pumping. Non-condensable gases at liquid N_2 temperature formed by decomposition of N_2O_4 were determined as a function of time and radiation dose by PVT relationships. The results of experiments at the dose rate of 5.76×10^5 rad/h for both the uninhibited and inhibited forms of N_2O_4 were displayed as mols of non-condensable gas formed per gram of liquid N_2O_4 as a function of radiation dose. The decomposition rate at a fixed dose rate appeared to be a function of the extent to which the sample vessel was filled, which suggested that the vapor is more

susceptible than the liquid to decomposition and that there is some interaction with the walls of the vessel. The major non-N₂O₄ component of the gas space was nitric oxide, NO, and its rate of formation appeared to be about the same in both cases at the dose rate used, 5.76×10^5 rad/h. For the uninhibited N₂O₄, the *G* value of $G(\text{N}_2) = 6.1 \times 10^{-2}$ molecules/100 eV which was similar to the results reported by Castorina of 5.2×10^{-2} . The only other product found in addition to NO and N₂ was nitrous oxide, N₂O, which was formed at a rate slightly greater than that of nitrogen in the case of the uninhibited nitrogen tetroxide and slightly less in the case of the inhibited form.

The liquid-phase radiolysis of NO solutions in N₂O₄ at nitrogen monoxide concentrations up to 15 mass-% was studied at 303–413 K (30–140 °C) and pressures of 1.2–6.0 MPa [270]. The radiation-chemical yield of decomposition of liquid N₂O₄ was found to be 1.5–2.0 orders of magnitude lower than that of gaseous N₂O₄. The dissolution of nitrogen monoxide (to 15 mass-%) in N₂O₄ increased the radiation-chemical yields of nitrogen and dinitrogen oxide from 0.03 ± 0.002 to 0.15 ± 0.002 and from 0.005 ± 0.0005 to 0.03 ± 0.001 , respectively.

It is thus unlikely that cosmic radiation affects the propellant properties of NTO during long space missions. Fuels such as N₂H₄ or MMH would suffer from radiolysis much worse than NTO would.

5.6 Reactions of Dinitrogen Tetroxide with Inorganic Compounds

Dry dinitrogen tetroxide reacts with many inorganic compounds, but its reactivity is greatly enhanced in the presence of traces of moisture. The main concern about reactions of liquid N₂O₄ with inorganic materials is about the corrosion of metal tanks during storage and flight use of N₂O₄, resulting in leached metals being dissolved as metal salts or precipitated as sludge causing flow decay problems.

Metal nitrate/N₂O₄ adducts of the type $\text{M}(\text{NO}_3)_x \cdot y\text{N}_2\text{O}_4$, in which N₂O₄ molecules are trapped in the metal nitrate lattice, were synthesized from the reaction of N₂O₄ and the corresponding metal salts [230]. Since liquid N₂O₄ evaporates at 294.3 K (21.15 °C) under atmospheric pressure, $\text{M}(\text{NO}_3)_x \cdot y\text{N}_2\text{O}_4$ adducts are a very convenient and thermally stable source of N₂O₄. The iron salt with a composition of $[\text{NO}]^+ [\text{Fe}(\text{NO}_3)_4]^-$ is the main culprit in flow decay in NTO, which has become saturated with this sparsely soluble compound and which precipitates if the NTO solvent is cooled. Upon contact with moisture, it is readily hydrolyzed to hydrated iron(III) nitrate. It can be sublimed under vacuum, but it decomposes to a similar compound $[\text{NO}_2]^+ [\text{Fe}(\text{NO}_3)_4]^-$ [271].

A five-phase program has been conducted to define and determine elimination techniques for flow decay, a troublesome phenomenon [272, 273]. Flow decay has been shown to arise from the deposition of N₂O₄-soluble iron compounds in valve orifices. This deposition impedes the flow of propellant and, in extreme cases, clogs the valve completely. The five phases of the program involved compound formation, compound identification, compound solubility, compound elimination,

and efficiency evaluation of removal techniques. The solubility of $\text{Fe}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_4$ in pure N_2O_4 over the temperature range of 273–311 K (0–37.8 °C/32–100 °F) is quite low, on the order of 0.1–2 ppm (in terms of Fe concentration), with a slight positive temperature coefficient of solubility. Water at the military specification limit (0.1 mass-%) and NO up to 1 mass-% had no effect on solubility. Higher water concentrations increased the solubility. The addition of acetonitrile, perfluoroacetonitrile, benzonitrile, perfluorobenzonitrile, ethyl acetate, or perfluoroacetone was tested in the hope that these compounds would prevent precipitation of $[\text{NO}]^+ [\text{Fe}(\text{NO}_3)_4]^-$. Acetonitrile added to N_2O_4 dissolved the deposit. The addition of 0.25 mass-% acetonitrile to N_2O_4 prevented the formation of deposits in a flow system. It was attempted to identify the compound in N_2O_4 by NMR or EPR, but the sensitivity of these methods in the presence of excessive $\text{NO}_2/\text{N}_2\text{O}_4$ was insufficient. A Mössbauer spectrum was taken of the anhydrous synthetic $\text{Fe}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_4$ to characterize this material more fully and to determine whether this technique would be useful in determining the structure of the actual flow-decay material. The isomer shift observed was ~ 0.25 mm/s. The broad line width was probably caused by a fairly long spin-spin relaxation time. The absence of a sizable quadrupole splitting suggested that the iron site (or sites) had essentially undistorted octahedral or tetrahedral symmetry. The spectrum observed for $\text{Fe}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_4$ was quite different from that of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, which has a shift ~ 0.1 mm/s less than the $\text{Fe}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_4$ and has a line width approximately twice as broad. The spectrum did not resemble spectra of the simple iron oxides.

The crystal structure of the adduct $\text{Fe}(\text{NO}_3)_3 \cdot 1.5\text{N}_2\text{O}_4$ indicated that it should be represented as $3\text{NO}^+ \text{NO}_3^- \cdot 2[\text{Fe}(\text{NO}_3)_4]^-$ [274]. Vibrational spectroscopy provided evidence for interaction between the NO_3^- and 3NO^+ ions, and the properties could be correlated in terms of a weakly bonded $[\text{N}_4\text{O}_6]^{2+}$ group that may also be present in solutions of N_2O_4 or the adduct in pure nitric acid.

5.6.1 Solubility of Iron Nitrate in Dinitrogen Tetroxide

The limited solubility of iron nitrate and its adducts in dinitrogen tetroxide is the cause for precipitation of solids or gels and flow decay. Several experimental studies were conducted to determine the solubility limit of iron nitrate in NTO and MON with different water and NO contents.

If the initial propellant composition is varied (within the limits of NAS 3620), the iron solubility changes. The most distinct change is the increase of iron solubility with NO content. If the composition is held constant and the temperature is increased, the solubility increases with an increase in temperature. In selecting the optimum operating temperature for a satellite propellant tank, increasing the temperature widens the soluble range, but it also accelerates the rate of corrosion. Researchers at NASA's WSTF conducted a series of tests to measure the solubility of the material that causes flow decay in MON-1 and MON-3 [11, 275–277]. The solubility was measured as a function of NO concentration, water equivalent concentration, and temperature. The

results indicated that the solubility is very dependent on NO content and to a lesser degree is affected by the water content. In a second series of tests, flow decay was deliberately induced when flowing MON through windowed orifices and a Space Shuttle RCS engine. The tests showed that the oxidizer needs to be supersaturated with iron nitrate to produce the flow decay phenomenon. Figure 44 shows the solubility of iron nitrate in MON as a function of temperature, with the NO content as a secondary variable but with constant water content (0.1% H₂O equivalent). Similar charts exist for water equivalent contents of 0.05% H₂O, 0.15% H₂O, and 0.20% H₂O, but they do not differ very much. The data from 350 data points were curve fitted and resulted

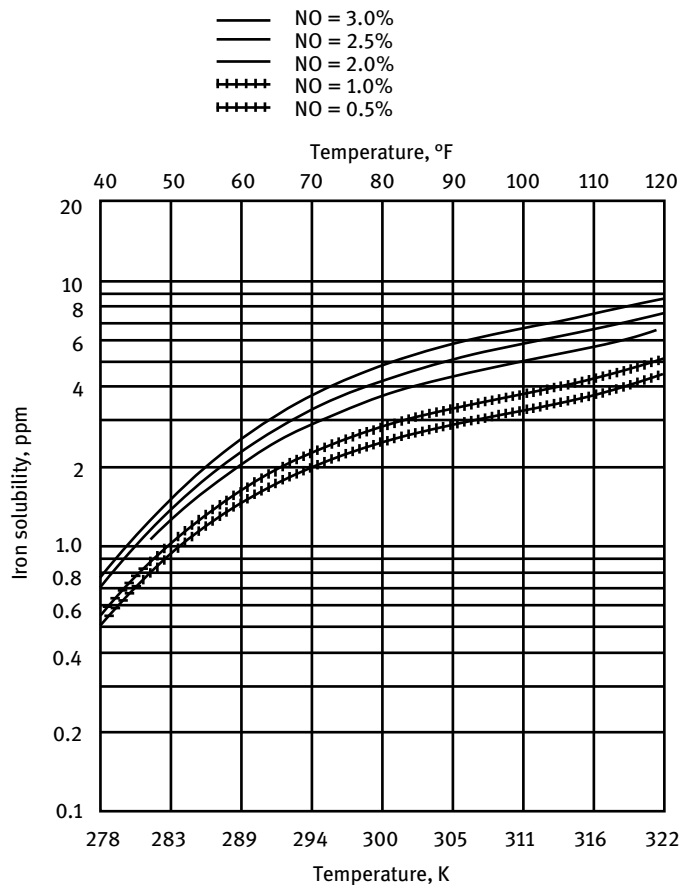


Figure 44: Solubility of iron nitrate in MON as a function of temperature and NO content. (Reproduced and modified from [11].)

in an equation that expresses the saturation concentration of iron nitrate in N_2O_4 as a function of temperature, NO content, and H_2O content:

log iron concentration (in parts per million)

$$\begin{aligned}
 = & -2.355 + 0.0929T - 0.00108T^2 + 4.153 \times 10^{-6}T^3 \\
 & + [-0.935 - 0.137T + 0.00305T^2 - 1.450 \times 10^{-5}T^3] \text{ water equivalent percent} \\
 & + [0.0311 + 0.000462T + 0.0000189T^2 - 1.417 \times 10^{-7}T^3] \text{ NO percent}
 \end{aligned}$$

where T is the temperature in kelvin.

When replotting the WSTF data in a format that shows the iron solubility as a function of water content with temperature as the secondary variable, it was noted that the slope of the iron solubility curves changed with temperature [278]. As shown in Figure 45, iron solubility increased with water content at high temperatures but decreased with water content at low temperatures.

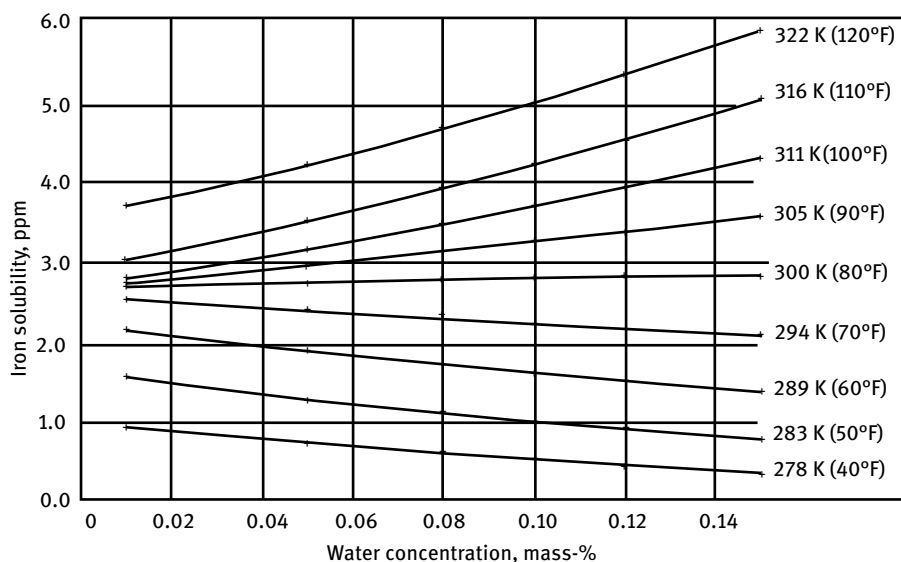


Figure 45: Iron solubility in MON-1 as a function of water content and temperature. (Reproduced and modified from [278].)

Applying this solubility information to the conditions inside the Galileo Jupiter space probe oxidizer tank containing MON-1 with 0.8% NO and 0.08% H_2O , it was predicted that flow decay problems might have to be expected if the temperature were allowed to drop to less than 263 K (10°C) (Figure 46) [279–281].

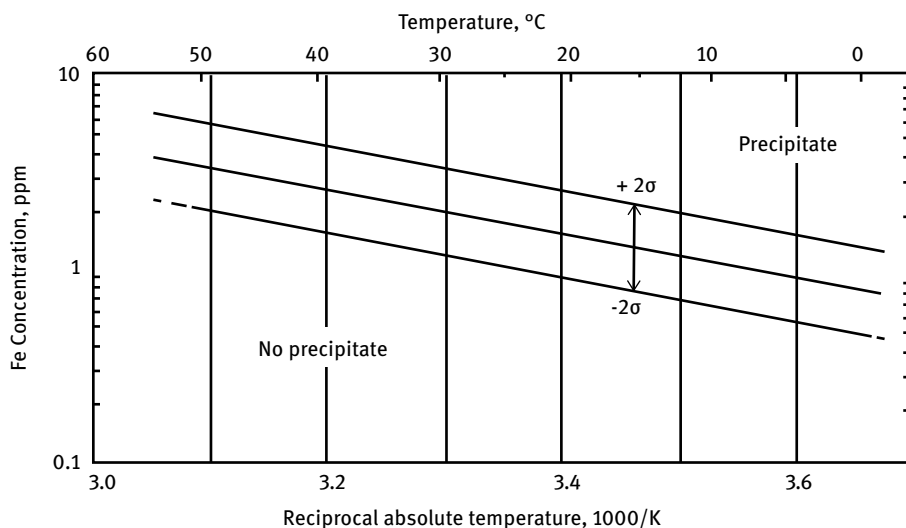


Figure 46: Iron solubility limits determine flow decay problems in MON oxidizer tank. (Reproduced and modified from [278].)

When studying the solubility of iron nitrate in MON-1 and MON-3, it was found that solubility is higher in MON-3 than in MON-1 [282]. Solubility increased with water content in the range of 0–0.1 mass-% H_2O equivalent and increased with temperature in the range of 278–308 K (5–35 °C). Filtration of MON saturated with iron nitrate through filters with pore sizes in the range of 0.2–1 μm showed that the finer membranes removed more iron. That indicates that iron nitrate exists in MON in particle sizes below the submicron level.

The solubilities of metal nitrates in liquid dinitrogen tetroxide containing 0.4–2% HNO_3 additive at 293 K were determined by emission spectrographic and colorimetric methods [283] (Table 39).

Table 39: Solubilities of metal nitrates in liquid dinitrogen tetroxide.

Nitrate Analysis method	Solubility, mass-% Spectrographic	Solubility, mass-% Colorimetric
Al(III)	4.6×10^{-4}	3.8×10^{-4}
Fe(III)	1.8×10^{-4}	4.0×10^{-4}
Ca(II)	3.9×10^{-5}	
Mg(II)	7.0×10^{-5}	
Ni(II)	3.7×10^{-5}	
Cr(III)	5.3×10^{-5}	

Data source: [283]

5.6.2 Reactions of Dinitrogen Tetroxide with Water

The reactions of dinitrogen tetroxide with water are essentially the same as those already discussed in the chapter “Nitrogen Dioxide” for reactions of nitrogen dioxide with water. Dinitrogen tetroxide has been described as the mixed anhydride of nitrous and nitric acids because of its reaction with water that gives a mixture of nitrous acid and nitric acid. When dinitrogen tetroxide is dissolved in a large excess of water in the absence of oxygen, nitrous and nitric acids are formed in equal amounts:



Nitrous acid is a weak acid ($K_a = 6 \times 10^{-4}$ at $303\text{ K} = 30^\circ\text{C}$), so it will not dissociate appreciably in aqueous solution. The un-ionized acid decomposes into nitric acid and nitric oxide, though only slowly at low temperatures, until equilibrium is reached. All the reactions are reversible. In the presence of dilute alkali, the reaction is no longer reversible. This is a key reaction for the removal of NO_2 and N_2O_4 vapors from pressurant gases vented from NTO tanks after a completed rocket test by passing the NO_x -loaded gases through a scrubber with an aqueous solution. This is also an important reaction in the manufacturing of nitric acid. The reaction also takes place between NO_x and moisture in the atmosphere and is part of the abiotic nitrogen fixation cycle.

Liquid dinitrogen tetroxide and water form two liquid phases over a wide range of compositions. The upper layer is largely aqueous nitric acid, and the lower layer is deep blue due to the presence of dinitrogen trioxide. At 273 K , the upper layer contains 47 mass-% N_2O_4 , and the lower layer contains 98 mass-% N_2O_4 . If the mixture is heated to 340 K (67°C), the two phases combine into one phase. In the presence of NO or N_2O_3 , the hydrolysis of N_2O_3 is much faster than the reaction of N_2O_4 with water.

Kinetic evidence has identified N_2O_4 as the chief reactant species in the $\text{NO}_2/\text{N}_2\text{O}_4/\text{H}_2\text{O}/\text{HNO}_3$ system [284, 285]. The equilibrium data for this system with an apparent temperature independence could be more accurately expressed in terms of N_2O_4 instead of NO_2 . The ionization of N_2O_4 in solution is a key step. The ionic nature of the reaction would seem to preclude the existence of a purely gas-phase reaction between these nitrogen oxides and water.

In the absence of oxygen, and with varying amounts of nitrogen to adjust the total pressure in the gas phase, the mixture consisting of N_2 , NO , NO_2 , N_2O_4 , N_2O_3 , HNO_2 , and HNO_3 is impossible to analyze with any given single method. Multiple methods have to be used to characterize the complex equilibria in this reacting mixture [286]. One could start with a known amount of concentrated nitric acid, allow an equilibrium amount of $\text{NO}_2/\text{N}_2\text{O}_4$ to dissolve in the liquid phase, and then analyze for NO and NO_2 in the gas phase. See also [287].

5.6.3 Reactions of Dinitrogen Tetroxide with Ammonia

The slow gas-phase reaction of N_2O_4 with NH_3 under conditions that avoid ignition leads to ammonium nitrate [288]:



Ammonia reacts even with solid N_2O_4 readily and extensively. Because of the secondary exothermic reactions, the N_2O_4 decomposition is complete.

Reactions of ammonia with NO , NO_2 , and NO_x have been investigated very thoroughly as part of the stack gas NO_x removal by injection of ammonia into hot stack gases (with or without the presence of a catalyst) to prevent atmospheric pollution.

5.7 Reactions of Dinitrogen Tetroxide with Organic Compounds

Many organic compounds dissolve in N_2O_4 at room temperature without reaction, e.g., saturated hydrocarbons, aromatic hydrocarbons, halocarbons, nitro-compounds, and carboxylic acids. Substances that react with it include unsaturated hydrocarbons, alcohols, amines, and ketones [39]. Ethers, tertiary amines, and many oxygen-containing and nitrogen-containing heterocyclic compounds form adducts similar to Lewis adducts. Most tertiary amine adducts contain two molecules of the base per each N_2O_4 molecule.

The reaction of N_2O_4 with alcohols parallels that with water and leads to an equilibrium with alkyl nitrites:



In the gas phase, a mist of nitric acid vapor is formed. In solution, two separate liquid layers are formed, one rich in nitric acid and the other rich in nitrite ester [289]. For additional information about reactions of NO_2 and N_2O_4 with organic compounds, we refer readers to other publications in the literature [290]. Other reactions are summarized in conference proceedings about nitration methods [291]. Similar reactions can be achieved by using N_2O_3 instead of N_2O_4 [292].

In nitration reactions, N_2O_4 may react in the form of nitrosonium nitrate NO^+NO_3^- , which can form by oxidation of NO in inert solvents at cryogenic temperatures. Nitrosonium nitrate may be an intermediate in the reaction of N_2O_4 with olefins [293].

In our book, we are mostly interested in the NTO and MON reactions that lead to hypergolic ignition with reactive fuels.

Reactions of N_2O_4 with secondary amines give nitrosamines as intermediate products. In ether solutions at low temperatures, reaction of N_2O_4 with tertiary amines forms molecular addition compounds that can be isolated as precipitates at low temperatures and are unstable at room temperature [294].

Because N_2O_4 reacts with many organic compounds, it has been very difficult to find elastomeric materials for gaskets, O-rings, valve seats, and expulsion bladders for use with N_2O_4 .

5.8 Analysis of Dinitrogen Tetroxide and Its Mixtures

In subdividing a chapter on the analysis of rocket propellants, one can either subdivide by the method used or by the analyte to be analyzed. In this chapter we have chosen to subdivide the following by the analytical method used.

Analytical methods are required for dinitrogen tetroxide and nitrogen dioxide for several tasks, which include ensuring the quality of liquid propellants filled into rockets at the launch pad and monitoring work spaces for safe breathing-air conditions. The methods described here are applicable to the rarely used pure N_2O_4 as well as the more commonly used mixed oxides of nitrogen, which consist of N_2O_4 with varying amounts of N_2O_3 as an additive. One of the more important analytical tasks in handling N_2O_4 and MON oxidizers is the analysis of the NO or N_2O_3 content in MON.

Because the composition of MON samples may change if the sampling of propellant from a large reservoir is not done properly or because contaminants may be introduced if incompatible sampling equipment is used, correct and reproducible analysis results can be obtained only if the sampling is done correctly [295].

NASA Specification KSC-SPEC-P-0018 [296] describes the sampling and analysis method for liquid NTO and MON that has been off-loaded from a spacecraft after a flight and stored in a storage tank. It was assumed to be contaminated and had to be analyzed, dried, NO-content-adjusted, and re-analyzed before it could be recycled for future use. This specification provides a means of categorizing recovered propellants for either reclamation for alternate reuse or for reprocessing to the original manufacturer's specification purity. See also [297].

5.8.1 Contaminants Commonly Found in Dinitrogen Tetroxide

Many contaminants that are potentially harmful to applications in rocket engines can be found in dinitrogen tetroxide that has not been properly manufactured and stored. These contaminants include volatile and non-volatile contaminants. Volatile contaminants are nitric acid, nitrosyl chloride, bromide, water, and nitrous acid.

Less volatile contaminants are sulfuric acid and nitrososulfuric acid. Non-volatile contaminants are typically metal salts of metals that were leached from container walls or flow control components, such as valves and filters.

5.8.1.1 Iron Contamination in Dinitrogen Tetroxide or MON

The most troublesome contaminant in dinitrogen tetroxide is partially hydrolyzed iron(III) nitrate or iron(III) nitrosyl tetranitrate, formed by the interaction of nitric acid with tank walls, surface tension screens, and filter screens. This material can form a gelatinous deposit in flow orifices, causing flow decay. For further investigations into causes of flow decay in N_2O_4 systems, see Section 6.3.

Appendices to a final report on flow decay [273] contain three different methods for the analysis of iron in NTO, including 4,7-diphenyl-1,10-phenanthroline or 1,10-phenanthroline spectrophotometric methods and a flame atomic absorption method.

The contaminants found in N_2O_4 causing flow blockage in ground service equipment at the launch site and collected on filter screens have been analyzed and identified as nitrosyl tetranitratoferrate $[NO]^+[Fe(NO_3)_4]^-$ [298, 299]. The stainless steel filter containing the contaminant was obtained from Vandenberg Air Force Base. Approximately 18000 gallons of N_2O_4 had been passed through this filter, which was located in the transfer line between the oxidizer transport trailers and the ready-storage vessel. An authentic sample of this material was synthesized in the laboratory for comparison purposes. The isolation and identification of this compound in actual NTO or MON propellant samples is difficult because it is very hygroscopic. Upon contact with moisture, it is readily hydrolyzed to hydrated iron(III) nitrate. It can be sublimed under vacuum, but it decomposes to a similar compound $[NO_2]^+[Fe(NO_3)_4]^-$ [271].

Some impurities have a pronounced effect on the corrosivity of N_2O_4 toward metals [300]. The main impurities in dinitrogen tetroxide are iron compounds leached from stainless steel container walls.

A comparison of two recommended methods for iron analysis, the Rocketdyne procedure MRTB 60-519 and the NASA procedure TR-248-001, showed that the Rocketdyne procedure worked well for iron contents above 0.5 mg Fe/kg N_2O_4 , but the NASA procedure, which used a hermetically closed system, could analyze iron content over a wider range of concentrations [301]. Either method would give erroneous results if iron existed in the form of a volatile iron compound (e.g., iron carbonyl or iron nitrosyl). It was shown that under the conditions of the NASA method, there are no volatile iron compounds in the samples. In order to test the suspected volatility of iron compounds, a sample of nitrosyl iron(III) tetranitrate had to be prepared, which would then be used to dope pure, iron-free NTO to generate known iron concentrations in the oxidizer [302]. The chosen method for preparation of nitrosyl iron(III) tetranitrate was the reaction of iron pentacarbonyl with dinitrogen tetroxide. The product contained ~19% Fe, while the theoretical iron content should have been 16.7% Fe.

The iron content in green dinitrogen tetroxide can be determined by flame atomic absorption spectrometry [303]. By optimizing working-condition and sample-handling methods, the detectable concentration of iron is 0.060 mg/L, the recovery is 98.8–101.4%, and the relative standard deviation is less than 2%.

5.8.1.2 Halogen Contamination in Dinitrogen Tetroxide or MON

One of the most troublesome contaminants in NTO is chloride in the form of nitrosyl chloride. The methods for chloride analysis in NTO have been improved by researchers at NASA's WSTF over the years [304, 305].

The military-specification method for chloride analysis in MON does not differentiate between chlorine and bromine and may not detect bromine if it is present in the form of bromate. It appears that bromide in MON becomes oxidized to bromate during hydrolysis with sodium hydroxide solution, and bromate escapes the analysis. A more accurate analysis and separation of chloride, bromide, and bromate is possible if a known amount of potassium iodide is added to the sample to be analyzed. Iodide reduces bromate to bromide. Total alkaline soluble chlorine and bromine containing compounds can be individually quantified using a solution procedure adapted from a WSTF procedure and an inductively coupled plasma-mass spectrometry (ICP-MS) procedure developed at TRW [117]. The TRW-developed ICP-MS method used to quantify these halogens is different from the methods described in the military-specification and the WSTF procedure. The sample is prepared by hydrolyzing 5 g of oxidized MON-3 in 50 mL of 5-N sodium hydroxide. The TRW method differentiates chloride and bromide using mass spectrometry, whereas the WSTF method differentiates these compounds using a potentiometric titration. In both cases, bromine-containing compounds were found to be the major halogen containing compounds present in some MON samples. The military-specification method, which is a simple silver nitrate titration, determines only the combined alkaline soluble chlorine and bromine-containing compounds concentration reported as a single chloride result, and bromate may be missed. The titration method detected 33% less alkaline soluble bromine.

5.8.1.3 Equivalent Water Present as Nitric Acid

Water is a common impurity in NTO or MON oxidizer, but the analytical problem it presents is that it is not present simply as H_2O but reacts with the nitrogen oxides that are present to produce both nitrous and nitric acid. Thus, the analysis of total water content must take into account these acids. The analytical methods commonly used consider the nitric oxide concentration and a measured value for the nitric acid, found by near-IR spectrophotometry. With knowledge of the equilibrium constants for the reactions forming the nitrous and nitric acids, and the disassociation of nitrous acid into nitric oxide and dinitrogen tetroxide, the total "water equivalent" can be calculated.

The analytical results of corresponding water in green dinitrogen tetroxide (MON-1) may be distorted by other effects. It has been suggested to revise the Chinese national military standard for MON-1 to avoid such difficulties [306].

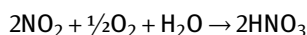
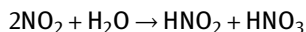
The method for determining equivalent water in NTO or MON by gas chromatography may have a number of shortcomings and is fraught with uncertainties about the form in which the water exists in the oxidizer, most of it being in the form of HNO_3 , which is difficult to run through a gas chromatograph without decomposition and cor-

rosion [307]. In order to determine the uncertainty of the equivalent water content in NTO and MON by gas chromatography, the equivalent water content of NTO was measured by SC-200 gas chromatograph apparatus according to the equivalent water-content chromatography measurement method specified by GJB 1964-1994 and GJB 1673-1993. GJB 1964-1994 and GJB 1673-1993 are analysis methods used at the Xichang Satellite Launch Center in Liangshan, China. The standard uncertainty, combined uncertainty, and expanded uncertainty were analyzed and evaluated, applying the measured data. The combined standard uncertainty was 0.0327%, and the expanded uncertainty was 0.065% (coverage factor $k = 2$).

5.8.2 Assay Methods for Dinitrogen Tetroxide

The procurement and transfer of rocket propellants is controlled by quality-control specifications that are frequently issued by the U.S. Armed Forces or other government agencies, such as NASA. The main document controlling the quality of dinitrogen tetroxide is MIL-P-26539, which has undergone many revisions during the past several decades. Table 41 in Section 5.8.8 summarizes the dates and scope of some of the most recent changes to this specification.

The most undesirable contaminant in N_2O_4 is water, which is readily absorbed from the air if the container is not securely closed; also, water is sometimes inadvertently left behind in freshly washed but poorly dried containers and transfer hoses. Water and N_2O_4 or NO_2 will gradually react, first forming nitrous acid and nitric acid and later, in the presence of air, forming more nitric acid, which causes the propellant to become more corrosive toward many materials of construction.



This is the same reaction that forms the basis for the production of nitric acid on an industrial scale. When reporting the results of analyses of NTO and reporting the water content as % H_2O , one must realize that the water will most likely have reacted to form HNO_3 , which in turn forms adducts such as $HNO_3 \cdot xH_2O$ or $HNO_3 \cdot xN_2O_4$. The water should be reported as “water equivalent.”

For the quality control of NTO at the rocket test site or in the field (military applications), direct-reading methods that provide an instant readout of the results are preferred [308].

At one time, a widely used but very crude method for the estimation of water in NTO was the evaporative method given in MIL-P-26539B. The procedure is to pass a stream of dry nitrogen through a known volume of N_2O_4 at 272–273 K (28–32 °F). N_2O_4 is evaporated until the concentration of residual water exceeds its solubility and the mixture takes on a cloudy appearance. The volume is then noted and correlated with

the initial water content. This crude method requires an experienced operator to determine the end point [309].

The old military-specification procedure for water analysis was based on the evaporation of dinitrogen tetroxide at 273 K (0 °C) with dry nitrogen gas until a two-phase system was obtained. At this point the turbid residue contains 1.6% water. The percentage of water present was calculated from the volume of the two-phase residue and the starting volume. It was assumed that only dinitrogen tetroxide and nitrogen dioxide were lost when dry nitrogen was bubbled through the liquid dinitrogen tetroxide at 273 K (0 °C). This may not be such an unreasonable assumption considering that the water in the dinitrogen tetroxide is present mostly as nitric acid. However, this assumption does not allow for the possibility of mechanically carrying away some of the nitric acid as a fine mist.

An assay method for N_2O_4 (after complete oxidation of all N_2O_3 and NO) in MON described in MIL-P-27408A, MIL-P-26539C, and MIL-PRF-26539E seals a weighed amount of the oxidizer in a glass vial and breaks it under 100 mL of water and 20 mL of 30% hydrogen peroxide in an Erlenmeyer flask with a ground-glass stopper (iodine number flask). The N_2O_4 is thereby oxidized to HNO_3 , which is then titrated acidimetrically with 0.5 N NaOH using methyl red or bromothymol blue as the indicator.

For the analysis of nitric oxide-dinitrogen tetroxide mixtures, the mixture of nitric oxide and nitrogen dioxide is first absorbed in sulfuric acid, and then the sum of nitric acid and nitrosyl nitrogen in solution is determined by means of a nitrometer, and nitrosyl nitrogen is analyzed by titration with a solution of potassium permanganate [310]. A recovery of 99.8% was obtained for pure dinitrogen tetroxide and 99.8% for pure nitric oxide. For synthetic mixtures containing 4 to 10% nitric oxide, the recoveries were 99.1% for nitric oxide, 99.8% for dinitrogen tetroxide, and 99.5% for total nitrogen. The analysis is performed in a system, carefully kept free from air and water, for absorbing the gases and including a special chamber for breaking ampoules containing the samples. The method is applicable to the assay of nitric oxide, dinitrogen tetroxide, and mixtures containing up to 50 mol-% of nitric oxide.

5.8.3 Gravimetric Analysis Methods for Dinitrogen Tetroxide

Due to the poor accuracy and the time-consuming need to dry and weigh the crucibles to constant weight before the analysis, gravimetric methods would be the least favorite of any analytical chemist. Nevertheless, a gravimetric method was once described for the determination of water in dinitrogen tetroxide.

In a gravimetric method for determining small amounts of water in dinitrogen tetroxide, the vapor, in a stream of dry nitrogen, was first passed over anhydrous sodium carbonate at 553 K (280 °C) and then over metallic copper at 873 K (600 °C) [311]. Most of the acidic substances were removed by anhydrous sodium carbonate, and remaining traces of oxides of nitrogen were completely removed by

passage over hot metallic copper. The water released by these reactions was absorbed by anhydrous calcium sulfate and weighed. For samples containing about 0.5% water, the precision of the determination corresponded to a standard deviation of 0.006% absolute. At JPL, the gravimetric weighing of the adsorbed water was replaced by condensing it in a cold trap, followed by gas chromatography analysis [295].

A method in MIL-P-27408A and MIL-PRF-26539E describes a gravimetric method for determining NO in MON containing 10–25% NO. The analysis is done by weighing a sample of MON into a 60-mL stainless steel cylinder, cooling to 273 K, and feeding pure oxygen into the cylinder until oxygen absorption has stopped, thus converting all NO and N₂O₃ to N₂O₄. The percentage of NO is calculated from

$$\text{NO} = \frac{[y - 0.003857(z - \frac{x+y}{1.49})]187.5}{x} - 0.15$$

where NO = mass-% NO, x = sample mass in g, y = oxygen mass in g, and z = volume of the cylinder in mL.

5.8.4 Electrochemical and High Frequency Microwave Analysis Methods for Dinitrogen Tetroxide

The water or nitric acid content of N₂O₄ can be measured with an electrical conductivity method as long as no other contaminants are present [312, 313]. This method is suitable only for less precise measurements. For more accurate determinations of the nitric acid content, one slowly evaporates all N₂O₄ and the eventually present N₂O₃ and then titrates the remaining, non-volatile nitric acid acidimetrically with standardized sodium hydroxide solutions.

The water content of NTO or MON can be measured by determining the dielectric constant ϵ by oscillometry [314]. The dielectric constant of a material is a measure of its polarization in an electric field, which induces electron shifts in its atoms, and of the statistically preferred orientation of electrically unsymmetrical molecules in an electric field. Water has one of the highest dielectric constants, $\epsilon = 80.4$ at 293 K (20 °C). NTO has a low value, $\epsilon = 2.5$, at 288 K (15 °C), and mixtures of the two compounds have intermediate values. The wide spread between the two values permits the accurate measurement of small amounts of water in N₂O₄ as a function of the dielectric constant. The instrument was calibrated with samples containing known amounts of water up to 1.5%. In operation it is convenient to have two oscillometer cells, one for benzene with a known amount of water and the other for the N₂O₄ sample to be analyzed.

5.8.5 Optical and Absorption Spectrophotometric Analysis Methods for Liquid Dinitrogen Tetroxide

There are only a few spectrophotometric analysis methods for the measurement of assay or contaminants in liquid N_2O_4 . Most spectrophotometric methods deal with the analysis of gaseous NO_2 in air, which is summarized in Section 5.8.5.

Chloride in green dinitrogen tetroxide can be determined by ammonia absorption spectrophotometry [315].

5.8.5.1 Infrared Spectrophotometric Analysis Methods for Liquid Dinitrogen Tetroxide

The specific band assignments for contaminants in N_2O_4 are $1.470\mu\text{m}$ for HNO_3 , $1.448\mu\text{m}$ for HNO_2 , and $1.404\mu\text{m}$ for H_2O . The $1.404\mu\text{m}$ H_2O band is well resolved but is in a region where the instrumental background under high sensitivity distorts the spectrum. The $1.448\mu\text{m}$ HNO_2 and $1.470\mu\text{m}$ HNO_3 bands overlap sufficiently so that it is difficult to detect and determine small amounts of HNO_2 in the presence of larger amounts of HNO_3 .

Water (assumed to have completely reacted to form nitric acid) in liquid dinitrogen tetroxide can be determined by measuring the IR absorbance of the nitric acid overtone peak at $1.47\mu\text{m}$ [316]. Nitric oxide must first be converted to NO_2 , and all H_2O or HNO_2 must be converted to HNO_3 . The method is applicable to water contents in the 0.01–0.17 mass-% H_2O range and is capable of detecting as little as 0.002 mass-% H_2O . If HNO_2 is not completely removed, an HNO_2 absorption peak will show up at $1.447\mu\text{m}$.

Solutions of N_2O_5 , N_2O_4 , and HNO_3 in methylene chloride can be analyzed by IR spectroscopy [317].

An IR spectrophotometric method for analysis of HNO_3 in NTO and MON is described in MIL-PRF-26539E. A scan in the near-IR between 1300 and 1650 nm (7692 and 6060cm^{-1}) will reveal an HNO_3 peak. The baseline can be found by connecting the minima at 1430 and 1615 nm (6993 and 6192cm^{-1}) with a straight line. The HNO_3 peak height is measured from this slanted baseline. The absorption coefficient of HNO_3 is 0.178.

MON mixtures with NO concentrations from 1% to 5 mass-% are common in current spacecraft applications. Higher NO concentrations, as high as 30 mass-% NO, are not as common yet but are being considered for hybrid and bipropellant rocket systems to be used in future missions to/from Mars and the moon, mainly due to their low freezing points and high performance. It may be possible to analyze the NO content of MON-25 or MON-30 by FTIR of diluted, evaporated samples of this oxidizer. The analysis of different compositions of MON oxidizers was investigated using a Cary 680 FTIR spectrometer equipped with a 10-m heated gas cell. Calibration curves were obtained for NO and NO_2 by themselves before trying to analyze NO/ NO_2 mixtures [174]. Preliminary tests provided calibration curves for the main components of MON, namely

NO and $\text{N}_2\text{O}_4/\text{NO}_2$. Calibration curves showed linear variations of absorbance with concentration for both components, which was in accordance with the Beer-Lambert law and is the basic requirement for FTIR analysis as a tool to examine the quality of unknown MON compositions. For the gaseous phase, MON-X samples will have to be diluted down to at least the maximum parts per million value obtained in this study (around 500 ppm) to provide meaningful absorbance data before one can use the calibration curves for individual gases. No N_2O_3 appears to survive in the vapor phase.

5.8.5.2 UV/Visible Spectrophotometric Analysis Methods for Liquid Dinitrogen Tetroxide

Dinitrogen trioxide in N_2O_4 is measured as N_2O_3 , but it is calculated as NO by measuring its broad electronic absorption band peaking at 700 nm. At high NO concentrations, the trailing of this absorption band extends into the 1550–1350-nm near-IR region where the protonated species are measured, and corrections, therefore, must be made. Additionally, at high NO concentrations, the 700–900 nm absorbance difference is too high to be read within the 0–1.0 absorbance range available.

Analysis of mixtures containing all oxides of nitrogen is very complicated. Nitrogen dioxide and associated dinitrogen tetroxide can be determined by UV absorption at 394 nm, where other oxides of nitrogen are known to be transparent [318]. Other remaining components can later be determined by mass spectrometry.

Small amounts of nitric oxide, when dissolved in liquid dinitrogen tetroxide, exist as dinitrogen trioxide N_2O_3 . The nitric oxide content of such solutions can be determined by measuring the intensity of the green color of the N_2O_3 at 273 K (0 °C) at 700 nm. This method, described in MIL-P-26539C as an alternate method, requires a specially designed cell that is constructed of materials resistant to dinitrogen tetroxide, capable of being cooled to and maintained at temperatures near 273 K (0 °C), leak-proof under moderate pressure and vacuum, and having a path length suitable for analysis of samples containing 0–1.5% nitric oxide [319].

If a MON sample is dissolved in aqueous KOH solution in the absence of oxygen, the resulting nitrate:nitrite ratio in the aqueous solution can be determined by UV spectrophotometry and can be used to backtrack to the $\text{N}_2\text{O}_4:\text{N}_2\text{O}_3$ ratio in the original sample [320].

Chloride in NTO or MON can be determined by slowly flowing approximately 10 g of the evaporated oxidizer into a gas-wash bottle filled with 50 mL of deionized water. The solution is then rinsed into a 1000-mL volumetric flask and neutralized with concentrated ammonia to an end point determined with dinitrophenol indicator. The volumetric flask is filled to the calibration mark with deionized water and mixed. An aliquot is reacted with iron(III)ammonium sulfate and mercury(II)thiocyanate. The reaction of chloride with mercury(II)thiocyanate precipitates insoluble mercury(II)chloride and releases thiocyanate ion. The red color of iron(III) thiocyanate is

then measured in a spectrophotometer at 460 nm, and the absorption is compared to concentrations in a previously prepared calibration chart.

This method is described in MIL-P-27408A, MIL-P-26539C, and MIL-PRF-26539E. A similar method can be used to determine chloride in hydrazine.

5.8.5.3 Emission Spectrophotometric Analysis Methods for Dinitrogen Tetroxide

Most methods discussed here are absorption spectrophotometric methods. However, there are also emission spectrophotometric methods for analysis of other contaminants in N_2O_4 that are equally well applicable to oxidizers like N_2O_4 and fuels like UDMH. Excessive contamination by alkali metals in either propellant would cause a high ionization density in the exhaust plume. The plume becomes impervious to radio signals, and radio telemetry may be disturbed by radio wave attenuation. The alkali metals in NTO can be determined by flame spectrophotometry [321]. Nowadays the same would be done more accurately with inductively coupled plasma emission instead of flame emission spectrophotometry.

The iron content of NTO can be determined by atomic absorption spectroscopy using the 248.8-nm resonance line of Fe [322]. A linear calibration chart was created for iron concentrations up to 6 ppm. The sensitivity for iron in NTO was five times better than that for iron dissolved in water.

5.8.5.4 Gas Chromatographic Analysis Methods for Dinitrogen Tetroxide

Because nitrogen dioxide reacts with most organic oils and porous polymers used as stationary phases in gas chromatography, it has been proposed to convert all NO_2 to HNO_3 and NO by reacting it with water that is pre-adsorbed on the surface and in the pores of a molecular sieve column [323]. NO does not react with most stationary phases/partitioning liquids used in gas-liquid chromatography. One mol of NO is formed for each three mols of NO_2 converted. The HNO_3 remains adsorbed on the molecular sieve along with the water. Oxygen has to be excluded from the sample gas and the carrier gas.

An electron capture detector was used in a gas chromatograph to measure parts per million quantities of nitrogen dioxide in a ternary mixture of nitrogen, oxygen, and nitrogen dioxide [324]. For concentrations of nitrogen dioxide from 5 to 150 ppm and for oxygen present to the extent of 9% by volume in nitrogen, the standard deviation of the best calibration curve through the points showing response versus concentration was 2 ppm, compared to about 3 ppm for wet chemical techniques. The main advantages of gas chromatography are the short time for analysis and the small sample size (0.5 mL) required.

Liquid dinitrogen tetroxide can be analyzed for water content by passing it through hot copper shavings at 1073 K (800 °C) contained in a column wherein all nitrogen-containing and hydrogen-containing compounds including HNO_3 and HNO_2

are converted quantitatively to dinitrogen and water [325, 326]. The effluent from the column is then passed into a gas chromatograph and separated on a Porapak-Q column, where the amount of water initially contained in the nitrogen tetroxide can be determined by integrating the area under the peak or, for narrow peaks, by the peak height method. Less than 10 minutes is required for an analysis, and as little as 0.1 g of water (0.01 mass-%) can be determined reproducibly. Organic compounds or dissolved carbon dioxide in the sample can also be determined by this method. If there are organic contaminants, the H_2O content detected must be corrected for H_2O resulting from the combustion of organic contaminants.

The gas chromatographic determination of water content in NTO or MON is fraught with uncertainties about the form in which the water exists in the oxidizer, most of it being in the form of HNO_3 , which is difficult to run through a gas chromatograph without decomposition and corrosion [307].

Another method to determine NO, CO_2 , N_2O , and NOCl in dinitrogen tetroxide has been suggested [327].

5.8.5.5 Mass Spectrometric Analysis Methods for Dinitrogen Tetroxide

During an effort to identify contributors to metal corrosion, the analysis of non-volatile residue in MON was hampered by the small amount of residue available for analysis, only 10–20 mg/L. Subsequently, the inlet of a mass spectrometer was modified to facilitate sample handling and to analyze the samples for NO content [328]. A method was developed to determine nitric oxide in N_2O_4 using a mass spectrometer. This was accomplished by some modification of the inlet system on the instrument and by the development of suitable handling techniques that prevented the loss of NO.

5.8.5.6 Nuclear Magnetic Resonance Analysis Methods for Dinitrogen Tetroxide

Researchers at the JPL developed an NMR procedure for the rapid quantitative analysis of water in dinitrogen tetroxide and MON oxidizers [195]. This technique was capable of detecting as little as 0.001 mass-% of H_2O (10 μg of water per gram of propellant) and gave results in the concentration range of 0.01–0.02 mass-% with a precision of about ± 0.002 mass-%. Because many samples of NTO/MON contain NO, a separate procedure for oxygen titration of NO prior to NMR analysis for H_2O was developed that gave the NO concentration accurately to within ± 0.05 mass-%. While this method employed the continuous wave method at modest magnetic field strengths, equivalent to resonance at up to 100 MHz, a newer method based on high-field Fourier transform proton NMR offered greatly improved sensitivity suitable for the determination of lower water contents. The newer method used a 250-MHz Fourier transform proton NMR and an internal proton-containing standard, deuteroacetonitrile, HD_2CCN with a known content of 1H, and it was able to analyze water down to 0.003 ± 0.0012 mass-% [329]. Dideuteroacetonitrile is chemically inert to N_2O_4 , but solutions of HD_2CCN in MON

are less stable than those in NTO. Because this method is an absolute method, it does not require calibration prior to analysis. Unlike previous NMR methods, paramagnetic NO does not have to be oxidized prior to analysis. The sample temperature during NMR measurement is not critical; it can be anywhere between 268 and 294 K. The deuteroacetonitrile used as internal standard was 99.5% D₃CCN and contained only a known trace of HD₂CCN. The H proton in HD₂CCN produced a non-binomial quintet at 1.93 ppm. The analysis was performed by distilling a known mass (40 μ L) of dideuteroacetonitrile in trideuteroacetonitrile into frozen NTO at 77 K and sealing the NMR tube. The NMR tube was allowed to warm slowly to room temperature and was then ready for analysis.

NMR spectra were determined for four N₂O₄ samples scanned from 0 to 10 ppm at room temperature [328]. Trimethylsilane was used as the external standard to determine the 0-ppm line, but it could not be used as an internal standard because it reacted with the samples. All samples exhibited one absorption between 8.5 and 11.0 ppm, which was probably from water protons in a highly electronegative environment such as would be provided by NO₂. It would be necessary to introduce an internal standard to determine any variations from one sample to the next.

A comparison of various analysis methods to determine the equivalent water content in dinitrogen tetroxide included gas chromatography, near-IR spectrometry, microwave, and NMR methods. The theory and the application of NMR methods were emphasized in this paper [330].

Equivalent water content in nitrogen tetroxide was determined by NMR spectroscopy (NMRS) using deuteroacetonitrile as internal standard [331]. The linearity range of the method was steady over 0.004–0.39% H₂O. The detection limit (3σ) was $1 \times 10^{-4}\%$. Relative deviations between the results found by the NMRS method and those found by gas chromatography were $\sim 3.8\%$. See also [332, 333].

Electron spin resonance (ESR) studies indicated the presence of several paramagnetic substances in the N₂O₄ samples, which made it very difficult to interpret ESR and NMR spectra.

5.8.6 Rapid Liquid Propellant Analysis Methods for Use in the Field

Rapid analysis methods are needed for use in the field to give a quick go/no go answer about the acceptability of a propellant for a given application [334]. Ideally this would be in the form of a dipstick probe with a direct readout.

Any launch vehicle delay or stacking mishap could potentially lead to the necessity to off-load the propellants from a satellite. This propellant would have to be returned into its transport container. Any off-load operation can potentially compromise the propellant composition, and in this situation, at remote launch sites in Eastern Europe or Asia or on floating launch platforms, there would be no way of determining

any contamination in the propellant without flying a propellant sample back to the home base in Europe or the United States, where chemistry labs with the necessary equipment and operator experience can do an accurate analysis. It was proposed to establish a portable modular laboratory capable of analyzing MON, N_2H_4 , and MMH that could be flown to the remote launch sites where no chemistry laboratory support was available. The mobile laboratory would have to be robust to allow for air transport and be minimal in size to reduce transport costs [335]. The instrumentation would be designed and modified to fit into standard-size air freight cases of approximately 1 cubic meter each, with a maximum of five flight cases required for a “complete” lab.

5.8.7 Analysis of Nitrogen Dioxide in the Air at the Work Place

Dinitrogen tetroxide that leaks into the work room air will quickly evaporate and dissociate into nitrogen dioxide, readily visible by its reddish-brown color. Work room air-analysis instruments for audible alert systems or continuously recording record-keeping are described in the chapter on nitrogen dioxide. In addition to active leak detectors that sound an alarm if a leak is detected, passive leak detectors such as color-changing paint will not only alert the observer but also locate the leak.

5.8.8 MIL and NASA Specifications

The AIAA Special Report [209] contains a first-hand historical account of the evolution of specifications for NTO and MON, quoted here:

One of the original applications for NTO as a rocket oxidizer was the Titan II intercontinental ballistic missile that used brown NTO. About the same time, NASA required an NTO with a lower freezing point for space missions. The requirement led to specifications MIL-P-27408A (1971) for NTO products designated MON-10 and later MON-25 that contained 10 and 25 mass-% nitric oxide, respectively. Sometime later NASA found in the Apollo program, that serious stress-crack corrosion problems occurred with titanium hardware when NTO that contained no nitric oxide was used. To overcome this corrosion problem, NASA created a specification (MSC-PPD-2 and later MSC-PPD-2A) for NTO similar to the military specification except for a requirement that the product contain $0.65 \pm 0.2\%$ nitric oxide (MON-1) to inhibit titanium stress crack corrosion. MSC-PPD-2 and later MSC-PPD-2A were incorporated into the military specification, MIL-P-26539C [336]. When the Minuteman ICBM was developed, the decision was made to use a prepackaged (sealed) liquid bipropellant propulsion subsystem for the fourth stage. The oxidizer chosen was an NTO formulation that contained 0.31 ± 0.2 mass-% nitric oxide designated by Bell Aerosystems as *Minuteman Grade*, Bell Specification 8477-947041. This nitric oxide level was selected to provide an additional margin of safety for long-term storage in stainless steel tankage [337]. Early in the development of the small bipropellant engines for Shuttle reaction control it was determined that the level of nitric oxide should be greater than that for MON-1 to allow for losses caused by repeated depressurization of storage vessels. This led to a decision by NASA to introduce another formulation of NTO containing 2.75 ± 0.25 mass-% nitric oxide, MON-3, which was incorporated

into MIL-P-26539C as Amendment 1. The result of the decisions by various organizations lead to the brief existence of at least five different specification documents for the various NTO formulations in use. The Aerospace Industries Association of America, a group of industrial organizations with a common interest in rocket propulsion, volunteered to consolidate the specifications for brown NTO, MON-1 and MON-3. The efforts resulted in a National Aerospace Standard, NAS-3620 [338], which contained all the requirements and the most recent analytical methods for three formulations of NTO used by the military and NASA [338]. Several years later the Air Force produced a military specification, MIL-P-26539D, a consolidation of NAS-3620 and the military specifications for MON-10 and MON-25.

The performance specification MIL-PRF-26539F is the current (2014) documentation used by the U.S. Department of Defense (DOD) and NASA for NTO procurement [339]. European space agencies and their contractors have developed their own set of propellant specifications for MON [340]. Table 40 is a summary of current and past (expired) propellant specifications for NTO and MON.

Table 40: Current and former military specifications for NTO and MON

Designation	Date issued	Date canceled or superseded	Propellants covered	Remarks
MIL-P-26539C	30 Mar 1970		NTO and MON-1	[336]
MIL-P-26539C amendment 1	1 Mar 1971			
MIL-P-26539C amendment 2	5 Apr 1976		NTO, MON-1, and MON-3	
MIL-P-26539D	28 Aug 1989	7 Oct 1997		
MIL-PRF-26539E	7 Oct 1997	17 Apr 2006	NTO, MON-1, MON-3, MON-10, and MON-25	
MIL-PRF-26539F	17 Apr 2006		NTO, MON-1, MON-3, MON-10, and MON-25	Maximum allowed iron content is 0.5 ppm
MIL-P-27408	31 Jul 1964		MON-10 and MON-25	
MIL-P-27408A	15 Oct 1971	6 Sep 1989	MON-10 and MON-25	[341]

Table 41 lists the purity requirements of NTO and MON according to MIL-PRF-26539F.

Table 41: NTO and MON specification requirements per PRF-26539-F

Composition Color	NTO Reddish- brown	MON-1 Green	MON-3 Green	MON-10 Green	MON-15 Green	MON-25 Green	Test paragraph
N ₂ O ₄ assay, %wt, MIN	99.5	—	—	—	—	—	4.3.3
NO content, %wt, MAX	*	1	3	11	16	26	4.3.2
NO content, %wt, MIN		0.6	2.5	10	15	25	
N ₂ O ₄ + NO, %wt, MIN	99.5	99.5	99.5	99.5	99.5	99.5	4.3.3
Water equivalent, %wt, MAX	0.17	0.17	0.17	0.17	0.17	0.17	4.3.4
Chloride content, %wt, MAX**	0.04	0.04	0.04	0.04	0.04	0.04	4.3.5
Non-volatile residue, mg/L, MAX	—	10	10	10	10	10	4.3.6
Iron content, ppm wt, MAX	—	0.5	0.5	0.5	0.5	0.5	4.3.7
Particulate, mg/L, MAX	10	10	10	10	10	10	4.3.8

* The NO content shall be limited to that which does not change the specified reddish-brown color of the propellant

** The chloride test does not need to be performed on any propellant type if the material was manufactured using the ammonia oxidation process

5.8.9 Round-Robin Analysis Results

An industry-wide and government-wide round-robin analysis exercise for military-specification and NASA-grade MON showed the need to standardize the methods and equipment in order to obtain reproducible and comparable results [342]. Twenty-two stainless steel cylinders were fitted with two valves on either end and were passivated with MON-3 for 20 weeks. Then 11 were filled with MON-1 and another 11 were filled with MON-3, and they were sent to participating laboratories to be analyzed for N₂O₄ assay, chloride, water, NO, and iron in triplicate as prescribed by NAS-3620. The results, reported by ten laboratories, were analyzed using statistical methods. Chloride analyses had the least outliers of any method. The iron analysis showed good repeatability within a laboratory but poor reproducibility between laboratories. The NO analysis had inhomogeneous variances for both MON-1 and MON-3, and two laboratories reported results that were outside the 95% confidence interval.

Since April 1996, dinitrogen tetroxide tank cars have been sampled and analyzed as soon as they arrive at NASA Kennedy Space Center and prior to passing the oxidizer

through a molecular sieve filter in preparation for loading on the Space Shuttle orbital maneuvering and reaction control systems [343]. Significant discrepancies were sometimes noted between NASA’s results and the manufacturer’s certification accompanying each shipment. Sometimes the propellant was “out of spec,” most often due to low NO content.

6 Materials of Construction for Dinitrogen Tetroxide

The presence of a few tenths of a percent of water in NTO or MON leads to rapid corrosion failure of containing metals. For all applications, the water content must be carefully controlled.

Dinitrogen tetroxide with and without the addition of small amounts of N₂O₃ is the most important storable oxidizer; consequently, a lot of work has been conducted to select the proper materials of construction. The following summaries in Table 42 provide a good starting point in the study of this topic. Most of the publications date back to the time when the Titan-II ICBM was developed and fielded in launch silos. Some of these reference publications need to be on the bookshelf of any spacecraft designer working with storable bipropellants.

Table 42: Summary of literature citations on materials compatibility with dinitrogen tetroxide.

Author	Year	References
Alley, Hayford, and Scott	1961	[344]
Bender	1963	[345]
Berman	1962	[346]
Suarez-Alfonso, Chambers, and Hatz	1961	[60]
Suarez-Alfonso, Chambers, and Hatz	1961	[66]
Liberto	1961	[347]
Liberto	1962	[348]
Liberto	1963a	[349]
Liberto	1963b	[350]
Letos	1970	[351]
Wright	1977	[2]
Swartz and Smith	1991	[352]
Li and Luo	1993	[353]
Wanhill and Windisch	2018	[354]

A design guidebook on material compatibility with space storable propellants contains sections on NTO/MON and also sections on MMH, B₂H₆, F₂, OF₂, and FLOX [355].

6.1 Compatibility Test Methods

Methods for testing the compatibility of existing and new materials of construction have been developed over the years by either the manufacturers of the propellants or by the rocket propulsion industry and government laboratories in support of the user community. This applies to materials testing for compatibility with NTO in particular because it is one of the more corrosive oxidizers.

In the 1960s it was considered necessary to standardize immersion test methods used at the many different laboratories throughout the United States, and the American Society for Testing and Materials (ASTM) issued specifications describing recommended methods for testing with dinitrogen tetroxide and its blends with dinitrogen trioxide [356].

A standardized test for the gross compatibility of materials with NTO as a function of exposure time and temperature is the immersion test described in *Reactivity of Materials in Aerospace Fluids (Test 15)* (NASA 1991). The unstressed material is immersed in NTO liquid at 344.1 K (160 °F) and is held for 48 h or until the pressure exceeds the normal vapor pressure of the NTO at the test conditions. Following the immersion, the samples are examined for weight loss, changes in surface appearance, and tensile properties.

One of the visually most explicit methods to study corrosion of metals at the molecular level is the use of a scanning tunneling electron surface microprobe [357].

Liquid-fueled missiles in submarines have been the cause of numerous submarine accidents in the Russian fleet (e.g., K-219, Project 667A in 1986). Corrosion is an important factor in missile reliability. Therefore, corrosion testing of the materials used to build these missiles has to be done beforehand, and it would be desirable to accelerate these tests in the laboratory. The service environment of submarine-launched missiles may directly affect their life span. An equivalent conversion method is used to establish the relationship between the corrosion equivalent acceleration and actual corrosion. A three-dimensional digital video microscope was adopted to observe the corroded surface of the metal specimens [358].

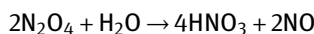
6.2 Corrosion of Metals in Dinitrogen Tetroxide

The selection of metals for propellant tanks and components that will be wetted by NTO or MON for long periods of time (decades) requires a thorough understanding of the mechanism of corrosion and the roles played by various contaminants in the oxidizer. There is sufficient published information on the corrosion of metals by NTO/MON to fill a book in its own right. Only a sampling of the most prominent publications in the available literature is offered here.

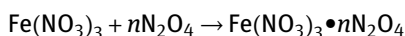
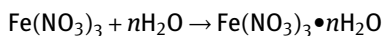
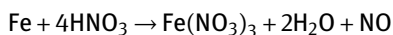
Some of the Material Safety Data Sheets for N_2O_4 written by chemical suppliers state, “Anhydrous nitrogen dioxide is non-corrosive to most metals at normal temperatures. It does corrode copper and its alloys.” This is surprising, considering the many corrosion problems the aerospace industry has had in dealing with this oxidizer. This statement was probably written by a marketing representative and not by a chemist.

6.2.1 Corrosion Mechanisms in Dry or Moist Dinitrogen Tetroxide or MON

The reaction that takes place in moist NTO in contact with metals is due to the formation of nitric acid from N_2O_4 and H_2O :



The nitric acid then will attack the metal and form metal nitrates and their adducts with N_2O_4 or H_2O :



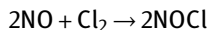
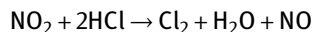
Because water and nitric acid are regenerated during some of the reactions, the corrosive attack will continue indefinitely [359]. The corrosion products can be in solution or in suspension in the NTO or MON oxidizer. The solubility of the corrosion products increases with the NO content of the oxidizer. A recognized method for recovery from flow-decay problems in an operating system is to raise the propellant temperature so that the contaminants go back into solution and remain in solution.

The corrosion of chromium/iron-alloys (50–80% Cr) by NTO at 300–400 K and 0.1–16 MPa results in the formation of an oxide crust layer consisting of the oxides of both elements [360]. The rate of corrosion is distinctly higher than that of Cr-Ni-Mo steels such as the Russian 09Kh16N15M3B. Annealing of the Cr/Fe steel at 1170 K can change the alloy structure and reduce the rate of corrosion, but only by a small amount. At higher temperatures (870–1270 K), the corrosion results in the formation of solid and volatile chromium oxides. The dominant effects on the rate of corrosion are due to the original O, N, and C content of the alloy.

6.2.2 Corrosion Effects of Chloride in Dinitrogen Tetroxide or MON

Chloride inadvertently introduced into dinitrogen tetroxide during manufacturing or transfer may accelerate corrosion of stainless steels and may cause stress corrosion in titanium alloys. Some degreasing solvents contain chlorine, and residues of degreasing solvents in a system that is later filled with NTO or MON will cause serious problems.

Chloride introduced as HCl or FeCl₃ will first be oxidized to free chlorine and then quickly convert to nitrosyl chloride NOCl, which is very volatile (boiling point 267.6 K [−5.5 °C]) and is totally soluble in NTO or MON.



The presence of chloride will accelerate the rate of iron solution from stainless steel in NTO or MON. Since the chloride is regenerated in the process, one atom of chloride will be responsible for dissolving many atoms of iron. Once the concentration of Fe(NO₃)₃•1.5N₂O₄ exceeds saturation, flow-decay problems may ensue.

Specifications MIL-P-26439D or NAS-3620 limit the amount of allowable chloride to 0.040% (400 ppm) maximum. It was surprising to see that a number this high is allowed. It seems that some NTO/MON users have instituted tighter chloride limits at the point of end use. There have been discussions about lowering the tolerable chloride levels in future revisions of the specifications.

It seems there were some incidents in which residual cleaning fluids (Freon-TF, Freon-PCA) contributed to metal corrosion in both NTO and hydrazine. Sometimes bromide may also have been present and was not recognized as such. Bromide would be just as bad as chloride. There would be no impact on propellant performance as long as chloride content does not exceed the specification limits. See also [361].

Chloride and other impurities have a pronounced effect on the corrosivity of N₂O₄ toward metals [300]. Water in N₂O₄ caused severe corrosion of Al-6061 or CRES-347, while the effect of NOCl or Cl[−] impurities on unstressed specimens was negligible. Ti-6Al-4V was much more resistant to attack by N₂O₄ than the other two metals. Possible corrosion mechanisms were proposed.

6.2.3 Electrochemistry of Corrosion in Dinitrogen Tetroxide or MON

Corrosion of metals is an electrochemical process that is enhanced in the presence of galvanic couples of elements with different electronegativity or where metals are separated by phase segregation in the heat-affected zone of welds. The difficulty with measuring polarographic potential in N₂O₄ is that the electrical conductivity of the electrolyte is very low, often below the threshold of sensitivity of commercially available potentiostats. Since 1978, advances in electrochemical instrumentation have enabled short-term, accelerated tests. The idea of using electrochemical techniques to study corrosion phenomena follows from the fact that corrosion phenomena can be explained in terms of electrochemical reactions. A unique advantage of electrochemical techniques is that they can yield kinetic and mechanistic information about processes occurring at the interface between material and solution. The electrochemical

information is obtained in a relatively short time and can subsequently be used to predict corrosion rates and compatibility.

The application of electrochemical compatibility test methods to metals exposed to N_2O_4 was difficult because it was found that pure N_2O_4 is not sufficiently conductive to permit electrochemical measurements to be carried out [192]. Researchers used electrochemical measurements in a limited potential region and showed that the polarization resistance measurements were in good agreement with the corrosion rate data obtained by weight loss and solution analysis for long-term tests. It was necessary to add an excessive amount of water in the concentration range of 10–11 mass-% in order to obtain compatibility data via the electrochemical method. This concentration corresponds to the high-density acid phase of the $\text{N}_2\text{O}_4/\text{H}_2\text{O}$ system. Above 1–2 mass-% water, a small portion of the high-density acid phase is formed, which can produce localized corrosion. It was suggested that corrosion in the high acid phase should be considered for further study even though the overall water concentration was quite low.

Electrochemical techniques for evaluating the long-term compatibility of liquid propellants in various containment materials require that the liquid and containment material be electrical conductors, that the exchange current be measurable, and that the propellant decomposition mechanism be known [362]. The time base can then altered by electrolysis of the system at some multiple of the natural decomposition rate. As a result, a simulated time scale can be achieved in which the propellant decomposition rate can be predicted for up to 15 years, while the actual time required for the tests is on the order of only 1–2 months, depending on the particular metal tested.

Electrochemical impedance spectroscopy was tested as a useful tool for the study of corrosion in electrolytes, even poorly conducting electrolytes such as dinitrogen tetroxide and hydrazine [363–366]. Although the methods in poorly conductive media like hydrazine operate at the limit of sensitivity for commercially available potentiostats, the selection of proper electrode geometry and the application of interrupter and feedback techniques enabled researchers to gain insight into the electrochemical processes leading to corrosion at the electrolyte-metal interface. The tests included CRES-430 with MON-1 spiked with water (0.19% H_2O), giving a conductivity high enough to permit some direct current (DC) measurements required for determination of approximate Tafel slope values, as well as the alternating current (AC) measurements, CRES-304L with MON-10 and Al-6061 with the same “MON-1” (actually NO-1.6%) oxidizer. In all cases, the electrochemical values for corrosion rates agreed to better than an order of magnitude with the (not exactly comparable) results from standard metal dissolution analysis, results that became available only after a much longer exposure time.

Theoretical studies predicted that with stainless steel/titanium couples immersed in NTO, the iron would act as a sacrificial anode, protecting the titanium it is in contact with. This would result in large amounts of iron going into solution but eventually exceeding the solubility in NTO and causing flow decay. A study of the corrosion of com-

ponents of a surface-tension PMD in the Intelsat VII propulsion subsystem used AC impedance measurements, immersion tests with chemical analysis of off-loaded propellant, and surface examination of exposed specimens to ensure the compatibility of the tank and its PMD with MON-3 for a 7-year satellite mission [367]. The following components were tested by themselves and in electrical contact with the other metal:

- CP Ti screen
- CRES-304L screen
- CP Ti foil (frame) attached to CP Ti screen
- CP Ti foil (frame) attached to CRES-304L screen
- Ti-6Al-4V tubing
- CRES-304L tubing
- Ti-6Al-4V tubing attached to CRES-304L tubing

All tests were conducted at 305 K (32°C; 90°F) and continued in three batches for 44, 90, or 180 d. The surface-to-volume ratios depended on the geometry of the specimens being tested, and they varied widely. The off-loaded propellant was filtered through a stack of Teflon filter membranes in which the first filter's pore size was 5 μm and the second and third filters' pore size was 0.2 μm . The exposed metal specimens were examined by optical microscope, scanning electron microscopy (SEM), electron spectroscopy for chemical analysis (ESCA), and Auger. Auger electron spectroscopy was done repeatedly on the same area of the specimen after intermittent ion etching to obtain element concentration profiles through the surface layers. Altogether, the tests demonstrated that the materials selected were satisfactory for the intended 7-year mission. Theoretical studies predicted that iron in contact with titanium alloys would act as a sacrificial anode, protecting titanium. The main concern was whether the iron concentration would exceed the solubility limit before the end of the 7-year mission.

Electrochemical methods for accelerated compatibility measurements of metals in NTO, MON, or nitric acids are DC polarization and AC impedance measurements [368]. These methods are supplemented by visual examination of corroded specimens under an optical microscope or by SEM, Auger, and ESCA surface analysis methods [369].

6.2.4 Corrosion Inhibitors for Dinitrogen Tetroxide

MON is used instead of pure NTO to prevent stress-corrosion cracking in titanium and steel tanks. Stress corrosion can be avoided by adding N_2O_3 to N_2O_4 .

In analogy to IRFNA, initial plans were to inhibit corrosion in NTO by adding a fluorine-containing oxidizer, F_3NO , but storability results showed that F_3NO is not compatible with NTO at elevated temperatures [370]. FNO_2 was substituted as the inhibiting fluorine oxidizer, and this propellant system was then called INTO-2. Its constituents were found to be compatible in the short term with most metals at 343 K (70°C), and long-term and short-term corrosivity tests were initiated. Results of 7-d

compatibility tests with non-metallics were completed in NTO, INTO-1, and INTO-2 and indicated that INTO-2 was more compatible than INTO-1 with the materials studied. There was little difference between NTO and INTO-2. INTO-2 was prepared by the reaction of fluorine with NTO. Fluorine reacts with water, and the resulting mixture was shown to react with intentionally added water, bringing the water equivalent down to 0.03 mass-%.

Corrosion tests of steel and aluminum alloys were conducted in wet NTO, dry NTO, and dry NTO + HF at ambient temperature for 30 d and for 20 months, and at 343 K (70 °C) for 30 d [371]. A definite passivation layer was noted both visually and by weight change on the aluminum samples exposed to INTO made from dry NTO. Storability tests of INTO in stainless steel, aluminum, and nickel containers at 343 K (70 °C) for 4 months showed no apparent change in the composition of the propellants. The electrical conductivity of INTO prepared from wet and dry NTO was 3.4×10^{-11} and $4.0 \times 10^{-11} \text{ ohm}^{-1} \text{ cm}^{-1}$, respectively.

Storability tests were conducted on INTO-2 at ambient temperature and at 343 K (70 °C) in aluminum and iron tanks of 10 to 18-gallon volume [372]. Two 24-gallon titanium 6Al-4V tanks that were to be tested during the program failed while fluorine was being bubbled into them to form FNO₂. This indicated that INTO is not storable in titanium 6Al-4V when formed *in situ*. Titanium 6Al-4V specimens were uniaxially stressed to 90000 psi and stored in INTO at ambient temperature and 343 K (70 °C) for 43 d. Stress-corrosion failure did not occur.

Detonation propagation, U-tube adiabatic compression, and drop-weight impact testing sensitivity tests of solutions of 3 and 8 mass-% FNO₂ in NTO were negative [373, 374]. Tensile elastic moduli were determined on stress-corrosion test specimens of 250 maraging steel, 347 stainless steel, and 2219 aluminum immersed in INTO, and samples of the same metals were exposed to INTO while stressed at 75% of their yield strengths. Atomic absorption methods were developed to analyze INTO and NTO for dissolved Fe, Cr, Cu, Ni, Ti, and Al, and detection limits for these six elements dissolved in NTO were improved four-fold.

Inhibited dinitrogen tetroxide (INTO) is N₂O₄ containing 1–3 mass-% FNO₂. The storability of INTO was investigated at room temperature and 343 K (70 °C) in tanks of 10 to 24-gallon capacity made from CRES-347, carbon steel 1018, maraging steel 250, Al-2219, Al-2014, and Ti-6Al-4V [375]. For the large tank storability tests, NO₂F was prepared *in situ* by bubbling difluorine gas directly into crude NTO that contained 0.22 mass-% H₂O equivalent and thus was deliberately out of spec. The *in situ* method for NO₂F addition introduced other problems and was abandoned after it was found that the tanks were not as well protected by INTO as earlier small-scale tests that had not used the *in situ* method had indicated. The rate of *in situ* formation of FNO₂ by the addition of F₂ to wet N₂O₄ was slower and more difficult than had been anticipated. Small-bomb storability tests in bomblets made from maraging steel 250, A286 steel, and Ti-6Al-4V were conducted with two INTO samples prepared from NTO that originally contained 0.08 mass-% H₂O or 0.2 mass-% H₂O, respectively. INTO was found

to be storable in A286 (14 months, ambient, and 343 K) but not in maraging steel 250 or Ti-6Al-4V. Additional small-bomb compatibility tests at ambient (25 months), 343 K (25 months), and 403 K (49 h) indicated that INTO was storable in CRES-304L, CRES-321, Al-6061, or nickel when the containers were sufficiently passivated. Stress-corrosion tests were conducted with two uninhibited propellant-grade NTOs, MIL-P-26539 and MSC-PPD-2A, but none of the samples ruptured.

Two 50-gallon batches of INTO were field-prepared, but severe tank corrosion and iron fluoride precipitation occurred, resulting in clogged feed lines and flowmeters [376]. Although rocket engine performance with N_2H_4 , MHF-3, or Ae-50 was not degraded by the inhibitor, the corrosion problems and physical properties made the use of INTO impractical for future Air Force applications. It was concluded that FNO_2 in 3–5% concentrations did not affect the performance of NTO when combusted with hydrazine, Aerozine-50, or MHF-3. INTO should be filtered between preparation and its addition to storage tanks, and it should be stored in unvented systems and assayed after any venting process because of the high evaporation rate of FNO_2 .

Only five of the corrosion inhibitor candidates were found to have some effect in reducing the corrosion of stainless steel, aluminum, or titanium in N_2O_4 [309]: phosphorus trifluoride, phosphorus pentafluoride, ammonium fluorosulfonate, potassium fluorosulfonate, and tetramethylammonium tetrafluoroborate.

Phosphorus pentoxide has been patented as a corrosion inhibitor for magnesium alloys in N_2O_4 [377]. However, ammonium hexafluorophosphate caused increased corrosion and was not suitable as an inhibitor.

6.3 Flow Decay in Dinitrogen Tetroxide

Corrosion products in NTO, mostly iron leached from the wall or screen in steel tanks and their PMDs, may initially remain in solution but will precipitate when the concentration exceeds the saturation level or the oxidizer tank cools down. Salts may also precipitate in high-shear flow with high-flow velocities. Suspended particles, often in the form of a gelatinous mass, may clog small flow passages such as in filters, metering orifices, and injector passages. The resulting restriction of flow passages causes increased pressure drop and reduced flow. This problem of flow decay received a significant amount of attention during a 2-decade period toward the end of the last century.

While much has been written and discussed about flow decay, what is missing are accurate accounts of problems with flow passage obstruction during ground testing and flight use. It is unknown how many satellites or space probes have encountered this problem in flight and subsequently had their mission cut short or had to have the spacecraft switch to a backup system sooner than expected. The problem would be encountered mostly with small bipropellant thrusters with thrust levels at or below

22N, and then only after the mission had already been in progress for some time, and not so much with 400-N engines that are often used for orbit insertion, midcourse correction, and apogee kick stages.

In 1965, a valve with a window into the area of the valve seat was flowed with NTO until a deposit between the seat and the needle could be observed and correlated with the flow decay. That was the first time the problem had been visualized. Flow decay could be induced at will by soaking the propellant tank at 311–319 K and then dropping the temperature at the same time when the flow test was started. In trying to identify the mechanisms leading to the formation of injector-clogging flow-decay-causing materials and in the search for a magic solvent that would dissolve the precipitates or prevent their formation in the first place, iron(III) nitrate complexes with N_2O_4 as an adduct with compositions similar to $\text{Fe}(\text{NO}_3)_3 \cdot n\text{N}_2\text{O}_4$ were synthesized in the laboratory by reaction of $\text{Fe}(\text{CO})_5$ with N_2O_4 and were compared with contaminants collected from actual propulsion subsystems [378, 379]. One of the samples analyzed was $\text{Fe}(\text{NO}_3)_{3.19} \cdot 1.03\text{N}_2\text{O}_4$. It was suspected that the deposits might also contain water, and NMR and EPR spectroscopy were used to search for water in the deposits. The $\text{Fe}(\text{NO}_3)_3 \cdot n\text{N}_2\text{O}_4$ adduct was soluble in acetonitrile, ethyl acetate, nitromethane, nitrobenzene, acetone, and acetophenone. Acetonitrile was compatible with N_2O_4 , but nitromethane was not.

Flow decay causing corrosion products can take the form of either a solid or a second liquid phase, the latter being ambiguously described as very viscous or gelatinous but sufficiently stiff to clog orifices [380]. Both types of deposits are derived from iron nitrate, the solid being assigned the chemical formula $\text{NOFe}(\text{NO}_3)_4$, the liquid being a complex mixture derived from the interaction of iron nitrate and water. Both are soluble in dinitrogen tetroxide, but only at a level of a few parts per million (as iron). Their presence in the propellant and their deposition are a function of the water-equivalent level of the propellant and of the temperature and pressure profiles that the propellant encounters before and during flow. In general, the deposition will occur whenever propellant has been cooled just prior to or during flow, and this change in temperature to bring about contaminant deposition and flow decay may be as small as 1–2 K (3–5 °F). It was found that the presence of excess water in amounts up to the general-use limit of 0.2% changed the characteristics of the deposits formed when NTO was heated and then cooled prior to or during flow [381]. Instead of the crystalline solid $[\text{NOFe}(\text{NO}_3)_4]$ that is deposited from dry propellant, gelatinous or viscous liquid phases were formed in wet propellant. The appearance of these deposits was governed by an equilibrium solubility limit similar to that observed for the solid deposits in dry propellant. The gelatinous or viscous liquid deposits were not observed to adhere to or plug valves and orifices, as did $[\text{NOFe}(\text{NO}_3)_4]$, but they did clog filters. Flow-decay concerns affected the propulsion system selection for a planned orbital workshop, a small-scale manned space station forerunner [382–384].

Flow-decay studies performed by TRW Systems Group examined clogging materials not only in NTO but also in hydrazine, oxygen difluoride, and diborane, all in the category of space-storable propellants [385–387].

A flow-decay study was performed on the feed lines, valves, and filters of a bipropellant propulsion subsystem intended for an early version of a manned space station called Orbital Workshop [384]. The system was exposed to off-limit (high and low) temperatures and fed with normal and artificially aged propellants. Engine flow decay due to increased pressure drop did not exceed 10% of the nominal flow rate when tested with military-specification-grade NTO and did not exceed 5% of the nominal flow rate when tested with artificially aged and temperature-cycled NTO.

The rate of dissolution of iron or chromium from steel in N_2O_4 and the solubility limit of corrosion products as a function of temperature, as well as the effects on the rate and solubility of adding small known amounts of the impurities H_2O , NOCl , and NO , were measured using a radioactive tracer technique by thermal neutron activation followed by γ -radiation counting [388–392]. It was found that N_2O_4 reacts initially with metallic iron to form a surface layer of iron nitrate, whereupon the iron nitrate dissolves in N_2O_4 . The detection limit was 0.1 ppm for iron, 0.01 ppm for zinc, and 0.001 ppm for chromium. In addition to metals leaching into NTO, metals leaching into anhydrous hydrazine were measured using the same method. See also [393].

The behavior of $\text{Fe}(\text{NO}_3)_3 \cdot n\text{N}_2\text{O}_4$ adducts has been studied in HNO_3 solution and in $\text{HNO}_3/\text{N}_2\text{O}_4$ mixtures, since the presence of HNO_3 in propellant N_2O_4 was suspected to influence the physical and chemical nature of the flow-decay deposit and may be partially or perhaps primarily responsible for corrosion of steel [394]. The properties of the $\text{Fe}(\text{NO}_3)_3 \cdot n\text{N}_2\text{O}_4$ and $\text{HNO}_3/\text{N}_2\text{O}_4$ system were interpreted in terms of a gross modification of the $\text{HNO}_3/\text{N}_2\text{O}_4$ phase diagram by $\text{Fe}(\text{NO}_3)_3 \cdot n\text{N}_2\text{O}_4$. A flow apparatus was then constructed so that flow-decay deposit could be collected and its chemical identity and physical form studied as a function of the “water” (HNO_3) content of the N_2O_4 analyzed (as monitored by NMR). The dissociation vapor pressures of $\text{Fe}(\text{NO}_3)_3 \cdot n\text{N}_2\text{O}_4$ were measured to elucidate the stoichiometry of stable adducts, and SEM of crystals was done before and after exposure to dilute solutions of NOCl in liquid N_2O_4 for known lengths of time. The IR spectrum of the initial (un-evacuated) $\text{Fe}(\text{NO}_3)_3 \cdot n\text{N}_2\text{O}_4$ showed a very intense band at 2230 cm^{-1} (Figure 47a), together with the expected bands due to molecular N_2O_4 . On evacuation of the compound (10^{-2} mm Hg) for 3 d, the molecular N_2O_4 bands and the band at 2230 cm^{-1} decreased in intensity, and a further band appeared at 2298 cm^{-1} (Figure 47b). After evacuation for a further 3 d, the two bands in the NO^+ region were of comparable intensity (Figure 47c), and after 2 weeks the 2298 cm^{-1} band was the more intense, with the 2230 cm^{-1} band as a shoulder (Figure 47d). On dissolving the evacuated compound in ethyl acetate and reprecipitating with N_2O_4 , the spectrum reverted to that of Figure 47a. These observations led to the conclusion that excess N_2O_4 may be associated in some way with the NO^+ cation in an analogous manner to that known for diethylnitrosamine, in which two molecules of this solvent coordinate to NO^+ ,

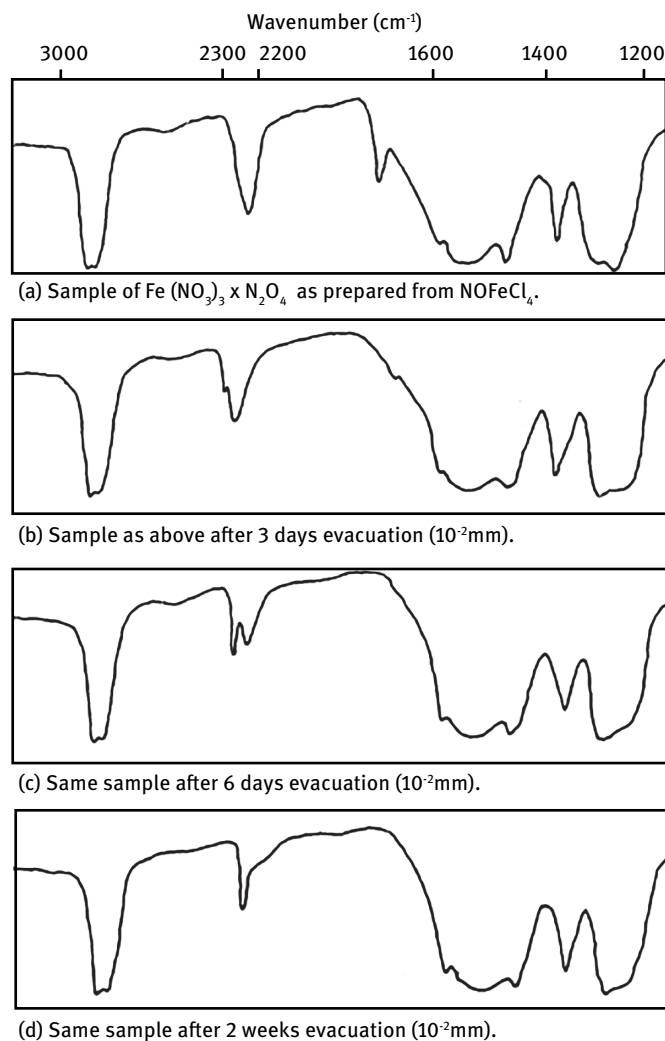


Figure 47: Changes in IR spectra of $\text{Fe}(\text{NO}_3)_3 \cdot n\text{N}_2\text{O}_4$ adduct with progressive evacuation. (Reproduced and modified from [394].)

producing a consequent shift in the IR absorption band. This observation supported the theory that the compound $[(\text{N}_2\text{O}_4)_2\text{NO}]^+[\text{Fe}(\text{NO}_3)_4]^-$ or $\text{Fe}(\text{NO}_3)_3 \cdot 3\text{N}_2\text{O}_4$ may be a discrete entity. Later tests supported the assumption that the adduct has the composition $\text{Fe}(\text{NO}_3)_3 \cdot 1.5\text{N}_2\text{O}_4$ [395]. Equilibrium vapor pressures were measured in the system $\text{Fe}(\text{NO}_3)_3 \cdot n\text{N}_2\text{O}_4$ ($n = 1 - 6$) to see at what ratio compound formation might occur. $\text{Fe}(\text{NO}_3)_3 \cdot 1.5\text{N}_2\text{O}_4$ was recognized as a solid phase in equilibrium with N_2O_4 . The presence of traces of HNO_3 in addition to N_2O_4 influences the physical properties

and the chemical behavior of the flow-decay deposit. The adduct was further characterized by Raman spectra, NMR, XRD, magnetic moment measurements, and Mössbauer spectra. The XRD crystal structure of the adduct $\text{Fe}(\text{NO}_3)_3 \cdot 1.5\text{N}_2\text{O}_4$ indicated that it should be represented as $3\text{NO}^+\text{NO}_3^- \cdot 2[\text{Fe}(\text{NO}_3)_4]^-$ [274].

The rates of dissolution of iron from Al-2014, Ti-6Al-4V, and CRES-347 stainless steel by N_2O_4 were measured by immersing radioactive samples of the alloys in N_2O_4 [5]. After immersion of the alloy, the samples were removed and the solutions examined for radioactivity. No iron was detected in the N_2O_4 containing the titanium or aluminum samples. However, radioactivity from some unidentified element was found in the N_2O_4 containing the titanium sample, which indicated that a reaction with the sample had occurred. The reaction rate of N_2O_4 with 347 stainless steel varied directly but not linearly with the sample surface to propellant volume ratio. Iron-free N_2O_4 , prepared by distillation, was stored for approximately 2 months in tanks made from the three sample alloys. Following storage, the N_2O_4 was flowed through a 2- μm stainless steel filter under conditions known to be conducive to flow decay. No decay was found with the N_2O_4 stored in the Al-2014 or CRES-347 stainless steel tanks. About 15% decay occurred with N_2O_4 stored in the Ti-6Al-4V tank. Flow decay resulting from passage of N_2O_4 through 2- μm nominal stainless steel filters was studied as a function of added iron concentration. With new filters, no flow decay occurred when less than 3.6 ppm iron (as iron nitrate) was added to the as-received N_2O_4 . Following successful laboratory experiments with molecular sieves, a larger molecular sieve filter, suitable for field use, was constructed for purifying N_2O_4 . Approximately 90 kg (200 lb_m) of as-received N_2O_4 (containing ~0.5 ppm Fe) was filtered through 0.9 kg (2 lb_m) of Linde type 13X molecular sieves of 100/120 mesh. During the filtration, a sample of that filtrate was withdrawn following each 8.1 kg (18 lb_m) increment of flow. These samples were examined by atomic absorption spectroscopy for iron concentration. No iron was detected in any of the samples since the readings did not exceed the instrumental detection threshold. The propellant-to-filter mass ratio was 1000, and the filtered propellant remained well within the specification limits. Filtration through molecular sieves thus appeared to be a practicable technique to eliminate flow decay as a problem from operational weapon and space systems. Samples of three metal alloys, Al-2014, Ti-6Al-4V, and CRES-347 stainless steel, were immersed in iron-free specification-grade brown N_2O_4 , and the rate of dissolution of iron from the metals was measured as a function of dissolution time, surface-to-volume ratio, state of agitation, and temperature. This was accomplished by activating coupons of these metals in a thermal neutron flux of $3 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ for 10 h ($^{58}\text{Fe} + \text{n} = ^{59}\text{Fe}$), immersing the coupons in N_2O_4 , and measuring the level of activity of radioactive Fe in the N_2O_4 after the coupons were removed. From the knowledge of the ratio of radioactive to non-radioactive iron atoms, the iron concentration in parts per million was then calculated.

Two methods of introducing known amounts of iron to the N_2O_4 were used to demonstrate the effectiveness of the purification method: In the first, known amounts

of iron were added to a tank of N_2O_4 in the form of iron(III) nitrate. In the second, iron-free N_2O_4 was stored in Al-2014, Ti-6Al-4V, and CRES-347 stainless steel tanks for an extended period of time, during which the N_2O_4 was allowed to react with the tank walls. One of the objectives of flow testing was to demonstrate elimination of flow decay by subsequently passing the propellant through a molecular sieve filter. This was accomplished by flowing contaminated N_2O_4 that was known to undergo severe flow decay through the molecular sieve filter and then again through the flow system to verify that flow decay no longer occurred. Since severe decay was experienced after the addition of 4 ppm iron, this was the point at which the use of molecular sieve purification appeared appropriate.

One has to assume that any commercially supplied dinitrogen tetroxide will have the potential of causing flow decay, if suitable (that is, adverse) conditions are present during flow. Rocketdyne conducted a number of investigations of various aspects of flow decay, beginning in 1964. An experimental and analytical program was conducted as part of a systematic engineering parametric study to establish the necessary engineering criteria for the prediction and prevention of flow decay in operational nitrogen tetroxide systems [396]. All materials of construction in the flow bench were selected to be compatible with NTO. The tanks, valves, fittings, and fluid lines were made of type 304, 316, 321, or 347 stainless steel. Valve seats and stem packings were made of either Teflon or Kel-F. Teflon tape was used as the thread lubricant on pipe fittings. Tests were done with both green and reddish-brown nitrogen tetroxide over ranges of seven other parameters: initial propellant temperature, temperature drop before reaching the test section, time during which the temperature drop was imposed, filter pore size, local velocity through the filter, total volume per unit filter area of propellant passing through the filter during a test, and iron-saturation condition. Flow decay was observed under some test conditions but was absent under other conditions. The rates of decay ranged up to 2.8%/min, although the mean rate was about 0.5%/min for all tests in which any significant flow decay occurred. It was possible to deduce information about the effects of these eight major independent variables on flow decay. However, it was found that the effects of these parameters were generally not simple or independent of each other; they exhibited many interdependencies. In addition, there were threshold effects for flow decay (i.e., an identifiable boundary between a range of variables for which no flow decay occurred, and a range for which flow decay occurred at varying rates). These thresholds were not sharp, and they further depended upon interactions of the independent variables.

In order to test the suspected volatility of iron compounds that would cause errors in iron analysis results, an authentic sample of nitrosyl iron(III) tetranitrate had to be prepared, which would then be used to dope pure, iron-free NTO to generate known iron concentrations in the oxidizer [302]. The chosen method for preparation of nitrosyl iron(III) tetranitrate was the reaction of iron pentacarbonyl with dinitrogen

tetroxide. The product contained ~19% Fe, while the theoretical iron content should have been 16.7% Fe. See also [397].

The flow-decay problem associated with NTO has become an important factor in the design of small, bipropellant propulsion systems that need to survive decades-long deep space missions such as Galileo at Jupiter or Cassini at Saturn. The objective of a program established at the JPL was to alleviate this problem by **(1)** developing a process to purify NTO to a level of contamination that would minimize the precipitation of iron-contaminated species, and **(2)** establishing component cleaning and passivation procedures that would prevent recontamination of the propellant [398]. While a number of potential methods for purification of nitrogen tetroxide existed, the method employing molecular-sieve column treatment appeared to offer the advantages of simplicity of implementation, relatively low cost, and, at that time, proven capability to operate in the field as well as the laboratory. In general, the molecular-sieve adsorption column treatment of mixed oxides of nitrogen (MON-1 or MON-3) resulted in little change in NO concentration (well within specifications), efficient removal of contaminant iron and other metals, efficient removal of water (HNO_3 and H_2O) when the column was activated, apparent removal of chloride impurity, and no introduction of deleterious material from leaching of the zeolites employed.

A 50-L cylindrical CRES-304L tank and a Ti-6Al-4V tank were filled with freshly distilled MON-1 and stored for 20 and 10 months, respectively, at a constant temperature of 313 K (40 °C) under a helium pad of 5 bar [399]. Because corrosion products are less soluble in MON-1 than in MON-3, this was considered a worst-situation test if later flights would use MON-3. Oxidizer samples were withdrawn from each tank after 1, 3, 6, 10, and 20 months of storage. Prior to sampling, the temperature was reduced to 293 K (20 °C), and the tanks were agitated by shaking. The initially high corrosion rate of CRES decreased after about 1 month. The iron concentration in the oxidizer remained constant at 0.7 ppm for the remainder of the test. The Ti-6Al-4V tank showed little corrosion, and it was mostly aluminum that was leached from the tank walls. No flow decay was encountered when the distilled and stored and off-loaded MON-1 propellant was passed through 10-N rocket thrusters intended for the ESA Olympus mission. However, flow decay in a 20- μm filter was a problem in similar tests with plain military-specification-grade NTO that had been stored in a mild steel tank for 96 months before being transferred to a CRES run tank containing 1.8–2.1 ppm Fe, particularly if the propellant was cooled from 313 K (40 °C) to 268 K (–5 °C) after it had been stored for a long time. It was therefore important to determine the causes of flow decay; find propellant purification, mode of operation, and material selection methods to avoid flow decay; and find recovery methods for an affected system during operational use in space. One method of recovery was to heat the propellant to 333 K (60 °C).

Flow decay depends on the rate of corrosion of stainless steel in contact with NTO and the solubility of iron nitrate and its hydrolysis products in NTO. Galileo was the first bipropellant-powered interplanetary spacecraft to orbit Jupiter, and its active mission duration was much longer than any of its bipropellant-powered predecessors,

which were only lunar orbiters or interplanetary fly-by probes. There was concern that flow decay might hamper the mission after several years in orbit. An effort was made to summarize the state of knowledge about flow-decay problems and their potential impact on the success of the Galileo mission [281]. Existing leaching-rate data were applied to exposed stainless steel surface-to-volume ratios on Galileo, and additional benchtop experiments were started with authentic components immersed in MON. When the launch of Galileo was postponed, the MON that was off-loaded after having spent several months in the tank could have been analyzed to obtain additional leaching-rate data.

The rate of formation of metal nitrates in dinitrogen tetroxide was fed into a computer model to predict the saturation point of metal nitrates in N_2O_4 [400]. Means of reaching the saturation point were examined, and a relationship was established for the reaction/formation rate and diffusion rate of metal nitrates in N_2O_4 .

6.4 Metallic Materials for Dinitrogen Tetroxide Service

The selection of metallic materials of construction for wetted use with N_2O_4 is simple compared with similar tasks for the various forms of nitric acid [401, 402]. Dinitrogen tetroxide and MON are less aggressive corrodents than nitric acid, but one must remember that it takes only a small amount of moisture for all the problems earlier encountered with nitric acid to resurface.

The corrosive effects of dinitrogen tetroxide on mild steel, aluminum, stainless steels, and titanium were determined quantitatively under static and dynamic flow conditions at six water concentrations up to 3.2 mass-% H_2O and four temperatures up to 343 K (74 °C) [403]. The corrosion of carbon steel (ASTM A-285 grade C) and Al-5086 was less than 0.5 mils per year in nitrogen tetroxide containing up to 0.21 mass-% water at 343 K, increasing to 50 mils per year at 3.2 mass-% water and 343 K. Negligible corrosion was observed under severe conditions with CRES-304L, titanium 75A, and Ti-6Al-4V, whereas high stress-corrosion cracking was observed in tests of carbon steel, high-strength steel, and aluminum in nitrogen tetroxide containing 0.1 mass-% water and 1.6 mass-% water at 343 K. Significant corrosion of CRES-304L occurred in the presence of Teflon. Dynamic tests showed no significant corrosion of CRES-304L or PH15-7Mo stainless steels, and average rates were seen of 0.05 mils per year for aluminum and 0.33 mils per year for carbon steel after 205 h of exposure to commercial dinitrogen tetroxide flowing at a velocity of 3 m/s (10 ft/s) at 303 K (30 °C).

The corrosion rates of carbon steel, stainless steel (304L and PH 15-7 Mo), aluminum (Al-5086), and titanium (75A and Ti-6Al-4V) in dry and wet nitrogen tetroxide were determined under static conditions of exposure at 264–347 K (–9 to 74 °C) [344]. Carbon steel and aluminum were attacked in proportion to water concentration and temperature. Stainless steel 304-L and titanium were not attacked, and PH 15-7 Mo was

only slightly attacked. Significant corrosion of stainless steel (CRES-304L) occurred in the presence of Teflon. Corrosion by dry nitrogen tetroxide under flow conditions was negligible. Teflon was the most resistant of the plastics exposed to nitrogen tetroxide.

When a wide range of different metals were tested for compatibility with N_2O_4 at 316.5 K (110 °F) for periods of 1.5–3 years, it was found that the least corroded metals were titanium alloys [404], iron alloys, cobalt alloys, some nickel alloys, and tantalum [405]. Molybdenum, magnesium, and some aluminum and nickel alloys were not compatible. The exposed metal samples were examined for weight loss, appearance of the corroded surface under the light microscope, and XRD of the corrosion products. The propellant used in the compatibility studies was analyzed for water by a gas chromatographic method, for nitric oxide by a spectrophotometric method, and for chloride by a wet chemical method.

Russia and its predecessor the USSR have launched thousands of rockets with N_2O_4 as the oxidizer, and, accordingly, they have amassed a substantial amount of experience in materials selection for N_2O_4 service. However, only very little of that literature has found its way into Western library collections [406].

Dinitrogen tetroxide corrosion phenomena and proposed mechanisms of corrosion with various metals, mostly stainless steels, are well described in [407].

Cryopanel in a vacuum space simulation chamber are periodically cycled between 77 and 300 K, and if the engine is operated oxidizer-rich during startup, N_2O_4 condensate on the panels melts and drips off after completion of a rocket test under simulated vacuum conditions. A black epoxy coating of CRES-304 panels suffered no apparent damage in one series of short tests, but pit formation in the coating, pitting beneath the coating, and intergranular corrosion in weld areas was detected in tests with longer exposure durations [408]. An epoxy-coated CRES-304L sample suffered microscopic cracking and blistering of the coating and surface pitting beneath the coating. In one worst-case test in which the N_2O_4 partial pressure in the chamber was 0.5 kPa (4 mm Hg), Al-1100, phosphorus-deoxidized copper, and stainless steel panels were exposed to vapor and condensate while subjected to external bending stresses similar to those from thermal differential expansion [409]. None of the panels cracked.

The JPL has done extensive materials compatibility testing with NTO, MON, and other rocket propellants, and some of the testing was extended for close to 20 years [410]. Interim status reports were published at 5-year intervals. The scope of the testing was to provide data necessary for the design of interplanetary spacecraft on long-term missions. The testing was done in “real time” at a constant temperature of 316 K (110 °F). Materials were tested in unstressed and stressed conditions and partially submerged conditions, such that there were liquid-exposed and vapor-exposed areas on each coupon. Groups of materials were tested in (1) bimetal separated, (2) bimetal contact, (3) welded, (4) brazed, (5) plated, and (6) coated configurations. Most of the materials originally placed into testing were identical to materials typically used in the Mars Viking Orbiter propulsion subsystem. The coupons were sealed in borosilicate (Pyrex) glass ampoules. Strain gauges attached

to the outside of the ampoules were supposed to allow inside pressure measurement, but the bond of the strain gauges to the glass failed, and pressure readings could not be obtained [411]. At the ten-year milestone, 38 samples removed indicated that most materials tested, with the exception of nickel, were compatible with MON-1 [412, 413]. On Al-6061-T6 the primary effects were corrosion and formation of a surface film; the oxide layer of the surface film may flake off and cause particulate contamination and clogging. In all CRES alloys (302, 303, 304L, 316, 321, 347, 17-4PH, and 17-7PH), only minor corrosion was seen. The amount of iron dissolved from the surface varied, with the most iron found in propellant off-loaded from 17-4PH and from a welded CRES-304L coupon. Titanium alloy samples had a substantial weight loss.

While most materials compatibility testing has been done under static, stagnant conditions, this is not what metals are exposed to in feed systems or rocket engines during operation of the rocket engine. More sophisticated corrosion testing of metals in flowing NTO exposed the specimens to more severe conditions than under static tests. As a consequence of the cavitation and turbulence on the surface, material corrosion may be accelerated due to the removal of passivating layers. One must be cautious when applying static corrosion-rate data to a dynamic environment.

A thorough and comprehensive summary of materials compatibility data of metals and non-metallic materials is contained in a NASA WSTF report that was later reissued as an AIAA Special Report [209]. It included a description of the criteria for rating metal degradation in NTO used by various investigators. In reviewing the literature on materials compatibility with NTO (and other propellants), one quickly realizes that the various investigators used different criteria to establish the compatibility ratings. Several materials NTO compatibility tables were compiled based on published data from four literature sources. This also included lists of materials that were found to be incompatible and must be avoided.

6.4.1 Compatibility of Ferrous Steels with Dinitrogen Tetroxide

One of the landmark studies investigated the corrosion of several pure metals and alloys in stagnant and flowing NTO containing six different levels of moisture up to 3.2 mass-% H_2O and at four different temperatures between 264 and 347 K (–9 to 74 °C) [403]. For example, a steel (ASTM A285-C) suffered in stagnant N_2O_4 with 0.2% H_2O at 347 K (74 °C) only a slow rate of corrosion (0.5 mm/a) (mm/a = millimeter/year), but at the upper range of the water content, at 3.2% H_2O , the rate of corrosion was several orders of magnitude faster, namely 50 mm/a. Comparing rates of corrosion in stagnant and flowing (3 m/s) N_2O_4 containing 0.20% H_2O at 303 K (30 °C), it was observed that the sample in flowing N_2O_4 corroded at only a moderately faster rate (0.33 mm/a) than quiescent N_2O_4 .

Precipitation-hardened PH-15-7-Mo steel suffered little attack, whereas CRES-304L was hardly attacked at all, and it still constitutes the material of choice for most tanks and conduits.

There have been sporadic reports that N_2O_4 in the presence of Teflon caused increased corrosion of stainless steel, but the cause for this observation has not been identified.

MS steel fittings for use in diesel fuel and hydraulic systems are often plated with cadmium to prevent rusting. Cadmium plating does not offer any protection for service with N_2O_4 because the coating will rapidly corrode and peel off. Protecting the cadmium by a coating of polyethylene may help to protect against NO_2 vapors but will not help much if liquid N_2O_4 leaks out.

Stainless steels of the types AISI-300, AISI-400, AM-350, AM-355, 17-4-PH, and 17-7-PH or alloys Superalloy A-286 and Haynes 16-25-6 can also be used for N_2O_4 service [66, 414].

An examination of the corrosion of Ch18N10T (18/10Ti) steel in dinitrogen tetroxide at high temperature and high pressure under radiation conditions in a nuclear reactor showed that the radiation had no aggravating effect on the corrosion of this steel under these extreme conditions [415].

Whereas in the beginning of the use of NTO and MON as rocket propellants the storage duration requirements were only of the order of a few years, later developments required safe storage for ten or more years. It became difficult to select stainless steels that would meet the long-term storage requirements without contamination of the propellant by leached corrosion products and with maintenance of the mechanical integrity of the tanks [416].

In addition to conventional metallurgical corrosion investigation techniques (mount, cut, polish, etch), electron-beam analysis and imaging techniques have been used to study the surface of cryoformed CRES-301 stainless steel samples before and after passivation and before and after immersion in MON-3 [417–419]. Electron-beam methods that can be used for surface analysis are electron microprobe, ESCA-XPS, SEM-EDAX, and Auger spectroscopy. In one case, it was demonstrated that an initial electrochemical attack on the metal by the propellant was retarded by the development of a protective film on the metal, accompanied by minor adulteration of the propellant. In clean propellant, there was no indication of pitting or intergranular corrosion.

CRES-301 and CRES-304L have been widely accepted as the material of choice for surface-tension screens in propellant management devices in tanks in zero-gravity operation or for the tank wall and pressure shell itself [420]. The surface has to be carefully cleaned and passivated for such applications, in particular satellites and planetary space probes with mission durations of 12–15 years and more. See also [421].

The resistance of steel 09Kh16N15M3B and alloy 65Cr31Fe3Al0.3Zr against corrosion by dinitrogen tetroxide can be improved by enriching the surface with chromium [422]. This can be achieved by treatment with water steam at 1120–1170 K, followed by reduction under hydrogen, which forms a chromium layer ~2 nm thick. Samples exposed to NTO under pressure at 420 K and 16 MPa for 2000 h were practically unchanged, whereas an untreated control sample was badly corroded.

The mass loss of the treated sample was 20 times less than that of the untreated sample.

The interaction of nitrogen tetroxide oxidizer (in the form of NTO or MON) with stainless steel (CRES) has been studied for a long time. In an effort to extend the CRES/NTO corrosion database, based on earlier assessments made prior to the launch of ESA's Olympus satellite and NASA's Galileo space probe in the 1980s, an extensive parametric study of CRES/NTO corrosion was conducted, intended to provide a reliable and comprehensive database to support future spacecraft design and operation [423]. Data were obtained showing the effects of propellant composition (H_2O , NO, Cl), steel specification, temperature, surface-to-volume ratio, and surface passivation processes on corrosion rates. It was found that the long-term (up to 250 d) corrosion rate of 304L stainless steel is

- strongly related to the water content (MON-1 containing 0.15% H_2O was ten times more corrosive than the same oxidizer with 0.01% H_2O)
- in MON-3 half of that in MON-1
- lowest for electropolished sheet material, which is five times less than non-passivated material (nitric acid passivation or pickling in nitric/hydrofluoric acid, followed by nitric acid passivation, gave intermediate corrosion resistance)
- doubled by raising the temperature from 278 to 308 K (41 to 95 °F)

Factors that did not significantly affect the corrosion rate, or were within experimental error, were the initial chloride or iron content. Effects of the alloy type (301, 304L, or 321) were overshadowed by surface treatment/passivation effects. The surface-to-volume ratio affected the concentration of dissolved iron but not the rate of corrosion.

Deposition of iron-containing corrosion products, mostly an iron(III) nitrate-dinitrogen tetroxide adduct, occurs after the solubility limit of the contaminant has been exceeded, and it has been the cause of numerous in-flight problems with spacecraft. In the absence of convection and agitation, the rate of diffusion of iron ions through dinitrogen tetroxide, a known electrolyte, has not been totally investigated. If it effectively diffused, then it would be less likely to precipitate near its formation area on the surface of steel. Precipitation of iron-nitrate adduct material occurs after iron saturation in the oxidizer, which is therefore a function of the solubility of iron, the initial iron concentration in the oxidizer, and the rate of diffusion of iron through the oxidizer. The precipitate structure has noted variability that appears to be based on the water content of the oxidizer. Low-water-content oxidizer yields a crystalline adduct, whereas higher-water-content oxidizer yields a sticky solid or a viscous insoluble gel, the cause of flow decay. Some mission planners have resorted to periodically flushing NTO that was stagnant in lines, filters, and valves by firing the thrusters even if there is no need to do any active propulsion for momentum wheel desaturation or orbit adjustment. Periodic flushing avoids the buildup and precipitation of iron compounds from corroded parts in the system. Calculations suggested that systems should be fired or flushed fairly often initially in order to prevent iron nitrate corrosion product from

harming the system. After 200 d of exposure, the amount of time between firings can be increased considerably. The power law data fit suggested that after around 3 years of on-orbit operation, thrusters need not be fired or flushed for another 3 years [424].

Some investigators claimed that the corrosion occurs only within the first 30 d and then stops. This conclusion was based on very limited data, namely two points at two test conditions.

6.4.2 Compatibility of Aluminum Alloys with Dinitrogen Tetroxide

While aluminum alloys as a structural material for NTO or MON tanks may be more economical than titanium alloy tanks and less susceptible to corrosion product leaching and flow decay than steel tanks, there is concern that the oxide coating that develops may flake off and that the aluminum oxide particles may clog filters.

Microscopic leaks of N_2O_4 through capillary cracks, pores, or microporosity under the earth's surface or underground storage conditions in a moist atmosphere would not be so disastrous if the chemical did not form nitric acid at the leak site and rapidly increase the size of the leakage path through crevice corrosion [425, 426]. Indicator paints have been developed that change color and provide an early visual warning where a microscopic leak has occurred. Residual cleaning agents or propellant may get trapped in narrow passages in propellant tanks and are difficult to remove. The mechanisms by which crevice corrosion can occur in a narrow passage of Al-2014 aluminum were studied both experimentally and theoretically for exposure to **(1)** water and fuel (a mixture of hydrazine and UDMH), and **(2)** water and oxidizer (dinitrogen tetroxide). With each of these two reacting systems, one may form two displacement systems. In one case it was assumed that the capillary was initially filled with water, which was later displaced by propellant. In the other case the capillary was initially filled with propellant, which was later displaced by water. The crevices of small diameter were open at one end to a propellant tank but were closed (dead-ended) at the other end. This included weld cracks or weld porosity.

Small containers made from Al-2014 and Al-6061 were subjected to short-term compatibility tests with N_2O_4 to determine the effect of different cleaning methods [427]. In other samples that were exposed for 46 months, only minor differences were noted in the pre-exposure and post-exposure appearance of the metal surfaces.

Aluminum 5086 corrodes in N_2O_4 with less than 0.2% H_2O at 347 K (74 °C) only very slowly (0.5 mm/a). Even in flowing N_2O_4 at 303 K (30 °C), the rate of corrosion is only 0.05 mm/a [403]. The rate of corrosion of aluminum is proportional to the water content of N_2O_4 and the immersion test temperature, similar to the behavior of stainless steels.

Aluminum alloys 1100, 5052, 6061, 6066, 356, B 356, and Tens 50 are suitable materials of construction [66, 428]. However, Al-2024 is not suitable for N_2O_4 service. Al-2219 can be used for pressurized tanks [429]. TIG-welded areas of Al-2219 are especially susceptible to corrosion in NTO [430]. Corrosion experiments of a TIG-welded

aluminum alloy structure were conducted under both mild and accelerated corrosion conditions by changing the water content in N_2O_4 . The experimental results indicated that both general and accelerated corrosion processes of the TIG-welded structure of aluminum alloy 2219 in N_2O_4 followed a linear equation for its time dependence, and the corrosion products were unchanged regardless of the water content in the N_2O_4 solution.

Pure aluminum has good resistance to dry N_2O_4 , but it is too soft and not strong enough for many applications. Aluminum alloys better suitable for N_2O_4 service are Al-3003 and Al-5052. There are some contradictory reports in the literature about the suitability of Al-6061 and Al-2024.

Aluminum Al-2024-T6 is compatible with dinitrogen tetroxide (N_2O_4 MIL-P-265398). However, experience has shown that N_2O_4 leakage can occur with this Al-2024-T6 material, usually in the heat-affected weld zone, in a humid environment (30% R.H.) [431]. It was observed that if the relative humidity was of the order of 30% or lower, the nitrogen dioxide vapor from a leak dissipated into the atmosphere and did nothing to aggravate the leakage. If the relative humidity was of the order of 40% or greater, however, it did not dissipate, but rather hydrolyzed, forming dilute nitric acid on the exterior surface in the immediate vicinity of the leak and causing attack from both sides of the tank wall. During the same tank storage program, Bullpup Al-2024-T6 tanks initially intended for IRFNA and MAF-2 were later tested with NTO with good results.

The corrosion rates of aluminum alloys in dry NTO are an order of magnitude higher than those of stainless steels. As with stainless steel, and contrary to the trend observed for titanium, the corrosion is worse when more water is present. With time, aluminum ions enter the MON and form adducts whose composition is similar to those of the iron nitrate adducts. Thick oxide films form on aluminum, but they are not necessarily protective because they tend to spall, contaminating the propellant with insoluble oxide. A dubious method to protect aluminum alloys would be to pair them with iron alloys. Iron would act as a sacrificial anode; iron goes into solution (potentially precipitating and causing flow decay), but the solution process is quickly arrested by the formation of a protective film on the steel.

Aluminum cylinders containing 4 L of NTO and made of Al-2024-T6 or Al-6061-T6 were used during a 2-month storage test [427]. Various anodizing treatments have been evaluated to make aluminum more compatible with NTO and MON. Soft aluminum gaskets (Voishan seals) are often used to obtain tight connections between steel-steel AN fittings, but they cannot be used with NTO because they deteriorate within a few days.

Aluminum alloy LD10 double-cantilever beam specimens were corroded under the conditions of UDMH, N_2O_4 , or 3.5% NaCl aqueous solution immersion [432]. The stress-corrosion crack propagation behavior of this aluminum alloy in N_2O_4 was relatively slight.

6.4.3 Compatibility of Titanium Alloys with Dinitrogen Tetroxide

The combination of high strength-to-weight ratio, excellent mechanical properties, and corrosion resistance makes titanium a material choice for many applications in corrosive environments and as structural materials. In most cases, titanium alloys are superior to aluminum alloys for applications where the material is in contact with N_2O_4 . Titanium tank half-shells are formed by spinning or explosive forming and are then welded at the girth, often including a surface-tension screen as a propellant management device for zero-gravity propellant expulsion. Because titanium wire and titanium screens are not always available, the surface-tension screens are usually made from stainless steel, setting up the potential for galvanic corrosion between dissimilar metals in electrical contact with each other. Pure, non-alloyed titanium parts that have minimum titanium contents ranging from about 98.6, to 99.5 mass-% are used primarily for corrosion resistance, but pure titanium is soft and not very strong. The most widely used titanium alloy is the Ti-6Al-4V α - β phase alloy [404, 433].

Typical red N_2O_4 attacks unstressed Ti-6Al-4V to a small but measurable degree at 345–347 K (72–74 °C), i.e., 0.8–0.9 mils/year. At room temperature the rate of attack is negligible, i.e., 0.06 mils/year. MON-0.4 and MON-0.8 showed no evidence of corrosive attack at 345–347 K (72–74 °C), i.e., 0.06 mils/year. One mil is one-thousandths of an inch.

Titanium Ti-75-A and Ti-6Al-4V were tested under similar conditions as the steel discussed above [403]. Neither of the two alloys suffered any corrosive attack, not even in very moist (3.2% H_2O) N_2O_4 and not even at the maximum temperature tested (347 K [74 °C]). This corrosion resistance is a substantial advantage of titanium alloys over aluminum alloys.

For several decades, materials scientists were so preoccupied with the problem of stress corrosion cracking with NTO in titanium alloys that reliable conventional corrosion data were hard to obtain.

In a storage test with 57-L tanks at the Air Force Rocket Propulsion Laboratory (AFRPL), all of the titanium tanks leaked within less than 35 d after loading with N_2O_4 [431]. Both the Ti-6Al-4V and the Ti-5Al-2.5 titanium alloys in the annealed condition leaked. At the beginning of the test program, consideration was given to the use of the NASA-grade N_2O_4 (MSC-PPC-2A specification [green]) in the loading of the titanium tanks because of the stress-corrosion problem encountered with MIL-P-26539B specification N_2O_4 (brown). The stress levels in the tankage, based on nominal loads and thickness, however, were considerably below the threshold for stress-corrosion cracking reported (16 versus 90 ksi). The test temperature was to be significantly below the temperatures at which problems were encountered (302.6 versus 316.5 K [85 versus 110 °F]). On the basis of these two considerations, stress corrosion was not thought to be significant, and the tanks were loaded with MIL-P-26539B specification N_2O_4 (brown). Fracture analysis of two of the five leaks revealed that stress-corrosion cracking was present in the failure area and was very probably responsible for the leaks. It is quite likely that warping loads that were

introduced by welding in the leak area resulted in residual stresses that significantly increased the local stress level above the calculated general-membrane stress level.

After the MON was off-loaded from Galileo due to a launch delay and the tank purged with dry nitrogen (it could not be evacuated), it was to be expected that a thin film of less volatile nitric acid would remain behind and might cause corrosion during the idle period of storage. In tests of the fracture toughness and stress-corrosion threshold of identical Ti-6Al-4V samples exposed to nitric acid, it was found that the tank's structural integrity was not degraded by nitric acid exposure [434].

Previous (prior to 1994) studies of corrosion of Ti-6Al-4V in NTO indicated that the corrosion of Ti-6Al-4V in NTO is uniform, "a light etching without pitting," although the Ti:Al ratio on the surface varied depending on the water and chloride content of the oxidizer.

Two corrosion products, $\text{TiO}(\text{NO}_3)_2$ and $\text{Ti}(\text{NO}_3)_4$, not typically found on the surface, are stable in contact with NTO [367]. Both are white solids that are readily hydrolyzed by traces of water. The tetranitrate $\text{Ti}(\text{NO}_3)_4$ is very volatile. The titanyl nitrate and its NTO solvate $\text{TiO}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ are less well characterized and would probably decompose to TiO_2 when heated.

Earlier attempts to quantify the rate of corrosion of Ti-6Al-4V in NTO or MON yielded ambiguous results because the mass losses of the coupons were too small to be measured, and the analytical methods to analyze dissolved corrosion products were not sensitive enough [367]. The investigators had to increase the surface-to-volume ratio to 6 cm^{-1} to obtain measurable quantities of corrosion products.

The concentration of leached metals was measured in off-loaded oxidizer after exposing Ti-6Al-4V coupons at a surface-to-volume ratio of 6 cm^{-1} at 303 K (30 °C) for up to 552 d to NTO or MON-3 with several different water contents [435, 436]. The results are summarized in Tables 43 and 44. Table 43 gives the concentration of dissolved metals, and Table 44 gives the corrosion rates derived from these numbers. The results showed that the corrosion of Ti-6Al-4V in both oxidizers proceeds to a limited extent and then stops. At 303 K and a surface-to-volume ratio of 6 cm^{-1} , the oxidation of the surface appeared to be complete within 55 d for NTO and 41 d for MON-3. The extent

Table 43: Leached metal amount from Ti-6Al-4V immersed in NTO or MON-3.

Oxidizer	Water content, mass-% H_2O equivalent	Duration, d	Total quantity of metal dissolved, ppm		
			Ti	Al	V
NTO	0.003	552	3.5 ± 0.5	0.43 ± 0.01	0.59 ± 0.02
NTO	0.02	55	6.95 ± 0.30	0.32 ± 0.01	0.85 ± 0.14
MON-3	0.01	49	0.21 ± 0.03	—	0.017 ± 0.003
MON-3	0.02	41	0.18 ± 0.01	—	0.016 ± 0.001
MON-3	0.15	43	0.25 ± 0.01	—	0.016 ± 0.001

Data source: [435]

Table 44: Time-averaged corrosion rates of Ti-6Al-4V immersed in NTO or MON-3 at 303 K.

Oxidizer	Water content, mass-% H ₂ O equivalent	Duration, d	Corrosion rate, mils/yr × 10 ⁶		
			Ti	Al	V
NTO	0.003	552	45*	95*	205*
NTO	0.02	55	1060	813	3230
MON-3	0.01	49	42	51	73
MON-3	0.02	41	36	98	67
MON-3	0.15	43	47	—	90

*Corrosion probably leveled off before vessel was opened after 552 d

Data source: [435]

Note: mil = 1/1000 inch

of MON-3 corrosion appeared to be unaffected by the water content in the range of 0.01–0.15 mass-% H₂O equivalent.

Dry (0.003 and 0.2 mass-% water equivalent) NTO is the more corrosive medium toward both alloys. The iron oxidation product dissolves more readily in MON-3, whereas the titanium alloy corrosion products are more soluble in the N₂O₃-free medium. In NTO, the oxidation penetrates to a depth of 30–40 Å.

For a long time there has been quite a concern that the impact of hypervelocity projectiles (meteorites) on N₂O₄-filled titanium tanks might cause an explosive combustion, but this situation would lead to system loss in either case, whether it is accompanied by a fire or not (Section 6.4.6). Initially the concern was so large that at one time titanium was not recommended to be used with N₂O₄. Hypervelocity impact tests with N₂O₄ in titanium, aluminum, steel, or fiberglass-reinforced plastic tanks did not result in explosions, whereas titanium tanks filled with liquid oxygen combusted with a fireball [437]. Titanium tubes filled with N₂O₄ and externally impacted with the bullet of a .30-06 cartridge showed evidence of burning over an area of about 1 inch from the point of impact.

The impact sensitivity of commercially pure titanium, Ti-6Al-4V, and precipitation-hardened 15-7 Mo stainless steel in liquid NTO was measured under a range of stimuli, including shearing, scraping, galling, impact by massive strikers, and high-velocity bullets [438]. See also [439–442].

Freshly exposed titanium surfaces at the point of tensile rupture may react spontaneously with NTO and ignite [443].

6.4.3.1 Stress-Corrosion Cracking of Titanium Alloys in Dinitrogen Tetroxide

Although dinitrogen tetroxide is less corrosive than RFNA, the potential for stress corrosion still exists and requires careful selection of materials of construction, clean manufacturing methods, and high-purity propellants [354].

The first reported indication of stress-corrosion failure came in early 1965 when a pressurized Ti-6Al-4V (solution-treated and aged) tank filled with liquid N₂O₄

ruptured at Bell Aerosystems Company. Failure came after 40 h of exposure at 314 K (105 °F) and a stress level of 620 MN/m² (90000 psi). Microscopic examination of the tank disclosed a considerable number of cracks that had formed in all areas where the stress level was above 276 MN/m² (40000 psi) [444]. Stress-corrosion cracking will usually occur in N₂O₄ when no significant or measurable amounts of NO (acting as an inhibitor) are present. In the absence of stress, titanium shows almost no corrosion in liquid or gaseous N₂O₄ in tests to 347 K (165 °F).

Another failure in late 1966 of a titanium-alloy tank by methanol-induced stress-corrosion cracking resulted in a flurry of activity to investigate the behavior of titanium and its alloys in various media such as the alcohols and fluorinated hydrocarbons. This particular tank that failed was being pressure tested with dry, reagent-grade methanol, which was used as a substitute fluid in place of the propellant that is intended for ultimate use. During the testing, which was a sustained-pressure test, it was noted that a leak developed in the heat-affected zone of the lower weld. A second tank failed catastrophically, also with methanol as a pressurized fluid. Failures of pressurized tanks occurred in as little as 3 h. Adding 1% water to the dry methanol inhibited the attack. The US Defense Metals Information Center sponsored a seminar on this subject in cooperation with NASA Manned Spaceflight Center. The seminar on "Accelerated Crack Propagation of Titanium by Methanol, Halogenated Hydrocarbons, and Other Solutions," was held at Battelle Memorial Institute in Columbus, Ohio, in March 1967 [445]. This was attended by 139 persons representing 78 individual companies and offices of the US government.

Concern about the potential fracture of Ti-6Al-4V tanks in dinitrogen tetroxide arose already before the spectacular failures in late 1966 of large tanks intended for the Apollo program. Smaller tanks intended for the Lunar Orbiter were examined for critical flaw sizes required for tank fracture, likeliness of small initial flaws to grow to critical size. It was determined if any necessary changes to operating stress levels, proof test or possible substitution with other tank materials would be required to assure mission success [446, 447].

The N₂O₄ stress-corrosion resistance of standard Ti-6Al-4V and extra-low interstitial Ti-6Al-4V alloy coupons with three different heat treatments was measured with specimens stressed 586 to 896 MN/m² (85–130 ksi) and heated to 314 K (105 °F) or 344 K (160 °F) until failure occurred or for a maximum of 30 d [448]. The heat treatments were the conventional solution-anneal-and-age treatment and two duplex treatments which included controlled-rate cooling from above the beta transition temperature followed by the conventional treatment.

Plane-strain cyclic and sustained load flaw growth characteristics were investigated for Ti-6Al-4V forgings and heat affected zones in weldments exposed to N₂O₄ inhibited with 0.49% NO Aerozine-50, MMH, NTO, methanol, Freon-MF, and distilled water (with and without sodium chromate additions) at 291 to 316 K (65 to 110 °F) [447]. Basis for evaluation was the determination of the threshold stress intensity values (that value below which sustained load flaw growth could not occur) in the various liq-

uid environments. The results showed that sustained load threshold values (in terms of initial-to-critical stress intensity ratios) were relatively high, exceeding 75%, with the exception of three environments: methanol, Freon-MF, and at test temperatures exceeding 302K (85°F), also dinitrogen tetroxide. Little or no difference in sustained load behavior was observed between base metal and weld HAZ except in the environment of Freon-MF. In this case, the flaw growth was significantly more pronounced in the HAZ than in base metal. At stress intensity levels below the sustained load threshold value, cyclic load flaw growth rates were quite low, and were not considered to be a serious problem. For the case of methanol, the base metal threshold value was 24% of the critical stress intensity. With regard to the failed Apollo SPS fuel tanks, this value indicated that initial flaws as small as about 0.003 in. deep could have grown to failure when exposed to methanol at maximum operating stress.

Traces of residual methanol and fluorocarbon cleaning solvents were suspected of causing tank ruptures when tanks were later filled with NTO [449, 450]. Subsequent to the stress-corrosion failure of several tanks and a nationwide campaign of coupon testing in the laboratory under carefully controlled conditions, it was noted that highly purified N_2O_4 still caused stress corrosion, but N_2O_4 contaminated (deliberately or not intentionally) by a little NO ("green NTO") did not. This was the discovery of the stress-corrosion inhibiting quality of NO and the beginning of routine use of MON instead of pure NTO. In addition to chemical inhibition, it was also found that glass-bead peening, which introduced residual compressive stresses, alleviated the stress-corrosion problem.

The appearance of tarnish on fracture surfaces, obtained on Ti-5Al-2.5Sn alloy in NTO, seemed to indicate that some similarities exist between tarnish which forms on α -brass in certain ammoniacal solutions and that found on titanium alloys failed in dinitrogen tetroxide [451]. It was suggested that tarnish-rupture mechanism first described brass-ammonia systems also may be involved in failure of titanium alloys in dinitrogen tetroxide.

In tests with a total of 464 titanium alloy specimens in N_2O_4 , 84 failed during the tests [452]. These specimens were tested at either room temperature or 347K (165°F) and at imposed stress levels of 206–930 MN/m² (30–135 ksi). These included 11 unnotched sustained-load type specimens, 20 notched sustained-load type, and 133 bend-test samples. The nitrogen tetroxide used was from a bulk storage cylinder, which came directly from the manufacturer and conformed to the MIL-P-26539A grade. To this grade of N_2O_4 were added various additives and/or contaminants. Some tests used a grade of N_2O_4 which had come to be known as NASA Spec-Grade NSC-PPD-2 and which contained an excess of NO. The Ti-6Al-4V material used was in the STA condition. Some of this was material salvaged from the original failed Apollo tanks while additional samples were prepared from newly purchased and heat-treated sheet. The parameters evaluated in the N_2O_4 test program included many variables of the manufacturing processes including cleaning prior to welding and/or heat treatment, bimetallic couples, various contaminants and inhibitors in

the N_2O_4 , effects of oxidation and heat-treating oxide scale, and anodizing and/or shot peening treatments on the surface of the Ti-6Al-4V tanks. In tests with methanol, of 236 tests completed, 163 of the coupons failed at stress levels of 204–862 MN/m² (30–125 ksi). The time to failure ranged from as little as 2½ h to a maximum of 15 d.

The stress-corrosion cracking (SCC) of Ti-6Al-4V in N_2O_4 was investigated using small coupons in the laboratory as well as full-size flight-weight tanks at 290–345 K (65–165 °F) and stress levels from 170 to 690 MN/m² (25–100 ksi) to determine the time elapsed to start of crack initiation [453]. Cracks initiated at all stress levels at about the same time. An excellent correlation was achieved between crack initiation on laboratory specimens and failure time of tanks. Tests were also conducted on specimens that had been treated with the intent to prevent or delay stress-corrosion attack. Organic and metallic coatings turned out to be unsatisfactory because of insufficient adherence or NTO permeation. Peening with glass beads introduced residual compressive stresses and delayed or prevented stress-corrosion cracking. The prevention of stress-corrosion cracking by adding 0.78 mass-% NO to the N_2O_4 was also substantiated in tests at 345 K (165 °F) extended for 170 h.

In a series of tests, aimed at establishing the chemical composition of reactive and non-reactive N_2O_4 , all 30 U-bend coupons of Ti-6Al-4V cracked during exposure to “red reactive” N_2O_4 , while no cracking was observed in 10 identical specimens exposed to “green” N_2O_4 containing 0.8% NO [19, 454–457]. The results were obtained in four separate tests with 10 specimens each at 348 K (167 °F) for 72 h. Twenty specimens with a radius of five times the thickness broke in half during exposure to red N_2O_4 at a stress level about 90% of the transverse or longitudinal yield strength. Another group of 5 pairs exposed to red N_2O_4 at stress levels of 30, 50, 70, 90 or 100% of the longitudinal yield strength cracked in less than 72 h. Some cracks developed within 24 h at 347 K (74 °C). Dehydrated N_2O_4 required more NO (500 ppm) than normal N_2O_4 (150–200 ppm) to inhibit SCC. The data showed that a cracking N_2O_4 system contained N_2O_4 , NO_2 , HNO_3 , and usually some dissolved O_2 . Non-cracking N_2O_4 contained N_2O_4 , NO_2 , N_2O_3 , HNO_3 , HNO_2 , and H_2O . Addition of O_2 to a reactive N_2O_4 system increased the rate and/or the extent of cracking but not in direct proportion to the O_2 concentration. However, the absence of dissolved O_2 did not prevent SCC. Normally, one would expect that addition of HNO_3 to N_2O_4 would aggravate corrosion problems, but the opposite was true for SCC. Normal red N_2O_4 contains 0.5–0.6 mass-% HNO_3 . Addition of anhydrous HNO_3 to increase the concentration to 1 and 2% caused significant inhibition of SCC at 313 K (40 °C). At 1% HNO_3 , crack density was greatly reduced; at the 2% HNO_3 level, no cracking occurred within 70 h. SCC could not be induced in stressed U-bend specimens by vapor phase contact with mixtures of NO_2 and O_2 at 347 K (74 °C). The N_2O_4 samples were analyzed for the following:

- (1) combined nitric oxide (visible spectrophotometry)
- (2) total protons (NMR)
- (3) distribution of protonated species (near-infrared spectrophotometry)
- (4) dissolved oxygen (gas chromatography)

- (5) combined chlorine (X-ray fluorescence)
- (6) metallic impurities (atomic absorption)

Titanium alloys are susceptible to SCC, not only in NTO but also in hot salt water environments. Methanol, which may have been used as a cleaning fluid, can also induce SCC in titanium alloys [458].

Stress-corrosion susceptibility of Ti-6Al-4V in a variety of fluids was examined after the unexpected failure of a Ti-6Al-4V tank following exposure to methanol and N_2O_4 [459]. Ti-6Al-4V is susceptible to SCC in absolute methanol in both the annealed and solution-treated-and-aged (STA) conditions. The threshold for the annealed alloy appears to be near 50 percent of the yield strength or approximately 482MN/m^2 (70 ksi), while the threshold for STA treated alloy is somewhat less. Long-term exposure tests of Ti-6Al-4V for 2yr to acetone, Aerozine-50, distilled water, absolute ethanol, Freon[®]-PCA, Freon[®]-MF, hydraulic oil, absolute isopropanol, methylhydrazine, kerosene RP-1 or trichloroethylene showed that Ti-6Al-4V is not susceptible to SCC in those fluids.

The stress-corrosion cracking behavior of titanium and Ti-6Al-4V alloy in liquid N_2O_4 has been investigated from a standpoint of thermodynamic considerations and supported by autoradiographic, chemical, and electrochemical potential studies [460]. A hydrogen embrittlement mechanism involving HNO_3 in the commercial N_2O_4 appeared improbable. Another electrochemical mechanism in which O_2 plays a major role has also been proposed.

The compatibility of four maraging high-toughness, low-strength steels (T-1, HY-140, HP-9-4-20, and 18Ni200) with N_2O_4 and UDMH propellants was investigated [461]. The compatibility was evaluated by general corrosion and stress-corrosion tests at temperatures up to 322 K (49°C [120°F]).

The effect of NO concentration levels in N_2O_4 on stress-corrosion cracking of Ti-6Al-4V was investigated repeatedly [462]. Tests were performed on pre-cracked specimens under sustained loading while being exposed to N_2O_4 with various concentrations of NO and at various temperatures for a period of 22–72 h. K_I is the stress field intensity, and K_{ISCC} is the threshold (critical) stress intensity factor. K_{ISCC} corresponds to the beginning of the crack growth before the critical value. When the criterion K_{ISCC} is used, the sensitivity of material to the action of the corrosion medium is characterized by the ratio K_{ISCC}/K_{IC} , where K_{IC} is the stress intensity factor when testing in air. K_{IC} is the plane-strain fracture toughness. Results indicated that at room temperature for a 0.09% NO concentration, the reduction factor K_{ISCC}/K_{IC} was less than 0.53. No additional tests were performed at room temperature. Tests carried out at temperatures up to 338 K (65°C) indicated that K_{ISCC} decreased sharply with NO concentrations less than 0.18%, the lowest measured K_{ISCC}/K_{IC} value being 0.41. The effect of NO concentration levels on stress-corrosion cracking of Ti-6Al-4V welds was not investigated. These test results are in contrast with those reported later, where pre-cracked samples exposed to pure N_2O_4 showed a reduction in K_{ISCC} corresponding only to 20–30%

K_{IC} [463]. It was suspected that the presence of residual fluorocarbons like Freon-PCA that might have been used as degreasing solvents may have aggravated the stress corrosion of titanium alloys in NTO.

A general 220-page survey of stress-corrosion cracking of titanium alloys in any media (not only rocket propellants) gives good background information about this troublesome phenomenon [464].

A test program with full-size tanks verified that this particular tank design fabricated from the Ti-15-3-3-3 alloy was equivalent or superior to the same design fabricated from the Ti-6Al-4V alloy. Solution treatment took place just prior to welding, and final aging was performed after all welding was complete. Twelve-month exposure tests in MON-1, MMH, or hydrazine showed the Ti-15-3-3-3 alloy to be compatible with these propellants [465, 466].

Eventually, very large (1.9 m [75 in] in diameter and 2.7 m [106 in] in length) tanks holding 6800 kg (15000 lb_m) of propellant were made from the Ti-15V-3Al-3Cr-3Sn alloy and qualified for use with NTO in satellites [467, 468]. In this tank the propellants were separated by a common bulkhead.

Because of the Rosetta satellite launch postponement from 2002 to 2004, possible adverse effects of subjecting the titanium propellant tanks to off-loading, decontamination, and subsequent refilling were considered by the European Space Agency [469]. It was unknown whether alterations of chemical composition of residuals in the tanks during this process could cause unacceptable stress-corrosion cracking damage of the tank material. Until then the susceptibility of Ti-6Al-4V alloy to stress-corrosion cracking in the MON-1 environment had been assessed only under nominal conditions of stress and chemical environment that were not sufficiently representative of real cases such as the off-loading, decontamination, and refilling of tanks. A test program was developed that had the objective of assessing the possibility of stress-corrosion cracking in Ti-6Al-4V propellant tanks in the case of tank off-loading, decontamination, and refilling by determination of crack-propagation stress-intensity threshold values of parent plate and weld material exposed to the propellant tank stress and chemical environment expected during off-loading and decontamination.

6.4.4 Compatibility of Other Metals with Dinitrogen Tetroxide

Many metals that are resistant to N_2O_4 by themselves may suffer galvanic corrosion if they are in electrical contact with metals of different electronegativity while immersed in N_2O_4 , in particular if the N_2O_4 is not perfectly dry.

Other metals suitable for handling of N_2O_4 are Inconel and chromium. Chromium is suitable as an electroplating protective coating for other metals, but it has to be free of pinholes.

Copper, bronze, brass, Monel, zinc, cadmium, nickel, and silver are not suitable for use with N_2O_4 .

Interplanetary space probes that are designed to land on planets where we search for life need to be sterilized before launch to make sure that no terrestrial life forms pollute the destination search area. Sterilization by heating imposes severe materials compatibility requirements on all the components [470].

6.4.5 Cleaning and Passivation Methods

6.4.5.1 Cleaning and Passivation Methods for Ferrous Steels

Prior to first usage, tankage and conduits from stainless steel are cleaned with a solution of hydrofluoric acid and nitric acid in water to remove residues of rust and weld spatter. Subsequently, all parts are passivated with 45–55 mass-% nitric acid in water, flushed with water, and thoroughly dried.

Carbon-containing steels can be cleaned and surface-etched with dilute hydrochloric acid, but one must make sure that all traces of chloride are removed before loading with NTO. The recommended passivation method for steel uses an aqueous buffered solution of 0.5% NaOH, 0.5% NaNO₃, 0.25% NaH₂PO₄, and 0.25% Na₂HPO₄.

A seven-step pickling and passivating sequence is supposed to slow down the rate of corrosion if the tank is subsequently filled with NTO or MON [471].

Vandenberg Air Force Base has been the main launch site for DELTA-II, TITAN-3, and TITAN-4, and as such has stored and flown more NTO than any other launch site in the United States. They have developed expertise in cleaning and passivating CRES-304 in ground service equipment and have developed their own cleaning and passivating procedure. Iron leaching from CRES-304 cleaned and passivated by the Vandenberg Air Force Base method has been measured and compared to other stainless steel pretreatment methods [472, 473].

Corrosion rates of CRES-304L coupons in MON-1 have been measured as a function of cleaning procedures, surface layer formation, propellant impurity levels, and exposure duration up to 90 d [474]. Soluble iron leached from the metal was measured as a function of time. Iron contamination in NTO or MON may cause flow decay. Surface treatments tested were combinations of cleaning, pickling, and passivation procedures. Examining and comparing the surfaces of untreated and passivated coupons by XPS-ESCA has revealed significant differences in the surface species present. The results indicated the need for a spacecraft-grade MON with lower water and chloride content than that allowed by military specifications.

The flow-decay problem associated with NTO has been an important factor in the design of small bipropellant propulsion systems. The objective of a program established at the JPL has been to alleviate this problem by **(1)** developing a process to purify NTO to a level of contamination that will minimize the precipitation of iron-contaminated species, and **(2)** establishing component cleaning and passivation procedures that will prevent recontamination of the propellant [398]. Although a number of potential methods for purification of NTO exist, the method employing molecular-sieve column treatment appears to offer the advantages of simplicity of implementation,

relatively low cost, and proven capability to operate in the field as well as in the laboratory. In general, the molecular-sieve adsorption column treatment of mixed oxides of nitrogen (e.g., MON-1 and MON-3) results in little change in nitric oxide (NO) concentration (well within specifications), efficient removal of contaminant iron and other metals, efficient removal of water (i.e., HNO_3 and H_2O) when the column is activated, apparent removal of chloride impurity, and no introduction of deleterious material from leaching of the zeolites employed.

One common multi-step sequence of CRES or Ti alloy tank cleaning and passivation methods used a solution of an industrial cleaner such as Turco 4181 with ultrasonic agitation for degreasing; deionized water rinsing; nitrogen blow drying; pickling with a solution of 20–25 vol-% HNO_3 , 2–5 vol-% HF, and the rest deionized water at 293–318 K (20–45 °C) for 10–25 min; deionized water rinsing; nitrogen purge; passivation with 20–45 vol-% HNO_3 at 303–313 K (30–40 °C) for 15–20 min; isopropanol rinsing; and nitrogen purge drying [399].

The JPL, in support of the Galileo interplanetary probe propellant loading and unloading effort, has evaluated several cleaning and passivation methods for CRES-304L by measuring the amount of iron leached in either military-specification MON or “dry” MON during 14 or 90-d immersion at 316 K (110 °F). Four different ten-step cleaning/passivating methods were compared, which differed in the type of acid used for step 6, using either citric acid, 10% HNO_3 , or 30% HNO_3 or no acid at all. The rates differed widely for military-specification MON but were very similar for dry MON-1. The passivating oxide layers produced by the various methods were analyzed by XPS, in particular for the Fe/Cr ratio. The rate of iron leaching was very high during the first 20 d and then leveled off during the remainder of the 90-d tests.

6.4.5.2 Cleaning and Passivation Methods for Aluminum Alloys

Anodized aluminum is not any more resistant toward N_2O_4 than non-anodized aluminum. Up to this time, no coatings have been found that would make aluminum more resistant to N_2O_4 , in particular none that would make it more resistant toward moist N_2O_4 .

One of the attempted surface-preparation methods recommends etching the surface with chromic acid solution in water until the surface is evenly clean, and then rinsing and passivating with 45% HNO_3 .

Reactivity of NTO with Cleaning Agents

The reactivities of several selected halogenated precision-cleaning solvents with MON-3 have been determined by analysis of the rates of formation of halide ion decomposition products [475]. The solvents tested were Asahiklin AK 225, Asahiklin AK 225 AES, HFE 7100, HFE 7100 DE, Vertrel XF, Vertrel MCA, Vertrel MCA Plus, 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113), and trans-1,2-dichloroethylene (DCE). HFE 7100 DE, Vertrel MCA, and Vertrel MCA Plus showed significant reactivity with MON-3 oxidizer.

6.4.6 Hypervelocity Impact Reactions with Dinitrogen Tetroxide

Any oxidizer contained in a metal vessel is liable to react with the metal when the tank is hit by a hypervelocity projectile, such as a meteorite or orbital debris. The main concern has been with tanks that are filled with liquid oxygen or dinitrogen tetroxide.

The impact sensitivity of commercially pure titanium, Ti-6Al-4V, and precipitation-hardened 15-7 Mo stainless steel was measured under a range of stimuli, including shearing, scraping, galling, and impact by massive strikers and high-velocity bullets [433, 438]. Titanium ignition was rarely evidenced by sparks or noises and usually resulted in small fused areas on the impacted metal surface. The reaction did not propagate, although there was sufficient NTO present to allow complete consumption of the metal. The nitrogen formed by the reaction may impede access of fresh oxidizer to the burning metal surface. Precipitation-hardened stainless steel PH-15-7Mo was not impact sensitive in liquid NTO. The falling-hammer impact apparatus used hammers weighing 4.5, 9.7, and 11.6 kg and were dropped from a height of 3 m (10 ft). The ignition frequency of titanium A55 as a function of impact energy in NTO was about the same order of magnitude as observed for fluorine or oxygen. With titanium, the impact threshold energy required for ignition decreased with time spent in the loaded state: About three times more energy was required for freshly covered samples compared to others stored for 24 h in the wetted state. Additional storage for up to 3 months did not change the sensitivity any further. Most of the tests were conducted with specimens cooled to near 273 K, except the bullet-impact tests, which were conducted at ambient temperatures between 288 and 300 K. For the bullet-impact tests, containers were made from 7.5-cm sections of 19-mm grade A titanium tubing and were filled to three-fourths of their capacity. The major concern about freshly sheared metal surfaces igniting in NTO is with the design and operation of pyro valves.

6.5 Non-metallic Materials of Construction for Dinitrogen Tetroxide

There are several literature summaries on the compatibility of polymers with NTO and similar corrosive oxidizers [476–478].

6.5.1 Elastomeric Materials for Gaskets and Seals

During the development of the Titan-II system, a large number of the failures were blamed on lack of resistance of non-metallic materials (gaskets, O-rings, bushings) once they were exposed to N_2O_4 [345]. There are numerous literature summaries on elastomeric material compatibility with NTO and other propellants [479]. These are needed for gaskets, O-rings, expulsion bladders, and personal protection equipment.

Valve seats and pistons may suffer worse degradation while exposed to N_2O_4 (NO_2) vapors than when in the liquid phase. Kel-F may suffer degradation of surfaces that are in frictional contact with each other. Teflon, which is otherwise a very resistant

polymer, caused problems because NO_2 vapors may diffuse and permeate through this polymer

Teflon may also swell once it is immersed in N_2O_4 . This can lead to blocked valves or frozen pump impellers.

Teflon may cold-flow when under compression. The cold flow can be reduced by filling the polymer with inert powders and fibers. Glass powder-filled Teflon (brand name Fluorogreen) can be used for valve seats. Teflon-impregnated asbestos has been recommended for gaskets and washers (brand names Armstrong AT-810 and AT-812).

The following reports give more information on non-metallic materials for use with N_2O_4 , such as polyvinylidene fluoride (Kynar) [480, 481]. The development of a nitroso terpolymer containing pendent carboxy groups resulted in a nitroso polymer with greater crosslinking versatility. This polymer could be cured with metal salts of organic and fluorocarbon acids, epoxy compounds, and epoxy/metal oxide mixtures. These carboxy nitroso rubber vulcanizates were resistant to N_2O_4 , showing no change in mechanical properties after 90 d of total immersion at 347 K (165 °F). See also [482].

A set of elastomer seals previously considered unsuitable for exposure to N_2O_4 has been re-examined and found to be qualified for long-term use with N_2O_4 [483, 484].

Different fluoropolymers were evaluated as bladder materials for NTO or hydrazine [485], in particular for an advanced liquid propulsion system under development at the JPL [486]. Fluoroelastomers were expected to be resistant to hydrazine as well as to dinitrogen tetroxide, but permeability problems persisted.

Alternate repair methods have been considered for situations in which a threaded connection starts leaking small amounts of NTO, MON, or MMH and cannot be stopped from leaking by tightening of the cap or B-nut with a wrench. A clamshell repair kit that wraps and clamps around the leaking fitting has been developed for last-minute repairs of small leaks that otherwise would require a launch postponement and expensive off-site repair [487].

Additional work on long-term exposure of Kalrez to NTO was conducted at Aerospace Corporation [488, 489].

The weight and Shore A hardness of Kalrez 1045, a perfluorinated copolymer, were determined from samples from two different lots after exposure to dinitrogen tetroxide at two different pressures, 7320 kPa (72.5 atm) and 101 kPa (1 atm), for times ranging between 1 and 80 d and for observation periods up to 21 days following their exposure [490]. The largest changes occurred in the first 8–10 d of exposure. The weight increased between 15 and 30%, and the Shore A hardness declined from 83 to 60. Both weight and hardness partially recovered to their original values after removal from liquid N_2O_4 and drying in air. However, samples exposed for more than 1 d never fully recovered. The chemical stability of the Kalrez as a function of time exposed to N_2O_4 was monitored with solid probe-mass spectrometry. The results indicated that there was no main chain scission for the first 30 d of exposure. Loss of the pendant groups from the main chain was observed within 16 h. Loss of the pendant group from the crosslink site monomer and loss of the crosslink itself occurred after 150 h of exposure

to N_2O_4 . The overall results indicated that Kalrez 1045 exhibited exceptional stability to N_2O_4 , and seals manufactured from this material should be superior to the butyl rubber that had been employed in the oxidizer circuits of some launch systems.

O-ring seals of selected elastomeric and compliant materials were evaluated for resistance to liquid rocket fuels in a simulated end-use test [491, 492]. The candidate elastomers were placed under compression in closed cells and exposed to the liquid and vapor of NTO in direct contact with the O-ring seals at 296 K (73 °F) for extended periods of time. Rate of fuel loss through the seal and the change in physical properties of the seal materials were determined. Metal-clad and polyethylene-encapsulated elastomeric O-rings were also tested for resistance to NTO at 296 K (73 °F). The effect of temperature on elastomer endurance was determined by exposing the O-rings to NTO at 344 K (160 °F). The effect of direct immersion in liquid rocket fuel on the physical properties of the seal materials was investigated by immersing promising O-ring candidates in NTO.

A continuously recording permeation measurement apparatus was designed and used to characterize the permeation of NO_2 through Teflon [493]. In view of all the known data about NO_2 permeation through Teflon, one wonders why Mars Observer was flown with only two Teflon check valve seats separating the NTO from the pressurant gas space and MMH feed lines during the 11-month cruise phase from Earth to Mars, resulting in the loss of the spacecraft when the system was activated prior to Mars orbit insertion on 21 August 1993. Mars Observer was scheduled to perform an orbital insertion maneuver on 24 August 1993. However, contact with the spacecraft was lost on 21 August 1993. A likely reason for spacecraft failure was the leakage of fuel and oxidizer vapors through the improperly designed polytetrafluoroethylene (PTFE) check valve to the common pressurization system. During interplanetary cruise, the vapor mix had accumulated in pressurant lines, resulting in explosion and their rupture after the system was activated for course correction [494–496]. A similar problem would later cripple the Japanese Akatsuki Venus Climate Orbiter space probe in 2010.

An O-ring material used in storable propellant components on many NASA spacecraft designs was discontinued by the manufacturer, and NASA's stockpiles were expected to be depleted soon thereafter. The NASA Engineering and Safety Center (NESC) initiated a materials compatibility characterization effort to evaluate multiple replacement material options. Material properties of multiple replacement candidates were tested, looking at weight change, swelling, hardness, compression set, and tensile strength in representative environments to help identify suitable replacements [497].

6.5.2 Elastomeric Materials for Positive Expulsion Diaphragms and Bladders

Teflon is compatible with N_2O_4 , but NO_2 vapors permeate Teflon quite quickly. It was attempted to reduce the permeability by coating the Teflon with vapor-deposited aluminum films [498]. It was difficult to achieve the strength and ductility required for a liquid propellant expulsion bladder. Teflon-aluminum laminates were produced

that had no permeability to N_2O_4 or NO_2 , with modulus below 125ksi and tensile strengths in excess of 4 ksi.

Various elastomers were evaluated at the JPL for large hemispherical expulsion bladders for dinitrogen tetroxide and hydrazine in an advanced liquid propulsion system (ALPS) where propellants were to be stored for 1 year at 293–323 K without degradation of either the expulsion bladders or the propellants [499]. The original design of the ALPS envisioned a pair of collapsible bags containing hypergolic propellants ($\text{NTO}/\text{N}_2\text{H}_4$) within a common pressure vessel. In retrospect, this was a two-component bomb waiting to explode. Permeation of both NTO and N_2H_4 into the pressurant gas space might have caused ignition or deposition of corrosive reaction products. It was then realized that polymeric membranes alone are not suitable for such a design. Adding an “ NTO getter” that would continuously remove the permeated NO_2 from the gas side of the bladder would overly complicate the system. Most “compatible” polymers such as polyfluorocarbons are swelled and softened by contact with NTO . Silastic LS-53, for instance, swells to 300% of its original volume in NTO . Metallic platings on Teflon intended to act as a permeation barrier have failed because of swelling of the elastomer when the Teflon side was exposed to NTO . The swelling problem may be aggravated by the markedly anomalous coefficient of thermal expansion behavior of Teflon, which undergoes a five-fold increase between 379 and 433 K and then returns to its former value at the 444-K mark. A number of fluoropolymers were evaluated for the bladder application, but none was found to meet the strength, compatibility, and permeability criteria.

Silastic, Fluorel, Viton A, Viton B, and cured polyethylene were tested by immersion in NTO for 1 and 7 d at room temperature. All elastomers showed substantial swelling. Hydrocarbon polymers swelled less than fluorinated polymers did. Viton B showed the best resistance to NTO [500–502]. Carboxy nitroso rubber was recommended for long-term exposure to NTO at 347 K (165 °F), while resin-cured butyl rubber was satisfactory only for limited application [503].

Fluorocarbon bladder films must be flexible and have low permeability for NO_2 . One criterion requires a low-molecular-mass polymer, and the other requires a high-molecular-mass polymer. One must optimize the merits of high-molecular-mass, high-melting, rigid Teflon TFE and its lower-molecular-mass, lower-melting, and more flexible copolymer, Teflon TFE fluorocarbon resin. The high/low molecular-mass polymer proportions can be pre-assessed by stress-strain analysis of the tensile curve [504].

When the permeation of NO_2 through PTFE membranes between 0.04 and 0.14 mm thick (0.0015 and 0.0057 in) was tested in the temperature range of 202–389 K (30–116 °C), the diffusion and permeation coefficients were found to be independent of membrane thickness [505]. For NO_2 – N_2O_4 , the temperature dependence of the permeation rate was complex, partially because it was dependent on the $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ dissociation equilibrium. Unlike permanent gases tests in the same series of experiments, NO_2 interacts strongly and reversibly with the polymer.

Standard Teflon/aluminum laminate bladders employed as NTO and MMH zero-gravity propellant management devices on the Mariner Mars 71 space probe failed because of cracks and tears near an aluminum seal ring that formed the mouth of the bladder [506]. These failures occurred during flight-acceptance tests with inert solvents (Freon TF and isopropanol) used as simulant fluids. It was found that one of the laminate polymers, FEP 120, was particularly solvent sensitive, and it was then eliminated from future laminates for expulsion bladders.

When selecting materials for expulsion bladders, there is a dual concern: permeability of the polymer material for the propellant in one direction and permeability of the material for pressurant gas in the other direction. These concerns were adequately addressed in the construction of the propellant tanks for the five Lunar Orbiter missions that were launched between August 1966 and August 1967 and operated for up to 339 d in space, mapping the moon in preparation for manned lunar landings. During a simulated mission ground test, a comparison was made of the nitrogen permeation through a Teflon bladder and a laminated Teflon-aluminum bladder. With plain Teflon, pressure had equilibrated on both sides of the bladder within 100 h, whereas no detectable nitrogen permeation took place with the laminated Teflon-aluminum bladder [507].

Viton-B, Kel-F, and modified poly(cyclized 1,2-polybutadiene) tolyl urethane (CPBU) elastomers were tested for use in NTO expulsion bladders [508, 509]. In parallel, valve seat and gasket materials were developed for use in dinitrogen tetroxide and Aerozine-50. One of the materials developed for this oxidizer application was AF-E-124D [510]. AF-E-124D is a terpolymer of tetrafluoroethylene, perfluoromethyl vinyl ether, and perfluorophenyl vinyl ether. See also [511].

Seamless Teflon positive expulsion bladders were used for NTO, MMH, and Aerozine-50 propellants on the Apollo command module, service module, lunar descent module, and even on the S-IVB upper-stage RCS [512]. A similar bladder was used for MMH on the unmanned Lunar Orbiter velocity control system.

Composite Teflon-aluminum foil bladders were evaluated for the Surveyor lunar lander vernier propulsion system in an effort to reduce helium permeation and propellant (MON-10 or MMH/H₂O) saturation with pressurant gas [513, 514]. If the propellants were partially or fully saturated with helium, the large quantities of gas coming out of solution and the resulting two-phase flow decreased the dynamic response of the vernier engines. Propellant permeation into the ullage space was only a minor problem.

Bladders tested were initially made of multiple sprayed layers of tetrafluoroethylene (TFE) and fluoroethylene propylene (FEP). Others used a “bag-in-a-bag” design. TFE was manufactured similarly to a sintered-powder metallurgical part by compressing the powder. FEP was similar in character to a true thermoplastic material. The major problem was bladder tearing during three-axis vibration, in particular at the lower temperature range [515, 516].

Elastomers developed for service with dinitrogen tetroxide included AF-E-124D (perfluorinated polymer) and carboxynitroso rubber/HYSTL composites. Polymerizations were conducted to prepare a perfluorinated elastomer cured by a (perfluoro) covalent mechanism. Diaphragms molded from AF-E-124R, intended for NTO, had problems with sticking to the mold and poor compaction in the seal bead.

6.5.2.1 Elastomeric Materials Degradation Mechanisms

The mechanism and cause of N_2O_4 attack on polymeric elastomers was studied by measuring the effects of interaction, crosslinking, and structural variations in polymers [517, 518]. Polyethylenes with varying molecular weight, degree of branching, and unsaturation were studied by IR spectroscopy to identify the weak links in the molecule where N_2O_4 attack weakens the structure. Mechanical changes in polymer strength were determined by linear creep measurements, permeability to N_2O_4 , and chemical changes under N_2O_4 exposure. Polymers that suffered chain scission exhibited much larger irreversible elongation than before exposure. Results indicated that the best mechanical performance with respect to resistance of polyethylene to N_2O_4 was offered by polymers of intermediate molecular weight and containing little vinyl side group unsaturation. Fluorinated ethylene propylene polymer showed little degradation after 7 d of exposure to liquid N_2O_4 .

6.5.2.2 Insulating, Coating, and Encapsulating Materials for N_2O_4 Service

Neopren, Mylar, Hypalon, Micarta thermosetting plastic, latex rubber, and natural rubber are not suitable for service with N_2O_4 . In particular, these materials should not be used as insulation in electrical installations where they may be exposed to N_2O_4 or NO_2 . Electrical cables in Titan-II underground installations were all insulated with butyl rubber.

Thermal conditioning jackets are often insulated with foamed-in-place polyurethane foam. This material may auto-ignite if it comes in contact with N_2O_4 .

A liquid level indicator that had been encapsulated in Teflon failed because sufficient NO_2 vapors had diffused through the plastic sheath such that the electrical sensors were destroyed. An epoxy-coated CRES-304L sample suffered microscopic cracking and blistering of the coating and surface pitting beneath the coating [408].

6.5.3 Lubricants for N_2O_4 Service

Common lubricants are not allowed for use with N_2O_4 . One has to be extra careful that all components are carefully degreased before allowing them to come into contact with N_2O_4 . Not even lubricants that are considered acceptable for use with liquid oxygen can be safely used with N_2O_4 because they often react with N_2O_4 . The following lubricants have been recommended: Dow Corning DC-II, Silicone Lubricant, and Drilube Type 822-MMSN 3068; Nordcoseal-147 or DO-234-S as well as NA2-205-

2-Alochlor-1254-Monsanto; and Molycote-Z and Fluorolube (may be useable). Reddy Lube-100 is not suitable because it will harden after a short time.

Lubricants considered acceptable for NTO service are Castrol Braycote 601, DuPont Krytox 204AC, and Solvay Plastics Fomblin Y25. Fomblin PFPE fluorinated lubricants are resistant to aggressive chemical environments, high temperatures, and wide working-temperature ranges.

Perfluorinated greases are typically used as a thread lubricant in the assembly of non-welded NTO oxidizer systems. These greases, typically a perfluoroalkylether with suspended PTFE micro-powder, have attractive lubricating properties toward threaded components and are relatively chemically inert toward NTO oxidizers. A major drawback, however, is that perfluoroalkylether greases are soluble or dispersible in NTO and can contaminate the propellant and deposit in other parts of the system (valves, filters, injectors). This problem is exacerbated when propellant is circulated or transferred between storage units and test stands, resulting in widespread contamination. Contaminated NTO fails the non-volatile residue (NVR) specification analyses and may have negative effects on test hardware performance and lifetime. Consequently, removal of the grease contaminants from NTO may be highly desirable. Methods for the removal of perfluorinated grease components from NTO oxidizers, including distillation, adsorption, filtration, and adjustment of temperature, were investigated [519]. Krytox 240 AC is a mixture of a perfluoroalkylether (73–82% Krytox 143 AC oil) and PTFE (18–27%). Solubility or dispersibility data for the perfluoroalkylether oil (Krytox 143 AC) component of Krytox 240 AC and for Krytox 240 AC itself in NTO were determined. The NVRs of Krytox 240 AC-spiked NTO (25 g in 360 mL NTO, agitated after filtration through a 0.2- μm PTFE filter) taken at two different times after spiking were $29 \pm 1 \text{ mg/L}$ after 3 h of contact time and $200 \pm 20 \text{ mg/L}$ after 4 d of contact time. The NVRs of Krytox 143 AC-spiked NTO that were equilibrated 5 d and then filtered through a 0.2- μm PTFE filter and determined sequentially were three to four times as high. Purification of the contaminated NTO was attempted by passing it through adsorption columns filled with high-surface-area aluminum oxide, diatomaceous earth, or porous PTFE beads. Column adsorption with aluminum oxide removed approximately 30% of the spiked Krytox 143 AC NVR.

Graphite bearings in pumps and graphite gaskets in the packing of valve stems may swell during exposure to NTO or MON. A soak test of four kinds of graphite sealing material was performed in N_2O_4 to verify the compatibility of graphite material and N_2O_4 [520]. Variables that influenced the sealing performance of graphite material were graphite porosity, impregnating resin, graphite substrate material, graphite element, and microstructure. Analysis results indicated that the graphite impurities and microstructure had an important influence on resistance graphite material to N_2O_4 . See also [521, 522].

6.5.4 Sealants for N_2O_4 Service

If one wants to make a preliminary seal of a connection that does not need to be opened, one can seal it with a mixture of sodium silicate (“water glass”) and graphite powder.

6.6 Plume Contamination by Dinitrogen Tetroxide

It is common practice to vent unused dinitrogen tetroxide after geostationary satellites have arrived at their intended orbit, having used their bipropellant LEO-GEO transfer and apogee insertion thrusters. Venting unused propellants prevents them from sloshing around and causing center-of-gravity shifts. However, the slowly diffusing cloud of corrosive dinitrogen tetroxide may adversely affect other components of the satellite, such as magnesium fluoride anti-reflection coatings on solar panels and lenses [523].

7 Components for Dinitrogen Tetroxide Service

7.1 Flight Tanks for Dinitrogen Tetroxide Service

Reading through the rocket propellant literature, it becomes apparent that the two most difficult propellants to design long-term storage, lightweight, flight-qualified propellant tanks for are dinitrogen tetroxide and anhydrous hydrazine. Some of the literature on NTO propellant tanks is summarized in Table 45. Many of the reports listed in this table may not be specific for NTO but concerned more than one propellant. Commonalty of tanks is desired for designing a satellite. It appears that once a tank design is able to handle the more corrosive oxidizer, a similar tank can be safely used for the less corrosive fuels. Although the same tanks or very similar tanks can also be used for IRFNA or hydrazine-type fuels, the list of propellant tanks will not be repeated in the IRFNA or fuels section.

Table 45: Summary of literature on dinitrogen tetroxide propellant tanks.

Topic	Author	Year	References
Construction materials for NTO containers	Evans	1960	[401]
High-strength materials for liquid propellant tankage	Ng and Walsh	1969	[524]
Liquid rocket metal tanks	Wagner and Keller	1974	[525]

In early 1966, two Apollo main propulsion system titanium alloy tanks successfully completed 30-d exposures to N_2O_4 under maximum operating stress (approximately 100ksi wall stress) [449, 526]. These tanks were about 1.29 m (51 in) in diameter and about 4.25 m (14 ft) in length, with wall thickness of approximately 1.4 mm (0.055 in). In January 1965, a smaller RCS titanium alloy tank failed a similar 30-d test at approximately the same stress level. Failure analysis by Bell Aerosystems and North American Aviation concluded that the failure mode was stress corrosion, and the probable cause was contamination by chlorides prior to heat treatment. Six cracks were observed in three discrete areas of the tank wall. This tank had a Teflon bladder that, theoretically, isolated the titanium from the N_2O_4 . To be safe, however, ten additional tanks (without bladders) were put into testing at Bell to represent a sample of production runs to ensure that the contamination problem was an isolated one or that it was associated with a particular production period. Thirty-four hours after the tanks had reached test temperature 314 K (105 °F) and pressure, the first tank failure occurred. Three other tanks burst within the next 9 h of the test. When the failed tanks were examined metallurgically, thousands of stress-corrosion cracks per tank were found. These cracks varied from very shallow (0.07 mm [0.003 in]) to cracks extending through the 0.43-mm-thick (0.017 in) wall. NASA and the Apollo contractors were faced with a serious materials compatibility problem.

7.1.1 Propellant Expulsion Bladders for Dinitrogen Tetroxide Service

The majority of NTO propellant tanks nowadays are surface tension tanks; however, smaller tanks may still use bellows, pistons, reversible diaphragms or collapsible bladders. There have been extended efforts to develop NTO-compatible elastomers for bladders and diaphragms, but in the end the permeation rates were too high with all the materials tested. It was attempted to reduce the permeation rates by metallizing the bladders or diaphragms. Other reversible diaphragms were made from soft aluminum [527] or stainless steel instead of elastomers. The problem with reversible metal diaphragms is that they can be reversed only once, and pre-flight tests for expulsion efficiency will consume a good tank.

The propellants for the Surveyor lunar lander vernier thrusters were kept in tanks with Teflon positive expulsion bladders, but that was only a very short mission in transit to the moon [514, 528]. The Apollo service module RCS needed to operate under a wide variety of acceleration and zero-gravity loads, so the propellant needed to be contained in a bladder [512, 529].

It was attempted to form a flexible rollonet rolling-diaphragm propellant expulsion device inside a tank by chemical vapor deposition of aluminum from an atmosphere of decomposing alkyl aluminum [530]. Such a tank could be used for NTO and other propellants.

7.1.2 Propellant Expulsion Pistons for Dinitrogen Tetroxide Service

Atlantic Research developed a tank with a traveling piston ring that also held a reversible diaphragm to more closely adapt to the hemispherical concave dome at either end of the domed cylindrical tank [531]. The elastomer seals on the piston ring were separated from the corrosive propellant by a metal shear strip that would rip when the tank was activated. By the time the piston ring had traveled the full length of the cylindrical section, the diaphragm in it would have reversed and now contoured the dome at the other end of the tank, thus improving expulsion efficiency.

7.1.3 Surface Tension Tanks for Dinitrogen Tetroxide Service

Surface tension and contact angles of liquid propellants must be known in order to design surface-tension tanks for use in a zero-gravity environment in space. Surface-tension tanks have fine-mesh screens in the forms of chimneys, vanes, and galleries to collect and hold propellants in position near the tank outlets, even in a zero-gravity environment [532–534]. Pressurant gas entrainment is a major operational problem with surface-tension tanks. The tanks have bubble traps to retain gas bubbles and prevent them from flowing out with the propellant. Pressurant gas entrainment is inevitable toward the end of the useful life of a satellite after the propellant supply is exhausted.

Because the wire mesh exposes a large surface area to the propellant, wire mesh material compatibility is an important design criterion. Traditionally, most surface-tension PMDs have been made from stainless steel wire, but the tank shell would be a titanium alloy. That sets up the potential for galvanic corrosion of dissimilar metals. It would be better if both the PMD and the shell were made from the same material, but it has been difficult to extrude titanium into thin wires and to weave titanium mesh.

The Space Shuttle RCS and OMS tanks used surface-tension PMDs to collect propellant under zero-gravity conditions [535]. The surface-tension screen was a 325×2300 twilled double-Dutch weave (TDDW) pattern from CRES-304L. The surface area was approximately 8 cm^2 per cm^2 of screen. Such a large surface area had the potential of leaching a large amount of iron and causing flow decay after the iron nitrate saturation of the NTO was exceeded. In a test program at NASA WSTF, the iron leaching from the surface-tension screen was tested by exposing screen samples to 50 mL of MON-3 at 300 K (80 °F) for 1–90 d [11, 536]. The samples were cleaned using the same procedure as that used by the tank manufacturer for flight hardware, but that procedure did not include a nitric acid pickling/passivation step. The off-loaded propellant was analyzed for soluble and particulate iron by passing it through a $5\text{-}\mu\text{m}$ membrane filter. The iron production rate decreased steadily during the 90-d period from $2 \times 10^{-6} \text{ g d}^{-1} \text{ in}^{-2}$ to $0.08 \times 10^{-6} \text{ g d}^{-1} \text{ in}^{-2}$. The iron was mostly in the soluble form, and only a little particulate was retained on the screen.

Instead of wire-mesh assemblies, stacks of etched discs can also be used as surface-tension PMDs [537, 538], and instead of etched discs, double-perforated plates can also serve as capillary barriers in surface-tension PMDs [539]. The gap between the plates fills with liquid. The advantage of either system is that there is a wider choice of metals to make the discs or plates from.

In order to investigate the corrosion behavior of CRES-304 stainless steel propellant retention screens in surface-tension propellant tanks, flight-standard devices were stored for 35 months in MON-1 at 323 K (50 °C) [540]. There was no degradation of the screen's bubble point, indicating that chemical reaction of the materials, if any, was rather small and did not impact the performance of the screen. The corrosion rate was in the order of 2×10^{-6} mm/year. Using this corrosion, the worst-case iron content in the oxidizer of a satellite was calculated.

The NEAR Shoemaker space probe was the first space probe to enter into an orbit around the asteroid Eros and eventually hard-land on it. In order to meet a tight development schedule, the oxidizer tank, with a diameter of 19 in, was a space-qualified diaphragm Ti-6Al-4V shell tank originally developed for the EXOSAT mission [541]. It was modified by

- elimination of the elastomeric diaphragm
- removal of the diaphragm support ring
- addition of an outlet tube near the tank equator
- modification of the pressurant and propellant tubes and tube supports
- addition of a vortex suppressor

A surface-tension PMD oxidizer tank for the Orbital Sciences Star-2 platform, which has flown on more than two dozen commercial geostationary communication satellites, was subjected to simulated launch conditions on the vibration table, and its slosh dynamics were modeled by a detailed three-dimensional computer program [542]. The vane-sponge-type PMD was custom-designed for the Star-2 spacecraft mission. To minimize cost, an existing tank shell was selected as the baseline design and was slightly modified for the mission. No modification was done to the tank membrane to maintain qualification by similarity. The propellant tank shell was constructed of solution-treated and aged (STA) Ti-6Al-4V. This material provided excellent strength-to-weight characteristics. The PMD was made of annealed Ti-6Al-4V and commercially pure titanium material. The MEOP was 2.068 MPa at 323 K (300 psia at 122 °F), the proof pressure was 2.585 MPa (375 psia), and the burst pressure was 3.10 MPa (450 psia). The inlet/outlet ports were made of Ti-3Al-2.5V. The expulsion efficiency was 99.79% minimum for depletion during liquid apogee engine firing, and the nominal NTO oxidizer load was 223.2 kg (492 lb). The propellant in the tank would remain near the outlet in the worst-case accidental flat spin at 5 rpm, and the perforated sheet could keep the gas from penetrating into the pick-up assembly.

7.1.4 Long-Term Tank Storage Tests

An effort to establish the operational limit of allowable iron in NTO for system worst-case conditions (2ppm Fe) and to verify that this operational limit would not be exceeded after missile long-term (10-year) storage in the field was based on a combination of existing flow-decay data from the literature and experimental testing of a representative PEACEKEEPER missile fourth-stage oxidizer tank. At Rocketdyne, a flight-worthy PEACEKEEPER propellant storage assembly consisting of a Ti-6Al-4V shell and nitric acid-passivated CRES-304L TDDW screens was filled with MON-1 and kept in storage for 8 months at ambient temperature; oxidizer samples were drawn periodically and analyzed [543]. The initial iron content prior to loading the oxidizer had been reduced to 0.23ppm. A rapid rise of iron content to 0.5ppm Fe was observed during the first months, and after that the rate of iron leaching dropped to zero. The sludge formed during the initial propellant pickling settled, and a protective film formed on the steel. The results were more encouraging than similar tests conducted earlier at Bell Aerospace.

At the date of the first report, a significant number of liquid propellant tanks, fabricated by typical production methods of forming and welding and subjected to the same degree of inspection and quality-control documentation as production tankage, had been evaluated in storage testing for nearly 2 years. A number of leaks were encountered in all three types of tankage metals, aluminum, steel, and titanium. In general, the failures were attributed more to quality discrepancies during fabrication and welding than to a lack of compatibility of the metals themselves [431]. It was observed that if the relative humidity was of the order of 30% or lower, the nitrogen dioxide vapor dissipated into the atmosphere and did nothing to aggravate the leakage. If the relative humidity was of the order of 40% or greater, however, it did not dissipate, but rather hydrolyzed, forming dilute nitric acid on the exterior surface in the immediate vicinity of the leak. The action of the nitric acid was to enlarge the original leakage path, working inward toward the source of the leak.

Tank storage tests under extreme conditions of relative humidity and temperature (constant 303 K [85 °F] and 85% relative humidity for oxidizer systems and cycling between 294 and 339 K [70 and 150 °F] for fuel systems) in progress for 3–4 years indicated that leakage of propellant can occur as a result of improper weld joint design, inadequate quality control in fabrication, and insufficient acceptance-leakage testing. During this period a total of 12 tanks were analyzed for cause of failure [544]. Later reports contained additional metallurgical examinations of failed tanks and connecting tubing [545–547]. Stress-corrosion cracking susceptibility of the tank material in combination with the propellant and trace quantities of foreign compounds/elements in the propellant can aggravate the situation.

Tanks that had held NTO and were stored in a storage environment at 303 K (85 °F) and 85% relative humidity for several months were emptied, cleaned, and dissected for metallurgical analysis [548]. The corrosion effects of the stored propellants on the internal metal surfaces were negligible, with no serious degradation of strength or

structural integrity occurring. Corrosion occurred primarily due to pitting, gas and liquid phase interactions occurring during storage, manufacturing defects, and corrosion occurred at the manifold tubing welds.

7.2 Valves for Dinitrogen Tetroxide Service

It would be tempting to make valve bodies from titanium alloys instead of stainless steel because titanium alloys are lighter weight and have better resistance to corrosion. This applies to solenoid valves and pyro valves. The selection of titanium alloy for a latch valve resulted in a low-weight (308 g [0.68 lb]) valve configuration and avoided the potential of ferric nitrate formation and flow decay in the oxidizer [549]. However, freshly sheared metal surfaces in pyro valves, in particular titanium alloy surfaces, may ignite in NTO [550].

7.3 Pressure Regulators for Dinitrogen Tetroxide Service

Dinitrogen tetroxide vapor-phase corrosion was suspected of having caused the failure of a ground-test helium pressurizing gas-pressure regulator at NASA WSTF [551]. In a subsequent failure investigation, coupons of CRES-304L and 15-5PH with several different surface finishes were exposed to MON-3 vapor for 14, 27, and 100 d. Post-exposure visual examination did not show any significant corrosion. Based on water-soluble iron ion analysis in the water rinse of the coupons, the corrosion rates in the vapor phase were similar to and not worse than those in the liquid phase in MON-3.

The INTELSAT 603 satellite was stranded in a low-earth orbit for 797 d after the separation of the TITAN-III upper (second) stage from the satellite failed, awaiting Space Shuttle rescue. In the storage orbit, helium leakage was observed through the primary pressure regulator and then through the redundant helium regulator. During this time, the pressure-regulation panel of the bipropellant propulsion subsystem was engaged. Flight-pressure telemetry indicated primary regulator leakage, eventually followed by leakage through the backup regulator [552]. The malfunction of the oxidizer and fuel-side pneumatic check valves followed Space Shuttle deployment, evidenced by failure of the propellant tanks to maintain regulated pressure during liquid apogee thruster firing.

A pressure-transducer diaphragm failed, causing N_2O_4 to leak into a volume filled with silicon oil and leading to an explosion and the release of approximately 2.8 L (3 quarts) of liquid NTO [553] Page 63–65; [554]. In March 2003, the NASA WSTF was performing a life-cycle test of a fast-acting valve, using NTO as the test fluid [555]. The test system was designed to circulate NTO from one 55-gallon cylinder through the test article to an identical receiving cylinder and back again. The test system was constructed of ~50 ft of $\frac{3}{4}$ -in and $\frac{1}{4}$ -in stainless steel tubing. All wetted components in the

test system were compatible with NTO. The supply of NTO was pressurized to 2.07 MPa gauge (~300 psig). The test article was opened for 80 ms each cycle and had a flow rate of 0.86 kg/s (1.91 lb/s). After ~36000 cycles had been performed, an explosion was heard from the test cell. The video camera in the test cell was quickly obscured by a cloud of NTO, preventing the test team from being able to immediately determine the cause or location of the leak. The test system was quickly powered down, and all valves were closed to minimize the spill. Test personnel were then sent into the test cell with totally encapsulating suits to survey the damage and begin the recovery efforts. During the inspection, it was immediately obvious that a pressure transducer on the test article inlet line had failed catastrophically, releasing liquid NTO into the test cell. The test team recovered the inlet port and body of the pressure transducer and approximately three-quarters of the failed diaphragm. The manufacturer of the pressure transducer had not made the users aware that the transducer contained silicone oil.

7.4 Filters for Dinitrogen Tetroxide Service

With flow decay observed on many spacecraft in orbit and during ground testing, the sizing of filters becomes a critical spacecraft design issue to prevent clogging of vital flow passages. If the filter-screen openings are too small, the pressure drop may become prohibitive. If the particle-retention capacity of the filter chosen is too large, one pays a weight and space penalty.

The GALILEO Jupiter space probe was the first bipropellant propulsion system to go on an extended interplanetary mission. Ground testing of flight spare components was conducted to determine the representative number and size distribution of particulate matter collected in flow tests [556]. For these tests and for filter qualification tests, a number of effects were examined. The influence of gravitational particle settling on ground test results versus the zero-gravity flight environment had to be considered.

The inlets to propellant valves are usually protected by filters to retain particles that might get lodged on the valve seat and cause the valve to leak when it is commanded shut. The screen material on the filters has to be compatible with the propellant, which in the case of IRFNA or NTO is a difficult task. The nitrate film growing on the thin metal wires might cause a narrowing of the passages and increase the pressure drop or embrittle the wires. Similar wire mesh is used in surface-tension PMDs in propellant tanks for zero-gravity operation. The long-term effects of propellant immersion on fine Micronic stainless steel wire cloth were studied for IRFNA and NTO and nine other propellants [557]. Immersion-time histories reported in the literature ranged from 3 months to 7 years.

7.5 Pumps for Dinitrogen Tetroxide Service

There are two types of pumps for NTO service: those on the launch vehicles and those in the ground service equipment (GSE) used to load propellant onto the launch vehicles. The difficulty is to find methods to lubricate the fast-rotating shafts. Conventional lubricants would react with NTO and constitute an explosive hazard. Pumps have been designed that are lubricated with the corrosive medium they are pumping, but minor irregularities (scraping blades) will cause ignition.

On 12 August 2003, at CCAFS launch pad LC-40 during the bleed-in operation for the TITAN-IV launch vehicle's second-stage propellant load, the oxidizer centrifugal pump exploded [553]. Along with the liquid N_2O_4 release of approximately 150 L (40 gallons), the explosion created a large amount of shrapnel that caused significant damage to the surrounding GSE. The pump was completely destroyed. Prior to the explosion, a reduced flow rate was noted while oxidizer was being loaded onto the first stage, and it was suspected that one of the filters became clogged with particulates. Following this event, all similar pumps at the Kennedy Space Center were replaced and surrounded by a shrapnel catch basket. There had been three other similar occurrences with oxidizer pumps in 1963, 1964, and 1980 throughout the history of the TITAN program.

Pumps, flow meters, valves, and pressure transducers for the TITAN-II missile were endurance-tested and calibrated in a closed-loop propellant pumping system containing two 22.7-m^3 (6000-gallon) tanks and two 984-L/min (260 gallons/min) pumps for NTO and Ae-50 [558].

A vacuum-tight electric drive was designed for a gear pump for pumped circulation of dinitrogen tetroxide [559]. The drive was designed for circulating dinitrogen tetroxide in a closed loop of a thermophysical high-pressure-flow test bench.

8 Handling of Dinitrogen Tetroxide

8.1 Handling and Ground-Service Equipment for Dinitrogen Tetroxide

The literature summaries listed in Table 46 provide useful information about the handling of N_2O_4 and other corrosive propellants. Most of these publications date back to the time in the early 1960s when TITAN-II missiles were under development and about to be placed in silos. Some of the publications deal with NTO as well as Aerozine-50 and other hypergolic propellants, so they are more of general industrial safety and historical interest.

Dinitrogen tetroxide is shipped as a liquid in steel cylinders and tank cars under its own vapor pressure (730 mm Hg [97 kPa] at 293 K [20 °C]). Dinitrogen tetroxide manufacturers will usually provide an instruction sheet with the shipment explaining how

Table 46: Literature summaries for handling of dinitrogen tetroxide and hypergolic propellants

Ross	Nitrogen tetroxide as an oxidizer in rocket propulsion	J. ARS	1950 [1]
Terlizzi and Streim	Liquid propellant handling, transfer, and storage	Ind. Eng. Chem.	1956 [560]
Tenenbaum	Testing with storables	ARS preprint 1263-60	1960 [561]
Liberto	Storable propellant data for the Titan-II program	Progr. rept. 8122-93	1961 [347]
Anonymous	Research on the hazard classification of new liquid rocket propellants, Vols I and II	Rocketdyne R-3217	1961 [562, 563]
Suarez-Alfonso	Nitrogen tetroxide handling manual	Rocketdyne R-3135	1961 [60]
Suarez-Alfonso	Mechanical system design-criteria manual for nitrogen tetroxide	Rocketdyne R-3131	1961 [66]
Fish	Storable liquid propellants, nitrogen tetroxide/Aerazine-50	LRP-198 (second edition)	1962 [564]
Anonymous	Storable liquid propellants	Aerojet General LRP 198	1962 [565]
Bender	Titan-II propellant handling and compatibility problems	AIAA preprint 63-086	1963 [345]
Anonymous	Handling and storage of liquid propellants, revised edition 1963	U.S. Office of the Director of Defense Res. and Engineering	1963 [566]
Anonymous	Handling and storage of nitrogen tetroxide	Chem. Corps U.S. Army, MD	1963 [567]
Wong	Material compatibility and corrosion control	SAE paper	1964 [568]
Carter	Liquid propellants safety handbook	NASA-TM-X-56611	1965
Cloyd and Murphy	Handling hazardous materials technology survey	NASA SP-5032	1965 [569]
Trulove (ed.)	Use of nitrogen tetroxide	AFAL-CP-88-003	1988 [570]

to best transfer the propellant from the delivery vehicle into stationary storage installations.

Hypergolic propellants, NTO, and MMH can be handled safely if propellant-loading personnel are properly trained. A 2-day training course for safe handling of hypergols was developed and routinely held at NASA WSTF [571].

The design of hypergolic propellant GSE for fueling launch vehicles and satellites at NASA KSC is outlined in [572].

8.1.1 Long-term Storage Tests of Prepackaged Systems

Storable prepackaged propellant systems of a liquid rocket propellant feed system were designed, fabricated, tested, and delivered by General Dynamics Convair for subsequent use in a storability investigation by the Air Force Rocket Propulsion Labora-

tory (AFRPL) [573]. The propellant tanks were fabricated of Al-2219 and had a volume of approximately 57 L (15 gallons). Each of the 23 delivered systems consisted of a 15-gallon propellant tank that contained either a surface-tension force-orientation device or a rolling-diaphragm positive expulsion device, along with one of three different pressurization subsystems. The pressurization subsystems included a liquid propellant (hydrazine) gas generator, a solid propellant LFT-3 (AN composite) gas generator, or a stored gas device. Within the gas-storage bottle, 90% nitrogen/10% helium gas was contained at 20.79 MPa (3015 psia) by an explosive valve. Each tank was welded closed such that the propellant was contained within an all-metal, welded tank. Metal rupture discs, welded in the tank inlet and outlet, would rupture for propellant discharge when pressurized by the pressurization subsystem. The systems were delivered to AFRPL, hermetically sealed, and loaded with their respective propellants: mixed hydrazine fuel (MHF-5), dinitrogen tetroxide (N_2O_4), or chlorine pentafluoride (ClF_5). In addition, four tanks were delivered empty to AFRPL. One sample of each of the storage subsystems was test-fired shortly after being loaded with propellants, and the pressure history and propellant flow rate were recorded. This was to serve as a baseline for later comparison when the stored units were to be tested using the same procedure. This report described only the pre-storage testing. The test results of the multi-year stored units would be published later in separate reports.

During the first two phases of a four-phase metallurgical analysis of post-storage tanks, approximately 40 tanks storing NTO, ClF_5 or IRFNA had been examined after being stored at 303 K (+85 °F) and 85% relative humidity for up to 6 years. Under the first phase of this program, storage containers with N_2O_4 or ClF_5 , stored for periods of time up to and including 6 years of pressurized exposure, were examined and chemically and metallurgically analyzed [574, 575]. Tankage materials included aluminum alloys 2021, 2014, 2024, 2219, 6061, 7039, X7007, and 5456, as well as Arde 301 stainless steel, steel A-286, and Inconel 718. Two types of N_2O_4 , oxygenated and unoxxygenated, were evaluated for compatibility. The evaluation of the storage containers revealed that the major source of degradation was external due to a corrosive atmosphere in the storage shed. The primary cause of corrosion was the dilute-acid, high-humidity storage area environment. Internal corrosion observed in a very limited number of containers was attributable to a lack of thorough rinsing after exposure. The majority of internal surfaces showed little or no degradation from either oxidizer. Corrosion effects on the internal surfaces of aluminum and stainless steel tanks were negligible, with no serious degradation of strength or structural integrity occurring. Problems were seen only with some of the weldments in the manifolds through which the tanks had been filled and drained. For the most part, corrosion occurred on the outside of units where some leakage took place.

The third phase of the program involved the examination of a complete Bullpup missile containing IRFNA and MAF-1; see *Encyclopedia of Oxidizers*, chapter “Red Fuming Nitric Acid.”

During the fourth phase of the metallurgy evaluation program, 37–55-L (10–15-gallon) cylindrical steel A-286 and cryostretched spherical CRES-301 tanks with ring-stiffened reversing diaphragms for propellant expulsion that had been in long-term storage for 5–8 years at AFRPL, Edwards Air Force Base, and contained NTO or ClF_5 were examined for corrosion and leakage [576].

8.1.2 Transportation of Dinitrogen Tetroxide

Dinitrogen tetroxide is shipped under Hazard Classification 2.3, UN1067, with oxidizer, corrosive, and inhalation hazard warning placards.

The USAF buys, stores, and transports liquid dinitrogen tetroxide (N_2O_4) in support of the nation's military, NASA, and commercial space programs. Until 1999, the Air Force contracted with the Vicksburg Chemical Company in Vicksburg, Mississippi, for the manufacture of this oxidizer. Commercial carriers transported N_2O_4 to Air Force, NASA, defense contractor, and commercial test facilities throughout the country. The Vicksburg facility went through several bankruptcies, ownership changes, and name changes during the past decades and was eventually shut down. The next procurement cycle was with Mississippi Chemical Corporation in Yazzo City, Mississippi. In 2004, Mississippi Chemical Corporation was acquired by Terra Industries Inc. As of 2012, NTO was supplied by Terra Mississippi Chemical Company (formerly Mississippi Chemical Corporation, now CF Industries) in Yazzo City, Mississippi. It shipped NTO in bulk quantities by tank trailers and by rail cars. Smaller quantities were also transported in cylinders by truck and ship. The Defense Logistics Agency – Energy, Aerospace Energy business unit at Kelly Air Force Base in San Antonio, Texas, manages the procurement, transportation, storage, and disposal of this oxidizer and many other propellants for the Air Force. Shipments are made under the direction of the directorate's Transportation Office. This office initiates many safeguards to ensure that shipments are made in the safest manner possible and constantly looks for ways to improve the safety of the transportation system.

The Transportation Office also publishes Emergency Response Plans that provide guidelines for responding to highway and rail accidents or incidents involving N_2O_4 . The Department of Transportation (DOT) requires such a plan for moving this product in bulk on public highways and railways. The Air Force conducts training exercises in accordance with these plans. The greatest potential for spills or leaks is during coupling or uncoupling of the hoses for loading or unloading of tankers.

Routes for the transportation of N_2O_4 are selected using a computerized route-risk assessment program. The program computes a risk factor for each proposed route, considering such things as population, probability of an accident, and the potential effect an accidental product leak could have on the population along that particular route. The routes are reviewed periodically to meet DOT exemption and approval requirements. In response to protests from California lawmakers, the shipment route to

Vandenberg Air Force Base was changed. In 1990, a 200-page study by the Air Force evaluated alternate modes of shipping (rail, barge) but concluded that transportation by truck tank cars was still the best method. The study found that the USAF practice of trucking the fuel through southern California was preferable to shipping it by barge through the Panama Canal or transporting it by rail. The Air Force rerouted the shipments after elected officials from the San Gabriel Valley, the San Fernando Valley, and Ventura County protested against shipping it through their communities. A northern highway route through less-populated Barstow, Mojave, Gorman, Mariposa, and Santa Maria was selected instead.

The Air Force recognizes the risk in transporting N_2O_4 and has taken many precautions over the years to enhance the safety of product shipment. These precautions have proven effective. There have been no accidents resulting in the loss of liquid product on public highways in more than 30 years. As of 1978, the Space Fuels Logistics branch had shipped approximately 1.7 million pounds of NTO, 1 million pounds of MON-1, and 0.4 million pounds of MON-3 over 250000 round trip miles each year. Personnel in the USAF Logistics Directorate could remember only four incidents involving NTO trailers while in transit [577]. Only two of the four incidents resulted in the release of NO_2 vapors to the environment. There have been no reported incidents of leakage involving tank cars or one-ton containers while in transit. There have been problems with leaks at the quick disconnects while unloading at Vandenberg Air Force Base. Occasionally, rail cars being used for storage developed gas leaks in the dome area.

The Air Force contracts only with long-established commercial motor carriers who have excellent, industry-proven safety records. The experience, qualifications, and training required of drivers exceed Code of Federal Regulations requirements for drivers of other hazardous materials. Two drivers are assigned to each tank trailer carrying the product. Two tank trailers comprise a normal shipment.

Drivers receive formal training every 2 years on the physical and chemical characteristics of N_2O_4 . Training includes instruction on authorized routes of movement and safe stopping places; actions to take in the event of mechanical breakdown, accident or product loss; and other responsibilities such as required documentation and special shipping instructions. A trained technical escort team accompanies all shipments. The team provides an immediate emergency response capability and communications link to local and federal emergency response resources. All team members are thoroughly trained on the physical and chemical properties as well as the hazards of the propellant and the characteristics of the cargo tank trailer. They also receive hands-on training for minor repairs of the trailer. They receive training on hazardous material incident response that satisfies the U.S. Environmental Protection Agency (EPA) training requirements for those who first respond to the scene of such an incident. In addition, they receive classroom training on the Emergency Response Plan.

An accompanying truck carries the emergency response equipment and tools that may be used, if needed, by the team to mitigate minor product leaks or spills. This includes personal protective gear, tools and equipment, decontamination equipment

and supplies, and first-aid equipment and supplies. Although federal law does not require escorts for each shipment, an escort team accompanies each N_2O_4 tank trailer shipment.

8.1.2.1 N_2O_4 Tank Trailers

Special MC 338 tank trailers are used for the bulk highway shipment of N_2O_4 . The trailers are equipped with state-of-the-art safety features that far exceed industry standards and current federal packaging specifications for equipment used to transport products with similar hazards. The cargo tank trailers have the capacity to haul 9500 L (2500 gallons) of product.

The trailers and equipment are constructed from rugged stainless steel. The tank consists of an inner tank and an outer jacket. The annular space contains a gaseous nitrogen blanket to maintain an inert corrosion-free environment. A honey-combed material similar to aluminum at the front of the trailer is designed to absorb energy if the trailer is involved in a head-on collision, greatly reducing the possibility of a spill.

Valves and piping are located on the top rear portion of the trailer and are enclosed in a retractable steel cover and roll bars for protection. The roll bars can withstand the full weight of the trailer and its contents in a rollover without damage to piping or valves. Also, the cover will not close if any of the valves are not completely shut off. An additional safety feature is that each trailer has an emergency valve-leak kit of color-coded canisters specifically fitted for each valve. When installed, the canisters seal off any leaking valve until more permanent repairs can be made.

8.1.2.2 N_2O_4 Rail Shipments

Air Force shipments of bulk N_2O_4 by rail have been made to Cape Canaveral Air Station, Florida, and major users include the Aerojet Propulsion Systems Plant in California. At one time there were eight tank cars in the N_2O_4 rail fleet. The rail tank cars were built to class DOT 105J500W specifications. The tank cars were insulated stainless steel pressure cars, with a manway nozzle designed for top loading and unloading. Bottom outlets or washouts were prohibited. The tank cars were fabricated from SA-240, type 304L stainless steel. The tank car was equipped with thermal protection, full head puncture resistance shields, and double shelf couplers. The tank cars had the capacity to haul 37800 L (10000 gallons) of N_2O_4 . All valves and piping on these cars were located on the top, within a lockable dome, near the center of the car. A valve-leak kit of color-coded canisters was designed to specifically fit each valve. When installed, the canisters seal off any leaking valve until more permanent repairs can be made.

Until 1987, the USAF transported NTO under DOT Exemption DOT E-3121. In the fifth revision of DOT E-3121, the DOT placed several additional requirements upon the USAF as a requirement for reissuance of the exemption. The new requirements included an emergency response plan, risk assessments, updates for highway routes of movement, and periodic updates of the risk assessments to ensure that routes remain the safest possible.

8.1.2.3 Cylinders

With the end of the TITAN-III/IV program and then again with the end of the DELTA 2 program, the volume of NTO shipments decreased by orders of magnitude. For example, in 2012 DLA Energy Aerospace Energy shipped only 180 cylinders with N_2O_4 .

In July 2013, the DOT granted a 4-year extension to special permit DOT-SP 10497 (eleventh revision) to Lockheed Martin Commercial Space Systems for the transport of N_2O_4 in cylinders of 30-in diameter and 7-ft length [578]. In December 2013 a special permit (fourteenth revision) was issued for construction of modified 4BW stainless steel cylinders DOT-SP 11580 [579].

8.2 Design of Dinitrogen Tetroxide Storage Facilities

Stationary storage tanks should be under cover to be protected from rain and sun, but without side walls to allow good ventilation. Building structures should not contain combustible materials such as wood or tar paper. Corrugated aluminum sheeting is often used because it combines chemical resistance with good reflectivity in hot climates.

Storage and transfer installations should have a suction duct into which brown fumes from transfer and purging operations can be safely vented. Relief valves and burst discs from storage tanks can be connected to this line. It is recommended to keep a spare empty tank on standby into which the contents of a leaking tank can be transferred in case of an emergency. The report [567] contains a detailed layout for NTO storage areas and shows designs for NTO disposal facilities.

8.3 Transfer of Dinitrogen Tetroxide

The transfer of N_2O_4 between shipping and storage tanks on the ground can be achieved by pressurization, gravity, or pumps. Because tanks usually do not have a bottom drain for safety reasons, gravity transfer is not always possible. Most NTO tanks have a stand pipe (dip tube) to withdraw liquid from the bottom of the tank.

The vapor pressure of N_2O_4 at room temperature is not sufficient to enable transfer of the liquid through a stand pipe under its own vapor pressure. Transport and storage containers carry at least two ports through which the tank can be pressurized or depressurized, and a third port is connected to a stand pipe. If the propellant is transferred by pumps, one must feed dry, inert gas back into the tank that is being emptied, or one must connect a vapor return line that allows gas and vapors from the tank being filled to escape to the tank being emptied.

The choice between pressure transfer and pump transfer depends on the size of the tank. Pump transfer is usually employed only for large tanks.

Propellants for the second stage of the Delta launch vehicle were loaded from the pretreatment unit into the rocket by pressurized transfer [580]. TITAN-III and TITAN-IV launch vehicles were loaded with pumps.

8.3.1 NTO Propellant Transfer for In-Orbit Refueling

The Russian space program has had significant experience in transferring propellants (N_2O_4 and UDMH) between supply space ships and orbiting space stations, starting with MIR and continuing with the International Space Station.

The transfer of NTO and MON is more difficult than the transfer of storable liquid fuels like hydrazine, MMH, and UDMH. In the case of MON, each transfer operation results in loss of some NO, which changes the stress-corrosion behavior of the remaining liquid oxidizer.

In most cases, propellant transfer for in-orbit refueling has been practiced with other, less volatile fluids first before the zero-gravity transfer of NTO or MON was attempted. Transfer of cryogenic fluids would be even more difficult. See also [581].

8.3.2 Propellant Feed Systems for NTO in Rockets

The design of propellant feed systems in rockets, satellites, and space probes is a chapter in its own right. We are summarizing here only chemical properties of N_2O_4 that may influence the design of such systems. Only large rockets, such as space boosters in the size category of TITAN-III, TITAN-IV, and ARIANE-I through ARIANE-IV, DELTA upper stages, DNEPR, and PROTON will use turbopumps to feed the propellants into the combustion chamber. Satellite and space probe propulsion subsystems will typically use pressure-fed propellants.

The chemical considerations in designing feed systems include the compatibility, i.e., non-reactivity of the oxidizer with the pressurant gas. In selecting an inert pressurant gas, the reactivity and solubility of the pressurant gas must be known. Helium and nitrogen can be used as pressurant gases for N_2O_4 or MON. The solubility of pressurant gases in N_2O_4 and MON is summarized in Section 3.11 and 4.1.8.

There has been a considerable amount of concern about pressure surges when liquid propellants are entering a propellant distribution manifold that has previously been evacuated or filled with low-pressure gas. The “priming” of propellant feed systems may cause severe pressure spikes, even with chemically inert fluids. Priming with chemically reactive fluids such as anhydrous hydrazine may lead to explosions if extreme surge pressures are allowed. No such concern exists with NTO, so the main concern is about a strictly mechanical, fluid-dynamic event leading to pressure spikes. Studies have looked at both priming pressure spikes and water hammer pressure spikes in propellant feed lines. It is possible to develop an analogy between the classic water hammer phenomenon and the priming water hammer caused by surge flow. Several of the studies that were primarily concerned with priming

of hydrazine or MMH feed lines have also included NTO in their calculations and experiments.

Experimental test results with water in simplified straight and 90°-bent-line geometries were compared to numerical simulations computed for MON, MMH, or water using ANABEL software [582]. This computer program can perform the computation of transient compressible/uncompressible monophasic or diphasic flow with separated phases in fluidic networks, allowing the prediction of water hammer and also pressure losses. With a push pressure of 40 bar, the predicted pressure spikes at the end of the line were 200 bar for MON, 172 bar for MMH, and 183 bar for water.

Fluid hammer experiments were conducted with NTO, MMH, or water in the propulsion laboratory of Office National d'Etudes et de Recherches Aérospatiales (ONERA) [583]. The objective of that study was to generate a reliable experimental database on the fluid hammer phenomenon with real propellants (NTO and MMH) to validate the physical models implemented in the numerical codes. Only one experiment was performed with NTO for a vacuum pipe pressure below the saturation pressure. Compared to MMH and water experiments performed under the same operating conditions, the fluid hammer amplitude and frequency with NTO were smaller. Regarding the peak temperature in the gas pocket, very small variations were recorded for water and MMH, whereas the temperature increase for NTO was more than 623 K (350 °C).

8.4 Decontamination of Dinitrogen Tetroxide Tanks

8.4.1 Decommissioning of N_2O_4 Systems

In the wake of and at the end of the Cold War, numerous missile launch silos containing storable hypergolic propellants had to be decommissioned and neutralized on both sides of the Iron Curtain.

The United States entered into the SALT-II agreement with the Commonwealth of Independent States (the successor to the USSR) to assist them in the removal and safeguarding of missiles and their payloads. Several conferences were held to exchange information on the decommissioning of the missiles and disposal of the propellants. In addition to NTO (code name Amyl), large quantities of RFNA (code name Melanj) had to be destroyed. In the evaluation of various disposal methods, methods were sought that would result in useful products, such as fertilizer.

Most hypergolic bipropellant engines undergo an acceptance test firing at the manufacturer's facility before they are mounted on a flight system. Subsequent to the acceptance test firing, the engines have to be thoroughly decontaminated. Decontamination methods differ for ground test equipment and flight systems. For flight systems, it would be best to fill them with propellants only once, immediately prior to launch. In some unforeseen circumstances, the launch may be postponed, and in those cases propellants have to be drained for storage or repair of the spacecraft. Dinitrogen tetrox-

ide, NTO, or MON is difficult to remove from ground test equipment or flight systems because even after all of the N_2O_4 evaporates, a thin film of nitric acid residues is left on the equipment, which may still be quite corrosive if not immediately removed.

In order to decommission a missile or a rocket test stand containing NTO, the first step is to drain the tanks and lines of liquid N_2O_4 , followed by a purge with hot, dry nitrogen [347]. After the purge gas is free from NO_2 , there usually remains a thin film of nitric acid and other less volatile or non-volatile residues on the tank walls. The complete removal of these residues can be achieved by rinsing with a dilute solution of triethanolamine, a method that was widely used for the cleaning of Titan-II engines [584].

8.4.1.1 Evaluation of N_2O_4 Equipment Decontamination Methods

Decontaminating a propulsion subsystem by pressure cycling by filling the tanks with nitrogen up to the maximum expected operating pressure (MEOP), allowing equilibration with the vapors, preferably at moderately elevated temperatures, and repeating this process many times may have advantages over solvent flushing. It was a serious error that continued use of methanol and Freon MF was recommended for decontaminating Apollo service module propellant tanks in spite of some concerns expressed by other metallurgists.

During the Apollo service module and lunar module development, the use of improper solvents (methanol) resulted in unexpected failure of an NTO tank. Subsequently improved methods were sought for propulsion subsystem decontamination that avoided the use of methanol. The compatibility of solvents with propellant and components was evaluated in a series of laboratory studies [585–587]. In addition, the methods for decontamination, sequence of solvents used, temperature dependence of solvent efficiency, diffusion rate of absorbed propellant from elastomers, removal of propellant from flushing solvents, and disposal of propellant-contaminated flushing solvents were studied. Even after all of the N_2O_4 is removed from a tank, the next question is how to remove the residual flushing solvent. Since the tanks cannot be evacuated because they would collapse, an extended dry inert gas (nitrogen) purge would be required to remove all solvent before the tank is put into storage or used again with a fresh load of propellant. Small spacecraft or propulsion subsystems could be placed into a vacuum chamber and vacuum applied to both sides of the tank to encourage residual solvents to evaporate.

There have been at least two incidents during which MON had to be downloaded from a spacecraft. The launch of Galileo was postponed in 1986. Because of safety concerns after the Challenger accident, NASA cancelled the planned use of the CENTAUR on the Space Shuttle, and Galileo was moved to the two-stage interim upper stage (IUS), later launched in October 1989 on STS-34.

The other incident happened in 2008 when an Orbital Sciences satellite on a STAR-2 platform had to be destacked from the launch vehicle because, a few days prior to the scheduled launch in Baikonur, a clumsy crane operator had accidentally bumped into

the antenna of the satellite and damaged it beyond on-site repair [588]. The satellite had to be destacked, off-loaded, and decontaminated before it could be flown back to the manufacturer's facility in the United States for antenna replacement. It took substantially longer to fully inert the hydrazine fuel tank than it took to inert the MON-3 oxidizer tank. All of the previous off-loading incidents had involved MMH instead of N_2H_4 as the fuel, which is more volatile and easier to remove than N_2H_4 .

The ROSETTA space probe was originally fueled in November 2002 and scheduled for January 2003, but after a failure of an ARIANE-5 launch vehicle on an earlier mission, the launch had to be postponed, and the MMH was off-loaded but the MON was not. Although the MON tank was neither off-loaded nor depressurized, it is interesting to follow the logic in the decision not to off-load the MON tank [469, 589–591].

8.5 Atmospheric Dispersion of NO_2 Fumes in Case of Accidental Releases

Of all rocket propellants flying at this time, the concern about toxicity effects of accidental spills is the highest with NTO and MON. The boiling point of these oxidizers is close to room temperature, the vapor pressure is close to atmospheric pressure, and the vapors are heavier than air, slowing down their dispersal. There are many computer models for predicting atmospheric dispersion of toxic chemical vapors under a variety of source strength and atmospheric conditions [592–594] and the modeling of an NTO spill is typically run as a test case because there are some real-life dispersion test data available to compare the accuracy of the model to. Most of the plume models are for emissions from stationary sources such as power plants, where the hot stack gases are buoyant and disperse more quickly than a spill of a vaporizing liquid at ground level. These models produce an elapsed-time-resolved three-dimensional map of the plume downwind of the spill site, compare it to the recommended maximum-allowable exposure limit for the general public, and determine the need to evacuate the population from the affected area. Some of the models allow for chemical interaction of spilled chemicals with atmospheric oxygen and moisture, as would be the case with spilled N_2O_4 or N_2H_4 .

One of the models widely used by the USAF during the time when most N_2O_4 was transported to and from TITAN launch sites was AFTOX, which was easy to run on a personal computer [595, 596]. AFTOX is a Gaussian puff dispersion model for uniform terrain and wind conditions. It can handle continuous or instantaneous releases, liquid or gas, and elevated or surface releases from a point or area source. AFTOX 14.0 represents an upgraded version based on comments from users after operating the model for 2 years in the field. The changes made the program more user-friendly and improved it technically.

Other models cover different spill-site geometries and atmospheric conditions to calculate toxic vapor corridors downwind or downhill from spill sites [597–599]. Reac-

tions of the chemicals, if any, with water vapor in the air are modeled and considered in some of the dispersion models [600]. Several other atmospheric dispersion models have been applied to modeling accidental NTO releases in the atmosphere.

Field diffusion tests were conducted at Cape Canaveral in Florida and Vandenberg Air Force Base in California during 1961 and 1962. These programs, nicknamed Ocean Breeze and Dry Gulch, respectively, were undertaken to establish quantitative diffusion predictions for use as range safety tools at the missile test ranges [601]. The programs culminated at each range with the installation of an automatic computer-controlled meteorological data acquisition and processing system for continuous operation at the bases.

A vapor cloud caused by either vaporization or reaction of hydrazine, UDMH, MMH, and NTO, as it was used on the Apollo spacecraft, was analyzed to determine the generation and concentration of toxic products and the safe toxic distances in case of a spill [602]. It was predicted that the process of vaporization of propellant without reaction creates the largest quantity of toxic products. Assuming that the total quantity of fuel or oxidizer aboard the APOLLO spacecraft would be spilled in sand and vaporized during unfavorable atmospheric conditions, it would have resulted in a maximum safe toxic distance of 5.5 km (3.4 miles). This safe toxic distance was considered to be the worst case, as the cooling effects of vaporization tend to reduce the actual rate of vaporization. Reaction of hydrazine, UDMH, or MMH with NTO will produce a smaller quantity of toxic products, thus reducing the toxicity hazard. When formed, these hot products, being above ambient temperature and buoyant, will rise and expand, creating a faster rate of product dilution.

SURFACE CHEMKIN is a widely available computer program developed for kinetic modeling of chemical vapor deposition that can be adapted for kinetic modeling of multi-phase chemistry in the atmosphere, such as vapor dispersion and absorption from an NTO spill [603, 604]. It can deal with multiple phases having different reaction paths in each phase. It can deal with gas, surface, and bulk reactions and mass transfer rates; it keeps track of the phase equilibria with realistic activities; and it can operate in an adiabatic mode to include the effect of heat release on the system. When applied to the problem of a dinitrogen tetroxide spill in the troposphere, the model is able to predict the formation of a nitric acid/water aerosol and follow the chemistry taking place in both the gas and liquid phases as the spill dilutes in the surrounding atmosphere. The model predicts that in such a spill, most (70–90%) of the nitrogen oxides released are converted to nitric acid over a wide range of relative humidity atmospheric conditions. The launch-abort problem is especially difficult because there are separate initial clouds of fuel and oxidizer, with regions of mixing between them. One way to deal with this problem is a “multi-bin” approach that treats the fuel and oxidizer and an interface as separate bins but keeps the computation tractable [605]. The model results showed that the outcome is highly dependent on initial conditions. A likely scenario for a Titan IV launch mishap may result in 24% of the initial oxi-

dizer remaining, of which at least half is transformed into nitric acid after reacting with atmospheric moisture, and with 2% of the initial fuel remaining. Heterogeneous chemistry modeling showed that half of the released N_2O_4 will convert to HNO_3 .

A mathematical model was developed to predict propellant vapor clouds released from a theoretical explosion involving a Titan II, Delta II, or Titan IV launch vehicle [606, 607]. The model was based on a variety of scientific and engineering input: the chemical description of interacting rocket propellants, data from previous accidents involving these or similar launch systems, an analysis of vehicle failure modes and propellant mixing characteristics, and thermochemical properties of reacting rocket propellants and their combustion products. Outputs of the model included the chemical composition and average molecular weight of the fireball cloud, the adiabatic flame temperature, the fireball size, and the total heat release. Required input variables to the model were time and altitude of the explosion, the mixing ratio for liquid propellants, amounts of unreacted liquid rocket propellants thermally decomposed, and the amount of air entrained into the fireball cloud. The mathematical model has been encoded into Fortran 77 for integration with the rocket exhaust effluent diffusion model once used at the Vandenberg Air Force Base space launch complex.

A photo of a dramatic launch-abort of a Titan-34D at Vandenberg Air Force Base in April 1986 showed brown clouds of evaporating NTO on top of a shower of burning chunks of solid propellant falling from the two destroyed strap-on boosters [608]. The self-destruct mechanism had to be activated by the range safety officer by remote command after irregularities in one of the two solid propellant strap-on boosters had been detected. It would have been interesting to have taken more photos of the rate of dispersion of the reddish-brown cloud and compared it to predictions of some of the computer models.

Predictions of a model of evaporation characteristics of N_2O_4 and UDMH propellant in the air were in good agreement with experimental results simulating a launch-abort of a Long March launch vehicle [609–612]. A different model was developed for evaporation of NTO from a stagnant pool of a contained open-air spill [613]. In this case, the experiment was designed by simulating the evaporation environment of NTO leaking to form a liquid pool in a storage area. The variables such as wind speed, liquid pool area, temperature, and humidity that affect the evaporation rate of NTO were studied. The results showed that the evaporation rate of NTO correspondingly increased with the increase of any one of these factors. A model of NTO evaporation was established to predict the evaporation rate under storage conditions. The experimental results provided reliable data for research on safe treatment and personal protection related to the harmful gas environment formed after NTO propellant leakage during storage.

If upper stages vent unused NTO after stage or payload separation and while coasting prior to reentry, or if they explode because of aerodynamic heating during reentry, large amounts of residual N_2O_4 and NO_2 may be released into the upper stratosphere

and interfere with the ozone layer [614]. The influence of dinitrogen tetroxide on the ozone layer was described by a quasi-three-dimensional model that described the processes of diffusion and of the ozone photochemical interaction with the admixture. Results of model calculations were presented for release points at altitudes of 25, 30, 35, 40, and 45 km in the atmosphere. After launch, first-stage boosters cease operation at altitudes of 40–60 km; after that, they separate and fall to the ground. During the descent the propellant tanks of the first stage are usually destroyed, and remnants of the propellants splash onto the soil. Second stages cease operation at altitudes of 150–300 km. The second stages then separate and, moving along a ballistic curve, enter the dense layers of the atmosphere with a high velocity and are destroyed at altitudes of 20–50 km, i.e., inside the atmospheric ozone layer. The model simulations demonstrated that the ozone in the NO_x cloud center would be destroyed during 2–3 s at all heights. Since the ozone reaction with nitrogen dioxide formed in the process of dinitrogen tetroxide dissociation is very slow, the primary process is the nitrogen dioxide photodissociation, and then the formed nitric oxide reacts with the ozone. The ozone photodissociation is by orders of magnitude a weaker source of oxygen atoms than the nitrogen dioxide photodissociation. Model calculations were made for the total ozone depletion under a release of 1000 kg of dinitrogen tetroxide at various heights. The estimates demonstrated that a local release of large quantities (1000 kg) of the ozonoactive nitrogen oxides as the result of destruction of a rocket's second stage in the atmosphere should not lead to a long-term, large-scale depletion of the total ozone. One must understand that typically about 1300 kg of nitric oxide are released into the ozonosphere (20–50 km) together with the normal exhaust of the rocket's first-stage propellant combustion (e.g., for a Proton rocket), which corresponds to about 2000 kg of nitrogen dioxide. Thus, the release of the propellant remnants in the process of a rocket's second-stage destruction are comparable to the amount of nitrogen oxides thrown into the atmosphere each time with the normal products of combustion. In addition, simultaneous release of excess oxidizer and excess fuel, often from hypergolic combinations, may start a fireball and accelerate the consumption of residuals in the atmosphere or on impact on the ground.

Residual liquid propellant that is sprayed into the atmosphere at high altitudes and low ambient pressure may result in propellant droplets instantly freezing from sudden evaporative cooling and falling greater distances before they are warmed and evaporated [615].

8.6 Venting and Passivation of Propulsion Subsystems in Space

Explosions and fragmentations of spent upper stages or decommissioned satellites in space have been blamed on residual propellants and have created clouds of orbital debris. International space policies now require that upper stages and satellites be emptied of all residual propellants and be passivated at end of life.

A numerical study was performed to evaluate the Ariane 5 third-stage inerting by separately venting NTO and MMH third-stage tanks to vacuum after the deployment of payloads and prior to reentry. Two-dimensional viscous flow calculations were performed through the venting nozzles, and two-dimensional simulations were used from the nozzle exit conditions to determine the plume characteristics [616, 617]. The flow-rate decay with decreasing feed pressure was analyzed, and correlations were proposed to describe the plume spatial and temporal distribution. The solid-liquid-vapor phase diagrams of NTO and MMH were required for the analysis, and equilibrium phase changes were examined. It was concluded that the gaseous species produced by the venting process will not condense on surfaces warmer than 250 K. The phase-change assessment requires further non-equilibrium condensation analysis, with experimental validation.

Venting surplus NTO or MON in space will create a cloud of frozen N_2O_4 crystals [618, 619]. The particle size of the N_2O_4 snow was determined by Rayleigh light scattering observation conditions. The light source was an Argon laser emitting a 5-mm-diameter beam normal to the direction of flow. It was deduced that condensation occurred inside the nozzle, and the size of the largely sub-micron-size particles increased with the distance from the throat.

Similar venting tests and thermodynamic calculations have been performed for venting hydrazine from upper stages. Hydrazine behaves similarly to water, and it might form chunks of frozen hydrazine that would clog the pipes or adhere to the spacecraft. There is less concern about clogging fuel lines when venting MMH or UDMH because they have lower freezing points than hydrazine or NTO.

Part of any dinitrogen tetroxide that has leaked into the vacuum of outer space will freeze and may cluster around the leak site. The frozen dinitrogen tetroxide will slowly melt and sublime [620].

8.7 Controlled Spill Tests with Dinitrogen Tetroxide

As part of the TITAN-II development program, the USAF performed controlled deliberate spill tests with both N_2O_4 and Aerozine-50 to simulate a worst-case scenario [621]. A series of tests was performed to determine the potential hazards of TITAN-II propellant handling mishaps. Twenty model missile spills using total propellant quantities of 22.7 and 136 kg (50 and 300 lbm) and two large-scale spills using total propellant quantities up to 726 kg (1600 lbm) were made at Haystack Butte, Edwards Air Force Base. The TITAN-II propellants, NTO and Aerozine-50, were also spilled in quantities up to 1.13 kg (2.5 lbm) of total propellant in a series of small-scale tests conducted at the Propulsion Field Laboratory. A biological survival field study was performed on one large-scale test at Haystack Butte.

While most of the other spill tests and computer model predictions dealt with spills of only one TITAN-II propellant at a time, conditions of a simultaneous spill

of both components were modeled only after an accident in one of the Titan-II silos destroyed the missile and caused a fatality [622]. In 1980, a TITAN II accident occurred near Damascus, Arkansas, in which the scenario was much different from the one for which the toxic hazard corridor plume dispersion calculation procedures had been developed. Leaking fuel within the silo eventually made contact with the oxidizer on board a TITAN-II, leading to a violent explosion that sent combustion products and possibly some unreacted propellant several thousand feet in the air, where the atmospheric dispersion process began. The model was designed to characterize the interactions of hypergolic liquid rocket propellants and to provide information pertinent to the development of a model that would describe the transport and diffusion process of the airborne combustion products and unreacted propellant vapors resulting from a catastrophic accident involving hypergolic liquid rocket propellants burning either in the open or in the confined space of an underground silo. The internal pressure required to lift the heavy silo lid and the TNT equivalence of the NTO/Ae-50 reaction were calculated. Volume 2 of the final report discussed the chemical and physical interactions of the combustion products with ambient air [623]. The atmospheric dispersion of the products was described by considering the coupled effects of convection, dispersion, and chemical reaction.

The measured source strength and downwind dispersion results of two controlled N_2O_4 spill tests were used to evaluate four different source strength and dispersion models [624]. One conclusion from these source strength comparisons was that the internal energy (evaporative cooling) heat source is a major contributor to the source strength.

Two field-scale releases of dinitrogen tetroxide were performed at Lawrence Livermore National Laboratory for the USAF as part of the Eagle series. Data gathered during this experiment were fitted to a computer atmospheric dispersion model, and corrections for interaction of $\text{N}_2\text{O}_4/\text{NO}_2$ with ambient humidity and oxygen were applied [625]. The reported source rate for one experiment was 2.9–3.4 kg/s, while the source rate for the other experiment was 1.6–1.9 kg/s. Reported NO_2 concentrations downwind of the source were corrected for the mass evolution rate, and these observed concentrations were compared with predicted concentrations using the Ocean Breeze/Dry Gulch model.

At a time when the TITAN II missiles were being decommissioned, resulting in an increase in the overland transportation of N_2O_4 , a series of instrumented, controlled large-scale spills of 3–5 m^3 of N_2O_4 were performed at the Nevada test site for the Air Force Engineering and Services Laboratory, Environics Division [626, 627].

Large-scale, extensively instrumented controlled spill tests of liquid ammonia and liquid dinitrogen tetroxide were performed at the Nevada test site, resulting in large amounts of data that can be used to quantitatively describe the observed phenomena [628]. Preliminary results from both test series indicated that aerosols played a very important role in dense gas dispersion. The test data were ideally suited

for model validation. Gaussian model calculations were found to be inadequate even at long distances downwind.

A series of large-scale dinitrogen tetroxide spill tests were conducted to determine the source strength characteristics and heavy-gas dispersion aspects of large N_2O_4 spills. The source strength and downwind dispersion results of two of the spills were used to evaluate several source strength and Gaussian dispersion models [629, 630]. It was concluded that the internal energy heat source is a major contributor to the source strength, that source strength models need improvement, that formation of a dense HNO_3 mist may account for much of the downwind mass transport of large N_2O_4 spills, and that all models evaluated underpredicted downwind gas concentrations. The purpose of these experiments was to study the evaporation rates and heavy gas-dispersion aspects of realistic size releases of N_2O_4 . Some typical results for one of the spills included the atmospheric boundary layer conditions in effect during the spill, the spill area heat flux and vapor temperature, the vapor flux measured at 25 m downwind, and the NO_2 gas concentration contours at 785 m. The measured NO_2 concentrations were compared to those calculated with the Air Force Ocean Breeze/Dry Gulch model.

Measured results from a total of 26 benchmark spill tests were chosen from the Lawrence Livermore National Laboratory Burro (LNG), Coyote (LNG), Desert Tortoise (ammonia), and Eagle (nitrogen tetroxide) tests; the Shell Research Maplin Sands tests (LNG and LPG); and the British Health and Safety Executive Thorney Island test (Freon-air mixtures) and were compared to model predictions [631]. Only continuous finite duration releases were selected for the test summaries because they were considered to better represent typical accidental releases from a storage vessel or transportation vehicle. The test summaries described the manner of release, the ambient meteorological conditions, and the resulting vapor cloud characteristics, including peak concentration, average centerline concentration, and average height and width of the cloud, all as functions of downwind distance.

8.8 Disposal and Spill Cleanup of Dinitrogen Tetroxide

Disposal and spill cleanup of dinitrogen tetroxide has been practiced for many decades, and there exists a good database on available methods for safe handling of this oxidizer, e.g., Chapter 3 in [632].

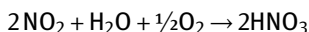
8.8.1 Absorption, Scrubbing, Neutralization, and Disposal of Vented Nitrogen Dioxide

If large quantities of N_2O_4 have to be disposed of, the choice is between wet absorption or combustion in a flare stack or solid absorbents in a canister. This problem usually occurs with the NO_2 -laden pressurant gases that are vented from storage, transport,

or run tanks when the liquid is transferred by pressurization instead of mechanical pumps. The *Hypergolic Propellants Handbook* contains an evaluation of various techniques for the destruction of NO₂ in vent gases from pressurized NTO tanks [561, 632]. The most economical method would seem to be to dissolve the vapors in aerated water, resulting in a dilute solution of nitric acid and nitrous acid. The acid solution then would have to be neutralized with caustic lime slurry before it could be released or sent to other applications. However, nitrogen dioxide dissolves only very slowly in water.

8.8.1.1 NO₂ Absorption with Wet Scrubbers

The problem with wet scrubbers is that NO₂ fumes do not dissolve in water very readily, and the reaction



takes a long time to go to completion [558, 633]. This reaction is part of the commercial process for production of nitric acid. The absorption rate of nitrogen dioxide-dinitrogen tetroxide gas mixtures from nitrogen into water plays an important role in industrial production of nitric acid and removal of NO₂ from gaseous mixtures. The results of a study of the mechanism of NO₂ absorption in a wetted wall, falling film column agreed well with known absorption mechanisms, and additional data were obtained on the liquid-side kinetics of this absorption process [634].

Instead of using plain water, a more effective method is to absorb the vapors in an aqueous solution of sodium hydroxide and sodium sulfite, where the sodium sulfite acts as a reducing agent. But such absorption towers/vapor scrubbers create a large volume of spent solutions that then need to be disposed of at substantial expense [635].

Experiments were conducted on a model wet scrubber in order to verify and rank the performances of several candidate scrubbing liquors. The most efficient scrubbing liquor found experimentally was a 10% sodium sulfite solution [636]. This was in agreement with a previous study by Exxon performed under a U.S. EPA contract. Other scrubbing solutions tested have been potassium permanganate (KMnO₄), ozone (O₃), sodium hydroxide (without sulfite), sodium hypochlorite, urea, triethanolamine, ammonia, and hydrogen peroxide (H₂O₂) solutions.

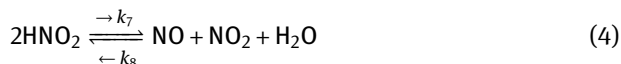
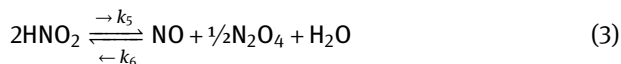
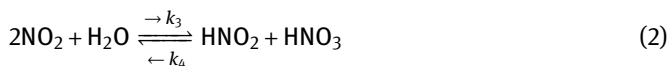
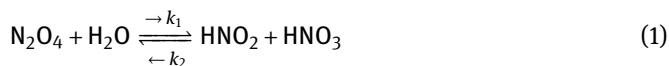
Pressurant gases vented from NTO/MON tanks were usually scrubbed with a sodium hydroxide/sodium sulfite solution, resulting in a hazardous liquid waste. As an environmentally more friendly alternative, the use of a solution of potassium hydroxide and hydrogen peroxide for the NTO/MON vent gas scrubber system was investigated [637]. The potassium nitrate solution formed could be potentially used as an agricultural fertilizer instead of having to be disposed of as a hazardous waste. The hydrogen peroxide was added to convert the potassium nitrite that was initially formed into the more useful and less toxic potassium nitrate. Small-scale laboratory tests were conducted to establish the storage stability of hydrogen peroxide in the

proposed scrubbing solution and to evaluate the effectiveness of hydrogen peroxide in converting nitrite to nitrate.

In order to find a more efficient method to reduce nitrogen oxide pollution when venting pressurized oxidizer tanks during propellant transfer or ground testing of rocket engines, pressurized absorption was studied with simulated waste gas [638]. The results showed that at lower pressures (0.1–0.4 MPa), the nitrogen oxides' absorption efficiency in water decreased with increases of the inlet concentration of nitrogen oxides, but at higher pressure (0.4–0.8 MPa) it increased with increases of the inlet concentration. The absorption efficiency increased with increases in the operation pressure, and the efficiency at 0.8 MPa was six times greater than that at atmospheric pressure, but the increase was less significant with pressures higher than 0.6 MPa. The optimum pressure was 0.4–0.6 MPa. The operating cost of pressurizing gas disposal can be compensated by the nitric acid recovery if a commercial use can be found for the dilute acid.

Nitric acid factories have designed special absorption towers to achieve dilute nitric acid, which subsequently has to be concentrated to obtain a commercial product. For a rocket test-stand waste-gas neutralization installation, one can use caustic (20% NaOH) solution instead of water in order to speed up the gas absorption process [639].

It was generally assumed in the past that the reactions between nitrogen dioxide and water occur by a mechanism in which gaseous nitrogen dioxide diffused into the liquid phase, where the chemical reactions take place. It was suggested that a gas-phase reaction may occur, and other investigations indicated that the gas-phase reaction may be of considerable importance in the overall reaction mechanism. To design efficient equipment for aqueous absorption of nitrogen dioxide, it is necessary to know whether the important chemical reactions occur in the gas phase or in the liquid phase. Other studies indicated that the rate of aqueous absorption of nitrogen dioxide is controlled by the rate of the chemical reaction rather than by diffusion. Therefore, by the use of chemical kinetics, it should be possible to predict the manner in which the concentration of the reactants affects the rate of nitrogen dioxide absorption. The chemical reaction of importance may be expressed by



These equations represent the reaction rate constants for the forward and reverse reactions. Reactions 1, 2, and 5 occur simultaneously, while reactions 3 and 4 are con-

secutive to reaction 1 and 2. The oxidation of nitric oxide (NO) to yield nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4) proceeds at a relatively slow rate. This reaction is not included here because experimental tests with a wetted-wall column indicated that the rate of nitric oxide oxidation was too slow to have any appreciable effect on the results. Even after all of the NO_2 is absorbed, there is still the question of how to dispose of the resulting solution containing sodium or calcium nitrite and nitrate.

For stationary installations used to neutralize the fumes after venting pressurized NTO tanks, spray nozzles can be arranged in such a way that they act like an aspirator and entrain the fumes or the vent gases from a tank that need to be neutralized. The caustic solution can be recirculated until it is saturated with nitrate and nitrite.

Hypergolic oxidizer and fuel pressurant gases are (were) vented during fueling and deservicing of the Space Shuttle and other spacecraft, which were cleansed of toxic propellant vapors before allowed to be vented to the environment. The scrubbers were not 100% efficient, and traces of propellant vapors may have passed through the apparatus. The environmental protection agencies wanted to know how much propellant vapor escaped entrapment. Scrubber emissions are difficult to measure due to the intermittent purge flow and the presence of suspended scrubber liquor droplets. An alternative method for emissions monitoring was introduced [640]. It was suggested that emissions can be determined from field scrubbers without direct measurement of vent flow rates and escaped hypergol vapor concentrations. This alternative approach was based on the scrubber efficiency, which had been previously measured during normal steady-state operations, and on the accumulated weight of hypergol captured in the scrubber liquor, which is part of the routine monitoring data of scrubber liquors. The emissions from scrubbers can be calculated by measuring the buildup of hypergol propellant in the liquor and then using the appropriate efficiency to calculate the fugitive emissions. An estimate of the total emissions from 16 scrubbers at NASA KSC indicated that 0.3 kg/year of fuel (MMH and hydrazine) and 234 kg/year of nitrogen dioxide were emitted [641].

It has been proposed to convert the NO_2 scrubber liquors to nitrate fertilizer that has commercial agricultural value. Used, unwanted scrubbing liquor consisting of an equimolar mixture of nitrate and nitrite dissolved in a highly alkaline solution (pH 13) was usually disposed of as hazardous waste. However, this waste liquor can be converted into nitrate fertilizer by oxidizing the nitrite to nitrate with ozone and neutralizing the alkali with nitric acid to form a nitrate solution at pH 7 [642–645]. The NO_2 scrubber liquor starts with 1% hydrogen peroxide at a pH of 7 in the first zone, and the process control system adds hydrogen peroxide and potassium hydroxide to the scrubber liquor in a second zone to maintain the initial pH and a slight excess of H_2O_2 . The result is the formation of a solution of potassium nitrate, which is sold as a fertilizer. This report describes the equipment and procedures used to monitor and control the conversion of the scrubber liquor to fertilizer, while at the same time reducing the scrubber emissions.

Hypergolic oxidizer used at most launch facilities is not pure N_2O_4 but is rather MON-1 or MON-3 with varying amounts of N_2O_3 added in the form of NO. The vapor phase above MON contains more NO than the liquid, and when vented, the NO is released first and may pass through the scrubber unchanged unless it has a chance to react with an excess of air to convert itself to NO_2 . The conversion of NO to NO_2 can be accelerated by UV illumination of gases entering the air-filled scrubber [646].

8.8.1.2 NO_2 Absorption into Dry Chemical Absorbents

A dry-chemistry $\text{NO}_2/\text{N}_2\text{O}_4$ disposal system without the need to pump and recirculate liquid absorbent solutions through an absorption tower would destroy the gaseous $\text{NO}_2/\text{N}_2\text{O}_4$ mixture by passing it over a hot bed of charcoal, coal, or coke, where the oxides of nitrogen would be reduced to nitrogen gas and CO/CO_2 [647]. If there is concern about the poisonous CO, it can be converted to CO_2 by adding more air and passing it over a heated copper oxide catalyst before releasing it above the roof.

8.8.1.3 NO_2 Condensation for Recycling

If NO_2 in vented pressurant gases has to be removed on a regular basis rather than only on an occasional basis, it may be more economical to collect the NO_2 by condensation in a cold trap in the form of N_2O_4 and recycle it [648]. Theoretical calculation results of the condensation recovery rate and the required cooling power of an engineering development unit showed that condensation recovery of N_2O_4 in the waste gas is feasible and profitable in engineering applications. A simulation computation model was performed by using HYSYS and condensate-recovery process flow charts. The test results of an engineering development apparatus based on these parameters at Jiuquan Satellite Launch Center indicated that the recovery efficiency can be greater than 90%, and the purity of N_2O_4 recovered can be up to 99.6%.

8.8.2 NO_x Vent Gas Scrubbers

Each time an NTO oxidizer tank in a stationary installation or in a reusable space transport returning from orbit has to be depressurized, the pressurant gas is saturated with $\text{N}_2\text{O}_4/\text{NO}_2$ and carries substantial amounts of toxic fumes that in most installations cannot be simply vented to the atmosphere. In the case of the Space Shuttle, the amount of vented NO_2 during loading was between 2 and 6 kg (4.5 and 14 lb_m) of NO_2 for the OMS and RCS tanks [649]. The vent gases are usually passed into a scrubber with an aqueous absorbing solution that is recirculated until it becomes saturated with NO_x . Although this can be done with plain water, various absorbing solutions have been tested that not only absorb NO_x but also neutralize it at the same time.

Solutions of sodium carbonate, sodium dichromate, or potassium permanganate have been evaluated as scrubber liquors for the absorption and neutralization of nitrogen dioxide [650].

A scrubber built by MMC for NASA Kennedy Space Center to NASA Kennedy Space Center design specifications consisted of four in series packed-bed (ceramic saddle) scrubbers with a common sump tank [651, 652]. Initially, testing was done with 2–8% NaOH solution. The desired output of 150 ppm NO_2 or less was not obtained with the 2–8% NaOH sump liquor. Several possibilities were investigated to evaluate whether the scrubber towers were flooding at certain test conditions or whether the gas was channeling in the towers so that maximum scrubbing would not be achieved. Subsequent tests were performed with 10 and 25% Na_2SO_3 solutions, which worked much better, and the exit gas concentration was below 150 ppm NO_2 . A mixture of 5% NaOH and 18% Na_2SO_3 in water was recommended as the sump liquor to be used in the oxidizer scrubber. An analysis of the test data from this system tried to normalize the operating conditions to identify the variables (gas flow rates, liquor flow rates, liquor composition and concentration, NO_2 inlet concentration, level of exhaustion of absorption capacity) that had the most impact on the performance of the system [653].

Part of the initial problem with using the wet scrubbers on vented hypergolic propellants was the ultimate disposal of the liquid scrubber wastes after the liquor absorption capacity was exhausted. Consideration was given to all possible methods of reducing the amounts of chemically bound nitrogen in the wastes to stay within the guidelines established by the state and federal agencies. These guidelines require that the total chemically bound nitrogen discharged to any body of water be no more than 5.0 ppm. One proposed method was the use of water hyacinths in open-air disposal ponds to reduce the waste concentration in the effluent to acceptable levels [635].

The scrubber used at DELTA second-stage fueling installations at Cape Canaveral Air Force Station and Vandenberg Air Force Base used a two-stage scrubber design using 5% sodium bicarbonate solution as a vapor-neutralizer scrubber liquor [580]. Design specifications were that the scrubber should be capable of reducing 115030 ppm NO_2 to 500 ppm from 400 scfm for 15 min.

Pilot-scale experiments of a packed-bed scrubber were conducted to investigate the effects of seven design and operating parameters on the removal of NO, NO_2 , and N_2O_4 from a nitrogen vent gas stream venting from an NTO/MON tank [654]. This was done to obtain design guidelines and scaling criteria for the design of a full-size caustic scrubber for a launch installation. The scaling criteria were in the form of a computer model that could be tweaked to obtain the optimum operating conditions. The reactions of NO, NO_2 , and N_2O_4 with a dilute NaOH solution with and without added air were analyzed. It was attempted to improve the performance of alkaline NO_x scrubbers by changing the packing material or operating conditions.

The absorption of nitrogen oxides in water was investigated experimentally in a column equipped with Helix structured packing for different operating conditions (NO_x inlet concentration, specific gas, and liquid flow rate) [655]. The experimental data were compared with the absorption efficiency predicted by three models, the first obtained by the open literature and the others developed in this work. Some conclu-

sions about the relative importance of the different mass-transfer mechanisms involving the absorption process were deduced.

An industrial reactive separation process for NO_x absorption into water and nitric acid was investigated, and gas-phase and liquid-phase concentrations were measured *in situ* while operating conditions such as temperature, pressure, and absorbent flow were varied [656]. A comprehensive mass transfer/reaction model was developed and compared to the field process data used for validation. The model accurately predicted NO_x removal from the gas (i.e., typically within 3.5% of the plant data). The model successfully predicted changes in performance when key operating parameters such as temperature and pressure were varied. The addition of a bleaching solution resulted in a significant improvement in NO_x removal.

At NASA Kennedy Space Center, a vent gas scrubber/fertilizer-producing system near launch pad 39A captured dinitrogen tetroxide vapor that was vented after it was transferred from ground storage tanks into the Space Shuttle flight tanks. The scrubber used dilute hydrogen peroxide to produce nitric acid, which was then neutralized by potassium hydroxide and converted to potassium nitrate, a fertilizer that was to be used on the on-site orange groves that Kennedy Space Center leases to outside companies [645].

Spent and saturated NO_x scrubber liquor can be destroyed in an incinerator [657].

8.8.2.1 Flare Stack Installations for NO_2 Disposal

Another method for disposal of N_2O_4 vapor is to feed it into a burner torch fueled with methane or natural gas and flare it off, but the NO_x destruction is not complete because such flames in air would form some NO_x even in the absence of any N_2O_4 fed into them. Some of the TITAN-II test installations had a flare stack with natural gas into which the nitrous fumes were fed into the fuel-rich kernel of the flame [658].

A flare burner for destruction of waste oxidizer vapors was designed and developed by Martin-Marietta during the late 1960s, and several burners were installed at NASA WSTF and Vandenberg Air Force Base, as well as at Martin-Marietta's Denver division. The unit was originally designed for use at TITAN-II sites. This unit consists of a cylinder 20 cm (8 in) in diameter and 0.9 m (3 ft) in length, containing a plenum into which propane and waste N_2O_4 vapors are injected, and a burner head. The plenum was designed in such a way that the propane and N_2O_4 do not come into contact with each other until they reach the exit plane of the burner. A wind shroud protects the head from flame-out. A continuous pilot is provided at the top of the burner head to ignite the gas mixture. Approximately 4.5 kg (10 lb_m) per minute of N_2O_4 can be destroyed in the case of the 8-in configuration.

8.8.3 Spill Response and Neutralization

Hazmat teams are specifically trained on how to deal with propellant spills, either off site or on site. A computer program can assess the type of response needed to bring the situation under control, depending on the type and quantity of propellant spilled, the proximity to populated areas, and geographic conditions [659].

Accidental and unintentional spills of N_2O_4 are an acute inhalation and potentially a fire hazard and need to be neutralized immediately. If organic insulating material (polyurethane foam, polystyrene foam) becomes soaked with N_2O_4 , it constitutes a fire and explosion hazard. The foam may auto-ignite on contact with N_2O_4 . Organic foams and fibers (often wrapped around thermal conditioning lines) must not be present near N_2O_4 test installations. The choice for a method of spill neutralization is between gaseous, liquid, or solid dispersion and neutralizing agents. The main concern in case of a propellant spill is the vapor containment and mitigation.

Before even trying to apply absorbent or neutralizing chemicals to the spill, one should try to suck up the puddles of liquid with a hose and collect them in a specially designed vacuum cleaner with cold traps [660].

Covering up a propellant spill with a layer of aqueous foam will not neutralize it, but it will prevent or retard vaporization for a limited time while plans for more permanent neutralization of the propellant spill are made and equipment for remote manipulation of the spill is put in place. High-expansion foams can both quench fires and form a temporary but sufficiently durable barrier to limit the concentrations of vapors from spilled combustible and/or toxic liquids to acceptable levels.

8.8.3.1 Dispersing Gas

Accelerating the evaporation and dispersing the fumes with hot air can only be used for small spills. This does not solve the spill problem; it only relocates it.

8.8.3.2 Liquid Neutralization Agents

Water mist can absorb NO_2 fumes as a first measure of control, but a substantial amount of unabsorbed NO_2 will escape [661]. The water should be cold because NO_2 dissolves more readily in cold water than in hot water. The water droplets should be finely dispersed to maximize the interface surface area where the physical absorption takes place. A water jet like that from a fire hose is less effective [662]. Laboratory-scale investigations showed that water fog provided one of the best means for controlling toxic fumes from individual spills of NTO, hydrazine, or UDMH.

In order to determine the rate of $\text{NO}_2/\text{N}_2\text{O}_4$ absorption in a water spray, laminar water jets of different lengths were exposed to a pure $\text{NO}_2/\text{N}_2\text{O}_4$ mixture at pressures between 0.06 and 0.3 atm [663]. The amounts of HNO_2 and HNO_3 found by chemical analysis in the liquid leaving this absorption system were interpreted in terms of the absorption of N_2O_4 and its subsequent reaction. The manner in which these N_2O_4 absorption rates depend on the partial N_2O_4 pressure and the jet length strongly supported the working hypothesis that N_2O_4 is preferentially absorbed under simultane-

ous reaction with water according to a fairly rapid first-order rate formula. From these measurements, values for

$$H\sqrt{k_1D}$$

at 293 and 303 K (20 and 30 °C) were obtained where H is the solubility coefficient of N_2O_4 in water, D is the diffusivity of N_2O_4 in water, and k_1 is the reaction velocity constant.

If insufficient water is applied to a puddle of N_2O_4 , the heat of reaction may actually accelerate the rate of evaporation of N_2O_4 and worsen the situation [558]. This is also the case if a dilute caustic solution is applied to a puddle of N_2O_4 , but in insufficient quantity [658, 664]. One poorly informed source of first-response information recommended the use of a caustic solution containing sodium dichromate or potassium dichromate, oxidizers that achieve a rapid conversion of nitrite into nitrate and more rapid solution of the fumes. However, chromium(VI) pollution in wastewater is much worse than a little nitrite!

8.8.3.3 Solid Material Spill Neutralization Kits

Uniform porous nano-sized spherical $Ca(OH)_2$ powder prepared by a CaO hydrolysis-azeotropic distillation method can be used to neutralize leaking liquid N_2O_4 in an emergency [665]. The particle size of $Ca(OH)_2$ should be 200–300 nm, the pore diameter should be 8–15 nm, and the specific surface area should be $63\text{ m}^2/\text{g}$. A portable leakage disposal device can be made by putting the prepared powder into a pressure bottle such as a dry chemical fire extinguisher. Leakage can be controlled by spraying the powder over the leakage under pressure. Experimental results showed that the removal rate of NO_2 gas can be up to 90%. Through combined adsorption, absorption, infiltration, and interfacial chemical reactions, $Ca(OH)_2$ powder captures NO_2 gas and covers up leaking liquid, preventing its evaporation and diffusion.

Spilled gelled NTO or RFNA would evaporate more slowly and constitute less of a hazard than ungelled NTO or RFNA. See also [658, 664, 666–670].

8.8.4 Demilitarization of Surplus Dinitrogen Tetroxide

In the wake of SALT and Strategic Arms Reduction Treaty (START) agreements between the United States and the USSR and its follow-on states, large quantities of hypergolic missile propellants off-loaded from demilitarized missiles had to be disposed of. The U.S. Department of Defense (DoD) concluded agreements with Ukraine and the Russian Federation under which the DoD was committed to providing both former Soviet Union states with equipment and other aid for use in eliminating their strategic offensive arms in accordance with schedules negotiated in the Strategic Arms Reduction Treaty. This effort was mostly concerned with IRFNA, HDA, and UDMH, but there was also some NTO (“Amyl”) that needed to be disposed of. The U.S. EPA Risk Reduction Engineering Laboratory conducted NTO and UDMH destruction tests in a rotary kiln

incinerator with afterburner and wet scrubber [671, 672]. N_2O_4 was fed to the diesel-fuel fired rotary kiln incinerator. The N_2O_4 oxidant was added to the burner primary air supply via an N_2O_4 feed system. For all three tests, the RKS afterburner was fired with natural gas to maintain a nominal afterburner exit gas temperature of 1363 K (1090 °C [2000 °F]). NO_x levels were quite high for the N_2O_4 tests, at 9300–10000 ppm (uncorrected) at the primary chamber exit; 8400–8800 ppm, lowered again due to dilution, at the secondary chamber exit; and 590–7100 ppm at the wet scrubber exit. Approximately 30–50% of the flue gas NO_x was NO_2 , the lower fractions corresponding to the scrubber exit location.

The disposal of RFNA (“Melanj”) and HDA will be described in *Encyclopedia of Oxidizers*, chapter “Red Fuming Nitric Acid.”

Several different methods were evaluated to not only dispose of but also convert the abandoned and unwanted rocket propellants, including Amyl and Melanj, into commercially useful products such as fertilizer.

8.9 NTO Leaks and Leak Detection

In a liquid propellant system we are concerned with internal leakage through a valve seat or burst diaphragm, as well as with external leakage. External leakage is easier to detect; internal leakage sometimes is detected only when it is already too late to correct it (as in the Mars Observer scenario). The main problem with NTO leaking into ambient air is the absorption of moisture and the formation of nitric acid, which can aggravate the leak situation and corrode metals in the vicinity of the leak. Crevice corrosion of tank shells and connectors will occur in moist environments and eat its way toward the source of the NTO at the center of the component.

Indicating paints will irreversibly change color at the point where the leakage occurred [673, 674]. They can be used for detection of NTO as well as UDMH, Aerozine-50, MMH, and hydrazine.

NTO or other propellants leaking into vacuum will cool by evaporation down to the triple-point temperature, and liquid droplets will soon freeze and turn into N_2O_4 snow. This condition was simulated by spraying liquid NTO into a vacuum chamber with visual (video camera) observation [675].

8.10 Personnel Protective Equipment for Handling of Dinitrogen Tetroxide

The level of required personnel protection will vary depending on the quantity of N_2O_4 or MON being transferred.

As a minimum of protection, personnel handling N_2O_4 must wear gloves, apron, boots, and a face shield made of N_2O_4 -resistant materials. The next level of protection would include a gas mask worn instead of or under a face shield.

Gloves, aprons, and boots can be made of PVC-coated non-combustible fabrics. If N_2O_4 is in prolonged contact with such protective clothing, it may diffuse through the fabric, and the protective gear must be discarded.

A self-contained breathing apparatus with compressed air should be available at the test site to be used in more severe emergencies.

NASA and USAF use completely enclosed self-contained air protective ensemble (SCAPE) suits during fueling operations with hypergolic propellants. The 1978 suit material was butyl-coated Nomex per MILC-38149. Boots, gloves, faceplate seal, and cuffs were butyl rubber. NO_2 has a very high permeability through many polymers, and an examination of the materials used in 1978 predicted that in a 100% NO_2 atmosphere surrounding the person, NO_2 concentration inside the SCAPE would exceed threshold limit value in 4 min. As of 1978, NASA was planning to test the whole suit in a test chamber with a 26% NO_2 concentration. This type of test had not been performed before on the SCAPE suit [676].

Full-sized operational SCAPE suits and fabric from the suits were subjected to a series of tests designed to determine the amount of exposure a wearer of the suit would receive if a spill of dinitrogen tetroxide (N_2O_4) should occur nearby [677]. The results of these tests showed that a wearer of a "stock" SCAPE suit equipped with a standard liquid air pack, if exposed to a spill resulting in a 26% increase of oxidizer in the surrounding atmosphere, would experiment no detectable concentration of NO_2 inside the suit for 15 min. Thereafter, the NO_2 concentration within the suit will increase for 35 min at a rate of 0.07 ppm per minute and then at a gradually decreasing rate until an equilibrium concentration of 3.4 ppm is attained after 100 min. The effects of liquid and vapor N_2O_4 and of liquid MMH on permeation rates and tensile strength of the SCAPE suit fabric were also investigated.

During the early years of SCAPE operations, the fabric of the suits was treated with tris(2,3-dibromopropyl) phosphate as a fire retardant. When it became apparent that tris is a mutagen and suspected carcinogen, methods were sought to wash off the fire retardant from the surface of the suits and to analyze the post-wash fabric for residual tris [678]. Soap-and-water washing was the most efficient method of removing the compound from fabricated SCAPE suits and unused material. Similar protective suits were used in TITAN-II missile silos [345] and at large TITAN-II installations and engine test sites [561].

Under normal operating conditions, a SCAPE suit is pressurized to about 12 mm (0.5 in) of water pressure from the environmental control unit airflow as regulated by the suit pressure relief valves. In order to answer a "What if ...?" question about what danger the operator might be exposed to when the suit is accidentally torn, two NO_2 sensors were installed inside a suit and tested in a $2.4 \times 2.4 \times 2.4$ -m ($8 \times 8 \times 8$ -ft) environmental chamber filled with NO_2 fumes [679]. When the suit was torn, the airflow escaped through the hole, and contaminated ambient could enter the suit very quickly.

A specification for an improved ensemble for propellant handlers was developed based on experience with existing suits that were about to be retired [680].

A group of 28 glove materials, nine suit materials, and three other materials were tested for permeability to hydrazine, MMH, and dinitrogen tetroxide following exposure to these propellants for 90 min [681, 682]. Breakthrough times were determined and correlated with static permeation rates.

An improved toxic-vapor permeation test apparatus that controlled temperature, absolute pressure, differential pressure, and equivalent concentration of NO_2 in the vapor phase more reproducibly than previously used permeating test setups was used to characterize three candidate fabric materials for propellant handlers' ensemble coveralls for hypergolic propellant servicing [683, 684]. The materials evaluated were a chlorobutyl fabric made by DuPont de Nemours and used in a rocket fuel handler's clothing outfit, another chlorobutyl fabric made by DuPont de Nemours proposed for a propellant handler's ensemble, and a chlorinated polyethylene (Cloropel) made by ILC Dover already used in a Chemtursion protective ensemble.

In hypergolic propellants spill tests at NASA WSTF, it was determined that the exterior of the protective equipment may be exposed to vapor concentrations as high as 2% N_2O_4 . These numbers were then used for permeation testing of different protective clothing materials [685, 686].

The permeability of rocket propellants through skin-protective materials was measured by weighing the propellant mass permeated per minute and per square centimeter. The detection limit was $100 \text{ pg cm}^{-2} \text{ min}^{-1}$ [687].

A comprehensive summary of protective clothing for all types of corrosive chemicals, as well as the hazards of permeation of aggressive chemicals through the protective clothing during use, is provided in [688, 689]. New designs provide for better visibility and more flexibility [690].

The efficiency of Mine Safety Appliance Company's rocket propellant canisters, model GMN-SSW, to provide protection against NO_2 and UDMH was tested [691]. Canisters manufactured in 1967 were compared to canisters made in 1971. Results of the study indicated that there was no statistically significant difference between the absorbing capacities of the new and old canisters for both contaminants. One of the built-in safety features of the canisters was a small viewing window containing a color indicator that changed from orange to blue-green when the absorbing capacity was 50–75% exhausted. The concentration $\times$ time product to a color change and to penetration at 1 ppm of NO_2 at 38 L/min was tested; penetration varied between 292000 and 517000 $\text{ppm} \cdot \text{min}$, but the color would change before that point. The study concluded that indicators on the new canisters were unsatisfactory for both UDMH and NO_2 .

If a large NTO spill occurs in the vicinity of air-conditioned office buildings, there should be a filter like a large gas mask at the air intake for the air conditioning unit [692]. A sample system has been constructed to test the ability of several types of filter materials to capture the NO_2 vapors prior to their penetration into the air conditioning system. The efficiencies of standard air conditioning filters, water wash

systems, and chemically impregnated filter materials for taking toxic vapors out of the incoming air stream were evaluated.

8.11 Reduced Spill Hazard of Gelled Dinitrogen Tetroxide

Gelling of dinitrogen tetroxide will reduce the spill hazard but will substantially increase the viscosity of the oxidizer, making it more difficult to inject it into a rocket engine and achieve atomization into small droplets. The effort to make gelled N_2O_4 often goes hand-in-hand with efforts to make gelled RFNA or gelled hypergolic fuels. Both of these applications would be very similar. Because N_2O_4 reacts with most organic gelling agents, the choice of gelling agents for N_2O_4 and MON is quite limited. Usually the same gelling agents (inorganic gelling agents, typically fumed silica) that have been tested for IRFNA will work for NTO/MON as well.

Usually, once the oxidizer is successfully gelled, the fuel to be used in the system with NTO will also be gelled. Various fuels intended to be used with gelled NTO have been tested, such as gelled MMH and gelled UDMH. The gelling agent concentration in NTO should be less than 3% [693, 694].

The saturated vapor pressure of gelled (“colloided”?) dinitrogen tetroxide was found to be lower than that of liquid dinitrogen tetroxide [695]. With increasing sample temperature, the difference of the saturated vapor pressure of dinitrogen tetroxide from liquid to gel increased. The influence of two gelling agents on the saturated vapor pressure of gelled dinitrogen tetroxide system was analyzed, and a theoretical formula of estimating the saturated vapor pressure of gelled dinitrogen tetroxide was derived. The estimated error of the formula was less than 5%.

Only very few organic gelling agents have been tested for NTO because most organics would be destroyed by reaction with N_2O_4 or might even form detonable mixtures. A copolymer of vinylidene halide and perhalogenated ethylene is chemically resistant to N_2O_4 and can be used as a gelling agent [696]. Similar polymers are available under trade names such as Kel-F. A viscous gel could be obtained by suspending 5–10% of the polymer in NTO.

9 Toxic Properties of Nitrogen Dioxide and Dinitrogen Tetroxide

Toxic properties of nitrogen dioxide and dinitrogen tetroxide could be discussed in either chapter on these two oxidizers. Often a leak originates as dinitrogen tetroxide, but by the time the fumes are accidentally inhaled by the victim, the main bad actor is nitrogen dioxide. For this reason, the dinitrogen tetroxide toxicity section is included in the chapter on nitrogen dioxide.

The hazard index, which is the vapor pressure divided by the toxicity number, of nitrogen dioxide and dinitrogen tetroxide is the highest among all currently used

rocket propellants. There have been dozens of industrial and agricultural worker fatalities due to nitrogen dioxide poisoning, although only a few of them were caused by the use of N_2O_4 as a rocket propellant. Although the previous sections in this book mostly concern N_2O_4 , the inhalation toxicity studies are done almost exclusively only with the dissociation product of N_2O_4 , NO_2 vapor, at low concentrations. In most cases the leakage and spill accidents we are concerned about will involve the equilibrium mixture of dinitrogen tetroxide and nitrogen dioxide at the natural boiling point, just above room temperature. The small percentage of N_2O_4 present in the vapor has been neglected by most investigators. The contribution of N_2O_4 to the NO_2 toxicity is unknown. In most cases, either of the two nitrogen oxides reacts quickly with water in body fluids to form nitric acid and nitrous acid. There are many summary publications on the toxicity of nitrogen oxides, mostly relating to the occurrence of nitrogen oxides in smog in polluted urban and industrial atmospheres. Relatively few experiments, many of those sponsored by rocket propellant-using agencies, have used pure nitrogen dioxide for animal exposure tests and establishment of safe tolerable limits of this pollutant.

9.1 Accident History of Dinitrogen Tetroxide

As is the case with almost all hazardous chemicals that are handled in bulk, there have been accidental spills with NTO, several fatalities, and numerous serious injuries of personnel transporting or transferring NTO or servicing NTO equipment. A very impressive summary of accidents in the United States with all hypergols, including NTO, was compiled in 2009 [553, 697, 698], and it serves as the database for “lessons learned”; anyone concerned with range safety must study these case reports and try to find a common denominator. Quite often the common denominator of accidents is human error. Another common cause is design flaw in GSE. For development of a new-hire training program for propellant handlers, a report like this should be mandatory reading.

Prior to the use of NTO in rockets and in the chemical process industry, the most frequent cause of NO_x poisoning was from NO_x evolving in top-loaded silage silos on agricultural farms. This type of poisoning is typically described under the name “silo filler’s disease” [699]. A literature search with these key words produces hundreds of publications and accident case studies.

9.1.1 N_2O_4 Accident Case Studies

Four firemen with acute toxic reactions to nitrogen dioxide inhalation were treated and observed over a period of 18 months [700]. A wide spectrum of responses was noted. All had initial symptoms of acute respiratory impairment. One subsequently developed chronic pulmonary insufficiency; the other three eventually became

asymptomatic. Because initial symptoms of acute toxic conditions are often not obvious, and delayed onset of respiratory distress and superimposed bacterial infection are distinct possibilities, patients with significant exposure to NO_2 should be hospitalized and observed for at least 48 h. After discharge from the hospital, these patients should be closely observed for at least an additional 6 weeks, since the second acute phase of the illness, which may be fatal, usually occurs with some delay.

On 7 May 1972, a tank cart at the San Diego Naval Air Station, while defueling the APOLLO 16 command module after its 27 April 1972 return from its mission to the moon, exploded because of overpressurization [701]. Forty-six persons suspected of inhaling toxic fumes were hospitalized, but examination revealed no symptoms of inhalation. An accident investigation board completed a report on the accident on 30 June 1972 [702].

While the command module RCS was being emptied of all remaining propellant using GSE designed to provide an acid/base neutralization of the propellant in both the liquid and gaseous phases so that it may be disposed of safely, the scrubber tank of the decontamination unit exploded, destroying the GSE unit and damaging the building that housed the operation. Only minor injuries were received by the personnel in the area, and the command module was not damaged. Test results showed that the failure was caused by an insufficient quantity of neutralizer for the quantity of oxidizer. This insufficiency led to exothermic nitration-type reactions that produced large quantities of gas at a very high rate and overpressurized and ruptured the decontamination tank. The ratio of neutralizer to oxidizer being detanked had been too low because of the extra oxidizer retained in the CM tanks as a result of the previous Apollo 15 parachute anomaly [703]. The decontamination unit used Delchem 2303C, a combustible fluid, as a neutralizer for the oxidizer. Delchem 2303C, manufactured by Pennsalt Chemical Company, was composed of the following materials:

riethanolamine (commercial grade)	70 mass-%
thylene glycol monoethylether	10 mass-%
ater	19 mass-%
etting agent	0.5 mass-%
nti-foaming agent	0.1 mass-%

Changes were made in GSE and the detanking procedure to prevent future overpressurization events.

A similar event had happened at NASA Eastern Test Range a few years earlier: During testing on 17 October 1965, on launch complex 19 of the Eastern Test Range, approximately 9.5 L (2.5 gallons) of dinitrogen tetroxide were drained into a 208-L (55-gallon) drum containing a mixture of 9.5 L (10 quarts) of water and 0.95 L (1 quart) of triethanolamine. The drum exploded while being moved away from the launch complex by a forklift truck.

On 24 July 1975, NTO poisoning affected the three U.S. astronauts on board an APOLLO command module during its final descent and parachute deployment while returning from the Apollo-Soyuz linkup in orbit. This was due to a switch left in the wrong position, which allowed NTO and MMH fumes to vent out of the Apollo spacecraft and then back in through the cabin air intake from the outside air after the external cabin vents were opened [704]. The NO_2 concentration was of the order of $300 \mu\text{L/L}$. The crew were exposed to the toxic gas from 24000 ft. (7.3 km) on down to landing (probably for more than 20 min). The crew members suffered from burning sensations of their eyes, faces, noses, throats, and lungs. One crewmember lost consciousness during descent. About an hour after landing, the crew developed pneumonia, and their lungs had pulmonary edema. They experienced shortness of breath and were hospitalized for 2 weeks. A week later their chest X-rays appeared to return to normal. Measurements of urinary hydroxylysine glycosides indicated that considerable collagen degradation had occurred due to their inhaling nitrogen dioxide, and the crew showed clinical and roentgenographic signs of diffuse chemical pneumonitis [705]. It was likely that collagen degradation occurred in the pulmonary parenchyma.

Another serious accident event is described in detail in [553], pages 9 through 13 and [697, 706]. Three crewmen were exposed to very high concentrations of the oxides of nitrogen. One died within minutes. Severe respiratory distress syndrome developed in the other two, one of whom survived. Twenty-one other workers were exposed to minimal to moderate concentrations of the gas. Most remained asymptomatic, whereas six had shortness of breath, cough, or hemoptysis. The three with persistent symptoms received corticosteroid therapy; the complaints resolved in two. Corticosteroid therapy for four asymptomatic patients who had moderate hypoxemia 2 weeks after the accident may have reduced the severity of the second stage of nitrogen dioxide injury. A detailed description of the event is reproduced here verbatim:

Titan II Silo Large Scale N_2O_4 Spill (8/24/1978, McConnell AFB Silo 533-7) On August 24, 1978, at McConnell AFB southeast of Wichita, Kansas, the worst reported unintentional N_2O_4 spill in US history took place. Approximately 13450 gallons of liquid N_2O_4 spilled into the underground missile silo. Two members of the 381st Strategic Missile Wing were killed and 25 more were injured from N_2O_4 liquid and vapor exposure. The silo also suffered extensive damage. The Titan II first and second stages were an A-50/ N_2O_4 bipropellant propulsion system. The loading operations were completed using a holding tanker located above ground. Once the N_2O_4 loading of the rocket's first and second stages had been completed, all that remained was disconnecting the quick disconnects (QDs) from the rocket air half couplings (AHC). The technicians wearing Rocket Fuel Handler Coverall Outfits (RFHCs) were unaware that a Teflon O-ring seal had dislodged from an upstream location, moved through the filter assembly (of which there were no filter elements installed), through the QD, and wedged itself in between the poppet of the AHC and its primary sealing surface on the Titan II (proximate cause) of the spill. This prevented the isolation of the bulk propellant in the first stage oxidizer tanks once the QD was removed. The RFHCs were similar to Self-Contained Atmospheric Protection Ensemble (SCAPE) suits that are used by the Space Shuttle Program. When the technician mechanically separated the QD from the

AHC, approximately 13450 gallons of liquid N_2O_4 poured out of the AHC and into the missile silo. Very high concentrations of NO_2 vapors traveled from the silo into the connecting cableway to the blast lock area, which was located just outside of the control center where several personnel were located. All the personnel located in the blast lock area managed to escape the vapors by exiting through the access portal at ground level. The personnel in the control center would normally be isolated from the silo, however, two technicians involved in the spill opened the airlock door to try and obtain assistance for their supervisor who was in need of immediate medical attention. The two technicians and four other control center personnel then evacuated through the emergency escape hatch, once they realized the immediate danger of the situation. The nearby town of Rock, Kansas had to evacuate about 100 people as a result of the vapors that were escaping from the silo. It was later discovered that the suit of the supervisor had failed, introducing him to dangerous levels of N_2O_4 (NO_2) vapors, which was ultimately fatal to him within minutes of being exposed. Two other technicians had removed their suit hoods while in the vapor cloud. One died nine days later. The extent of the injuries of the other technician is uncertain, however, he did survive. Repairs to the damaged 533-7 silo were attempted, but later discontinued for budgetary reasons. The silo was never returned to alert status.

Three young men died of rapidly progressive pulmonary edema of delayed onset after they inhaled fumes from an accidental nitric acid explosion [707]. Electron microscopy of their lung tissue revealed altered neutrophils and necrotic endothelial cells in alveolar capillaries. Immunohistochemistry showed small and large serum proteins, including immunoglobulin M, in the edema fluid and hyaline membranes. Increased permeability is a consequence of direct microvascular injury by inhaled nitrogen dioxide.

In the worst commercial NTO spill on record, on 23 October 1995 a cloud of dinitrogen tetroxide/nitrogen dioxide escaped from a railroad tanker car in Bogalusa, Louisiana, exposing an estimated 4000 citizens to the gas. This is an excerpt from the U.S. National Transportation Safety Board report [708]:

At 3:55 p.m. on October 23, 1995, at the Gaylord Chemical Corporation plant in Bogalusa, Louisiana, yellow-brown vapors began leaking from the dome of the DOT class 105A railroad tank car UTLX 82329 that contained a mixture of nitrogen tetroxide, which is a liquefied poisonous gas and oxidizer, and water. The vapors initially formed a plume between 10 and 15 feet in diameter. Plant personnel notified emergency response agencies and used two plant fire hoses to spray water into the plume to suppress the vapors. About 4:30 p.m. Bogalusa fire personnel arrived at the plant and set up fire hoses to help-suppress the vapors.

The head on the B-end of the tank car failed about 4:45 p.m., resulting in one end of the tank car jacket being torn away and thrown about 350 feet. The tank car was then propelled 35 feet down the track and derailed at a track bumping block. A large reddish-brown vapor cloud was released from the tank car. Vapors continued to be released from the opening in the tank car for another 36 hours until the chemical reaction that had occurred within the tank was brought under control through neutralization and dilution.

Some 3000 people were evacuated from the area as a result of the vapor cloud. Of 4710 people who were treated at local hospitals, 81 people were admitted.

It appears that the tank car had contained water that entered the tank when a leaking valve had been doused with water before it was replaced a month before the accident.

The tank car that was sent to be refilled at the N_2O_4 supplier was thought to be empty, but it still contained water when it was filled because the tare weight before filling was above the number on record. The off-normal tare weight should have alerted the operators. The mixture of water and N_2O_4 corroded the tank. Following the Bogalusa accident, the most thorough study of the health effects of N_2O_4 release from a railroad tank car was undertaken; it included measuring the association between acute low-level exposure and pulmonary symptoms; reviewing the records of three emergency departments; surveying 80 emergency department patients, 552 community residents, 21 chemical plant workers, and 29 emergency workers; and conducting a case-control study [709]. Pulmonary case status was defined as having an objective pulmonary finding noted on the emergency department record, reporting that the onset of symptoms was subsequent to the release, and being within the city limits at the time of the release. Self-reported case status was defined as reporting one or more symptoms consistent with exposure to nitrogen dioxide in the week after the release and having been within the city limits at the time of the release. Chemical exposure was characterized by proximity to, direction from, and being outdoors within 1 h after the release. Duration of potential exposure was not measured. Local emergency department visits increased fivefold in the week after the release. The most common complaints recorded in a systematic sample of 528 visits in the first 30 h after the release were headache (31%), burning eyes (30%), and sore throat (24%). Objective pulmonary findings were recorded for 41 patients in the week before and 165 in the week after the release. The odds of being a pulmonary case increased by 40% for each quarter-mile increment in proximity to the release, while the odds of being a self-reported case increased by 20% for each quarter-mile increment in proximity. People who met the pulmonary case definition were 2.5 times more likely than control subjects to have been outdoors and 6.4 times more likely to report a preexisting pulmonary condition. Emergency department visits increased five-fold, but serious acute health effects were uncommon. People who met the pulmonary case definition were six times more likely to report pulmonary symptoms than those without preexisting conditions. This study was not designed to determine any potential long-term effects of exposure.

In further evaluating reactive airway dysfunction syndrome (RADS) after exposure to dinitrogen tetroxide, a different sample of 234 patients with respiratory complaints after the Bogalusa spill in October 1995 received a complete history and physical examination, a symptom questionnaire, and pulmonary function tests [710]. Patients whose previously undocumented asthma-like symptoms persisted for 3 months after exposure to N_2O_4 had methacholine challenge testing. Of the 234 patients evaluated, six met the criteria for a diagnosis of RADS. The distance of these six patients from the source of the leak, their durations of exposure, and initial symptoms were not different from those of the sample patients who did not have RADS.

Even 13 years later, the patient questionnaire database was again subjected to another statistical epidemiologic examination and led to similar conclusions [711]. Environmental exposures from sudden events may adversely impact community residents,

often resulting in a variety of health concerns. Litigation often follows, and sorting those with effects due to the exposure from those without is often complicated and difficult. The study examined the effects of two different exposure models on claimed effects to nitrogen tetroxide from the 1995 Bogalusa railroad tank car explosion. Symptoms and physical injuries were sorted into 17 different categories and analyzed by the use of exposure models. Data from 16592 individuals who completed questionnaires dealing with their claimed adverse-health effects resulting from being in the locale of the explosion were used to assess the differences in symptoms and physical conditions for each exposure model. The data illustrated the importance of exposure assessment in evaluating sometimes-bogus claims of adverse health from an environmental exposure. The data also demonstrate the difficulties in assessing litigious, publicity, and recruitment factors. See also [712–716].

In spite of the treatment with a combination of dexamethasone and anisodamine, two victims of an NTO accident died after the treatment [717]. They had suffered severe damage of respiratory and circulation function and finally died from respiratory and circulatory failure.

10 Safety Properties of Dinitrogen Tetroxide

10.1 Detonability of Dinitrogen Tetroxide

Unlike nitrous oxide or nitric oxide, liquid nitrogen dioxide and dinitrogen tetroxide do not have a positive enthalpy of formation, and they cannot be used as monopropellants without the presence of a fuel. Just looking at the thermodynamic properties of liquid N_2O_4 , one would not expect this oxidizer to be detonable. But just to be on the safe side, the detonability of liquid N_2O_4 was tested in a setup similar to that used for card gap sensitivity testing of monopropellants and liquid explosives. Using the techniques previously developed for detonability testing of nitric oxide and nitrous oxide, the detonation characteristics of dinitrogen tetroxide as a non-boiling liquid were examined [718]. In contrast to liquid nitric oxide, liquid dinitrogen tetroxide is not detonable. Liquid N_2O_4 (273 K, 0.1 MPa) confined in a steel pipe 26.6 mm in diameter with 3.38-mm wall thickness failed to detonate when shocked with a 50-g tetryl donor close-coupled to a 0.08-mm-thick polyethylene foil or a 1.27-mm-thick steel foil attenuator that sealed the bottom of the container.

However, mixtures of N_2O_4 with toluene or nitrobenzene are detonable and have been proposed as binary explosives in bombs, where the initially separated components are mixed by an air-driven propeller only after the bomb has left the bomb-bay of the bomber aircraft and before it impacts the ground.

Confined mixtures of NTO and silicone oil may explode on contact.

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Dinitrogen Trioxide

Coverage of nitrogen oxides had to be spread out over seven chapters because a single chapter devoted to the topic would have been unwieldy and made it more difficult for readers to find information on a specific compound; in addition, such an approach would have made it difficult to arrange 30 chapters among 5 subvolumes in such a way that each subvolume was about the same size. Briefer chapters made our task much easier. The other six chapters in this series are titled “Nitrogen Oxides,” “Nitrous Oxide,” “Nitric Oxide,” “Nitrogen Dioxide,” “Dinitrogen Tetroxide,” and “Dinitrogen Pentoxide.”

This chapter covers dinitrogen trioxide, N_2O_3 , which exists as a pure substance only at very low temperatures. Nitrogen forms at least six covalently bound oxides, and N_2O_3 is one of them. The peculiar property of dinitrogen trioxide is its blue color. The main application of dinitrogen trioxide is as a stabilizer and anticorrosion agent in mixed oxides of nitrogen (MON).

Pure dinitrogen trioxide, which is also known as nitrous acid anhydride, nitrogen sesquioxide, nitrogen trioxide, CAS RN [10544-73-7], exists only in the solid state [1, 2]. It starts to decompose already slightly above its melting point and converts to a blue liquid consisting of a mixture of N_2O_3 and N_2O_4 . If the temperature is allowed to increase further, and the pressure buildup is allowed to vent, the mixture begins to lose nitric oxide and becomes gradually enriched with N_2O_4 . For this reason, pure dinitrogen trioxide is not suitable as a rocket propellant oxidizer, but it is used widely in mixtures with dinitrogen tetroxide. These mixtures are called **mixed oxides of nitrogen**, or MON for short. The MON designation is followed by a number that indicates the mass-% of NO in the mixture, e.g., MON-1 or MON-3. The main reason for adding N_2O_3 (or NO) to N_2O_4 is to reduce the potential of stress corrosion of stainless-steel and titanium-alloy tanks. Next to dinitrogen tetroxide, dinitrogen trioxide is the most important oxidizer among the group of nitrogen oxides.

Pure liquid dinitrogen trioxide $\text{N}_2\text{O}_3(\text{L})$ theoretically contains 65.2 mass-% NO and in the MON designation scheme could be called MON-65.2. There should be no MON with numbers higher than 65.2.

If pure dinitrogen trioxide were used as a rocket propellant, its composition would change each time the tank was vented or the propellant was transferred from a supply tank to an empty tank. On the other hand, the low freezing point of dinitrogen trioxide makes it more attractive than pure dinitrogen tetroxide, which has a relatively high freezing point. The best compromise between vapor pressure, vapor phase losses, and composition changes during transfer and a low-freezing-point oxidizer are the $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures containing less than 30% N_2O_3 , which were discussed in detail in *Encyclopedia of Oxidizers*, in the chapter “Dinitrogen Tetroxide.”

1 Production of Dinitrogen Trioxide

Dinitrogen trioxide can be prepared by bubbling nitric oxide gas into liquid dinitrogen tetroxide until the liquid is totally saturated with NO or by slowly adding a stoichiometric amount of oxygen to pure nitric oxide and condensing the product.

Concentrated nitric acid distilled with arsenious oxide and concentrated sulfuric acid yields nitrous acid anhydride (N_2O_3) mixed with some nitrogen dioxide.

2 Physical Properties of Dinitrogen Trioxide

The physical properties other than the melting point and the solid density of pure dinitrogen trioxide (N_2O_3) are not very well known, because this compound begins to decompose as soon as the temperature exceeds its melting point. Some of the properties are known only for equilibrium mixtures, which may contain varying amounts of dinitrogen trioxide, nitric oxide, nitrogen dioxide, and dinitrogen tetroxide (Table 1). Published data of physical properties for such mixtures vary widely, depending on the purity of the sample and the methods used for measurements. An excellent summary of the physical and chemical properties of N_2O_3 is published in Reference [2]. In many instances, the undesirable premature dissociation of N_2O_3 is suppressed by applying an overpressure of NO while the physical properties are being measured.

Determination of the physical properties of N_2O_3 is complicated by the existence of two dissociation equilibria that are not independent of each other. Both temperature and pressure affect these properties.

Table 1: Physical properties of dinitrogen trioxide.

Property name	Physical state	Property data		Literature
		SI Units	Other Units	References
Molecular mass		76.0116 g/mol	13.1559 mol/kg	[3]
Melting point	solid	171.1 K	−102 °C	[4]
Boiling point	liquid	246 K	−27 °C (extrapolated)	[4]
Density at −195 °C	solid		1.782 g/cm ³	[4]
Enthalpy of formation, (ΔH) ₂₉₈	gaseous	+82.8 kJ/mol	+19.80 kcal/mol	[5]

NIST Chemistry WebBook [3] has more reliable data, but only for the gas phase

Liquid dinitrogen trioxide at low temperatures just barely above its melting point is a dark blue liquid. At 223 K (−50 °C) it is totally opaque. The blue color of dinitrogen trioxide can be briefly observed if one acidifies alkali metal nitrite salts, where it is formed as a short-lived intermediate in the decomposition of nitrous acid HNO_2 . Solid

dinitrogen trioxide is not soluble in liquid air or in liquid oxygen (LOX). When heating liquid N_2O_3 in air, one can only observe the red-brown vapors of nitrogen dioxide.

The physical properties of pure dinitrogen trioxide are not as important as the physical properties of some of its mixtures with dinitrogen tetroxide, or MON. The physical properties of $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixtures will be discussed following the chapter on the physical properties of dinitrogen tetroxide.

2.1 Freezing Point and Phase Behavior of Dinitrogen Trioxide

The freezing point and vapor pressure of the $\text{NO}/\text{N}_2\text{O}_4$ system were determined to be in the range 0–16.85 mass-% NO and 288 to 233 K (15 to -40°C) [6]. These data were subsequently confirmed using data obtained by Beattie and Vosper [7].

The freezing points of mixtures of dinitrogen tetroxide and dinitrogen trioxide, as well as those of the pure components, have been accurately determined [8]. The phase diagram of the binary mixture was discussed in *Encyclopedia of Oxidizers*, in the chapter “Dinitrogen Tetroxide.” Dinitrogen trioxide behaves as a pure compound at its freezing point. The freezing point of dinitrogen trioxide was found to be at 172.4 K (-100.7°C).

2.1.1 Phase Changes at Very High Pressures

Some nitrogen oxides transition to other nitrogen oxides at very high pressures. In the case of dinitrogen trioxide, isotope exchange occurs in mixtures of liquid N_2O_3 and NO at low temperatures and high pressures [9].

2.2 Boiling Point of Dinitrogen Trioxide

The boiling point of dinitrogen trioxide cannot be determined directly because it decomposes already before it begins to boil [1]. This happens at about 276 K (3°C). Extrapolating from vapor pressure measurements of mixtures of N_2O_3 with N_2O_4 gives only a rough estimate of the boiling point of pure N_2O_3 : 246 K (-27°C).

2.3 Density of Dinitrogen Trioxide

The density of liquid dinitrogen trioxide at 275 K (2°C) is 1.447 g/cm^3 (from CRC Handbook). Dinitrogen trioxide decomposes before it reaches critical point conditions, and an equation of state for liquid dinitrogen trioxide cannot be established. Table 2 gives density data for temperatures down to almost the freezing point of the liquid.

The density of frozen N_2O_3 at 78 K is 1.782 g/cm^3 [10].

Table 2: Density of liquid dinitrogen trioxide.

Temperature		Density
K	°C	g/cm ³
265	−8	1.464
269	−4	1.455
272	−1	1.451
275	+2	1.447
268	−5	1.444
263	−10	1.453
253	−20	1.476
78	−195	1.782
158	−115	1.694

Data source: As referenced in [2] Beattie 1963

2.4 Vapor Pressure and Vapor Phase Composition of Dinitrogen Trioxide

A study was made of the vapor composition above liquid mixtures of nitrogen dioxide and nitric oxide [1, 7]. The vapor in equilibrium with a liquid containing equimolar

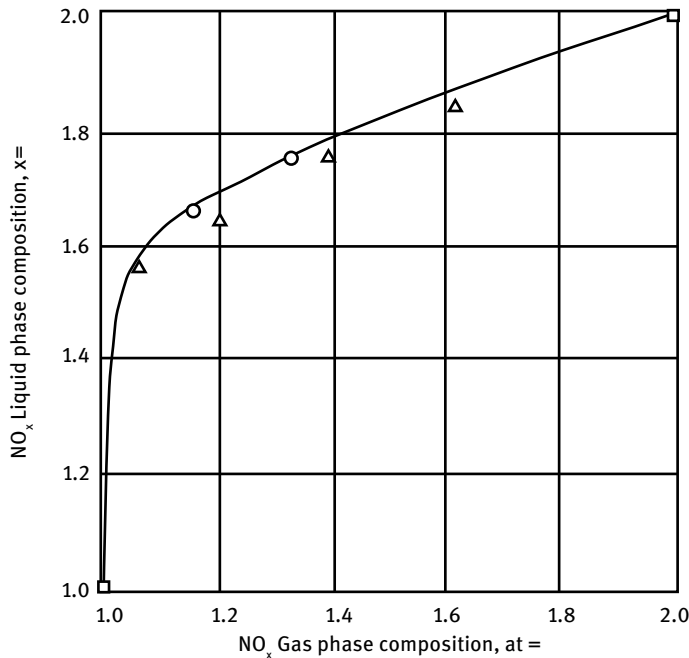


Figure 1: Vapor phase composition as a function of the liquid phase composition of NO/NO₂ mixtures. (Modified from [7]. Reprinted with permission from © 1961 The Royal Society of Chemistry.)

amounts of nitrogen dioxide and nitric oxide is almost exclusively nitric oxide. The composition of the vapor above liquid mixtures of nitric oxide and nitrogen dioxide is nearly independent of temperature for a particular liquid composition.

Figure 1 shows the vapor phase composition as a function of the liquid phase composition of NO/NO₂ (i.e., N₂O₃/N₂O₄) mixtures. The parameter x is the oxygen atom fraction expressed in multiples of the nitrogen atom fraction for a fictitious compound NO _{x} . The abscissa scale shows the fractional x of the NO _{x} vapor composition, and the ordinate scale shows the fractional x of the NO _{x} liquid phase composition. It can be seen that up to liquid $x = 1.4$ the vapor composition stays close to that of NO_{1.0}. The squares designate the pure compounds NO and NO₂ (i.e., N₂O₄) at either end of the curve.

2.5 Thermodynamic Properties of Dinitrogen Trioxide

The ideal gas chemical thermodynamic properties for NO, NO₂, N₂O₃, and N₂O₄ for the temperature range 50 to 5000 K were evaluated by a statistical thermodynamic method using an updated set of molecular parameters [11].

2.5.1 Heat Capacity of Dinitrogen Trioxide

The heat capacity of gaseous dinitrogen trioxide at 298 K is 65.615 J mol⁻¹ K⁻¹. The heat capacity as a function of temperature can be calculated from the following polynomial equation:

$$C_p^\circ = A + B \times \tau + C \times \tau^2 + D \times \tau^3 + \frac{E}{\tau^2}$$

where C_p is the heat capacity in J mol⁻¹ K⁻¹, τ is the temperature in kelvin divided by 1000, and A, B, C, D, and E are constants listed in Table 3 for two different temperature ranges. Note that N₂O₃ is unstable at temperatures above 298 K and the column for the higher temperature range 1100–6000 K is strictly of academic interest. It is not very practical to list thermodynamic data for a compound that is unstable at the tem-

Table 3: Thermodynamic property polynomial equation coefficients for dinitrogen trioxide gas.

Temperature Range, K	298–1100	1100–6000
A	39.09663	100.8737
B	114.8006	1.690785
C	-81.97125	-0.339747
D	21.77249	0.023407
E	-0.088738	-8.849160
F	66.46786	30.72094
G	324.5776	399.7498
H	82.84320	82.84320

Data source: [3]

perature range listed. It is much more important to have accurate thermodynamic data for liquid mixtures of dinitrogen trioxide with dinitrogen tetroxide.

2.5.2 Enthalpy of Formation of Dinitrogen Trioxide

The standard enthalpy of formation of gaseous dinitrogen trioxide at 298 K (if it existed at this temperature) would be +82.843 kJ/mol [3]. The JANAF Table listed it as +19.80 ± 0.2 kcal/mol [5]. The differential enthalpy of formation of gaseous dinitrogen trioxide as a function of temperature can be calculated from the following polynomial equation:

$$H^\circ - H^\circ_{298.15} = A\tau + \frac{B \times \tau^2}{2} + \frac{C \times \tau^3}{3} + \frac{D \times \tau^4}{4} - \frac{E}{\tau} + F - H$$

where H is the enthalpy in kJ/mol, τ is the temperature in kelvin divided by 1000, and A, B, C, D, E, and F are constants listed in Table 3 for two different temperature ranges.

2.5.3 Heat of Dissociation of Dinitrogen Trioxide

The equilibrium constant K_2 for the dissociation of N_2O_3 is

$$K_2 = \frac{[p_{NO}][p_{NO_2}]}{[p_{N_2O_3}]}$$

The equilibrium constant for the dissociation of N_2O_3 as a function of NO_2 concentration and temperature is presented graphically in Figure 2. The diameter of the circles indicates the mean deviation of the data points. The presence of NO or NO_2 retards the dissociation of N_2O_3 .

When plotting the logarithm of the equilibrium constant versus the reciprocal absolute temperature, one can derive the activation energy and heat of reaction from the slope (Figure 3). The result was 39.86 ± 0.4 kJ/mol (9.527 ± 0.096) kcal/mol for the heat of reaction [1]. The corresponding entropy change for the reaction was 139 ± 1.5 J mol⁻¹ K⁻¹ (33.25 ± 0.35 cal mol⁻¹ °C⁻¹).

2.5.4 Entropy of Dinitrogen Trioxide

The standard entropy of formation of gaseous dinitrogen trioxide at 298 K and 101 kPa is 308.54 J mol⁻¹ K⁻¹ [3]. The entropy of gaseous dinitrogen trioxide as a function of temperature can be calculated from the following polynomial equation:

$$S^\circ = A \times \ln(\tau) + B \times \tau + \frac{C \times \tau^2}{2} + \frac{D \times \tau^3}{3} - \frac{E}{2 \times \tau^2} + G$$

where S° is the enthalpy in J mol⁻¹ K⁻¹, τ is the temperature in kelvin divided by 1000, and A, B, C, D, E, and G are constants listed in Table 3 for two different temperature ranges.

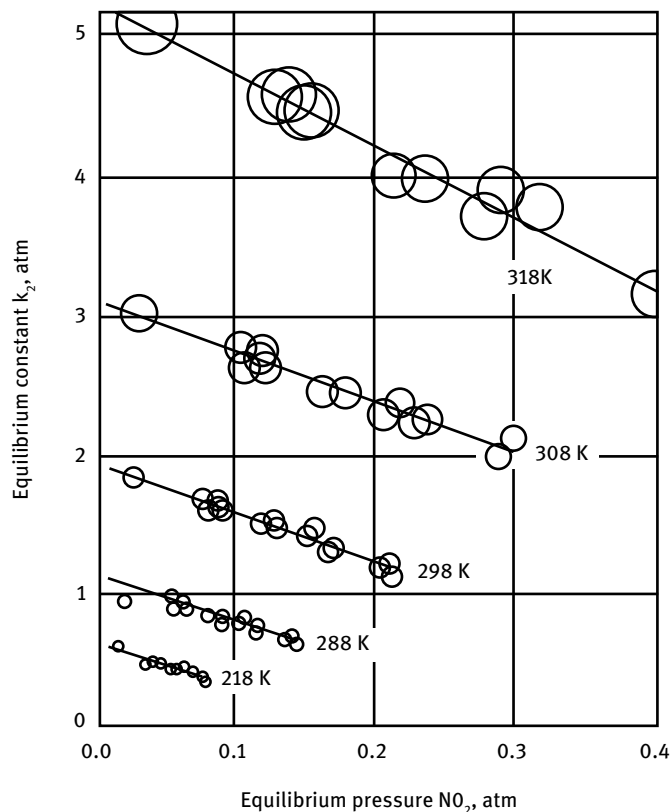


Figure 2: Equilibrium constant for the dissociation of N_2O_3 as a function of NO_2 concentration and temperature. (Modified from [1]. Reprinted with permission from © 1957 The Royal Society of Chemistry)

2.6 Molecular Properties, Crystal Structure, Dipole Moment, Molecular Orbital Calculations of Dinitrogen Trioxide

Data on the molecular structure of N_2O_3 are difficult to obtain. The lack of precise gas phase structural data is largely due to the readiness with which N_2O_3 dissociates to NO and NO_2 . The peculiar blue color of N_2O_3 must be explained by transitions of electronic states in the molecule.

2.6.1 Molecular Structure of Dinitrogen Trioxide

Adducts like N_2O_3 , which are formed by association of two molecules that can exist in monomer and dimer form, are also called heterodimers. The molecular structure of

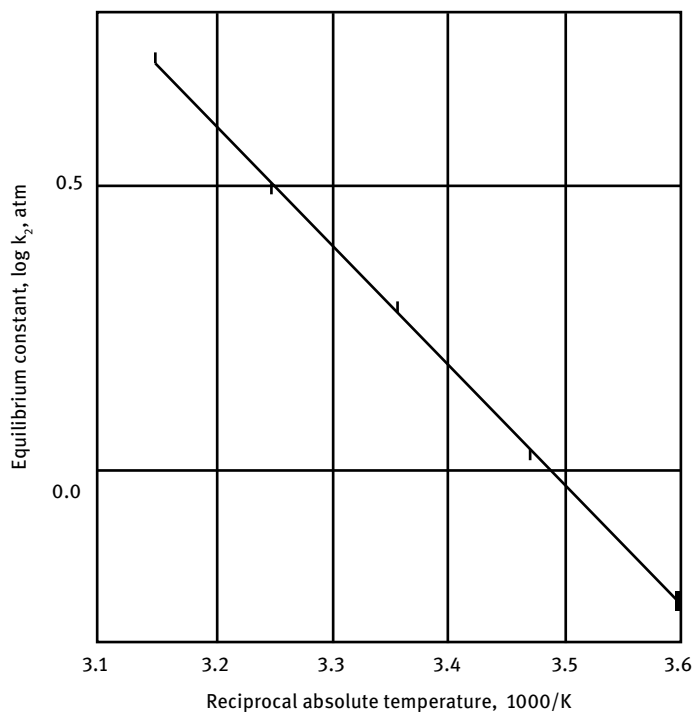


Figure 3: Arrhenius plot for the equilibrium constant for the dissociation of N_2O_3 . (Modified from [1]. Reprinted with permission from © 1957 The Royal Society of Chemistry.)

dinitrogen trioxide with interatomic distances and bond angles is shown in Figure 4. The molecule is a planar asymmetric rotor. The dashed lines marked a and b mark the two principal axes around which the asymmetric molecule can spin.

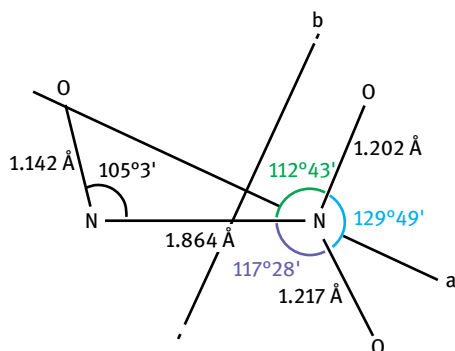
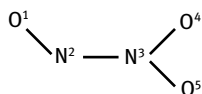


Figure 4: Molecular structure of asymmetric dinitrogen trioxide. (Redrawn and patterned after [12].)

The molecules $(\text{NO})_2$, N_2O_4 , and N_2O_3 , which form by association from other nitrogen oxides, contain weak N—N chemical bonds. They are also called homodimers $[(\text{NO})_2, \text{N}_2\text{O}_4]$ and heterodimers $[\text{N}_2\text{O}_3]$. The enthalpies of dissociation of these dimers are $\Delta H_{298} = 4.5, 57.1, \text{ and } 40.9 \text{ kJ/mol}$, respectively.

N_2O_3 has two forms, the unstable ONONO isomer and the more stable ONNO₂ form. The structure of N_2O_3 was determined from the microwave spectrum of seven isotopic species [13].

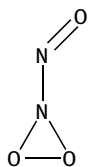


The detailed structure associated with the following planar configuration is: $d(\text{N}^2\text{N}^3) = 1.864 \text{ \AA}$; $d(\text{N}^2\text{O}^1) = 1.142 \text{ \AA}$; $d(\text{N}^3\text{O}^4) = 1.202 \text{ \AA}$; $d(\text{N}^3\text{O}^5) = 1.217 \text{ \AA}$; $\angle \text{O}^1\text{N}^2\text{N}^3 = 105.1^\circ$; $\angle \text{O}^4\text{N}^3\text{N}^2 = 112.7^\circ$; $\angle \text{O}^5\text{N}^3\text{N}^2 = 117.5^\circ$. These numbers are very similar to those shown in Figure 4.

Dinitrogen trioxide can exist both as asymmetric dinitrogen trioxide (O_2NNO) and symmetric dinitrogen trioxide (ONONO). There are other possibilities for nitrogen oxides that also have the gross formula N_2O_3 but a different structure [14]. Similar speculative structures were considered for the N_2O_3 molecule. One such theoretical isomer would be a symmetrical 2,4,5-trioxa-1,3-diazabicyclo[1.1.1]pentane, CAS RN [224950-18-9], also called the cage isomer:



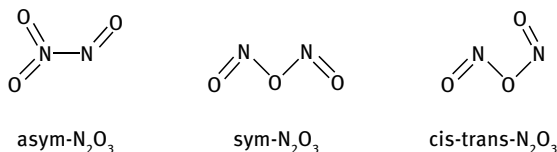
or nitroso-dioxaziridine, CAS RN [132871-99-9]:



None of these compounds has ever been isolated, but they already have their own CAS Registry Numbers. Thus, keep looking for any evidence that they actually exist, perhaps only at very low temperatures.

Conformers of N_2O_3 can be isolated in a low-temperature matrix and analyzed by Fourier transform infrared (FTIR) spectroscopy [15]. The irradiation of an argon matrix containing NO and NO₂ with a pulsed laser at 355 nm caused the enhancement of

a new set of vibrational bands, which may result from the conversion of *asym*-N₂O₃ to a new conformer, *trans-cis* N₂O₃, reported at [15] for the first time. The observed vibrational frequencies and relative intensities of the conformer were in good agreement with density functional theory (DFT) calculations at the BLYP/6-31G* level. Upon annealing, a thermally induced conversion of the *trans-cis* N₂O₃ into the not quite stable intermediate *sym*-N₂O₃ takes place:



The existence of the *trans-cis* N₂O₃ was confirmed by measuring IR absorption lines of NO/NO₂/Ar or NO/O₂/Ar mixtures condensed onto a cold target at 13 K [16]. In that study, two isomers of N₂O₃, *asym*-N₂O₃ and *sym*-N₂O₃, were identified by IR absorption in an argon matrix at 13 K. Upon irradiation with a XeCl excimer laser at 308 nm, *asym*-N₂O₃ was converted to *sym*-N₂O₃ and a new form of N₂O₃, *trans-cis* N₂O₃. The latter was readily photo-converted to *sym*-N₂O₃ upon further irradiation with red light. Assignments of IR absorption lines to each conformer in its isotopic variants were based on ¹⁸O-isotopic substitution and photoconversion experiments. *Trans-cis* N₂O₃ with an *asym*. ONONO structure was identified with absorption lines at 1704.5, 1665.7, 877.8, and 243.0 cm⁻¹. Isotopic substitution indicated that this species contains two nearly isolated N=O groups. Spectral assignments were further supported by theoretical calculations with DFT methods. Previous assignments of low-energy vibrational modes of *asym*-N₂O₃ and *sym*-N₂O₃ had to be revised based on comparison with new calculations.

Structures of eight isomers of N₂O₃, including five new conformers, were investigated by computational chemistry methods [17]. The computational results showed that *asym*-N₂O₃, *sym*-N₂O₃, and *trans-cis* N₂O₃ are stable isomers, and *asym*-N₂O₃ was predicted to be the most stable. The five new isomers were much more energetic, and therefore less stable, than *asym*-N₂O₃ by an additional 314–343 kJ/mol (75–82 kcal/mol). All eight isomers were able to convert among each other through one-step or multi-step reactions. Results obtained in this work lead to the conclusion that along with the known *asym*-N₂O₃ being the nitrosating active form for N₂O₃, the *sym*-N₂O₃ and *trans-cis* N₂O₃ isomers also have relatively strong nitrosating abilities when N₂O₃ reacts with secondary aliphatic amines.

2.6.1.1 Crystal Structure of Frozen Dinitrogen Trioxide

The crystal structure of solid N₂O₃ at 113 K (–160 °C) is orthorhombic, space group *P*2₁2₁2₁, with *a* = 5.0686(4) Å, *b* = 6.4796(5) Å, and *c* = 8.6326(6) Å; *d*_c = 1.781 g/cm³ for

$Z = 4$ [18]. The structures were solved by direct methods and refined by least-squares to $R = 0.022$.

Mixtures of N_2O_3 and N_2O_4 were prepared from measured volumes of NO and O_2 for the purpose of studying phase relations in the system N_2O_3/N_2O_4 , which depend on the composition of the samples and on the temperature. Single crystals of phases A and B of N_2O_3 were grown *in situ* on a diffractometer and studied at temperatures between 166 and 103 K (−107 and −170 °C) by XRD [19]. The structural analysis of A- N_2O_3 (tetragonal, space group $I4_1/a$ at 103 K [−170 °C], $a = 16.2557(16)$ Å, $c = 8.8049(13)$ Å, $Z = 32$, $R_1 = 0.051$) was hampered by twinning and additional disorder of one of two crystallographically independent molecules. B- N_2O_3 is nicely ordered with one molecule in the asymmetrical unit (orthorhombic, space group $P2_12_12_1$, at $T = 113$ K = −160 °C, $a = 5.0686(4)$ Å, $b = 6.4796(5)$ Å, $c = 8.6326(6)$ Å, $Z = 4$, $R_1 = 0.023$). The most interesting features of the N_2O_3 molecule are its planarity and the extraordinarily long N—N bond (1.890(1) Å).

2.6.1.2 Rotational Barriers in Dinitrogen Trioxide Molecule

The rotation of two halves of the molecule around the long axis of the N_2O_3 molecule is not unhindered but similar to situations in N_2O_4 or N_2H_4 , where the rotation has barriers where the orbitals of the outer atoms overlap and repel each other. Torsional energy potentials for N_2O_4 and N_2O_3 were calculated based on optimized geometries of the respective 90°-twisted saddle points [20]. These potentials were refined by obtaining potential energies of points along the intrinsic reaction coordinate. A comparison was made between these *ab initio* potentials and an analytical form based on a two-term cosine expansion in terms of the N—N dihedral angle. The shapes of these two potential curves were in close agreement. The torsional barriers in N_2O_4 and N_2O_3 obtained from the calculations were 2333 and 1704 cm^{-1} , respectively. In the case of N_2O_3 , the torsional frequency found from the intrinsic reaction coordinate potential, 144 cm^{-1} , was considerably larger than the reported experimental values 63–76 cm^{-1} . Consistent with this discrepancy, the torsional barrier obtained from several different calculations, 1417–1718 cm^{-1} , was higher than the value of 350 cm^{-1} deduced from experimental studies. It was suggested that the assignment of the torsional mode in N_2O_3 should be reexamined. Both N_2O_4 and N_2O_3 exhibit strong hyperconjugative interactions of in-plane O lone pairs with the central N—N σ^* antibond. The torsional barriers in these molecules arise principally from a combination of 1,4 interactions and hyperconjugation.

2.6.1.3 Bond Energies and Bond Lengths of Dinitrogen Trioxide

The N_2O_3 molecule can be described as a complex formed between NO_2 and NO. It has a binding energy of about 40 kJ/mol, which is higher than that of a van der Waals adduct but much lower than that of a typical covalent bond. The N—N bond length of 1.864 Å is between that of $(NO)_2$ ($r_{N-N} = 2.236$ Å) and that of $(NO_2)_2$ ($r_{N-N} = 1.75$ Å).

In equilibrium mixtures of NO and NO₂, there is a large concentration of N₂O₄ and a smaller but significant concentration of N₂O₃, depending on the temperature.

Over the course of an all-electron STO-6G valence-bond study of the origin of the long, weak N—N bond of *asym*-N₂O₃, special attention was given to the valence-bond structures, which differ in the locations of eight electrons among five overlapping nitrogen and oxygen atomic orbitals, designated as p1, h2, and p3 for NO₂, and h4 and p5 for NO [21]. These orbitals accommodate the electrons of the N—N s-bond and oxygen lone-pair electrons prior to any delocalization of the latter electrons. The calculations were parametrized so that estimates of the atomic spin densities for NO₂ and NO were approximately reproduced when their odd electrons were assumed to occupy these overlapping atomic orbitals. The origin of the N—N bond lengthening was shown to be associated with **(1)** the orientation of the h4 atomic orbital and **(2)** some delocalization of oxygen p electrons into the nitrogen h2 and h4 atomic orbitals when the latter orbitals are initially singly occupied. Covalent-ionic resonance



can stabilize the N₂O₃ relative to the NO₂ and NO dissociation products.

2.6.1.4 Molecular Orbital Calculations of Dinitrogen Trioxide

Because it is so difficult to measure physical and thermodynamic properties of pure dinitrogen trioxide due to its incipient decomposition, computational chemistry had to step in and fill some of the data gaps.

Localized molecular orbitals were derived from the molecular orbitals calculated by a Complete Neglect of Differential Overlap (CNDO) method for N₂O₂, N₂O₃, and N₂O₄, and the theoretical Lewis structures were given [22]. The molecules have σ-type nitrogen-nitrogen bonds of high p-orbital character, but no π bonds. Oxygen lone electron pair delocalization to both nitrogen atoms is antibonding, reducing the strength of the nitrogen-nitrogen bond. These results from a semi-empirical CNDO method were in good agreement with those from previous *ab initio* studies.

The structure of symmetric N₂O₃ was investigated using *ab initio* methods and results were compared with density functional calculations of the symmetric and asymmetric forms of this molecule [23]. Bond lengths and bond angles were determined using both SCF and MP2 theory. At the highest level of theory considered, the N—O bond was determined to be 1.492 Å, the N—O bond was 1.168 Å, the ∠N—O—N angle was 103.5°, and the ∠O—N—O bond angle was found to be 109.9°. The molecule was determined to be planar at all levels of theory considered. Vibrational frequencies were computed for the symmetric structure of N₂O₃. The calculated vibrational frequencies were in better agreement with the alternate assignments than the preferred assignments reported previously. An attempt was made to determine the relative stability of the symmetric and asymmetric forms of this molecule.

Equilibrium geometries, dipole moments, harmonic vibrational frequencies, and IR intensities were calculated for a set of dinitrogen trioxide conformers by *ab initio*

calculations at the MP2 level [24]. The calculation results satisfactorily reproduced the experimental structural and vibrational spectral features of *asym*-N₂O₃ and *sym*-N₂O₃. Calculations at the same levels indicated that the *trans-cis* N₂O₃ is actually a stable conformer of N₂O₃, and previously observed matrix IR spectral features that were not properly assigned should be attributed to the *trans-cis* structure of dinitrogen trioxide. However, other results showed that the other two estimated conformers, *cis* N₂O₃ and *cis-cis* N₂O₃, must be considered to be transition states.

Ab initio calculations on three hypothetical nitrogen-oxygen clusters, N₂O₃, N₄O₆, and N₈O₁₂, with highly symmetrical geometries, *D*_{3h}, *T*_d, and *O*_h symmetry, respectively, showed that these structures have local minima, with energies very high above the products of a fragmentation reaction (N₂ and O₂) [25].

The geometrical, electronic, and thermodynamic parameters of three known isomers of N₂O₃, including the structure of the asymmetrical isomer, NONO₂, were calculated by DFT [26]. From the calculation of vibrational frequencies it followed that the structure of NONO₂ has a local potential energy minimum and corresponds to the stationary state of the N₂O₃ isomer. The molecular structure of NONO₂ is characterized by a substantial negative charge on the NO₂ fragment and positive charge on the NO fragment. The electronic structure of the NO⁺NO₂⁻ isomer can be characterized as nitrosonium nitrite, which can be oxidized to nitrite and participate in nitrosylation in accordance with the biogenic characteristics of the NO_x intermediate, assumed to be formed in biological systems during the oxidation of NO.

The cage isomer of N₂O₃ (c-N₂O₃) is an intriguing energetic oxidizer if only it could be made cheaply (from air?) and stabilized. *Ab initio* electronic structure calculations showed that c-N₂O₃ is vibrationally stable with a large heat of formation of +7.95 kJ/g [27]. Combustion reactions with c-N₂O₃ as the oxidizer would produce larger enthalpies of combustion than other commonly used oxidizers such as ammonium perchlorate (AP), Liquid **O**Xygen (LOX), or Di**N**itrogen **T**etr**O**xide (NTO). c-N₂O₃ was shown to have a unimolecular decomposition barrier of 24.4 kJ/mol at the **C**oupled **C**luster **S**ingles and **D**oubles (CCSD)(T)/CBS(Q-5) level of theory and a dimer-induced decomposition barrier of 100.8 kJ/mol. Unfortunately, although c-N₂O₃ is predicted to perform well as an oxidizer, the low barrier to unimolecular decomposition is likely to render it impractical as an energetic oxidizer.

2.7 Optical Properties of Dinitrogen Trioxide

The most peculiar property of dinitrogen trioxide is its deep blue color. The analysis of a mixture of nitric oxide, nitrogen dioxide, dinitrogen tetroxide, and dinitrogen trioxide by UV spectroscopy is simplified by the fact that nitric oxide is transparent above 2300 Å at normal pressure, while dinitrogen tetroxide is transparent above 4000 Å. Optical methods are important for the analysis of mixtures of nitrogen oxides.

2.7.1 Ultraviolet/Visible Absorption Spectra of Dinitrogen Trioxide

Early workers studying absorption spectra of liquid N_2O_3 found a band system in the 3000–4000 Å region that was initially attributed to dinitrogen trioxide. However, it was suspected that this spectrum was due to the presence of nitrous acid which would have to be expected if the reacting gases were not perfectly dry. This was supported by a study of the isotopic shift effect for the band system, where H_2O or D_2O was deliberately added to a mixture of nitric oxide and nitrogen dioxide. It was also noted that the absorption in the red or orange that leads to the blue color of liquid N_2O_3 has not been observed in the gas.

The spectrum of dinitrogen trioxide in several solvents has shown the presence of a weak absorption maximum at about 7000 Å and an intense absorption, similar to that in the gas phase, below 3500 Å. The blue color is due to a weak band in the red region, at 6620 Å in toluene, with an absorption coefficient of 4.5×10^{-4} . The visible band shifts toward the blue with increasing polarity of the solvent [28]. If one assumes that dinitrogen trioxide is fully associated in toluene at 193 K (–80 °C), it is possible to calculate extinction coefficients for quantitative analytical purposes.

The visible spectra and absorption coefficients of liquid mixtures of nitrogen dioxide and nitric oxide have been determined over a range of temperatures [29]. When corrected for changes in density, the spectra were temperature-independent. Further, the amount of dinitrogen trioxide present was nearly equal to the quantity of nitric oxide absorbed. Thus, it appears that the only major molecular species present in this system are dinitrogen trioxide and dinitrogen tetroxide. Existing data were used to relate the stability of dinitrogen trioxide at a given temperature to the partial pressure of nitric oxide in equilibrium with the liquid.

2.7.2 IR Absorption Spectra of Dinitrogen Trioxide

Dinitrogen trioxide is a planar, near prolate asymmetric top molecule with several low-frequency vibrational modes. Consequently, each of its IR bands contains a multitude of lines because many rovibrational levels are thermally populated and each can undergo transitions of significant intensity to a number of rotational states in a given upper vibrational level. The patterns are complex so that no simple pattern of lines is evident. Because of the spectral congestion caused by the small rotational constants of N_2O_3 and the presence of several overlapping hot bands, there are no reports of a completely rotationally resolved IR spectrum of N_2O_3 .

Dinitrogen tetroxide was an unwanted contaminant during the recording of IR spectra of N_2O_3 in the gaseous, liquid, and solid states. Therefore, a sample of mostly N_2O_3 in N_2O_4 was prepared and the IR spectrum measured [30]. Table 4 gives the wavenumbers of absorption bands that were only found in the $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixture and that were **not** previously seen in the “pure” N_2O_4 sample.

Dinitrogen trioxide may have additional absorption bands not shown in the table above but that overlap with N_2O_4 absorption bands.

Table 4: IR spectrum of dinitrogen trioxide.

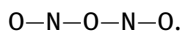
Physical state	Wavenumber, cm^{-1}	
	Solid	Gas
Temperature, K	93	293
Temperature, $^{\circ}\text{C}$	-180	20
		2164
	2090 w	2053
	1870 s	1830
	1590 s	1615
	1304 s	1309
	782 m	770

* s = strong, m = medium, w = weak.

Data source: [30]

Gaseous N_2O_3 was produced by the equilibrium reaction of NO with NO_2 . By careful selection of the temperature and pressure, the relative concentration of N_2O_3 was high and its IR spectrum was obtained without interference from other nitrogen oxide absorptions. The gas-phase IR spectrum of N_2O_3 between 300 and 2000 cm^{-1} was then recorded at $1\text{--}5\text{ cm}^{-1}$ resolution [31]. The spectrum revealed new features previously unreported including sequence bands containing torsional vibrations and provided a tentative assignment of all the N_2O_3 vibrational frequencies. An estimate of the internal rotation potential function indicates a barrier height of the order of 1 kcal/mol. Some of the frequency assignments, in particular the assignment of an absorption at 337 cm^{-1} to ν_8 in contrast to an earlier assignment of $600\text{--}700\text{ cm}^{-1}$ for this fundamental, later had to be revised in the light of Raman studies of N_2O_3 . The Raman spectrum showed a strong band at 627 cm^{-1} , which must be due to a fundamental vibration to account for its intensity.

When dinitrogen trioxide was formed in a frozen nitrogen matrix, it displayed a vibrational spectrum very similar to that of the gas-phase, asymmetrical molecule (*asym*- N_2O_3). On near-IR irradiation at 20 K, however, this structure was converted to an isomeric form with absorptions at 1689.7, 1661.0, 969.4, 704.3, 387.4, and 365.5 cm^{-1} [32]. Both ^{15}N and ^{18}O labeling showed that this isomer (*sym*- N_2O_3) had conventional, nitrite-like bonding and an extended, symmetric configuration:



The spectral region responsible for the matrix-photolytic conversion of *asym*- N_2O_3 into *sym*- N_2O_3 was $7000\text{--}9000\text{ \AA}$, a region in which *asym*- N_2O_3 absorbed (maximum, near $7200\text{ \AA}$). The *sym*- N_2O_3 could be converted quantitatively back into *asym*- N_2O_3 through irradiation in the UV region, $3700\text{--}4800\text{ \AA}$. UV absorption features at 3630, 3810, and $3980\text{ \AA}$ appeared in the spectra of matrix samples during IR-photolytic production of *sym*- N_2O_3 . These features disappeared during the UV conversion of *sym*- N_2O_3 back

into *asym*-N₂O₃. It was estimated that the symmetric nitrite-like structure of *sym*-N₂O₃ was no more than 5±10 kcal less stable than the asymmetric form. See also [33].

It is difficult to obtain pure samples of N₂O₃ for measuring its absorption spectra because even at low temperatures there is usually some NO that had formed as a result of N₂O₃ dissociating in reversal of its formation from NO₂ and NO. The fundamental and first three overtone bands associated with the ν_1 (N—O stretching) vibration of the planar, asymmetric top molecule N₂O₃ low-pressure (1–92 mm Hg) vapor were studied at 230 K using a high-resolution FTIR spectrometer and 20-m path lengths [12]. Even for the ν_1 band, where the spectrum was obtained at a resolution of 0.005 cm⁻¹, the complexity of the rotational structure defied complete analysis. However, it is possible to deduce the wavenumbers of the band origins ($\nu_1^\circ = 1829.535(2)$, $2\nu_1^\circ = 3628.03(5)$, $3\nu_1 = 5394.124(10)$, and $4\nu_1^\circ = 7128.5 \pm 1 \text{ cm}^{-1}$) and, for ν_1 , $2\nu_1$, and $3\nu_1$, the rotational constants A' , B' , and C' . Hot bands made a considerable contribution to the spectra in the region of each main band. Both the $2\nu_1$ and $3\nu_1$ vibrational levels lie well above the dissociation limit for the weak N—N bond in N₂O₃. The upper states of the overtone bands all lie above the dissociation limit for N₂O₃ → NO + NO₂. The linewidths observed for some transitions in the $2\nu_1$ and $3\nu_1$ bands indicated lifetimes of (180–300) ps and >150 ps, respectively, indicating that intramolecular energy flow from the ν_1 mode is relatively slow and that, in this respect, N₂O₃ exhibits unusual behavior. The wavenumbers for the fundamental modes in N₂O₃ are given in Table 5.

Table 5: Fundamental modes of vibration and band assignments in N₂O₃.

Fundamental mode	Wave number, cm ⁻¹
ν_1	1832
ν_2	1652
ν_3	1305
ν_4	774
ν_5	415
ν_6	241
ν_7	(205) ??
ν_8	622
ν_9	70

Data source: [31] and [12]

Figure 5 shows low-dispersion spectra of the ν_1 , ν_2 , ν_3 , and ν_4 bands of N₂O₃ at 230 K. The sharp lines in these spectra must be attributed to NO or other impurities.

At higher resolution, the ν_1 area around 1838 cm⁻¹ showed a multitude of resonances with two bands standing out due to their intensity (Figure 6). The congestion of the N₂O₃ IR bands is so great that a full analysis of the rotational structure would probably be impossible, even if greater instrumental resolution were available.

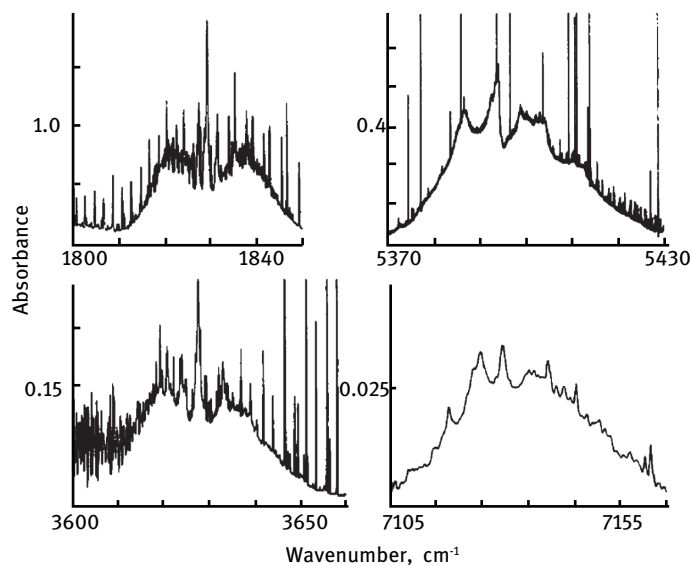


Figure 5: Low-dispersion spectra of ν_1 , ν_2 , ν_3 , and ν_4 bands of gaseous N_2O_3 at 230 K. (Reproduced from [12] with permission granted by Taylor & Francis, www.tandfonline.com.)

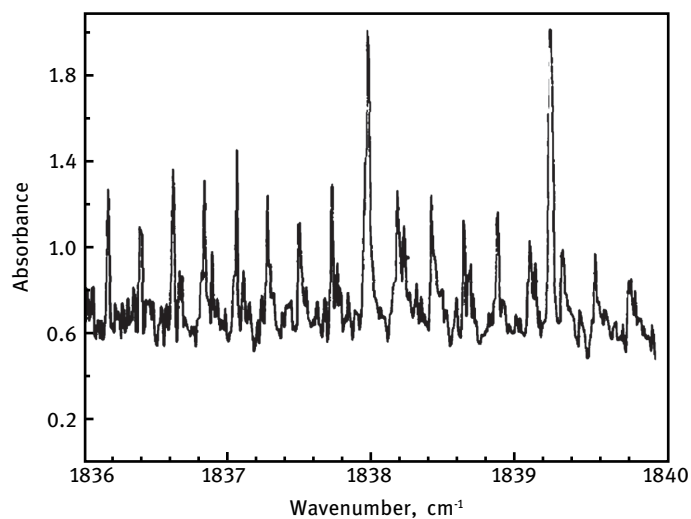


Figure 6: High-dispersion spectra of a small section of the ν_1 band of gaseous N_2O_3 at 230 K. (Reproduced from [12] with permission granted by Taylor & Francis, www.tandfonline.com.)

The IR spectrum of the ν_3 band of N_2O_3 in the dilute subatmospheric gaseous state has been measured at 1304 cm^{-1} using a slit-jet cooled tunable-diode-laser spectrometer [34]. A total of 439 IR transitions were fitted to a precision of 0.0003 cm^{-1} . Improved ground state rotational constants were calculated from ground state combination differences up to $J'' = 20$, $K''a = 10$. A number of weak perturbations were seen in the spectrum characterized by interaction matrix elements of $0.002\text{--}0.01\text{ cm}^{-1}$. The ν_3 band of N_2O_3 was scanned from 1297 to 1310 cm^{-1} with approximately 60% wavenumber coverage using two diodes. The linewidths were typically about 45 MHz, and center frequencies were estimated to be precise to about $\pm 0.0003\text{ cm}^{-1}$. The gas mixture used to study the N_2O_3 spectrum was 6.6 kPa (50 mm Hg) NO_2 and 20 kPa (150 mm Hg) NO diluted to a total pressure of 80 kPa (600 mm Hg) with Ar. A reference sample of pure N_2O was used to obtain absolute wavenumber calibration.

The ν_1 fundamental band in N_2O_3 gas was recorded in absorption at high spectral resolution with a Fourier transform interferometer, under jet-cooled experimental conditions [35]. The rotational structure, corresponding to 44 K rotational temperatures, could be analyzed, leading to a set of precise upper state parameters. The absence of b-type lines in the spectrum, expected to occur from the direction of the Q_1 normal coordinate with respect to the principal axes of inertia, can be justified by supporting *ab initio* calculations, confirming the decisive role of the polarizing NO_2 chromophore in tilting the corresponding induced dipole moment toward the direction of the a axis.

The rotational spectra of the ground vibrational state and the $\nu_9 = 1$ torsional state were reinvestigated and accurate spectroscopic constants of *asym*- N_2O_3 determined [36]. The torsional frequency, $\nu_9 = 70(15)\text{ cm}^{-1}$, was determined by relative intensity measurements. The assignment of the IR spectrum was slightly revised and an accurate harmonic force field calculated. The equilibrium structure was determined using various complementary methods – experimental, semi-experimental, and *ab initio* methods – leading to a bond length of $r_{\text{N-N}} = 1.870(2)\text{ \AA}$.

While N_2O_3 spectra had been observed in the gas phase, in solution, and as a solid at low temperatures, its spectra had not been measured adsorbed on solids at room temperature prior to 2000 [37]. The adsorbed N_2O_3 species adsorbed on dust has been postulated as a precursor to HONO in the lower atmosphere, where it plays an important role in atmospheric pollution. The IR spectra of N_2O_3 adsorbed on a porous glass surface at room temperature from the precursors NO and NO_2 were measured using transmission FTIR spectroscopy. The spectrum of the porous glass in the presence of NO and NO_2 showed broad peaks at approximately 1870 and 1600 cm^{-1} attributed to surface-adsorbed *asym*- N_2O_3 (ONNO_2). These peaks shifted by $30\text{--}40\text{ cm}^{-1}$ to lower wavenumbers when ^{15}N -labeled NO was used, consistent with absorption bands previously assigned by other researchers to solid *asym*- N_2O_3 at low temperature. See also [38].

2.7.3 Raman Spectra of Dinitrogen Trioxide

The Raman spectrum of N_2O_3 in methylene chloride solution was measured at low temperatures, and six lines in this Raman spectrum were assigned to N_2O_3 [39]. These Raman lines together with the IR spectrum obtained previously made possible the assignment of all fundamentals of the N_2O_3 molecule except the torsional mode. From the spectral data and from the available thermodynamic data, certain conclusions concerning the torsional frequency and the molecular structure were drawn.

Raman spectra of both asymmetric dinitrogen trioxide (O_2NNO) and symmetric dinitrogen trioxide (ONONO) were collected by stabilizing these species in nitric oxide matrices at 12 K [40]. Laser irradiation at wavelengths from 5682 to 7526 Å converted *asym*- N_2O_3 to *sym*- N_2O_3 , but wavelengths of 5145 or 4880 Å converted the symmetric isomer back to the asymmetric one. The Raman data, along with the IR spectra of several isotopic species (labeled ^{15}N and/or ^{18}O), for both molecules made it possible to resolve previous ambiguities in the vibrational assignments of these isomers and to carry out meaningful force constant calculations for both of them. The N—N stretching frequency at 266 cm^{-1} for *asym*- N_2O_3 and its stretching force constant of $f_{\text{N-N}} = 0.57\text{ mdyn/Å}$ are both characteristic of a very weak bond, although these values are higher than previously proposed. The N—O single bond stretching force constant for *sym*- N_2O_3 was determined to be 3.61 mdyn/Å .

2.7.4 Microwave Spectra of Dinitrogen Trioxide

The equilibrium data for the N_2O_3 dissociation reaction indicate that for typical pressures used in microwave spectroscopy ($\sim 10\text{ N/m}^2$) the amount of N_2O_3 is about 0.5% at 195 K (-78°C) and even less at higher temperatures. The microwave spectrum can be observed, however, and some structural information concerning the N—N bond length and planarity can be obtained [13]. The structure of N_2O_3 was determined from the microwave spectrum of seven isotopic species. The torsional vibrational frequency was measured as $124 \pm 25\text{ cm}^{-1}$. The quadrupole coupling constants for the nitrosyl nitrogen are $\chi_{\text{aa}} = -2.34\text{ MHz}$, $\chi_{\text{bb}} = 1.12\text{ MHz}$, and $\chi_{\text{cc}} = 1.22\text{ MHz}$. The dipole moments were determined as $|\mu_{\text{a}}| = 2.05\text{ D}$, $|\mu_{\text{b}}| = 0.54\text{ D}$, and $|\mu_{\text{t}}| = 2.12\text{ D}$ inclined at an angle of 9.1° to the N—N bond.

2.7.5 Refractive Index of Dinitrogen Trioxide

The refractive index of pure N_2O_3 could not be directly measured due to its instability. The refractive index of $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ mixtures containing up to 47 mol-% of N_2O_3 were obtained at room temperature using the method of minimum deviation [41]. The results for N_2O_4 were in good agreement with the literature values. It was found experimentally that the molar refraction of an $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ mixture could be expressed as the weighted sum of the molar refraction of the two components (see *Encyclopedia of Oxidizers*, in the chapter “Dinitrogen Tetroxide,” for $\text{N}_2\text{O}_4/\text{N}_2\text{O}_3$ mixtures). A plot of molar refraction against a mol fraction of N_2O_3 gave a straight line, which could be

extrapolated to $X \text{ N}_2\text{O}_3 = 1.0$ in order to estimate values of molar refraction and refractive index for pure N_2O_3 . Since N_2O_3 absorbs in the red region of the spectrum, the most reliable values were obtained using the mercury blue and blue-green lines. The extrapolated values for the refractive index of N_2O_3 were $n_{453.8}^{18} = 1.410$ and $n_{491.6}^{18} = 1.402$. Because of the experimental difficulties and the extrapolation of the results, these numbers are not very accurate.

2.8 Electrical Properties of Dinitrogen Trioxide

Liquid dinitrogen trioxide was treated as a non-aqueous solvent, similar to liquid dinitrogen tetroxide. The relative permittivity and electrolytic conductivity of N_2O_3 , N_2O_4 , and their mixtures were measured over a range of temperatures limited by the freezing point of the system on the one hand and its vapor pressure on the other [41]. The results for N_2O_3 are presented in Table 6.

Table 6: Electrical physical properties of liquid N_2O_3 .

Temperature, K	243	233	223	213	203
Temperature, °C	−30	−40	−50	−60	−70
Relative permittivity $\epsilon \text{ N}_2\text{O}_3$	26.41	26.65	28.01	29.50	31.13
Molar polarization P , $\text{cm}^3 \text{ mol}^{-1}$	46.5	46.3	46.0	45.7	45.3
Electrolytic conductivity $\lambda \times 10^8$, $\Omega^{-1} \text{ cm}^{-1}$	13.1	10.2	7.85	5.86	4.25
Ionic product $K' \times 10^{12}$	4.70	4.17	3.76	3.30	2.87
Equilibrium constant $K \times 10^{13}$	2.46	2.16	1.92	1.67	1.43

Data source: [41]

The values of $\epsilon \text{ N}_2\text{O}_3$ are typical for a polar but unassociated liquid and exceed slightly the corresponding values for NH_3 or NOCl at the same temperature. N_2O_3 might be expected to act as an ionizing non-aqueous solvent. The molar polarization P increased slightly with increasing temperature, as is the case for other polar liquids, e.g., SO_2 and NH_3 . For N_2O_3 , the molar polarization P and molar refraction R were estimated to be 45 and $13 \text{ cm}^3 \text{ mol}^{-1}$ at room temperature, respectively. To obtain these values, it was necessary to extrapolate the results for the density and relative permittivity of N_2O_3 from about 243 K (−30 °C) to room temperature. The large difference between P and R confirms that this molecule has a significant dipole moment. The dipole moment of N_2O_3 was estimated from the values of P and R using the Onsager relationship and a value of $2.7 \pm 0.3 \text{ D}$ was obtained ($1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$). This exceeds the value for gaseous N_2O_3 ($2.12 \pm 0.01 \text{ D}$), but in view of the uncertainty in the values of P and R and the approximations involved in the Onsager equation, the agreement was as good

as could be expected. Measurements of N_2O_3 in an inert solvent gave a dipole moment of $2.07 \pm 0.03 D$. Other sources reported a dipole moment of $2.572 D$.

To measure the electrical conductivity of N_2O_3 , it is essential that N_2O_4 be absent. At each temperature measurements were made with increasing partial pressures of NO above the liquid until a constant value was obtained that was characteristic of N_2O_3 . The results showed that N_2O_3 has significant electrolytic conductivity due to self-ionization. The most likely process involves the simple heterolytic dissociation of the $\text{N}-\text{N}$ bond, i.e.,



This agrees with the polarity of N_2O_3 and its chemical reactions.

2.9 Magnetic Properties of Dinitrogen Trioxide

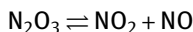
Liquid dinitrogen trioxide is diamagnetic with a specific susceptibility of $\chi = -0.26 \times 10^{-6}$ CGS. For comparison, the specific susceptibility of water is -0.72×10^{-6} CGS.

3 Chemical Properties of Dinitrogen Trioxide

If N_2O_3 is allowed to evaporate in air, the NO that escapes first will oxidize to NO_2 , and the vapor space above the liquid will consist mostly of the red-brown NO_2 gas. For all practical purposes, N_2O_3 is an oxidizer, although it is rarely used as such in rocket applications in the pure form.

3.1 Dissociation of Dinitrogen Trioxide

The polar N_2O_3 molecule can undergo heterolytic and homolytic dissociation producing NO^+ and NO_2^- ions or NO and NO_2 radicals, respectively. Both of these reactions occur in the liquid state, but in the vapor state it is mostly the homolytic splitting that is also of interest for the atmospheric chemistry of air pollutants [42]:



The heat of dissociation of dinitrogen trioxide was already described in Section 2.5.3, which also contains several graphs describing the dissociation equilibria.

The rate at which N_2O_3 dissociates to NO_2 and NO (or, inversely, the rate of N_2O_3 formation from NO_2 and NO) can be measured by doping the sample with an isotope-labeled nitrogen oxide and monitor the establishment of an equilibrium [43]. See also [44].

The homolytic dissociation of dinitrogen trioxide in a number of organic inert solvents has been studied and relevant thermodynamic data were calculated [45]. The stability of dinitrogen trioxide varied considerably and could be correlated with the electron donor properties of the solvent.

For the dissociation of N_2O_3 at much higher temperatures, the ideal gas chemical thermodynamic properties for N_2O_3 and its dissociation products for the temperature range 50 to 5000 K were evaluated by a statistical thermodynamic method using an updated set of molecular parameters [11].

Extensive kinetic measurements were made on the system $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$ in the gas phase. Equilibrium mixtures of nitrogen oxides containing an excess of NO at 208 ± 5 K diluted with inert gases were perturbed by flash photolysis and the rate of relaxation back to equilibrium was monitored by observing the transmittance of a line from a CO continuous-wave laser selected to coincide with the ν_1 band of N_2O_3 [46]. Despite the weakness of the N–N bond, the kinetics appeared to be well represented by the rate theories formulated on the basis of rapid and complete randomization of internal energy as well as by looking at high-resolution spectra of the ν_1 , $2\nu_1$, $3\nu_1$, and $4\nu_1$ bands of N_2O_3 .

3.2 Photolysis of Dinitrogen Trioxide

Depending on the wavelength and energy of the incident light and depending on the physical state of N_2O_3 , light can have different effects on the molecule. Moderate illumination can bring about interconversions of different isomers of frozen *sym*- and *asym*- N_2O_3 . Intense illumination will cause photolysis and dissociation of N_2O_3 .

Classical trajectories were used to calculate vibrational predissociation rates of *asym*- N_2O_3 for initial conditions that include excitation of the ν_1 (NO stretch), the ν_2 (NO_2 asymmetric stretch), the ν_3 (NO_2 symmetric stretch), and the ν_4 (NO_2 bend) vibrational modes and combinations of these modes [47]. The results showed strong mode selectivity. This selectivity is in accord with the experimental results of Chewter, Smith, and Yarwood [12], which showed that intramolecular energy flow from the ν_1 mode is relatively slow and that N_2O_3 exhibits “non-Rice-Ramsperger-Kassel-Marcus (RRKM) behavior.”

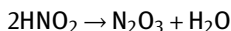
3.3 Reactions of Dinitrogen Trioxide

Dinitrogen trioxide is a nitrosating agent. It reacts with primary and secondary amines [48]. All secondary amines formed the corresponding N-nitrosamine. Primary aromatic amines gave the diazonium nitrite, but the corresponding aliphatic compounds gave a variety of products, including alkyl ammonium nitrites, alkyl

nitrites, and alkenes. In some cases *n*-alkyl amines gave products with a branched alkyl group.

3.3.1 Hydrolysis of Dinitrogen Trioxide

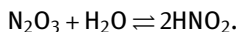
Dinitrogen trioxide is the anhydride of nitrous acid HNO_2 . As such, one would expect its hydrolysis to yield a dilute aqueous solution of HNO_2 . But the reverse reaction also occurs in strongly acidic solutions of HNO_2 , where N_2O_3 can be found by spectroscopic analysis. Solutions of HNO_2 in 5-M HClO_4 exhibit a contribution to the UV absorbance that is quadratic in the $[\text{HNO}_2]$ concentration [49]. From the measured spectrum and the extinction vs. wavelength in the range 245–260 nm, the equilibrium constant of



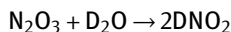
$$K_1 = \frac{[\text{N}_2\text{O}_3]}{[\text{HNO}_2]^2}$$

was determined to be $3.03 \pm 0.23 \times 10^{-3} \text{ mol}^{-1}$. This information can then be used to calculate the Henry's law coefficient for the solubility of N_2O_3 in water, a reaction that would take place in a scrubber that is supposed to wash out NO_x in the pressurant gas of MON tanks that is vented. In practice, however, one would use an alkaline solution and not just plain water as the absorbent solution. N_2O_3 reacts with water only very slowly and is partially soluble in water without reaction. Addition of water to liquid " N_2O_3 " under pressure gives two layers, a dark blue lower layer and a lighter blue upper layer.

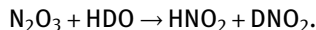
The energy differences between the lowest states of *cis* and *trans* conformers of HNO_2 and DNO_2 were determined by microwave intensity measurements [50]. The results were $\Delta E = 372 \pm 40 \text{ cal}$ for HNO_2 and $488 \pm 35 \text{ cal}$ for DNO_2 . The thermodynamic properties of HNO_2 were recalculated and yielded $\Delta H_0 = 540 (+600/-100) \text{ cal}$ for the reaction



The value of ΔH°_0 for the reaction was obtained from microwave intensity measurements of the species involved in the related reactions



and



The best value of $\Delta H_0 = 1050 \pm 300 \text{ cal}$ was in reasonable agreement with the value obtained from third-law calculations.

3.4 Analysis of Dinitrogen Trioxide

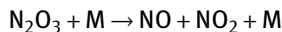
Because pure dinitrogen trioxide is not used as a rocket oxidizer, there is no need to analyze it in the pure state. However, the mixtures of N_2O_3 with N_2O_4 called mixed oxides of nitrogen (MON) need to be analyzed quite often, and those analysis methods are summarized in *Encyclopedia of Oxidizers*, chapter “Dinitrogen Tetroxide.” A vast amount of literature exists about the quantitative analysis of nitrogen oxides, including N_2O_3 , in the atmosphere, where they play an important role in air pollution and ozone depletion.

3.5 Decomposition and Thermal Stability of Dinitrogen Trioxide

Dinitrogen trioxide starts to dissociate reversibly as soon as it melts and by the time it reaches the gas phase, much of it is dissociated and short-lived. The presence of an excess of nitric oxide can retard the decomposition by the law of mass action.

While the N—N bond energy in N_2O_4 is about 56.4 kJ/mol, the N—N bond dissociation energy in N_2O_3 is lower, being close to 41.0 kJ/mol. The N_2O_3 vibrational frequencies necessary for such calculations are well known from the literature, they range from $\nu = 70\text{ cm}^{-1}$ for the torsional mode around the N—N bond to 1832 cm^{-1} for the stretching mode of the N—O bond.

The kinetics of N_2O_3 dissociation were investigated mostly in conjunction with similar studies for the dissociation of N_2O_4 , both being atmospheric pollutants. The kinetics of the



dissociation reaction was studied over a wide range of pressures by a laser-induced temperature jump relaxation method. Equilibrium mixtures at 225 K containing nitrogen dioxide, dinitrogen trioxide, dinitrogen tetroxide, and nitric oxide in argon were rapidly heated by a short pulse of CO_2 laser radiation [51]. The induced temperature jump, between 0.5 and 3 K, displaced the equilibrium toward NO_2 and NO formation. The rate of relaxation to the new equilibrium concentrations at higher temperature was monitored by observing spectroscopically the time dependence of the N_2O_3 absorption in the UV range. The following high- and low-pressure limiting rate constants for the $\text{NO} + \text{NO}_2$ recombination at 227 K were extrapolated from the experimental data:

$$k_{\text{recomb}\infty} = (3.5 \pm 1.0) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

and

$$k_{\text{recomb}0}/[\text{Ar}] = (1.0 \pm 0.5) \times 10^{15} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

respectively. The temperature dependence of the recombination rate constant, measured experimentally between 227 and 260 K, yielded the following expressions for the high-pressure and the low-pressure limiting rate constants, respectively:

$$k_{\text{recomb } \infty}(T) = (1.61 \pm 1.6) \times 10^9 T^{(1.4 \pm 0.2)} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

and

$$k_{\text{recomb } 0}(T)/[\text{Ar}] = (1.0 \pm 1) \times 10^{33} T^{-(7.8 \pm 0.8)} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

4 Toxicity of Dinitrogen Trioxide

The toxicity of dinitrogen trioxide vapor in air is essentially the same as that of nitrogen dioxide. The vapor toxicity of nitrogen dioxide is summarized in *Encyclopedia of Oxidizers*, in the chapter “Nitrogen Dioxide.” There is little chance that liquid dinitrogen trioxide would be ingested by other routes, but if it is, it would be very disastrous.

The cutaneous toxicity of liquid dinitrogen trioxide spilled on the skin would essentially be the same as that of liquid dinitrogen tetroxide, and precautions for the safe handling of these compounds are listed in the chapter on MON.

5 Handling of Dinitrogen Trioxide

Dinitrogen trioxide exists only in the solid state. The precautions for handling the liquid dinitrogen trioxide that forms as soon as the solid melts are the same as those widely practiced in the handling of liquid NTO or MON by experienced propellant handling personnel. Because liquid dinitrogen trioxide at temperatures a few degrees above its melting point is rarely used in the pure state, the risk of exposure is low in comparison to the risks involved in handling large amounts of NTO or MON.

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Fluorine

Elemental fluorine, difluorine, F₂, CAS RN [7782-41-4], is one of the most powerful oxidizers.

The potential of achieving the utmost in specific impulse with chemical rocket propellants by using fluorine instead of oxygen as an oxidizer has kept many propellant chemists busy working over the years and decades. However, in the end, it was more the concern about toxicity and environmental pollution than the desire for an extremely high specific impulse that determined the types of rocket propellants that are being used today. Nevertheless, for special applications where specific impulse is at a premium, fluorine-containing rocket propellants may still fly one day in the distant future. Many non-rocket applications, such as chemical lasers and fluorine-containing pharmaceutical drugs and agrochemicals, have benefited from the fundamental work that was done for fluorine-containing rocket propellants, just as rocket applications of fluorine in the 1960s benefited from the previous use of fluorine for uranium isotope separation during the Manhattan Project at the end of WW-II. Work on chemical lasers continued even after work on fluorine rocket propellants was abandoned. Fluorine chemistry has other, often underappreciated benefits. Examples for the use of fluorine in biologically active materials are the pharmaceutical drugs LIPITOR (for high cholesterol), ADVAIR DISKUS (for asthma), and PREVACID (for gastric reflux), three of the top ten pharmaceuticals sold in 2007, containing one or more fluorine atoms. And for more than 40 years, 5-fluorouracil has been one of the leading drugs used in topical cancer chemotherapy, where it operates by altering the synthesis of deoxyribonucleic acid (DNA) in cancer cells leading to apoptosis, inhibiting growth. The antidepressant Prozac contains a -CF₃ group. Fluorine chemistry, following the pioneering footsteps of rocket propellant chemists, has developed selective fluorinating agents that allow the synthesis of such pharmaceuticals. However, the presence of fluoroalkyl groups in water-repellent plasticizers, fire-proof fabrics, and cosmetic lotions has caused concern about potential toxic effects when the chemicals accumulate in fatty tissue in the body of humans.

It is partially with the ongoing laser applications and other future non-rocket applications of fluorine and fluorine compounds in mind that this chapter on fluorine in the book at hand has been updated and it continues to be an essential part of any book on rocket propellants (or on the history of rocket propellants). Otherwise it would only be a history book. Industrial fluorine history spans about a hundred years and admittedly has had negative environmental effects such as hydrofluoric acid pollution caused by fumes from aluminum smelters and ozone depletion due to chlorofluorocarbon solvent and refrigerant emissions.

Besides the physical properties of fluorine that are of interest for those readers evaluating fluorine as a rocket propellant, this chapter contains information on materials compatibility and handling precautions for fluorine. This information material was updated and included here again in the hope that it will be of some use to engineers looking at other future non-rocket applications of fluorine. The problems arising from handling liquid fluorine and the neutralization of exhaust gases make the use of fluorine as a rocket or laser propellant an extremely difficult task. Have rocket propellant chemists of the 1960s been overly optimistic and have they ignored the critics that derided them as falling victim to their own overly optimistic imagination, chasing an illusion? The perspective from the early twenty-first century is quite different from the prevailing optimism that characterized the rocket propellant scene in the 1950s and 1960s when the author first started working on rocket propellants, including several fluorine oxidizer compounds. Since 2016, hardly any liquid fluorine is transported over public highways any longer. For many years, until after World War II (WW-II), fluorine (gaseous or liquid) was not available commercially. Then the industry geared up and offered it in various forms, including gaseous and liquefied. However, today most elemental fluorine is produced only for captive use and converted soon after to other more inert products at the same chemical plant location. Some of the fluorides prepared in this way can also be used as rocket propellants, laser propellants, or torpedo propellants. This includes non-metallic fluorides such as ClF_3 , ClF_5 , OF_2 , NF_3 , and SF_6 (see *Encyclopedia of Oxidizers*, Chapters on Halogen Fluorides, Oxygen Fluorides and Nitrogen Fluorides). When looking for additional information on fluorine oxidizers and their potential use as rocket propellants, the reader may also want to consult the literature references collected in the following Table 1. This table also contains several bibliographies on fluorine and fluorine compounds.

During the second half of the twentieth century, acute interest in the use of fluorine and fluorine compounds as rocket propellants developed not only in the US, but also in many other countries, including Russia [19], France [20], Germany [21], and the UK [22]. In spite of this multi-national effort, no actual flight uses can be reported.

The specific impulse of liquid rocket propellants is determined by the choice of oxidizers and fuels. There are many oxidizers that give a better specific impulse than the mainstay oxidizer, liquid oxygen. Of all these high-energy oxidizers, only fluorine and ozone are manufactured in industrial quantities.

It is now only of historical interest to backtrack the different opinions on the pros and cons of using liquid fluorine or liquid ozone as a rocket propellant, because we have progressed from the beginning of the space age to a mature rocket propulsion industry [23]. In the beginning, there was a short period when fluorine and ozone were competing and both were given the same chance of becoming the high-energy oxidizer of the future. Time and experience has shown that neither one seems to be worth the extra expense or increased risk.

Table 1: Bibliographies and reviews on fluorine chemistry.

Author(s)	Year	Topic	References
Doescher	1949	Properties	[1]
Simons, J. H. (Ed.)	1950–1964	Fluorine chemistry	[2]
Jonas	1956	Fluorine and inorganic fluorine compounds	[3]
Sharpe	1957	Inorganic chemistry of fluorine	[4]
Gall	1959	Fluorine chemistry and technology	[5]
Schmidt	1960	Properties	[6]
Stacey, Tatlow, and Sharpe	1960–1973	Advances in fluorine chemistry	[7]
George	1963	Properties	[8]
Cabaniss	1964	Bibliography on fluorine and fluorine oxygen oxidizers	[9]
Schmidt and Harper	1967	Handling and use of fluorine and fluorine–oxygen mixtures	[10]
Sharpe	1967	Physical chemistry	[11]
Emeleus	1969	Chemistry of fluorine	[12]
O'Donnell	1973	Chemistry of fluorine	[13]
Naumann	1980	Fluorine and fluorine compounds	[14]
Detamore	1983	Compendium of fluorine data	[15]
Howe-Grant (Ed.)	1995	Fluorine chemistry	[16]
Jaccaud	2000	Fluorine	[17]
Shia	2003	Fluorine	[18]

1 Production of Fluorine

The main driver for starting and increasing the production of elemental fluorine was the use of uranium hexafluoride for isotope separation in diffusion plants, starting with the secret Project Manhattan during WW-II, continuing through the years of the Cold War, and transitioning into commercial nuclear power plants and their supply chain. The use of fluorine during the several decades while it was actively evaluated as an oxidizer in rocket propellants has benefited from this existing infrastructure in the nuclear industry.

1.1 Fluorine Resources

Because of its enormous reactivity with anything it comes in contact with, fluorine does not occur naturally in the elemental form but only in the form of fluoride compounds. Fluoride minerals that serve as a source of fluoride and fluorine are listed in Table 2.

Table 2: Fluoride minerals as sources of fluorine.

Compound name	Chemical formula	Fluoride content, mass-%	Alternative names
Fluorite	CaF_2	48.7	Fluorspar
Cryolite	$\text{Na}_3[\text{AlF}_6]$	54.3	
Apatite	$\text{Ca}_5(\text{PO}_4)_3\text{F}$	3.8	Fluorapatite

In apatite, the fluoride can be partially substituted by hydroxyl, chloride or carbonate. The hydroxyl group in hydroxylapatite, the main constituent of tooth enamel and bones, is readily exchanged for fluoride because this is one of the first known natural ion exchange column packing materials.

Looking at the elemental abundance of fluorine (fluoride) in the Earth's crust, it is surprising to learn that 0.06 mass-% of the crust consists of fluorine and that fluorine is actually more abundant than chlorine. Among the elements, fluorine ranks 24th in universal abundance and 13th in terrestrial abundance.

Most of the fluoride minerals used in the US are imported. There have been repeated (but now outdated) reports [5], lamenting the limited availability of fluoride minerals and predicting exhaustion of fluoride resources within a century. In 2014, the leading suppliers of fluorspar to the US were Mexico (77%), South Africa (9%), Mongolia (5%), and Vietnam (4%). Under these prospects it would have been unwise to build a rocket propulsion industry that will be knowingly dependent on a limited resource. However, the amount of fluorine used for rocket propulsion would have been only a small fraction of the total fluorine compound consumption. The main competing uses for fluorine are flux and molten electrolyte bath materials for aluminum electrowinning, fluorinated organic compounds (refrigerants, fire extinguishing agents, fluoropolymers, fluoro lubricants, fluoro surfactants), plate glass, and uranium isotope separation [3]. With the identification of halocarbons (predominantly fluorochlorocarbons) as causing ozone depletion and increased ultraviolet (UV) transmission of the high atmosphere, a ban on the use and release of halocarbons as pressurants ("propellants") for cosmetic aerosols and spray paint cans has reduced the amount of halocarbons produced for that application. The production of re-formulated refrigerants (R-134a replacing R-12 and R-22) still uses some fluorine, but they have a lower ozone depletion potential. The silicon chip-integrated circuit-producing industry needs extremely high purity (electronic grade) fluorine gas (diluted with inert gases) or nitrogen fluoride as an etchant in ion guns and for cleaning the vapor deposition chambers. Hydrofluoric acid is used for etching the glass of light bulbs and making window glass opaque (less transparent). Fluoride in the form of dihydrogen hexafluorosilicate (hexafluorosilicic acid) is added to drinking water in some communities where there is an inadequate natural fluoride mineral concentration to prevent tooth decay.

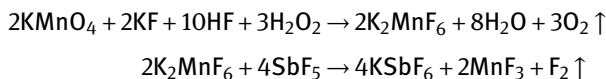
We are summarizing the supply situation for fluoride minerals here mostly in order to show that the limited availability of fluoride minerals would not be an impediment to the future use of fluorine or halogen fluorides as rocket propellants for specific upper stage (i.e., kick stage) space propulsion applications where the high specific impulse becomes mission-enabling and/or results in a substantial reduction of the overall vehicle launch mass.

In 2013, 134000 tons of fluorite equivalent was recovered in the US from all sources, but a multiple of that, 625000 tons had to be imported. The US dependence on imports is near 100% [24].

Additional information on the availability and production statistics of fluorine raw materials is contained in [25–28]. If a shortage of fluorite should develop, one would need to depend to a larger extent on fluoride recovered during the processing of apatite ores in the process of making phosphate fertilizers and phosphoric acid. Many phosphate minerals contain up to 3% fluoride, which is often an unwanted contaminant and cannot be safely vented to the atmosphere when the phosphate is processed with sulfuric acid into fertilizer. Downwind environmental contamination due to traces of fluoride in stack gases from fertilizer factories has caused severe problems to plant and animal life [29].

1.2 Production Methods for Fluorine

We are listing the methods of fluorine production here because elemental fluorine is (was) not industrially available in many countries and some rocket propellant development laboratories chose to make their own elemental fluorine on site. For the first hundred years of the known existence of fluorine as a free element, electrolysis of fluoride melts was the main method of fluorine production. Whereas the other halogens can be liberated from their salts by strong oxidizers, there is no oxidizer stronger than fluorine that could be used to liberate the free element from its salts. Fluorine is the element with the highest electronegativity. Only on the occasion of commemorating the centennial of the discovery of elemental fluorine was a new non-electrolytic method for the preparation of fluorine by chemical means announced by [30–32]:



During World War II, Germany had developed a substantial capability in fluorine production. A historical summary of the development of the elemental fluorine process in Germany during the war described the suitability of the various metals as anode materials and it was concluded that nickel was the most satisfactory metal up to 373 K (100 °C) [33, 34]. Different types of graphite anodes and electrolytes were tested. It was concluded that graphite was a suitable anode material at temperatures around

523 K (250 °C) and that specially prepared carbon anodes could be used between 338 and 363 K (65 and 90 °C). Operating details were given for two German cells, the high-temperature (518 K = 245 °C) Falkenhagen cell and the low-temperature (348 K = 75 °C) Leverkusen cell.

Historically, both the US and Germany developed fluorine production technology during WW-II as part of the war effort [35]. Whereas in the US, all of this effort was aimed at the production of UF_6 for isotope separation, in Germany much of the fluorine produced was converted to chlorine trifluoride, which was easier to store and which was intended as a hypergolic source of ignition for flame throwers.

When the interest in fluorine as a rocket propellant developed in the 1950s, rocket applications benefited substantially from the availability of fluorine for uranium isotope separation. The US had developed a substantial elemental fluorine production capacity as part of the Manhattan Project (development of the atomic bomb) during WW-II for making UF_6 and separating natural uranium isotopes ^{235}U and ^{238}U by diffusion of the UF_6 vapors. Fluorine is monoisotopic, so any mass differences between UF_6 molecules are due to the presence of ^{235}U or ^{238}U , enabling uranium enrichment via gaseous diffusion or gas centrifuge.

The raw material for electrochemical production of elemental fluorine is anhydrous hydrofluoric acid, which is available industrially in large quantities because it is used for many other applications. The electrolyte must not contain any water because otherwise the product would be oxygen difluoride instead of elemental fluorine. The electrolyte is a solution of potassium fluoride or potassium hydrogen difluoride in anhydrous hydrofluoric acid. The electrolyte melts at 303 to 513 K (30 to 240 °C), depending on the KHF_2 content. Three electrolysis processes have been used:

1. electrolysis of a melt consisting of $\text{KF} \cdot 2.5\text{-HF}$ on platinum or nickel anodes at 303 to 343 K (30 to 70 °C);
2. electrolysis of a melt consisting of $\text{KF} \cdot 2\text{-HF}$ on hard carbon (graphite) anodes at 353 to 393 K (80 to 120 °C);
3. electrolysis of melted KHF_2 on graphite anodes at about 523 K (~250 °C).

There are at least 40 different designs for fluorine electrolysis cells described in the scientific and patent literature. There are small cells for laboratory use with a capacity of 140 g/h, whereas large industrial units can produce more than 10 kg/h. Typically, several of these cells are combined in units that share heat sources, electrolyte maintenance, and product purification, but are wired individually. One of the early cell designs drew a current of 600 A [36].

Medium-temperature fluorine cells operated at 373 to 378 K (100 to 105 °C) using a fused-salt bath of $\text{KF} \cdot 2\text{HF}$ (melting point 344.2 K = 71.7 °C) [37, 38]. The fluorine was liberated at a carbon anode and hydrogen was liberated at a steel cathode. The cell body consisted of a welded Monel tank with a steel jacket through which water flowed for cooling and heating. In order to obtain fluorine free of oxygen and oxygen di-

fluoride contamination, the electrolyte has to be analyzed for water content prior to use [39].

A 36-cell fluorine plant was designed and operated by the Carbide and Carbon Chemicals Co. under contract to the US Atomic Energy Commission at Oak Ridge, TN, in the 1950s [40]. The plant was capable of producing, continuously, 1800 kg (4000 lb) of fluorine a day using cells that can be operated at a maximum output of 61 kg (134 lb) of fluorine per day.

Allied Chemical and other companies began to offer fluorine gas in compressed gas cylinders in 1946. Figure 1 shows a view of one of Allied Chemicals' production units in Metropolis, IL, used in the early 1960s.

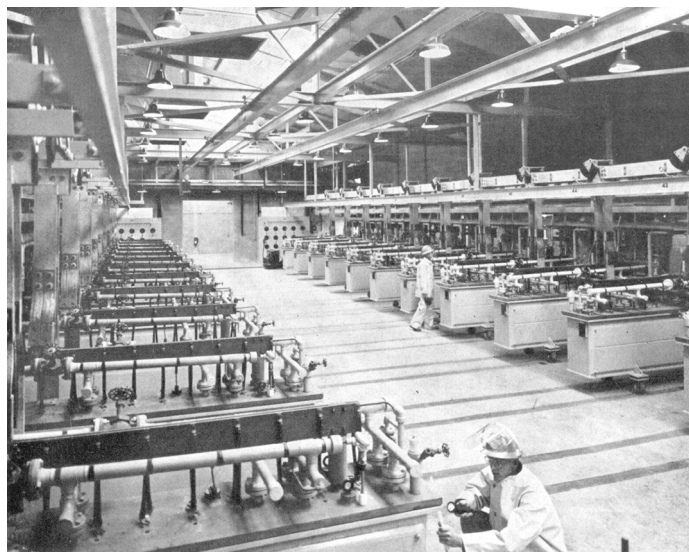


Figure 1: Fluorine electrolysis production units. (Photo: Courtesy of Allied Chemical.)

Technical details on fluorine production can be found in some of the references listed in Table 3.

Improvements in the fluorine production process may be obtained by forming a ternary conducting layer $\text{CF}_x \bullet \text{M}_y$ at the surface of carbon anodes (where M is a metal: Li, Mg, Al). Electron transfer at the interface is thus enhanced and the wettability of the electrode by the $\text{KF} \bullet 2\text{HF}$ melt is improved. It was shown that polishing the carbon electrodes with alumina or magnesia actually dopes the carbon by mechanically imbedding the latter compounds [55]. Scanning electron microscopy experiments showed that particles of aluminum oxide or magnesium oxide were inserted during the polishing process and they formed the corresponding fluorides during electrolysis in the $\text{KF} \bullet 2\text{HF}$ melt. A ternary conducting compound is formed on the surface, as in the case

Table 3: Summary of monographs on fluorine chemistry.

Author(s)	Year	Topic(s)	References
Monographs			
Ruff	1920	Chemistry of fluorine	[41]
Haszeldine and Sharpe	1951	Fluorine and its compounds	[42]
Simons	1950– 1964	Fluorine chemistry, 5 volumes	[43]
Slessor and Schram	1951	Preparation, properties and technology of fluorine	[44]
Rudge	1962	Manufacture and use of fluorine and its compounds	[45]
Single publications on individual topics relating to production of fluorine			
Downing et al.	1947	Electrolytic cells for production of fluorine	[46]
Gall and Miller	1947	Small-scale production and handling of fluorine	[47]
Murray, Osborne, and Kircher	1947	Carbon-anode fluorine cell	[48]
Pinkston	1947	Preparation of fluorine	[49]
Schumb, Young, and Radimer	1947	Electrolytic generation of fluorine	[50]
Leech	1949	Laboratory and technical production of fluorine	[51]
Kwasnik	1964	Fluorine manufacture	[52]
Rudge	1966	Anode material and electrolyte purity	[53]
Nakajima, Ogawa, and Watanabe	1987	LiF addition to HF/KF electrolyte ^a	[54]

^a HF/KF, hydrogen fluoride/potassium fluoride.

of electrodes doped by additions of LiF or AlF_3 into the melt. The electrochemical behavior of the polished electrodes was then studied by cyclic voltammetry experiments and impedance measurements.

The effect of the addition of LiF or AlF_3 to $\text{KF} \cdot 2\text{HF}$ melts on the behavior of the anodic carbon material during the preparation of elemental fluorine was studied using cyclic voltammetry [56]. These additions were intended to reduce the passivation of the anode. This effect was attributed to the formation of a conducting ternary compound at the interface between electrode and electrolyte. This compound is thought to enhance electron transfer at the interface and to improve the wettability of the electrode by the melt.

Fluorine is usually produced by electrolysis of molten $\text{KF} \cdot 2\text{HF}$ in medium-temperature cells at 353 to 393 K (80 to 120 °C). Non-graphitized carbon is the material that can usually be used for the anodes. However, a high anodic overvoltage is observed (~3 V in industrial cells), which results in the low energy efficiency of the process. This is caused by the formation of a passivating film of graphite fluoride at the surface of the electrodes [57]. During the direct current electrolysis of $\text{KF} \cdot n\text{HF}$ melts, a passivating film of graphite fluoride (CF_x) is formed on the carbon electrodes, leading to high anodic overvoltage. Pulsed electrolysis enables fluorine production with significant improvements [58]. Rectangular or sinusoidal wave forms have been studied.

1.3 Purification of Fluorine Gas

Fluorine produced by electrolysis of KHF_2 contains contaminants such as hydrogen fluoride (HF) carried over from the electrolyte, CF_4 , from reaction with the carbon or graphite anodes, or O_2 , O_3 , CO, and OF_2 , depending on the purity and the anhydrous operating conditions of the electrolyte in the bath. Except for O_2 , these contaminants can be condensed in cold traps. Some, but not all O_2 can be condensed in a cold trap kept at 93 K (-180°C). Oxygen is adsorbed by charcoal more than fluorine at 93 K (-180°C), and this phenomenon can be utilized for the purification of fluorine. Fluorine with a purity of 99.4% was obtained by this procedure [59]. One must remember that oxygen or fluorine condensed on charcoal constitutes an **explosive** mixture.

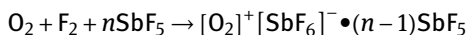
Hydrogen fluoride can be absorbed in towers filled with potassium fluoride (KF) or sodium fluoride (NaF) powder or granules. The absorption of HF into NaF forming the double salt NaHF_2 is so complete that this method has been used for the analysis of HF/ F_2 mixtures [60].

The exhausted absorbents in the HF absorption towers can be regenerated by heating them to 548–573 K ($275\text{--}300^\circ\text{C}$) in a stream of nitrogen gas. The regenerated NaF thus formed is very porous, has a high surface area, and is a very active absorbent for HF. A recommended method for the purification of gaseous fluorine is a combination of cold traps and absorption [61, 62]. The gas is first passed through a cold trap at 203 K (-70°C) and then through an absorption tower filled with NaF. If only one cold trap is used and it is cooled to below 190 K (-83°C), a problem may arise from solid HF clogging the trap. This method can be used in a continuous mode if two parallel trains of cold traps and absorption towers are available, one is on active duty while the other one is being regenerated and cleaned.

If large quantities of fluorine need to be purified, this can be done by fractionated cryogenic distillation using a 1.5-m-long distillation column with a vacuum jacket and filled with 1.5-mm nickel Helipak column packings [63]. The contaminants accumulated in the pot were analyzed by infrared (IR) and mass spectroscopy and shown to contain N_2 , O_2 , CO_2 , NF_3 , HF, CF_4 , C_2F_6 , C_3F_8 , OF_2 , and Ar. OF_2 can be removed and decomposed by passing it over copper shavings at 523 K (250°C).

Commercial fluorine gas may contain 1–2% impurities, primarily O_2 , N_2 , and HF with trace amounts of Ar, CO_2 , CF_4 , C_2F_6 , C_3F_8 , COF_2 , OF_2 , SiF_4 , SF_6 , O_2F_2 , and others. For most preparative purposes the O_2 content of fluorine does not interfere with the desired reactions and the purification of F_2 can be limited to the removal of HF by a NaF scrubber. There are applications where oxygen-free fluorine is needed. A typical example is the HF–deuterium fluoride (DF) chemical laser. It is known that molecular oxygen acts as an inhibitor for the chain-branching fluorine atom-generating reaction of H_2 and F_2 . In addition, the presence of O_2 causes the formation of water, which is a very strong deactivator for vibrationally excited HF or DF. In order to obtain meaningful baseline data, oxygen-free fluorine is required.

It was found that the well-known reaction



is ideally suited for the removal of oxygen impurities from fluorine [64]. Either heating or UV illumination can be used for activation of the reaction. Of these two activation energy sources, thermal activation is preferred for scalability and simplicity. In a typical example, crude F_2 (17 g = 500 mMol) and SbF_5 (2.1 g = 100 mMol) in a 1.2-L Monel reactor were heated for 2 h to 460 K. The vessel was cooled to 90 K and the F_2 was distilled into a trap kept at 77 K. The excess of unreacted SbF_5 was removed from the Monel vessel by pumping at room temperature. The vessel was opened in a dry box and contained 1.1 g of a white solid, which was identified by its vibrational spectra as $[\text{O}_2]^+ [\text{SbF}_6]^-$.

The low-temperature UV photolysis for the removal of O_2 from F_2 involves the irradiation of liquid fluorine in a quartz apparatus to convert O_2 to the less volatile O_2F_2 , followed by a distillation at 90 K [65].

The most troublesome contaminants in liquid fluorine are those that are insoluble and are carried along in particulate form, clogging filters and injection orifices. Filtration of liquefied fluorine would remove these contaminants. The fluorine could further be purified by distillation.

Filtration of the liquid was accomplished by condensing the gas in a Monel cell and forcing it through a Hoke 5–12-micron filter [66]. The filtered fluorine was analyzed by taking a sample in an IR cell or by distilling the fluorine and collecting the contaminants if any were present. In most instances, the fluorine was passed through an NaF bed to absorb troublesome HF before filtration.

If the material $\text{KF} \cdot \text{HF}$ used in the electrolysis for production of fluorine contains 0.17% Cl, the resulting fluorine may be contaminated by chlorine. The chlorine contamination occurred only at the beginning of electrolysis and ceased as the electrolysis proceeded [67].

The electrolysis of wet HF or wet $\text{KF} \cdot \text{HF}$ may also produce some ozone as a contaminant in the gas. The ozone concentration in fluorine or oxygen difluoride can be measured by gas chromatography [68].

1.4 Production Capacity for Elemental Fluorine

Most of the fluorine produced in the US during and shortly after WW-II was used for isotope separation and the capacity of these production units was classified information at that time.

From 1947 to 1960, approximately 340000 tons of liquid fluorine were produced in the USA. In many cases the liquid fluorine was not used as such, but liquefying and transporting it in cryogenic tanks from the production plants to the various customers was the most economical method, similar to the widely accepted practice of

transporting liquid oxygen to end users where it is evaporated back to gaseous oxygen. The capacity of one of the plants used by Allied Chemicals in the early 1960s was estimated at 1000 tons/year. Another source estimated the capacity as 1500 tons/year. Yet other writers estimated the capacity at 2400 tons/year [52]. For historical information on the production of fluorine the reader can consult [69–73]. For the European point of view, see [22], which explains the main ways in which British fluorine production installations differed from American ones.

2 Physical Properties of Fluorine

The physical properties of fluorine in its various states (gas, liquid, solid) are summarized in the following tables. The most comprehensive summaries of the physical properties of fluorine were compiled by researchers at the US National Bureau of Standards in Boulder, CO [74].

Fluorine has 18 isotopes, but only one of those is stable and occurs naturally. Seventeen radioisotopes with mass numbers from 14 to 31 have been synthesized, of which ^{18}F is the most stable, with a half-life of 109.7 min, and is used in medical diagnostic tools. The molecular mass of difluorine with natural isotope distribution (IUPAC 1962) is 37.9968 g/mol. See also [75].

2.1 Freezing Point of Liquid Fluorine

Liquid fluorine freezes at 53.54 K ($-219.62^\circ\text{C} = -363^\circ\text{F}$) at atmospheric pressure.

Fluorine has two solid forms, α - and β -fluorine. The latter crystallizes at 53 K ($-220^\circ\text{C} = -364^\circ\text{F}$) and is transparent and soft, with the same disordered cubic structure of freshly crystallized solid oxygen, unlike the orthorhombic systems of other solid halogens. Further cooling to 45 K ($-228^\circ\text{C} = -378^\circ\text{F}$) induces a phase transition into opaque and hard α -fluorine, which has a monoclinic structure with dense, angled layers of molecules. The transition from β - to α -fluorine is more exothermic than the condensation of fluorine, and can be violent.

2.2 Boiling Point of Liquid Fluorine

The boiling point of liquid fluorine is below that of liquid nitrogen, such that fluorine can conveniently be kept as a liquid in a surrounding bath of liquid nitrogen. The physical properties summarized in Table 4 are those fixed points that are temperature independent and a few where data were available only for one fixed temperature.

Table 4: Fundamental physical properties of fluorine.

Property	SI Units	Common Units	US Units	References
Atomic mass (F) (IUPAC 1962)	18.9984 g/g-atom			[76]
Molecular mass (F ₂) (IUPAC 1962)	37.9968 g/mol	26.3180 mol/kg		[76]
Solid fluorine phase change temperature	45.55 K	−227.61 °C	−377 °F	[77]
Melting point	53.54 K	−219.62 °C	−363 °F	[77]
Boiling point	85.02 ± 0.02 K	−188.14 °C	−307 °F	[77]
	85.21 K	−187.94 °C	−306 °F	
	84.93 K	−188.22 °C	−307 °F	[78]
Density, gas at 273.15 K and 1 bar		1.696 g/L		[79]
Triple point	53.481 K	−219.7 °C	−363 °F	[80]
Magnetic susceptibility, mass units		−3.447 × 10 ^{−7} cgs.em-Units/g		
Magnetic susceptibility, atomic units		−65.5 × 10 ^{−7} cgs.em-Units/g-Atom		

2.3 Density and Partial Molar Volumina of Gaseous and Liquid Fluorine

The liquid–gas phase diagram of fluorine is given in Figure 2.

2.3.1 Density of Gaseous Fluorine

The most accurate gaseous density data for gaseous fluorine were derived from a set of pressure, volume, temperature (PVT) measurements performed at the US National Bureau of Standards (NBS) [81]. A separate NBS report [82] contains PVT measurements, virial coefficients, and a Joule–Thomson inversion curve of fluorine. The equations were derived such that the densities are represented accurately even in the proximity of the critical point. The vapor density can be fitted to the data using the following equation:

$$\ln(\rho/\rho_c) = C_1[Z/(Z-1)] + C_2Z^{0.35} + \sum_{i=3}^7 C_i Z^{i-2}$$

where $Z = 1 - T/T_c$ and the following constants apply for C_1 through C_7 :

C_1 4.85547085

C_2 −1.96015519

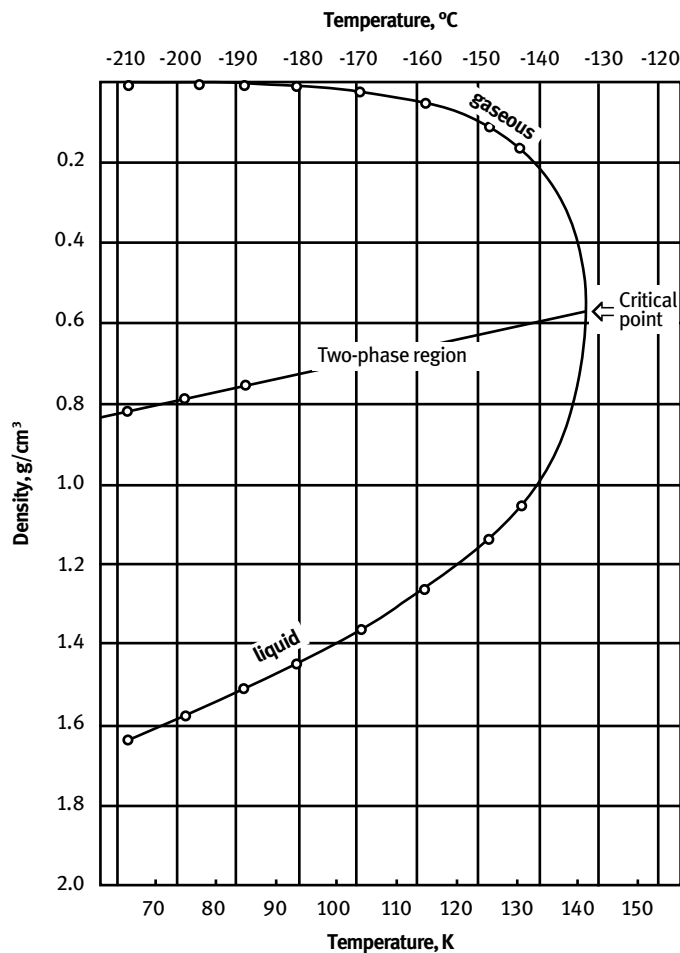


Figure 2: Liquid–gas phase diagram of fluorine. (Reproduced and modified from [79].)

$$C_3 \quad -1.88066900\text{E}-01$$

$$C_4 \quad 6.21165939$$

$$C_5 \quad -2.29600897\text{E}+01$$

$$C_6 \quad 4.69524623\text{E}+01$$

$$C_7 \quad -4.30650270\text{E}+01$$

and the following critical point properties were used to connect the data: $T_c = 144.31 \text{ K}$, $\rho_c = 15.10 \text{ mol/L} = 0.574 \text{ g/cm}^3$. A similar equation is given further down for liquid fluorine.

2.3.2 Density of Liquid Fluorine

For a long time dating from the discovery of fluorine by Moissan in 1886 until the 1940s, the density of liquid fluorine was reported to be much too low, owing to the lack of purity of the fluorine samples used. It was not until the 1950s that several investigators measured the density using high-purity fluorine and pointed out the error [83]. They reported a single data point of $1.54 \pm 0.02 \text{ g/cm}^3$ at 77 K (-196°C), substantially higher than any fluorine densities published up to that time. Additional data are presented in Table 5.

Table 5: Density of liquid fluorine.

Temperature			Density	
K	$^\circ\text{C}$	$^\circ\text{F}$	g/cm^3	lb/ft^3
65.78	-207.4	-341.3	1.638	102.26
71.76	-201.4	-330.5	1.594	99.51
74.93	-198.2	-324.8	1.578	98.51
78.59	-194.6	-318.2	1.550	96.77
78.62	-194.5	-318.2	1.553	96.95
81.72	-191.4	-312.6	1.532	95.64
84.34	-188.8	-307.9	1.514	94.52
85.05	-188.1	-306.6	1.505	93.96
85.67	-187.5	-305.5	1.505	93.96
86.91	-186.2	-303.2	1.496	93.39
88.26	-184.9	-300.8	1.481	92.46
90.08	-183.1	-297.5	1.472	91.90
91.55	-181.6	-294.9	1.458	91.02
94.73	-178.4	-289.2	1.434	89.52
97.56	-175.6	-284.1	1.412	88.15
100.21	-172.9	-279.3	1.391	86.84
102.75	-170.4	-274.7	1.370	85.53

Data source: [84, 85].

The data in Table 5 have been curve-fitted and can be represented by a polynomial equation that represents the data between 65 and 102K with much better accuracy than the linear equation proposed by White, Hu, and Johnston:

$$\rho = 1.907 - 2.201 \times 10^{-3}T - 2.948 \times 10^{-5}T^2$$

where ρ is the density in g/cm^3 and T is the temperature in kelvin. The uncertainty in the density was estimated to be $\pm 0.1\%$.

The liquid fluorine density data from the Jet Propulsion Lab (JPL) [86, 87] are tabulated in Table 6 and shown graphically in Figure 3 in comparison with data from other sources.

Additional liquid fluorine density data are tabulated in Table 7 and shown graphically in Figure 3 in comparison with data from other sources [88].

Table 6: Density of liquid fluorine.

Temperature, K	Density, g/cm ³
65.4	1.639 ± 0.002
67.1	1.630 ± 0.002
70.0	1.613 ± 0.002
74.1	1.587 ± 0.002
75.4	1.578 ± 0.002
77.8	1.562 ± 0.002
80.0	1.547 ± 0.002
81.0	1.539 ± 0.002
82.1	1.531 ± 0.002
83.4	1.522 ± 0.002
84.3	1.516 ± 0.002
85.2	1.509 ± 0.002

Data source: [87]

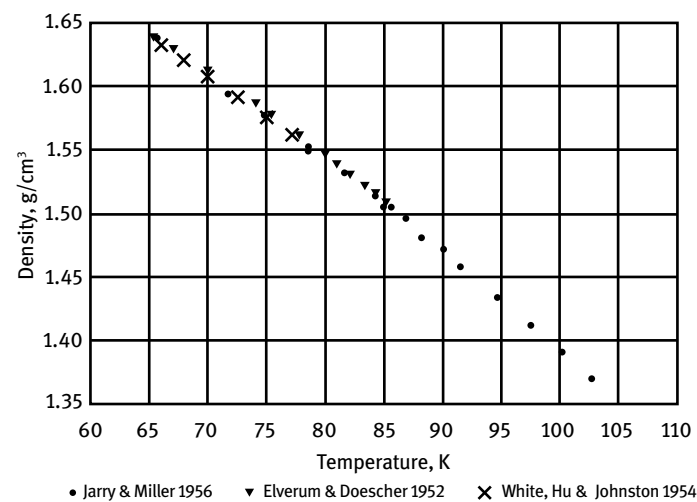


Figure 3: Density of liquid fluorine, exponential fit of three sets of data.

Table 7: Density of liquid fluorine.

Temperature, K	Density, g/cm ³
66.03	1.6331
67.98	1.6218
70.00	1.6081
72.55	1.5920
75.01	1.5761
77.22	1.5622

Data source: [88]

The density as a function of temperature between 66 and 77 K can be expressed by the following linear function [88]:

$$\rho = 1.5127 + 0.00635(85.02 - T)$$

where ρ is the density in g/cm³ and T is the temperature in kelvin. This equation gives only poor accuracy if one extrapolates to beyond 77 K.

The density of saturated liquid fluorine along the vapor–liquid coexistence boundary was measured more accurately by the US National Bureau of Standards and the data are now considered the most accurate because they were also normalized based on the International Practical Temperature 1968 Scale [81].

The very accurate experimental density data consisting of 97 data points can be represented by the following equation, which provides a smooth transition to the gas density in proximity of the critical point:

$$[(\rho - \rho_c)/\rho_c] = B_1 Z^{0.35} + \sum_{i=2}^6 B_i Z^{i-1}$$

where $Z = 1 - (T/T_c)$ and the following constants apply for B_1 through B_6 :

$$B_1 \quad 1.81881076$$

$$B_2 \quad 8.75236491\text{E-}01$$

$$B_3 \quad -8.50458910\text{E-}01$$

$$B_4 \quad 1.37284761$$

$$B_5 \quad -1.01331503$$

$$B_6 \quad 2.73840128\text{E-}01$$

and the following critical point properties are used to connect the data: $T_c = 144.31$ K, $\rho_c = 15.10$ mol/L = 0.574 g/cm³.

Table 8 in Section 2.4 on compressibility and velocity of sound contains two additional sets of data on the density of liquid fluorine at very high pressures up to 21 MPa.

2.3.3 Equation of State of Gaseous Fluorine

Like all gases, fluorine gas at higher pressures and lower temperatures does not behave as an ideal gas. The intermolecular force constants of gaseous fluorine in the region 80–300 K have been determined from measurements of the second virial coefficients [89]. On the assumption that gas imperfection resulted only from binary collisions of spherical non-polar molecules, the force constants obtained were $r_0 = 3.61 \pm 0.04 \text{ \AA}$ and $\varepsilon_0/k = 121 \pm 3 \text{ K}$. These force constants yielded viscosities that were in good agreement with the experimental data of Kanda if high temperature data points were discarded.

The form of a reduced Helmholtz energy function was used to derive an equation of state that included an equation to represent the behavior of the ideal gas [90, 91]. The coefficients in the equation were determined by a least-squares method where the terms used were selected statistically from a given data bank, thus reducing intercorrelation.

The analytical equation of state of Song and Mason was applied to calculate the compressed and saturation thermodynamic properties of fluorine [92, 93]. It was based on a statistical–mechanical perturbation theory of hard convex bodies and was a fifth-order polynomial in the density. The equation of state has been used to calculate thermodynamic parameters, including the critical constants, the vapor pressure curve, the compressibility factor, the fugacity coefficient, the enthalpy, the entropy, the heat capacity at constant pressure, the ratio of heat capacities, the Joule–Thomson coefficient, the Joule–Thomson inversion curve, and the velocity of sound for fluorine.

Thermophysical properties of fluorine were calculated with the Goharshadi–Morsali–Abbaspour (GMA) equation of state under critical conditions, including density, volumetric, and thermodynamic properties over extended ranges of pressure and temperature [94]. The results showed that the GMA equation of state reproduced the experimental PVT data of fluorine within experimental errors throughout the liquid phase. The calculated results differed only by a few percent from the experimental data.

2.4 Compressibility and Velocity of Sound of Liquid Fluorine

The bulk modulus is the reciprocal of compressibility. Two types of compressibility are generally measured and reported in the literature, the *isothermal* and the *adiabatic* compressibility. The coefficient of thermal expansion α and compressibility β can be calculated from partition functions, which also lead to values for heat capacities at constant volume or constant pressure.

The velocity of sound in liquid fluorine was measured along two isotherms (110 and 130 K) at pressures up to 21 MPa [95, 96]. The uncertainty in the measured velocity of sound data was estimated to be less than $\pm 0.05\%$. The results are summarized in

Table 8, also including density data obtained in a PVT apparatus at the same temperature and pressure.

Table 8: Velocity of sound in liquid fluorine.

Temperature K	Pressure MPa	Density mol/L	Velocity of sound, experimental m/s
130	21.049	33.059	621.6
130	19.567	32.838	610.0
130	18.330	32.645	599.0
130	15.321	32.132	573.5
130	12.326	31.547	543.9
130	9.101	30.797	506.5
130	6.171	29.946	464.5
130	3.066	28.701	403.4
110	18.806	36.508	740.6
110	15.527	36.188	721.1
110	12.003	35.817	698.5
110	8.512	35.414	674.1
110	5.139	34.982	647.9
110	1.247	34.417	613.4
110 ^a	0.888	34.361	609.9

^a saturated liquid

Data source: [95]

The validity of an approximate equation of state of real fluids and the expression for surface tension of hard-sphere molecules in liquids was tested for the case of fluorine and the results were compared with those measured by other authors [97] (Table 9). The expressions for the pressure coefficient of bulk modulus (C_1) and acoustical parameter (K) can also be derived from the measured surface tension of liquid fluorine. The acoustical parameter K is defined as the ratio of the temperature coefficient of ultrasonic velocity to the thermal expansion coefficient (α). Unfortunately, Sharma [97] was using the obsolete Kanda [98] surface tension data for comparison, which were obtained with impure fluorine and are not reliable.

Because the microscopic adiabatic heating at the knots of standing sound waves can already dissociate some of the fluorine, the propagation and attenuation of sound in fluorine gas is different than that in other gases. Thermal relaxation of sound waves can be used to measure dissociation and recombination kinetics [99]. See also [100, 101].

Table 9: Calculated and measured surface tension and acoustical parameter of liquid fluorine.

Temperature, K	Surface tension, Kanda, N/m	Surface tension, Sharma, N/m	Pressure coefficient of bulk modulus (C1)	Acoustical parameter K
55	—	15.40×10^{-3}	—	—
60	14.2×10^{-3}	14.97×10^{-3}	5.511	2.469
65	13.3×10^{-3}	14.60×10^{-3}	4.591	2.090
70	12.2×10^{-3}	13.74×10^{-3}	4.100	1.764
75	11.6×10^{-3}	13.23×10^{-3}	3.741	1.584
80	10.8×10^{-3}	12.76×10^{-3}	3.418	1.422
85	9.85×10^{-3}	11.11×10^{-3}	—	—

Data source: [98, 97]

2.5 Vapor Pressure of Liquid Fluorine

The vapor pressure of liquid fluorine has been measured by several investigators up to temperatures slightly above the normal boiling point. We provide several curve fits of experimental data, but would prefer the data published by NIST on the ChemWeb web site [102]. Curve fits are useful for interpolation of data but should not be used to extrapolate to temperatures outside their valid range. Table 10 compares measured vapor pressures and calculated data from two different curve fits.

The vapor pressure between 53 and 90 K can be expressed by the following equation [77]:

$$\log p_V = 7.08718 - 357.258/T - 1.3155 \times 10^{13}/T^8$$

where p_V is the vapor pressure in mm Hg and T is the temperature in kelvin. The boiling point derived from this equation is 85.02 ± 0.02 K.

The vapor pressure curve shown in Figure 4 is based on vapor pressure measurements by [78]:

$$\log p_V = 8.3317 - 406.8/T - 0.007785 T$$

where p_V is the vapor pressure in mm Hg and T is the temperature in kelvin.

Figure 5 is a comparison of vapor pressure data from several different sources. The three curves are very close to each other.

After taking 140 data points on three different samples between 68 and 85 K, the curve fits of vapor pressure data resulted in the following equation [103]:

$$\log p_V = 8.7202 - 462.66/T - 0.01656 T + 1$$

where p_V is the vapor pressure in mm Hg and T is the temperature in kelvin. This equation, once referenced on page 294 of [104] was in error by one order of magnitude because the original source had given the pressures in cm Hg instead of mm Hg. This error has now been corrected by adding 1.0 to the $\log p_V =$ equation.

Table 10: Vapor pressure of liquid fluorine.

Source			Hu, White, and Johnston [77] measured		Hu, White, and Johnston [77] calculated from formula $p_v =$		Allied Chemical calculated from formula $p_v =$	
Temperature			Vapor pressure					
K	°C	°F	kPa	mm Hg	kPa	mm Hg	kPa	mm Hg
53.56	-219.6	-363.3	0.2	1.7	0.2	1.7	0.3	2.1
53.84	-219.3	-362.8	0.2	1.8	0.2	1.8	0.3	2.3
54.99	-218.2	-360.7	0.4	2.7	0.4	2.7	0.4	3.2
55.69	-217.5	-359.4	0.5	3.5	0.5	3.4	0.5	3.9
57.56	-215.6	-356.1	0.8	5.9	0.8	5.9	0.9	6.5
59.03	-214.1	-353.4	1.2	8.8	1.2	8.8	1.3	9.6
60.50	-212.7	-350.8	1.7	12.9	1.7	12.8	1.8	13.7
61.95	-211.2	-348.2	2.4	18.3	2.4	18.2	2.6	19.2
63.49	-209.7	-345.4	3.5	25.9	3.4	25.7	3.6	26.9
65.02	-208.1	-342.6	4.7	35.3	4.7	35.6	4.9	37.1
66.52	-206.6	-339.9	6.4	48.1	6.4	48.1	6.7	49.9
68.00	-205.2	-337.3	8.5	63.7	8.5	63.8	8.8	66.1
69.57	-203.6	-334.4	11.2	84.3	11.3	84.7	11.7	87.6
71.07	-202.1	-331.7	14.6	109.2	14.6	109.7	15.1	113.4
72.56	-200.6	-329.1	18.6	139.7	18.7	140.1	19.3	144.7
75.59	-197.6	-323.6	29.8	223.7	29.7	223.1	30.6	229.9
77.17	-196.0	-320.8	37.4	280.4	37.3	280	38.4	288
78.54	-194.6	-318.3	45.2	338.9	45.1	338.3	46.3	347.3
80.03	-193.1	-315.6	55.0	412.8	55.0	412.4	56.3	422.3
81.59	-191.6	-312.8	67.2	504.1	67.1	503.2	68.5	513.6
83.06	-190.1	-310.2	80.5	604.1	80.3	602.8	81.7	612.9
84.58	-188.6	-307.4	96.4	723	96.2	721.5	97.4	730.5
85.05	-188.1	-306.6	101.7	763.1	101.5	761.7	102.6	770
86.60	-186.6	-303.8	120.9	907.1	120.9	907.1	121.6	912.1
87.52	-185.6	-302.1	133.7	1003	133.7	1003	134.0	1005.3
88.59	-184.6	-300.2	149.6	1122	150.0	1125	149.6	1122.2
89.40	-183.8	-298.8	162.6	1220	163.1	1224	162.3	1217.3

The vapor pressure of liquid fluorine for the temperature range 53.99–143.99 K can be expressed in the form of an Antoine equation based on the Straty and Prydz data [105]:

$$\log_{10} P = 4.02355 - [322.067 / (T - 4.748)]$$

where P is the vapor pressure in bar and T is the temperature in kelvin.

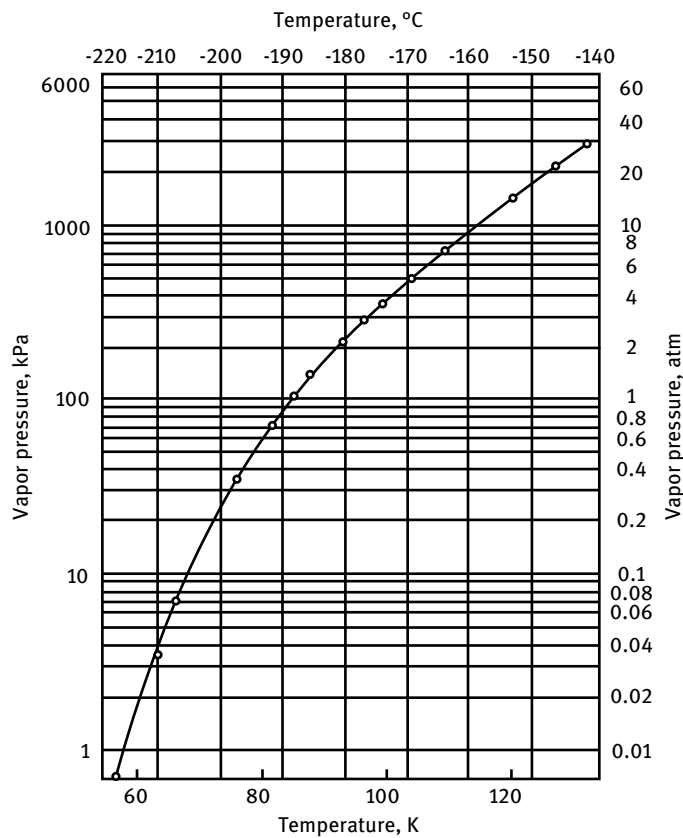


Figure 4: Vapor pressure of liquid fluorine. (Reproduced and modified from [79].)

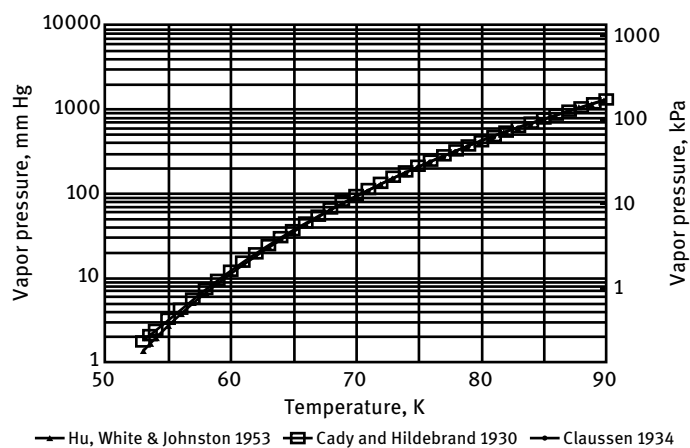


Figure 5: Vapor pressure of liquid fluorine; combining data from three different sources.

The original data were re-evaluated and after applying an update for the temperature standard scale, and were expressed by the following equation from [81]:

$$\ln(P/P_t) = D_1X + D_2X^2 + D_3X^3 + D_4X(1-X)^{D_5}$$

where $X = [1 - (T_t/T)]/[1 - (T_t/T_c)]$ and the subscripts t refer to the triple point and the subscripts c refer to the critical point. The constants D_1 through D_5 are as follows:

$$D_1 = 7.89592346$$

$$D_2 = 3.38765063$$

$$D_3 = -1.34590196$$

$$D_4 = 2.73138936$$

$$D_5 = 1.4327$$

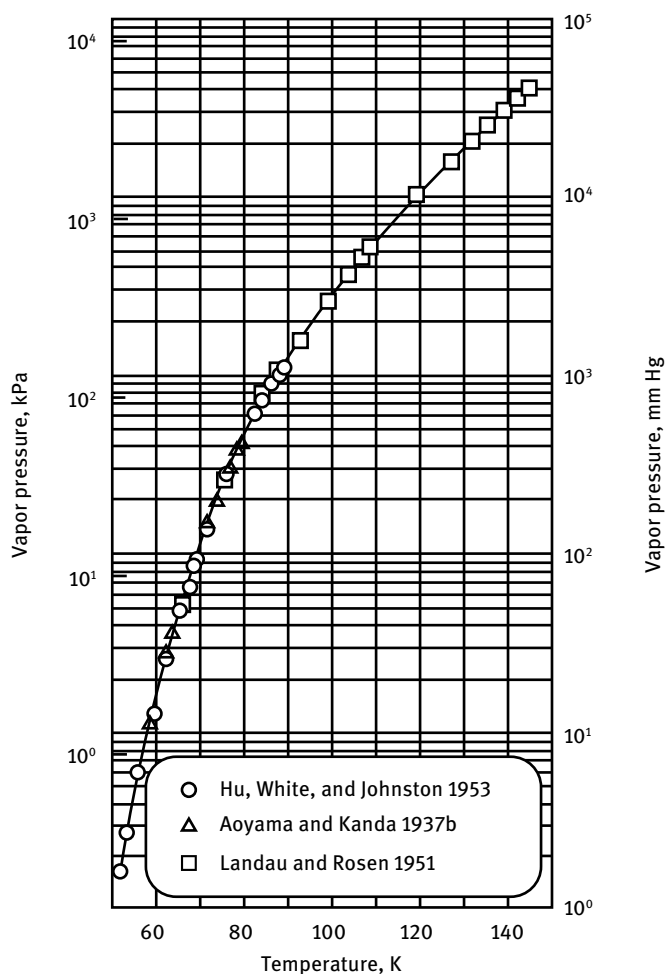


Figure 6: Vapor pressure of liquid fluorine. (Reproduced and modified from [10].)

$$\begin{aligned}
 T_t &= 53.4811 \text{ K} \\
 P_t &= 2.52 \times 10^{-4} \text{ MN m}^{-2} \\
 T_c &= 144.31 \text{ K}
 \end{aligned}$$

The normal boiling point of liquid fluorine derived from this equation is $84.95 \pm 0.003 \text{ K}$.

In Figure 6, vapor pressure data from three other sources [77, 106, 107] were plotted together on the same scale and compared with results from a curve-fitted polynomial equation. The data fit the curve-fitted solid line quite accurately.

The vapor pressure data reported by [106] and marked as triangles in Figure 6 are now considered unreliable because they were obtained on impure fluorine. They had reported a vapor pressure equation

$$\log p = -(442.72/T) + 9.1975 - 0.013150 T$$

where p is the vapor pressure in mmHg and T is the temperature in kelvin. These data should be ignored. In the same paper, the heat of evaporation was reported as 1970 cal/mol (8.24 kJ/mol) and the heat of fusion as 390 cal/mol (1.63 J/mol).

2.6 Viscosity of Liquid and Gaseous Fluorine

There are two common definitions of viscosity in use, the absolute (dynamic) viscosity μ defined as the force per unit area necessary to maintain a unit velocity gradient at right angles to the direction of flow between two plates a unit distance apart. The SI unit for absolute viscosity is Pa s or N s m^{-2} . One Poise (abbreviated as Ps) corresponds to $0.1 \text{ Pa s} = 1 \text{ g cm}^{-1} \text{ s}^{-1} = 0.001 \times 0.01 \text{ kg m}^{-1} \text{ s}^{-1} = 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$. A common but now obsolete unit for dynamic viscosity is centipoise, (cPs); $1 \text{ cPs} = 10^{-3} \text{ N s/m}^2 = 1 \text{ mPa s}$, where mPa is pressure in millipascal (a pressure unit) and s is time in seconds. Viscosity expressed in $\mu\text{g cm}^{-1} \text{ s}^{-1}$ corresponds to 10^{-7} Pa s . The kinematic viscosity σ is defined by

$$\sigma = \frac{\mu}{\rho}$$

where ρ is the density of the incompressible fluid. The common but now obsolete unit for kinematic viscosity is centistokes (cSt); $1 \text{ cSt} = 10^{-6} \text{ m}^2/\text{s} = 1 \text{ mm}^2/\text{s}$. Kinematic viscosity data can be converted back to dynamic viscosity by multiplying with the density:

$$\mu = \sigma \times \rho.$$

The theorem of corresponding states (excess functions) and measured second virial coefficients of the equation of state for fluorine have been used to calculate theoretical viscosities and thermal conductivities for liquid and compressed gaseous fluorine

over a wide range of temperatures and pressures [108]. Tabulated data were presented for temperatures from 70 to 300 K and pressures from 1 to 200 atm, but may be inaccurate by up to 10% at conditions near the critical point. At lower pressures, the agreement with experimental data is modestly good (Figure 7 and 8 [viscosity] and Figure 12 [thermal conductivity]).

2.6.1 Viscosity of Gaseous Fluorine

A torsionally oscillating quartz crystal was used to measure the coefficient of shear viscosity for gaseous fluorine from 155 to 300 K at pressures up to 20 MPa, and for saturated liquid fluorine for temperatures from 70 to 144 K [109]. The accuracy of the results was estimated to be of the order of 2%, with the precision somewhat better, approximately 0.5%. The dependence of the viscosity on density has been investigated by representing the gaseous data along isotherms in power-series expansions. Figure 7 is a comparison of measured and calculated viscosity data for gaseous fluorine. Table 11 is a summary of gaseous viscosity data from two different sources.

Figure 8 shows the viscosity of gaseous fluorine at elevated pressures.

Viscosity and thermal conductivity of fluorine gas in the range 100–2500 K and 0.25–2.0 atm pressure were computed using the Chapman–Enskog first approximation equations for the thermal equilibrium binary mixture of fluorine atoms and molecules [111, 112]. The procedures accounted for inelastic encounters for the fluorine molecules and assignment of the change in rotational collision numbers with temperature. Computed data agreed well with experimental viscosity and thermal conductivity data over

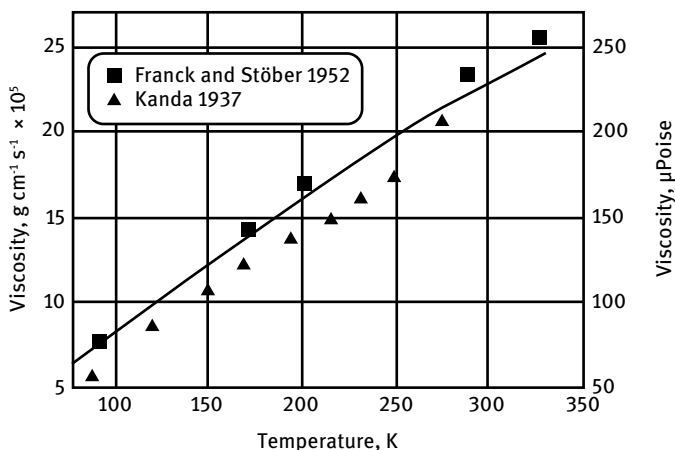


Figure 7: Measured and calculated viscosity of gaseous fluorine. (Republished and modified from [108], with permission of © 1972 American Institute of Physics; permission conveyed through Copyright Clearance Center Inc.)

Table 11: Viscosity of gaseous fluorine.

Temperature			Pressure	Dynamic viscosity	References
K	°C	°F	MPa	μPs	
90.0 ± 0.5	-183.2	-297.7	0.101	76.7 ± 1.0	[110]
169.3 ± 0.5	-103.8	-154.9	0.101	142.4 ± 1.8	[110]
200.0 ± 1.5	-73.1	-99.7	0.101	168.0 ± 2.5	[110]
289.1 ± 0.5	16.0	60.7	0.101	234.5 ± 2.4	[110]
327.1 ± 1.0	54.0	129.1	0.101	254.7 ± 2.3	[110]
426.7 ± 1.5	153.6	308.4	0.101	308.0 ± 4.5	[110]
471.0 ± 1.5	197.9	388.1	0.101	329.0 ± 6.0	[110]
155	-118	-181	0.485	128.4	[109] ^a
155	-118	-181	20.977	698.0	[109]
170	-103	-154	0.479	139.1	[109]
170	-103	-154	20.088	523.8	[109]
185	-88	-127	0.471	150.4	[109]
185	-88	-127	21.045	430.4	[109]
200	-73	-100	0.380	162.1	[109]
200	-73	-100	20.958	365.2	[109]
220	-53	-64	0.398	176.6	[109]
220	-53	-64	20.558	315.7	[109]
240	-33	-28	0.390	189.4	[109]
240	-33	-28	20.303	296.0	[109]
270	-3	26	0.389	208.9	[109]
270	-3	26	20.039	289.3	[109]
300	27	80	0.403	227.1	[109]
300	27	80	20.580	297.6	[109]

^a Additional intermediate data are available in the original source of these data.

Conversion factors: $1 \text{ g cm}^{-1} \text{ s}^{-1} = 1 \text{ Ps} = 0.1 \text{ N s m}^{-2} =$

$1 \mu\text{g cm}^{-1} \text{ s}^{-1} = 10^{-6} \text{ Ps} = 10^{-4} \text{ cPs} = 1 \mu\text{Ps}$

$1 \mu\text{g cm}^{-1} \text{ s}^{-1} = 10^{-7} \text{ Pa s}$

the temperature range where measurements were available. For example, the viscosity at 300 K and 101 kPa was calculated to be $227.1 \times 10^{-6} \text{ g cm}^{-1} \text{ s}^{-1}$.

2.6.2 Viscosity of Liquid Fluorine

Older viscosity and other physical properties data for liquid fluorine from [113], which have been cited by many authors, are not reliable and have since been replaced by more accurate data, as shown in Table 12. Figure 9 shows the measured and calculated viscosity of saturated liquid fluorine as a function of temperature.

Table 13 contains viscosity data for liquid fluorine under pressure at temperatures above its normal boiling point.

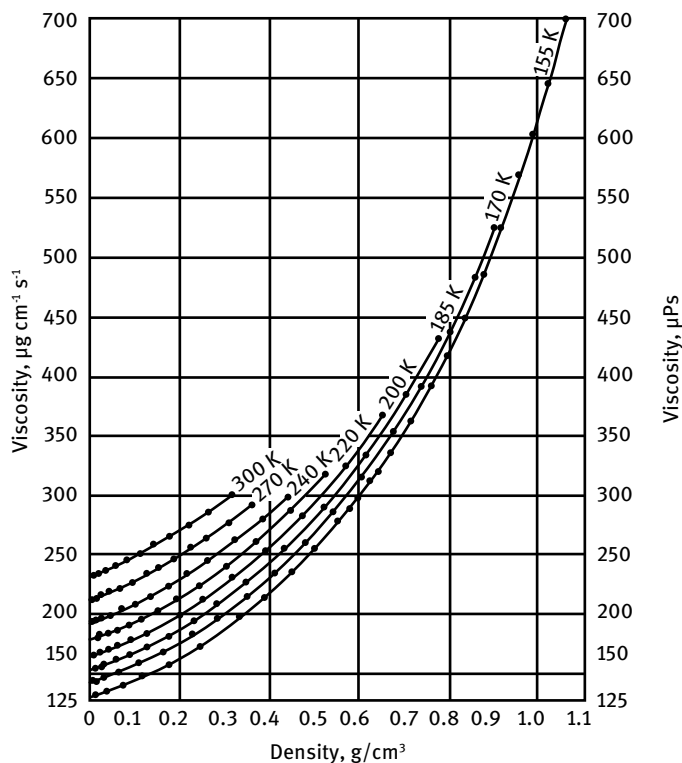


Figure 8: Viscosity of gaseous fluorine at elevated pressures. (Reprinted and modified from [109], with permission from © 1974 Elsevier; permission conveyed through RightsLink.)

The viscosity of liquid fluorine can be calculated from the following equation [86, 87]:

$$\eta = 2.43 \times 10^{-4} \exp(194/T)$$

where η is the viscosity in cPs and T is the temperature in kelvin.

The viscosity of liquid fluorine can be calculated from the equation

$$\log \eta = -2.5818 + 1.0170E + 02/T + 1.6489E - 02 \times T - 8.9947E - 05 \times T^2$$

where η is the viscosity in cPs and T is the temperature in kelvin. A sample calculation for $T = 100$ K gives the viscosity as 0.153 cPs [114, 115].

In addition to sea level pressure measurements, the coefficient of shear viscosity of liquid fluorine was measured using a torsionally oscillating quartz crystal for compressed liquid fluorine from 90 to 140 K at pressures up to 20 MPa, and for saturated liquid fluorine for temperatures from 70 to 144 K [109]. The results are illustrated in Figure 10.

Table 12: Viscosity of saturated liquid fluorine at 0.101 MPa.

Temperature			Viscosity		References
K	°C	°F	cPs	$\mu\text{g cm}^{-1} \text{s}^{-1}$	
69.2	-204	-335.1	0.414	4140	[86, 87]
73.2	-200	-327.9	0.349	3490	[86, 87]
75.3	-197.8	-324.1	0.328	3280	[86, 87]
78.2	-195	-318.9	0.299	2990	[86, 87]
80.9	-192.2	-314.1	0.275	2750	[86, 87]
85.2	-188	-306.3	0.257	2570	[86, 87]
70	-203	-334	0.377	3766	[109]
75	-198	-325	0.319	3193	[109]
80	-193	-316	0.271	2713	[109]
85	-188	-307	0.233	2327	[109]
90	-183	-298	0.200	1999	[109]
95	-178	-289	0.176	1755	[109]
100	-173	-280	0.153	1530	[109]
105	-168	-271	0.136	1359	[109]
110	-163	-262	0.121	1214	[109]
115	-158	-253	0.108	1080	[109]
120	-153	-244	0.096	960	[109]
125	-148	-235	0.086	856	[109]
130	-143	-226	0.074	740	[109]
135	-138	-217	0.063	630	[109]
140	-133	-208	0.049	492	[109]
144	-129	-200	0.034	341	[109]

Table 13: Viscosity of compressed liquid fluorine.

Temperature			Pressure		Viscosity		
K	°C	°F	MPa	psia	$\mu\text{Pa s}$	$\mu\text{g cm}^{-1} \text{s}^{-1}$	cPs
90	-183	-298	0.459	67	203	2026	0.203
90	-183	-298	21.983	3188	244	2440	0.244
100	-173	-280	0.485	70	153	1532	0.153
100	-173	-280	20.290	2943	189	1891	0.189
110	-163	-262	1.286	187	122	1215	0.122
110	-163	-262	21.620	3136	155	1547	0.155
120	-153	-244	1.892	274	97	966	0.097
120	-153	-244	22.094	3204	129	1285	0.129
140	-133	-208	4.658	676	53	529	0.053
140	-133	-208	21.563	3127	91	907	0.091

Data source: [109]

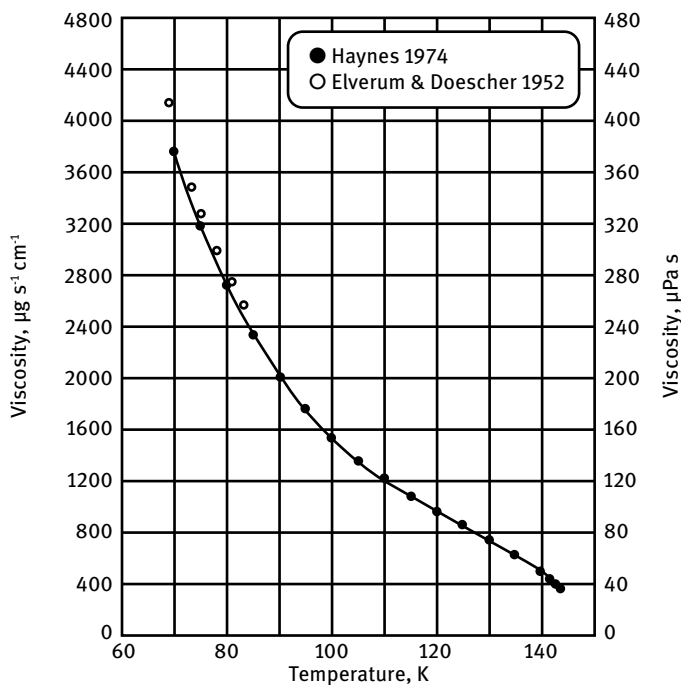


Figure 9: Viscosity of saturated liquid fluorine. (Reprinted and modified from [109], with permission from © 1974 Elsevier; permission conveyed through RightsLink.)

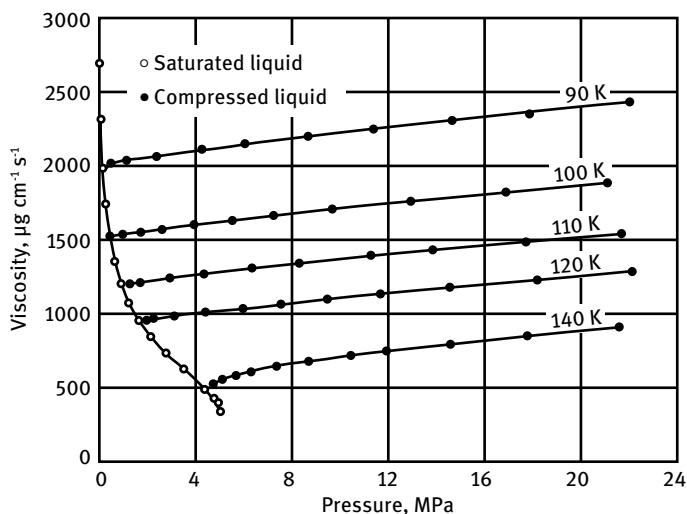


Figure 10: Viscosity of liquid fluorine at elevated pressures. (Reprinted and modified from [109], with permission from © 1974 Elsevier; permission conveyed through RightsLink.)

2.7 Surface Tension of Liquid Fluorine

The surface tension of liquid fluorine is summarized in Tables 14 and 15 and illustrated in Figure 11. Preliminary surface tension data were already shown in Table 9 above.

Table 14: Surface tension of liquid fluorine.

Temperature			Surface tension	
K	°C	°F	dyn/cm	N/m
66.21	−206.9	−340.5	18.85	0.01885
70.26	−202.9	−333.2	17.7	0.0177
70.68	−202.5	−332.4	17.4	0.0174
72.05	−201.1	−330.0	17.02	0.01702
73.35	−199.8	−327.6	16.86	0.01686
75.09	−198.1	−324.5	16.49	0.01649
75.19	−198.0	−324.3	16.28	0.01628
77.15	−196.0	−320.8	15.73	0.01573
79.9	−193.2	−315.9	14.81	0.01481

Data source: [88]

Conversion: $10^5 \text{ dyn} = 1 \text{ N}$; $1 \text{ cm} = 10^{-2} \text{ m}$; $1 \text{ dyn/cm} = 10^{-5} \text{ N/cm} = 10^{-3} \text{ N/m}$

Table 15: Surface tension of liquid fluorine.

Temperature			Surface tension	
K	°C	°F	dyn/cm	N/m
69.2	−204.0	−335.1	17.9	0.0179
71.2	−202.0	−331.5	17.4	0.0174
73.2	−200.0	−327.9	16.7	0.0167
75.3	−197.8	−324.1	16.2	0.0162
76.4	−196.7	−322.2	15.9	0.0159
78.2	−195.0	−318.9	15.4	0.0154
81.0	−192.2	−313.9	14.6	0.0146

Data source: [86, 87]

Conversion: $10^5 \text{ dyn} = 1 \text{ N}$; $1 \text{ cm} = 10^{-2} \text{ m}$; $1 \text{ dyn/cm} = 10^{-5} \text{ N/cm} = 10^{-3} \text{ N/m}$

Surface tension can be expressed by the McLeod equation:

$$\gamma^{1/4}/(D_{\text{Liq}} - D_{\text{Gas}}) = 1.276 \pm 0.002$$

where $D_{\text{Liq}} - D_{\text{Gas}}$ is liquid density minus the vapor density and 1.276 is the McLeod constant which appeared to be constant to within $\pm 0.06\%$ for the entire temperature range investigated.

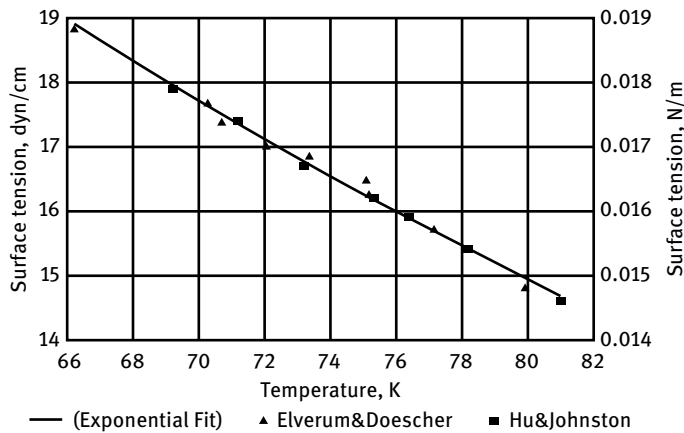


Figure 11: Surface tension of liquid fluorine, data from two different sources.

Table 16: Surface tension of liquid fluorine.

Temperature	Surface tension	
K	N/m	dyn/cm
61.41	0.0138	13.85
65.30	0.0132	13.17
71.00	0.0122	12.20
81.50	0.0104	10.41

Data source: [98]

Surface tension data from two different sources are compared in Figure 11 with an exponential fit of the experimental data. Older surface tension data for fluorine shown in Table 16 are less reliable [116].

2.8 Thermal Conductivity of Gaseous and Liquid Fluorine

The thermal conductivity of gaseous fluorine increases with temperature, whereas the thermal conductivity of liquid fluorine decreases with temperature. A similar trend is observed for oxygen. The theorem of corresponding states (excess functions) and measured second virial coefficients of the equation of state for fluorine have been used to calculate theoretical thermal conductivities for liquid and compressed gaseous fluorine over a wide range of temperatures and pressures [108]. Tabulated data were presented for temperatures from 70 to 300 K and pressures from 1 to 200 atm, but may be inaccurate by up to 10% at conditions near the critical point. At lower pressures, the agreement with experimental data is modestly good (Figure 12).

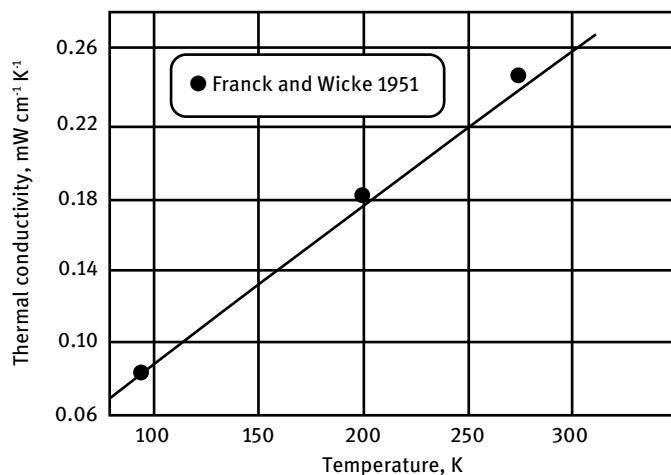


Figure 12: Measured and calculated thermal conductivity of gaseous fluorine. (Chart created by Schmidt 2016 based on data from [108].)

Assuming a heat of dissociation of 167 to 209 kJ/mol (40 to 50 kcal/mol), the difluorine molecule should already be dissociated into atoms at 873 K and 101 kPa (600 °C and 1 atm) to an extent of about 0.1 to 1%. Therefore, if thermal conductivity measurements extend to that temperature, the dissociation of difluorine molecules at the hot end and the recombination of fluorine atoms at the cold end contribute to the purely physical heat transfer through sensible heat and convection.

2.8.1 Thermal Conductivity of Gaseous Fluorine

The thermal conductivity of gaseous fluorine was measured by a hot wire method using a resistance-heated nickel wire [117, 118]. Complications arose as soon as the nickel wire reached higher temperatures and became coated with a layer of nickel fluoride. The λ values measured at the highest temperature (788 K = 515 °C), however, taking into account their range of uncertainty, fit into the curve to be expected for “normal” (no dissociation) thermal conductivity. At this temperature a total of 12 measurements with fluorine were carried out in the pressure range 50 to 340 mm Hg, and yield the mean value

$$\lambda \text{ (at 788 K = 515 °C)} = 1.46 \pm 0.06 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ °C}^{-1}$$

A pronounced dependence on total pressure, as would be expected by the influence of dissociation, was not observed in this measurement. This experiment was conducted as part of an effort to determine the heat of dissociation of difluorine, and the results speak against values smaller than 180 kJ/mol (43 kcal/mol) for this property.

A pure sample of fluorine needed for the determination of thermal conductivity was prepared by decomposition of chlorine trifluoride. The thermal conductivity of

fluorine gas was then measured at temperatures up to 800 K [119]. A Nernst formula was used to calculate the theoretically to be expected temperature dependence of the thermal conductivity, based on the degree of dissociation predicted for different temperatures. A comparison of the measured temperature dependence of the thermal conductivity for N_2 , O_2 , and F_2 showed that the three gases behaved very similarly between 100 and 800 K. There was no indication of excessive dissociation in the case of F_2 . Also, even at the highest experimental temperature, the thermal conductivity of difluorine was independent of pressure. For comparison, with iodine vapor, which has a lower dissociation energy (148 kJ/mol = 35.4 kcal/mol), the increase in thermal conductivity due to dissociation was quite measurable.

The temperature dependence of thermal conductivity of a dissociating gas is determined by the speed at which a dissociation equilibrium establishes itself in the gas phase and at the interphase with the hot surface that provides the energy for the dissociation. A function was derived for difluorine that predicts the temperature dependence of thermal conductivity of F_2 with the aid of the relaxation time and a coefficient of accommodation [120]. Although the measurements and predictions agreed well with each other for bromine vapor, the lack of a dissociation effect on the thermal conductivity of F_2 at temperatures up to 973 K (700 °C) was blamed on the inadequate rate of reaction in the gas phase and a very small coefficient of accommodation (10^{-4} to 10^{-3} ; Table 17). The coating of the hot wire with nickel fluoride also interfered with some of the measurements.

Table 17: Thermal conductivity of gaseous fluorine.

Temperature, K	Thermal conductivity	
	$\text{cal cm}^{-1} \text{s}^{-1} \text{K}^{-1} \times 10^7$	$\text{W cm}^{-1} \text{K}^{-1} \times 10^7$
100	206 ± 2	862
150	321 ± 2	1343
200	436 ± 2	1824
273	592 ± 2	2477
300	643	2690
400	823 ± 10	3443
500	993 ± 10	4155
600	1166 ± 10	4879
700	1336	5590
800	1503 ± 50	6289
900	1660 ± 100	6945
1000	1850 ± 150	7740

Data source: [120]

2.8.2 Thermal Conductivity of Liquid Fluorine

Figure 13 is a comparison of measured and calculated data for the thermal conductivity of liquid fluorine. For data on the thermal conductivity of liquid fluorine see also [121].

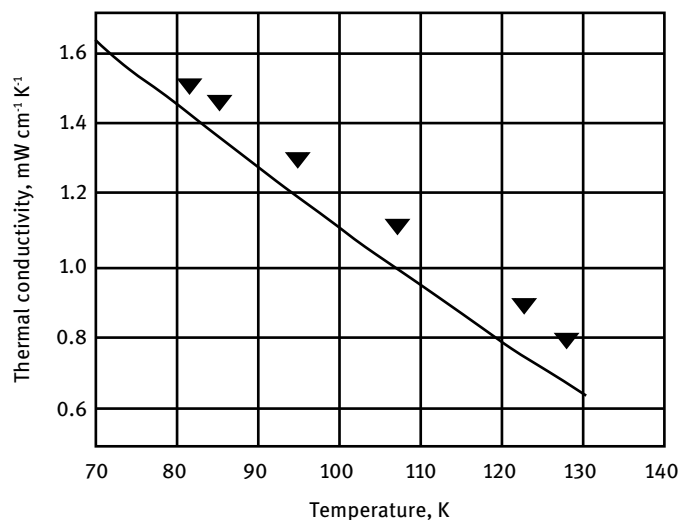


Figure 13: Measured and calculated thermal conductivity of saturated liquid fluorine. (Chart created by Schmidt 2016 based on data from [108].)

Triangles represent measured data from an inaccessible source (Smith, Ohio State University)

2.8.3 Heat Transfer Coefficient of Liquid Fluorine

Measuring the heat transfer from injectors or vaporizers to liquid fluorine requires extreme precaution and careful design of the experiment [122]. Only a few materials are resistant to hot and flowing fluorine. Incorrect choice of materials for this experiment could cause leakage and ignition accidents. Fluorine cannot be used for regenerative cooling of rocket engines [123].

2.9 Critical Constants of Fluorine

Table 18 lists the critical constants for fluorine [124].

Table 18: Critical point data for fluorine.

T_c , K	p_c , atm	ρ_c , g/cm ³	References
144.16	55		[79]
144.31	51.47	0.574	[82]
144	55		[78]

2.10 Solubility, Miscibility, and Solutions of Liquid Fluorine

The solubilities of various compounds in liquid fluorine are summarized in Table 19. The most troublesome contaminants in liquid fluorine are those that are insoluble and are carried along in particulate form, clogging filters and injection orifices.

Table 19: Solubility of fluoride compounds in liquid fluorine.

Material	Solubility at 77 K = -196 °C = -320 °F, mol percent
Carbon tetrafluoride	87.5
Oxygen difluoride	10.0
Silicon tetrafluoride	<0.05
Hydrogen fluoride	<0.5
Sulfur hexafluoride	<0.1
Nitrogen trifluoride	0.12
Hexafluoroethane	2.87
Perchloryl fluoride	0.33

Data source: [125]

Additional contaminant solubility data are contained in [66]. Chlorine will initially dissolve in liquid fluorine, but when the mixture thaws, the two gases will begin to react, forming ClF and ClF₃ [67]. A special apparatus was devised for the purpose of taking a sample of the mixture for analysis, and used in the analysis of liquid air and a solution of chlorine in liquid fluorine.

Data on the solubility of fluorine gas in various fluorocarbons and concentrated acids are contained in [126].

Solubilities of several substances in liquid fluorine were determined, such as carbon tetrafluoride (CF₄), perfluoroethane (C₂F₆), perchloryl fluoride (ClO₃F), nitryl flu-

oride (NO_2F), silicon tetrafluoride (SiF_4), boron trifluoride (BF_3), tetrafluoroethylene polymer, cobalt trifluoride (CoF_3), and aluminum trifluoride (AlF_3) [127]. In addition, the liquid–liquid systems nitrogen/fluorine (N_2/F_2) and nitrogen trifluoride/fluorine (NF_3/F_2) were investigated. All solutions were studied within the temperature range 68 to 83 K by vapor–pressure measurements. The NF_3/F_2 system behaved as a nearly ideal solution throughout the entire composition range of 0 to 100% NF_3 as determined by vapor–pressure measurements between 68 and 78 K. The nitrogen/fluorine system was completely miscible at 77.5 K. Powdered tetrafluoroethylene polymer, SiF_4 , BF_3 , CoF_3 , and AlF_3 were all less soluble than could be determined by the experimental apparatus used.

2.11 Thermodynamic Properties of Liquid and Gaseous Fluorine

Thermodynamic properties of fluorine summarized in this section and Table 20 through Table 23 are heat capacity, enthalpy of formation, entropy of formation, and enthalpies involved with phase changes. The heat of dissociation of difluorine has been uncertain for a long time, and has had some influence on the thermodynamic property data measured and calculated for many other fluorine compounds. In order to calculate theoretical specific impulse of a rocket propellant, thermodynamic data are needed not only for rocket propellants that go into the combustion chamber but also for combustion products that flow out through the nozzle. Thermodynamic data for HF (and DF, a chemical laser product) have also received a lot of attention and are equally important [128].

For entropies, it is common practice to give the values in “entropy units”, abbreviated as “e.u.”. One e.u. is $1 \text{ cal g}^{-1} \text{ K}^{-1}$.

One book chapter contains a summary of information on the dissociation energy of difluorine, the heat of formation of HF, fluorine bomb calorimetry at constant volume, and various other types of calorimetry for the determination of thermochemical properties of fluorine compounds [130].

Bibliographic information on physical property data for difluorine between 0 and 300 K collected from 51 references is given in [131].

Thermodynamic functions of fluorine that were first published in 1939 were later revised based on the availability of more accurate electron diffraction and Raman spectra [132]. The molar heat capacity at 298 K was $31.24 \text{ J mol}^{-1} \text{ K}^{-1}$ ($7.466 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$).

Thermodynamic functions of fluorine were included in a review of the status of mathematical models and correlations for the calculation of thermodynamic properties of cryogenic fluids [133]. This review included references to the original works that contain details of the mathematical models and correlation methods, and provided sources of information about using the computer formulations for applications and Internet access to computer programs for thermodynamic properties of the fluids.

Table 20: Thermodynamic properties of difluorine.

Property	SI units	Other units	References
Enthalpy of formation, gas, (ΔH) at 298 K	0.0 kJ/mol	0.0 kcal/mol (by definition)	
Enthalpy of formation, liquid, (ΔH) at 85 K	-12.96 kJ/mol	-3.098 kcal/mol	[129]
Heat of phase change, (ΔH)Phase	728 J/mol	173.9 ± 0.04 cal/mol	[77]
Heat of fusion, (ΔH)fusion	510 J/mol	121.98 ± 0.5 cal/mol	[77]
Heat of vaporization, at normal boiling point		See separate table further down	
Entropy of ideal gas at 85.02 K, from calorimetric data		39.58 ± 0.16 e.u.	[77]
Entropy of phase change, (ΔS)phase	$16.0 \text{ J mol}^{-1} \text{ K}^{-1}$	$3.82 \text{ cal mol}^{-1} \text{ }^{\circ}\text{C}^{-1}$	[77]
Entropy of fusion, (ΔS)fusion	$9.54 \text{ J mol}^{-1} \text{ K}^{-1}$	$2.28 \text{ cal mol}^{-1} \text{ }^{\circ}\text{C}^{-1}$	[77]
Entropy of vaporization, (ΔS) _{evap} , at normal boiling point and 1 atm	$76.9 \text{ J mol}^{-1} \text{ K}^{-1}$	$18.38 \text{ cal mol}^{-1} \text{ }^{\circ}\text{C}^{-1}$	[77]
Entropy of vaporization		$18.3 \text{ cal mol}^{-1} \text{ }^{\circ}\text{C}^{-1}$	[103]

Thermodynamic properties of fluorine are summarized in Table 20 through Table 23.

The data published by [134] and summarized in Table 22 were criticized for containing small errors scattered throughout because the relation $(F^0 - H^0)/T = (H_0^0 - H_0^0)/T - S^0$ was not always satisfied [128]. A new set of calculations was based on improved spectroscopic data for HF(G) and DF(G) and thermophysical data for F and F₂ were tabulated for temperatures from 298 to 5000 K in 100-K increments (Table 23).

An apparatus to measure vapor pressure and PVT data of fluorine from the triple point to 300 K at pressures up to about 24 MPa was constructed and used to measure PVT data of fluorine [135]. A network of isotherm and isochore polynomials and a truncated virial equation were used to represent all PVT data. Additional comparisons were made to measure specific heats and latent heats of vaporization. Extensive tables of thermodynamic properties of fluorine included pressure, temperature, density, isotherm and isochore derivatives, internal energy, enthalpy, entropy, specific heats at constant pressure, and volume and velocity of sound. Some erroneous values for the internal energy and enthalpy of the compressed liquid below 135 K, published previously, had to be corrected in a revision.

Accurately measured PVT and specific heat data were then used to calculate thermodynamic functions of gaseous and liquid fluorine up to pressures of 21 MN/m² = 21 MPa (1 MN/m² = 9.86923 atm) and temperatures between 50 and 310 K [136, 137].

Table 21: Thermodynamic properties of solid and liquid difluorine.

Temperature K	Molar heat capacity, C_p		Entropy		$H - H_0/T$		$-(F - H_0/T)$	
	$\text{cal mol}^{-1} \text{ } ^\circ\text{C}^{-1}$	$\text{J mol}^{-1} \text{ K}^{-1}$	$\text{cal mol}^{-1} \text{ } ^\circ\text{C}^{-1}$	$\text{J mol}^{-1} \text{ K}^{-1}$	$\text{cal mol}^{-1} \text{ } ^\circ\text{C}^{-1}$	$\text{J mol}^{-1} \text{ K}^{-1}$	$\text{cal mol}^{-1} \text{ } ^\circ\text{C}^{-1}$	$\text{J mol}^{-1} \text{ K}^{-1}$
Solid phase I								
15	1.745	7.301	0.741	3.100	0.523	2.187	0.218	0.912
20	3.104	12.987	1.422	5.950	0.992	4.148	0.431	1.803
25	4.609	19.284	2.276	9.523	1.564	6.544	0.712	2.979
30	6.031	25.234	3.245	13.577	2.192	9.171	1.053	4.406
35	7.427	31.075	4.281	17.912	2.842	11.891	1.439	6.021
40	8.778	36.727	5.363	22.439	3.502	14.652	1.861	7.786
45	10.142	42.434	6.475	27.091	4.164	17.422	2.311	9.669
45.55	10.290	43.053	6.599	27.610	4.237	17.728	2.362	9.883
Solid phase II								
45.55	11.120	46.526	10.417	43.585	8.055	33.702	2.362	9.883
50	11.792	49.338	11.486	48.057	8.359	34.974	3.127	13.083
53.54	12.210	51.087	12.308	51.497	8.600	35.982	3.708	15.514
Liquid phase								
53.54	13.700	57.321	14.586	61.028	10.879	45.518	3.708	15.514
55	13.698	57.312	14.955	62.572	10.954	45.832	4.001	16.740
60	13.680	57.237	16.146	67.555	11.182	46.785	4.964	20.769
65	13.607	56.932	17.239	72.128	11.372	47.580	5.867	24.548
70	13.558	56.727	18.245	76.337	11.529	48.237	6.716	28.100
75	13.642	57.078	19.182	80.257	11.666	48.811	7.516	31.447
77 ^a	13.702	57.331						
80	13.793	57.710	20.067	83.960	11.794	49.346	8.273	34.614
85	13.948	58.358	20.907	87.475	11.916	49.857	8.991	37.618
85.02 ^b	13.948	58.358	20.909	87.483	11.917	49.861	8.992	37.623
85.02 ^c			39.287	164.38	30.281	126.70	8.996	37.639
85.02 ^d			39.577	165.59	—	—	—	—

^a interpolated; ^b liquid; ^c vapor; ^d ideal gas

Data source: [77]

Ideal gas properties, which constituted the starting point for the calculations, have been recomputed based on the latest available data. Derived thermofunctions, heat of vaporization, and sound velocities, for the single- and two-phase regions were tabulated.

Table 22: Thermodynamic properties of difluorine as ideal gas.

Tem- perature K	Molar heat capacity		Entropy		$F_0 - E_0/T$		$H_0 - E_0/T$	
	cal mol ⁻¹ °C ⁻¹	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹	J mol ⁻¹ K ⁻¹
100	6.957	29.107	40.756	170.52	33.804	141.44	6.950	29.078
200	7.097	29.693	45.604	190.81	38.630	161.63	6.979	29.200
298.16	7.487	31.326	48.506	202.95	41.432	173.35	7.079	29.616
300	7.495	31.359	48.553	203.15	41.475	173.53	7.081	29.628
400	7.895	33.031	50.761	212.38	43.534	182.15	7.236	30.277
500	8.200	34.308	52.562	219.92	45.165	188.97	7.400	30.962
600	8.420	35.231	54.077	226.26	46.527	194.67	7.553	31.601
700	8.581	35.904	55.388	231.74	47.702	199.59	7.689	32.170
800	8.702	36.410	56.272	235.44	48.737	203.92	7.804	32.652
900	8.796	36.803	57.573	240.89	49.673	207.83	7.913	33.108
1000	8.872	37.119	58.504	244.78	50.503	211.30	8.005	33.494
1500	9.111	38.120	62.151	260.04	53.818	225.17	8.338	34.887
2000	9.262	38.751	64.794	271.10	56.247	235.34	8.551	35.778
2500	9.384	39.263	66.874	279.80	58.171	243.39	8.706	36.425
3000	9.496	39.730	68.595	287.00	59.769	250.07	8.828	36.937
3500	9.601	40.171	70.067	293.16	61.139	255.81	8.931	37.368
4000	9.705	40.604	71.356	298.55	62.337	260.82	9.022	37.746
4500	9.806	41.028	72.505	303.36	63.406	265.29	9.103	38.087
5000	9.906	41.448	73.542	307.70	64.369	269.32	9.178	38.402

Data source: calculated values, from [134]

Table 23: Thermodynamic functions of difluorine in the ideal gas state.

T K	$-(F_0 - H_0^0)/T$		C_{p_0}		S_0		$(H_0 - H_0^0)/T$	
	JK ⁻¹ mol ⁻¹	cal °C ⁻¹ mol ⁻¹	JK ⁻¹ mol ⁻¹	cal °C ⁻¹ mol ⁻¹	JK ⁻¹ mol ⁻¹	cal °C ⁻¹ mol ⁻¹	JK ⁻¹ mol ⁻¹	cal °C ⁻¹ mol ⁻¹
298.16	173.1	41.369	31.32	7.485	202.7	48.445	29.60	7.075
300	173.3	41.413	31.35	7.493	202.9	48.491	29.61	7.078
400	181.9	43.470	33.01	7.890	212.1	50.703	30.26	7.233
500	188.7	45.101	34.27	8.191	219.7	52.498	30.94	7.396
600	194.4	46.464	35.18	8.408	226.0	54.011	31.58	7.548
700	199.3	47.637	35.84	8.566	231.5	55.320	32.15	7.683
800	203.6	48.671	36.33	8.683	236.0	56.412	32.64	7.800
900	207.5	49.596	33.95	8.114	240.6	57.500	33.07	7.904
1000	211.0	50.434	37.01	8.846	244.5	58.428	33.45	7.995
1100	214.2	51.199	37.26	8.905	248.0	59.274	33.79	8.075
1200	217.2	51.905	37.46	8.954	251.3	60.051	34.08	8.146
1300	219.9	52.560	37.64	8.997	254.3	60.770	34.35	8.210
1400	222.5	53.170	37.80	9.035	257.1	61.438	34.59	8.268

Table 23: (continued)

T	$-(F_0 - H_0^0)/T$		C_{p_0}		S_0		$(H_0 - H_0^0)/T$	
K	$\text{JK}^{-1} \text{mol}^{-1}$	$\text{cal}^\circ\text{C}^{-1} \text{mol}^{-1}$	$\text{JK}^{-1} \text{mol}^{-1}$	$\text{cal}^\circ\text{C}^{-1} \text{mol}^{-1}$	$\text{JK}^{-1} \text{mol}^{-1}$	$\text{cal}^\circ\text{C}^{-1} \text{mol}^{-1}$	$\text{JK}^{-1} \text{mol}^{-1}$	$\text{cal}^\circ\text{C}^{-1} \text{mol}^{-1}$
1500	222.3	53.142	37.94	9.069	259.7	62.062	34.81	8.320
1600	227.1	54.281	38.07	9.100	262.1	62.649	35.01	8.368
1100	229.2	54.790	38.20	9.129	264.4	63.201	35.20	8.412
1900	231.3	55.272	38.31	9.156	266.6	63.724	35.36	8.452
1900	233.2	55.730	38.41	9.181	268.7	64.219	35.52	8.490
2000	235.0	56.166	38.51	9.205	270.7	64.691	35.67	8.525
2100	236.7	56.583	38.61	9.228	272.5	65.141	35.81	8.558
2200	238.4	56.981	38.70	9.250	274.3	65.570	35.94	8.589
2300	240.0	57.364	38.79	9.272	276.1	65.982	36.06	8.618
2400	239.0	57.131	38.88	9.293	277.7	66.377	36.17	8.646
2500	243.0	58.085	38.97	9.313	279.3	66.757	36.03	8.612
2600	244.5	58.425	39.05	9.333	280.8	67.123	36.39	8.697
2700	243.3	58.154	39.13	9.353	282.3	67.475	36.49	8.721
2800	247.2	59.072	39.21	9.372	283.7	67.816	36.58	8.744
2900	248.2	59.319	39.29	9.391	285.1	68.145	36.68	8.766
3000	249.7	59.676	39.37	9.410	286.5	68.464	36.76	8.787
3100	250.9	59.965	39.45	9.429	287.7	68.772	36.82	8.801
3200	252.1	60.245	39.53	9.447	289.0	69.072	36.91	8.821
3300	253.2	60.511	39.61	9.466	290.2	69.363	37.01	8.846
3400	254.3	60.781	39.68	9.484	291.4	69.646	37.09	8.865
3500	255.4	61.038	39.76	9.502	292.5	69.921	37.17	8.883
3600	256.4	61.289	39.83	9.520	293.7	70.189	37.24	8.900
3700	257.5	61.533	39.90	9.537	294.8	70.450	37.31	8.917
3800	258.4	61.771	39.98	9.555	295.8	70.705	37.38	8.934
3900	259.4	62.003	39.80	9.513	45.8	10.953	37.45	8.950
4000	260.4	62.230	40.12	9.590	297.9	71.196	37.51	8.966
4100	261.3	62.452	40.20	9.608	298.9	71.433	37.58	8.981
4200	262.2	62.668	40.27	9.625	299.8	71.664	37.64	8.996
4300	263.1	62.880	40.35	9.643	300.8	71.891	37.70	9.011
4400	264.0	63.087	40.42	9.660	301.7	72.113	37.76	9.026
4500	264.8	63.290	40.46	9.671	302.6	72.330	37.82	9.040
4600	265.6	63.489	40.56	9.695	52.5	12.543	37.88	9.054
4700	266.5	63.684	40.64	9.712	304.4	72.752	37.94	9.068
4800	267.3	63.875	40.71	9.729	305.3	72.957	37.99	9.081
4900	268.0	64.063	40.78	9.746	306.1	73.157	38.05	9.095
5000	268.8	64.246	40.85	9.763	306.9	73.354	38.11	9.108

Data source: [128]

2.11.1 Heat Capacity of Solid, Liquid, and Gaseous Fluorine

2.11.1.1 Heat Capacity of Solid Fluorine

When measuring the heat capacity of solid fluorine between 14 and 85 K, it was noticed that a phase transition took place that documented itself in a sudden increase in heat capacity [77]. The phase transition took place at 45.55 ± 0.02 K, with an enthalpy change of $728 \text{ J/mol} = 173.90 \pm 0.04 \text{ cal/mol}$. Similar phase transitions have been observed with solid nitrogen and solid oxygen. At the phase transition temperature, an anharmonic torsion oscillation changes into a not totally free, somewhat hindered rotation of the molecule.

2.11.1.2 Heat Capacity of Liquid Fluorine

Experimental specific heats of fluorine at constant total volume were measured for the two-phase, liquid vapor system from the triple to the critical point. The constant volume heat capacity of two-phase liquid fluorine was measured at five different loading densities ranging from 6.77 to 34.10 mol/L [138]. Specific heats of liquid along the two-phase saturated liquid coexistence path were derived by the use of PVT data for the two-phase system, and were represented by a formula to facilitate computations of thermodynamic properties. The subscript σ stands for the saturated two-phase condition. Figure 14 shows $C_{V\sigma}$ for the liquid on the path along the saturation line. On the scale of this plot, the data appear to be linear in temperatures below boiling point (85 K).

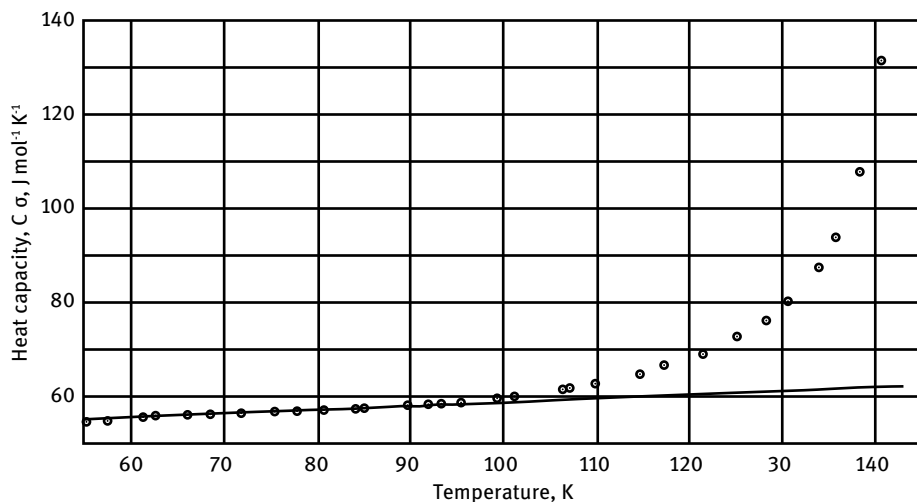


Figure 14: Heat capacity of two-phase liquid fluorine along the saturation line. (Reproduced and modified from [138].)

Specific heat along the saturation (coexistence) path of T ; P conditions can be expressed by the equation

$$C_{v\sigma} = C_v - \frac{T_a}{\rho} \left\{ \frac{1}{\rho} \frac{d\rho}{dT} \frac{dP}{dT} + \left[\frac{\rho V_b}{N_b} - 1 \right] \frac{d^2P}{dT^2} \right\}$$

where $C_{v\sigma}$ is the heat capacity at saturation, T_a is the average temperature of the temperature interval over which C_v was measured, ρ is the density, V_b is the volume of the calorimeter bomb, and N_b is the gram mols of fluid in the bomb.

2.11.1.3 Heat Capacity of Gaseous Fluorine

The gas phase heat capacity, excess enthalpy, and standard entropy can be calculated from the following polynomial equations (Shomate Equation). The constants are given in Table 24 below.

$$\begin{aligned} C_p^\circ &= A + B\tau + C\tau^2 + D\tau^3 + E/\tau^2 \\ H^\circ - H^\circ_{298.15} &= A\tau + B\tau^2/2 + C\tau^3/3 + D\tau^4/4 - E/\tau + F - H \\ S^\circ &= A \times \ln(\tau) + B\tau + C\tau^2/2 + D\tau^3/3 - E/(2\tau^2) + G \end{aligned}$$

where C_p is the heat capacity in $\text{J mol}^{-1} \text{K}^{-1}$, H° is the standard enthalpy in kJ/mol , S° is the standard entropy in $\text{J mol}^{-1} \text{K}^{-1}$, and τ is the fractional temperature in $\text{K}/1000$. The constants in Table 24 are valid for a temperature range from 298 to 6000 K.

Table 24: Shomate equation constants for heat capacity of gaseous fluorine.

A	31.44510
B	8.413831
C	-2.778850
D	0.218104
E	-0.211175
F	-10.43260
G	237.2770
H	0.000000

Data source: [76, 129]

The single-phase heat capacity of fluorine at constant volume was measured over a wide range of temperatures, 80 to 300 K, pressures up to 23 MPa, and loading densities up to 26.3 mol/L [139]. For a wide range of densities about the critical isochore, the specific heat increased sharply as the temperature approaches the two-phase envelope, which was to be expected. At densities far removed from the critical, the temperature dependence was relatively weak. A graph showed isochores of heat capacity versus temperature for six different loading densities between 6.5 and 26.3 mol/L.

2.11.2 Enthalpy of Formation of Liquid and Gaseous Fluorine

2.11.2.1 Enthalpy of Dissociation

Because of the difficulty in determining the heat of dissociation of the difluorine molecule into atomic fluorine, the thermodynamic data given for atomic fluorine in the literature vary substantially. It is difficult to determine the heat of dissociation of difluorine from spectroscopic data because the spectrum does not show discrete ground states. Instead, it shows a continuous absorption band that stretches from 2300 to 3500 Å. There has been a controversy raging over several decades about which enthalpy of dissociation data of difluorine should be used to calculate the derived thermodynamic functions. The data seemed to be very dependent on the method used for their determination. Several research groups attacked this problem, but their results did not agree. The heat capacity C_p , enthalpy function H/T , and entropy S_0 for the free F atom was calculated based on the enthalpy of dissociation for difluorine that had been determined earlier [140].

Spectroscopic and thermal data cast doubt about the heat of dissociation of fluorine, which at one time was reported to be as high as 251 kJ/mol (60 kcal/mol). The thermal conductivity of difluorine gas was measured and found to be almost identical to that of dinitrogen, which indicated that no dissociation occurred and led to the erroneous assumption that the heat of dissociation was very high. Renewed interpretation of the absorption spectrum indicated that the lower value was more accurate [141].

For a long time the first published value for the dissociation energy of difluorine (239 kJ/mol = 57.2 kcal/mol) was considered a reliable data point. Other sources gave 268 kJ/mol = 64 kcal/mol. Until 1954, a dissociation energy of 156 kJ/mol = 37.4 kcal/mol was considered reliable, but that assumption was quickly proven wrong. Table 25 shows a compilation of data for the dissociation energy of difluorine, determined by different methods and leading to different results.

Using a method first described by [118], who estimated the value to be between 40 and 50 kcal/mol, the dissociation energy of difluorine was determined using an explosion method in a closed bomb and found to be 154.8 ± 8 kJ/mol = 37.0 ± 2 kcal/mol [153].

Dissociation and recombination kinetics are often studied by monitoring the decay of dissociation products behind a shock wave in a shock tube. This method was used by several other investigators to measure the heat of dissociation of fluorine [154, 155].

Doescher's method consisted essentially in directly comparing the pressure variation with temperature of a quantity of fluorine and that of a quantity of nitrogen. Twenty-four determinations of the equilibrium constant were made, and $\ln K$ was plotted as a function of reciprocal absolute temperature, giving the activation energy of the dissociation [156].

The convergence boundary of the vacuum UV absorption bands of the F_2 molecule was used to derive a dissociation energy of 135.1 ± 9.6 kJ/mol = 32.3 ± 2.3 kcal/mol [157–

Table 25: Dissociation energy of difluorine.

Author	Method	Date	Dissociation energy ^a		References
			kJ/mol	kcal/mol	
Diesen	shock tube	1966	113	27	[142]
Wray and Hornig	shock tube	1956	130 ± 18	31 ± 4.3	[143]
Stricker	spectroscopic	1967	135.1 ± 9.6	32.3 ± 2.3	
Gole and Margrave	UV spectroscopic	1972	138.3	33.05	[144]
Gilles and Margrave	manometric	1953	151 ± 12.5	36 ± 3	[145]
Doescher		1952	153.6	36.71	
Wicke and Fritz	explosion	1953	154.8 ± 8	37.0 ± 2	[146]
Rees	IR spectra	1957	155.2 ± 3.56	37.1 ± 0.85	[147]
de Corpo et al.	mass spectrometer	1970	156.9 ± 9.6	37.5 ± 2.3	[148]
Iczkowski and Margrave	UV spectra	1959	156.9 ± 8.4	37.5 ± 2	[149]
Wise	effusion	1954	157 ± 3.3	37.6 ± 0.8	[150]
Doescher	manometric	1951	157.7 ± 1.7	37.7 ± 0.4	[151]
Stamper and Barrow	theoretical	1958	157.8	37.72	[152]

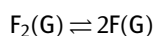
^a Data sorted by ascending dissociation energy values

159]. For most other dissociating polyatomic gases one can use the more energetic (toward shorter wavelengths) edge of the absorption band as an indication of beginning dissociation by photolysis. For fluorine, this method does not give the expected results [160].

The dissociation of <1% F₂ in Ar, Kr, or Ne in a shock tube was studied over a range from 1665 to 2670 K and the temperature dependence of the rate constants used to calculate the heat of dissociation [142]. Rate constants were determined from both fluorine molecule and atom analysis in mixtures containing 1% F₂ or less. The activation energy was 113 kJ/mol = 27 kcal/mol. See also Eucken and Wicke [117], Evans et al. [161], Gaydon [162], and Sanderson [163].

Altogether, the dissociation energy of difluorine is much lower than one would expect by extrapolation from the dissociation energies of the other halogens. This number has to be known accurately to predict flame temperatures for fluorine flames and to predict the performance of fluorine and non-metallic fluorides as rocket propellants.

For a direct determination of the heat of dissociation of difluorine the gas effusion method is particularly suitable as the measurements are performed at low pressures (molecular-flow region) and therefore a measurable degree of dissociation is attained at relatively low temperatures [150]. The rate of gas effusion was determined over the temperature range from 500 to 800 K at a total pressure of 4×10^{-4} mm Hg. The results of these measurements yield for the reaction



a value of $\Delta H_{\text{diss}} = 157 \pm 3.3 \text{ kJ/mol} = 37.6 \pm 0.8 \text{ kcal/mol}$.

2.11.2.2 Enthalpy of Formation of Gaseous and Liquid Fluorine

The enthalpy of formation of gaseous difluorine under standard conditions is by definition zero. The enthalpy of formation data for liquid difluorine collected from different literature sources are summarized in Table 26.

Table 26: Enthalpy of formation data for liquid fluorine.

Author(s)	Year	Temperature	Enthalpy of formation				References
		K	kJ/mol	kcal/mol	J/g	cal/g	
Crampel	1968	85.02	−6.52	−1.56	−172	−41	[164]
Siegel and Schieler	1964	85	−12.55	−3.0	−330	−79	[165]
PEPCODED.DAT	2000	85	−13.036	−3.116	−343	−82	[166]
PEPCODED.DAT	2000	85	−12.082	−2.888	−318	−76	[166]
NASA CEA	1966	85.02	−13.091	−3.129	−345	−82	[167]
JANAF Ser. D	1966	85.02	−12.96 ± 0.08	−3.098 ± 0.02	−341	−81.5	[168]

Molecular mass of F₂: 37.9968 g/mol (IUPAC 1962)

The high specific impulse of fluorine with hydrogen or hydrogen compounds is based on the high enthalpy of formation of HF. This number must be known very precisely so that the theoretical rocket performance can be calculated accurately. The US National Bureau of Standards [169] has developed a calorimeter that can be used to determine the heat of reaction of fluorine with other gases, for instance, ammonia.

2.11.3 Enthalpy of Fusion and Solid-State Phase Transitions of Solid Fluorine

Enthalpy of fusion data for solid fluorine are summarized in Table 27.

Table 27: Enthalpy of fusion data for solid fluorine.

Author(s)	Year	Enthalpy of fusion				Temperature
		kJ/mol	kcal/mol	J/g	cal/g	K
Aoyama and Kanda	1937	1.632	0.390	42.9	10.3	
Kanda	1937	1.556	0.372	40.9	9.8	55.2
Hu, White, and Johnston	1953	0.510	0.12198 ± 0.0005	13.4	3.2	
Kit & Evered (second-hand data)	1960	1.632	0.390	42.9	10.3	53.55

Molecular mass of F₂: 37.9968 g/mol (IUPAC 1962)

Solid fluorine can exist in two different phases, α -F₂ and β -F₂. Physical properties such as the heat of fusion or the heat of sublimation depend on the type of phase existing at the moment of melting or sublimation.

The heat of fusion data reported by [170] were unfortunately obtained on impure fluorine and are not very accurate.

2.11.4 Enthalpy of Vaporization of Liquid Fluorine

The heat of vaporization of liquid fluorine (and any other liquid) is determined most often by the Clausius–Clapeyron equation rather than through direct calorimetric measurements. Data from various sources are summarized in Table 28.

Table 28: Heat of vaporization of liquid fluorine.

Source	Year	Temperature, K	Heat of vaporization		References
			kJ/mol	kcal/mol	
Hu, White, and Johnston	1953	84.71 (at 738 mm Hg)	6.544	1.56398 ± 0.003 ^a	[77]
Claussen	1934	85.21	6.527	1.560	[103]
Cady and Hildebrand	1930	84.93	6.69	1.600	[78]
Aoyama and Kanda	1937		8.24	1.970	[106]
Prydz, Straty, and Timmerhaus	1970	53.481	7.437	1.777	[81]
		60	7.257	1.734	[81]
		70	6.963	1.664	[81]
		80	6.689	1.599	[81]
		84.71	6.555	1.567	[81]
		84.93	6.548	1.565	[81]
		85.03	6.545	1.564	[81]
		85.19	6.541	1.563	[81]
		85.21	6.540	1.563	[81]
		90	6.388	1.527	[81]
		100	6.004	1.435	[81]
		110	5.503	1.315	[81]
		120	4.853	1.160	[81]
		130	3.963	0.947	[81]
		140	2.472	0.591	[81]
		144	0.935	0.223	[81]
Kit & Evered	1960	85.2	6.527	1.560	[171]

^a calorimetric data

2.11.5 Heat of Mixing of Liquid Fluorine

The heat of mixing of liquid fluorine and liquid oxygen is minimal and not measurable. Therefore, the enthalpy of formation of fluorine–oxygen (FLOX) is assumed to be additive without heat of mixing.

2.11.6 Entropy of Liquid Fluorine

Values calculated from spectroscopic data [134, 172], (39.56 ± 0.01 and 39.62 ± 0.02 e.u., respectively) were in good agreement with the calorimetric value (39.58 ± 0.16 e.u.) [77].

The National Institute of Standards and Technology (NIST) WebBook data base gives the entropy of the ideal gas at 1 bar as $202.791 \pm 0.005 \text{ J mol}^{-1} \text{ K}^{-1}$ and the source is a Committee on Data Review value [173]. An alternative value found in the literature is $202.80 \text{ J mol}^{-1} \text{ K}^{-1}$ from the NIST/Joint Army, Navy, Air Force (JANAF) Tables [129]. The entropy of vaporization was calculated to be 18.427 e.u. [174], in good agreement with measured data 18.378 e.u. from [77]. See also [175, 176].

2.12 Molecular Structure of Liquid Fluorine

A better understanding of the molecular structure of gaseous, liquid, and solid fluorine will be useful in predicting thermodynamic and other physical properties of this rocket propellant oxidizer.

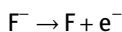
Another method of analyzing the experimental atom–atom pair distribution functions based on the corresponding state principle has been applied to liquid fluorine to explain the large discrepancies found when comparing experimental and simulated molecular interaction forces as a function of intermolecular distance [177]. The microscopic structure of liquid fluorine must be very different from that of other liquid halogens. The interatomic distance of fluorine atoms in the difluorine molecule in the vapor state is $1.435 \pm 0.010 \text{ \AA}$ [178].

Measurements of the neutron scattering static structure factor $S(Q)$ of orthobaric liquid fluorine at 77 K and the atom–atom correlation function were compared with those of other halogens and oxygen [179]. From the $d = f(r)$ pair distribution function it was shown that liquid fluorine has a coordination number of first neighbors more similar to that of liquid oxygen than other halogens. The number of atoms in the first and second coordination shell is in good agreement with a closely packed arrangement of atoms.

2.12.1 Electron Affinity

Because fluorine was thought to be the most electronegative of the elements, along with its high oxidative powers, the electron affinity of fluorine has undergone extensive investigation. This property is important in calculating thermodynamic data for fluorine atoms, ions, and molecules, and, ultimately, calculating the performance of fluorine as a rocket propellant. The tendency to complete the second shell with eight electrons is the driving force for the extreme chemical activity of fluorine (known as the octant rule). This gives fluorine the highest electronegativity, with a potential of -2.85 V , compared with -1.36 V for chlorine and -1.22 V for oxygen. At the first glance, electron affinity appears to be a property of mostly academic interest, but when looked at more closely, it is one of the driving forces behind the reactivity of fluorine and the polarity of chemical bonds in the structure of fluorine compounds.

The electron affinity, E_{ea} , of an atom or molecule is the energy required to detach an electron from a singly charged negative ion such as would occur in the following process:



An alternative definition is the energy released ($E_{\text{initial}} - E_{\text{final}}$) when an electron is attached to a neutral atom or molecule. It should be noted that the sign convention for E_{ea} is the opposite to most thermodynamic quantities: a positive electron affinity indicates that energy is released on going from atom to anion. All elements have a positive electron affinity. Atoms whose anions are relatively more stable than neutral atoms have a smaller E_{ea} . When comparing the electron affinities of the halogens, it is surprising to note that the gradual increase in the group from iodine (295 kJ/mol) over bromine (343 kJ/mol) to chlorine (349 kJ/mol) is disrupted when going from chlorine to fluorine. All of a sudden, the electron affinity drops instead of increasing further. The commonly accepted value for fluorine is 328 kJ/mol . Of all the elements, chlorine most strongly attracts extra electrons.

Table 29 gives a summary of publications on the electron affinity of fluorine that relate to its reactivity in many oxidation reactions.

Table 29: Summary of publications on the electron affinity of fluorine.

Author(s)	Year	Measured data		References
Bernstein and Metlay	1954	344.8 kJ/mol	82.4 kcal/mol	[180]
Bailey	1958	$343.5 \pm 8.8\text{ kJ/mol}$	$82.1 \pm 2.1\text{ kcal/mol}$	[181]
Margrave	1954	$348.1 \pm 1.2\text{ kJ/mol}$	$83.2 \pm 0.3\text{ kcal/mol}$	[182]

2.12.2 Other Thermodynamic Data

Additional physical and thermodynamic properties of difluorine and the fluorine atom and on the electron affinity of the F atom, the refractive index, viscosity, the electrical polarization, and the diameter of the F_2 molecule are described in [140]. That paper also contains data on thermal conductivity and the rate of dissociation of gaseous difluorine.

When designing a rocket engine running on liquid fluorine as the oxidizer, it helps to know the ease of atomization, the rate of evaporation and the mean droplet size of liquid fluorine. These numbers enter into calculations for the necessary L^* of a rocket engine. Next to liquid oxygen, liquid fluorine was one of the propellants that evaporated the fastest [183]. Other propellants investigated in this study were O_2 , $n\text{-}C_7H_{16}$, NH_3 , and N_2H_4 .

The performance of fluorine as a rocket propellant has to be calculated from accurate thermodynamic data for both the reactants and the combustion products. All propellant combinations with fluorine as the oxidizer have HF as a combustion product. In the liquid state under standard conditions at 298 K, HF is associated and its formula is H_2F_2 .

The enthalpy of formation of liquid H_2F_2 was measured using a bomb calorimeter and measuring the heat released during the combustion of H_2 gas in F_2 gas. The standard molar enthalpy of formation of liquid HF ΔH_f° (HF, L) was found to be $-303.56 \pm 0.27 \text{ kJ mol}^{-1}$ at $T = 298.15 \text{ K}$ and $p_o = 101.325 \text{ kPa}$ by direct reaction of gaseous hydrogen and fluorine in a bomb calorimeter [184]. The enthalpy of formation of monomeric ideal gas HF under standard conditions is $-272.5 \text{ kJ/mol} = -65.14 \text{ kcal/mol}$.

2.12.3 Molecular Orbital Calculations of Molecular Structure of Liquid Fluorine

Two difluorine molecules may associate in the liquid state to form a dimer $(F_2)_2$ that affects the density and compressibility of the liquid. Two possibilities for the potential energy surface of the $(F_2)_2$ dimer were constructed on the basis of *ab initio* calculations [185]. The best estimate of the complete basis set limit of interaction energy was derived for analysis of basis set incompleteness errors. The most stable structure of the dimer was obtained at $R = 6.82 \text{ au}$, $\theta_a = 12.9^\circ$, $\theta_b = 76.0^\circ$, and $\varphi = 180^\circ$, with a well depth of $716 \mu\text{Eh}$. Two other minima were found for canted and X-shaped configurations. The quality of potentials was tested by computing values of the second virial coefficient, which was supposed to give a more reasonable agreement with experimental values.

2.12.4 Molecular Orbital Calculations of the Molecular Structure of Solid Fluorine

It is unlikely that solid fluorine will ever be used as a rocket propellant, but the properties of solid fluorine are included here nevertheless because they affect the thermodynamic properties of liquid fluorine. Solid fluorine can exist in two different phases, $\alpha\text{-}F_2$ and $\beta\text{-}F_2$. Physical properties such as the heat of fusion or the heat of sublimation depend on the type of phase existing at the moment of melting or sublimation. $\alpha\text{-}$

Fluorine has a regular pattern of molecules and is a crystalline solid, but its molecules do not have a specific orientation. β -Fluorine molecules have fixed locations and minimal rotational uncertainty, which affects the specific heat. Solid fluorine was reported to undergo a transition at 45.55 K with a heat of transition of 728 J/mol = 173.9 cal/mol.

The equilibrium structure and orientations of solid fluorine were calculated by optimizing a general monoclinic lattice with two molecules per unit cell [186]. In addition to the lattice parameters and orientations, the molar volume, sublimation energy, and gas phase second virial coefficients were calculated. Both the proposed $C2/c$ and $C2/m$ structures were found, for which nearly identical sublimation energies were calculated. The quadrupole moment θ was assumed to be 0.65×10^{-26} esu cm² in this work. Pressurizing solid fluorine up to 100 kbar will not bring about any new phases [187].

One e.u. is 1 cal g⁻¹ K⁻¹. Solid fluorine has a normal entropy of fusion (2.28 e.u. = 9.54 J g⁻¹ K⁻¹ = 362 J K⁻¹ mol⁻¹) and has a first-order solid-state transition at about 8 K below its melting point. This indicates that fluorine probably rotates in the solid state at melting point. The significant structure theory of liquids can be applied to calculate physical and thermophysical properties of liquid fluorine in comparison to better investigated liquids such as liquid nitrogen [174]. This theory is based on partition functions and accurately predicts entropy of vaporization, vapor pressure, density, heat capacity, and surface tension to within $\pm 5\%$. The agreement between calculated and observed properties for fluorine was satisfactory. The largest deviations occurred in the comparisons with the critical point and the heat capacity, both of which involved higher-order differentials of the partition function.

The crystal structure of α -fluorine, stable below 45.6 K, has been investigated from XRD patterns [188]. Alpha fluorine is monoclinic, probably space group $C2/m$, but space group $C2/c$ cannot be ruled out completely. There are four molecules per unit cell. At 23 K, the cell dimensions were found to be: $a = 5.50 \pm 0.01$ Å, $b = 3.28 \pm 0.01$ Å, $c = 10.01 \pm 0.01$ Å, $\beta = 134.66 \pm 0.02^\circ$. The unit-cell volume at 23 K was 128.4 Å³, the calculated density was 1.97 g/cm³ and the calculated molar volume was 19.3 cm³/mol. The structure of solid fluorine is very similar to that of α -O₂, the main difference being that the molecules are tilted, probably only by about 11° to alternate sides of the normal to the basal plane in alternate layers, leading to a doubling of the unit cell in the c direction compared with α -O₂.

A re-interpretation of the XRD powder pattern reported by Meyer, Barrett, and Greer concluded that the space group is $C/2c$, with eight F in the unit cell, cell dimensions $a = 5.50$ Å, $b = 3.28$ Å, $c = 7.28$ Å, $\beta = 102.17^\circ$, with $x = 0.285$, $y = 0.317$, $z = 0.0997$ [189].

Reasonable agreement of the calculated external vibration frequencies for solid α -F₂ with observed Raman and far IR spectra was obtained for the $C2/m$ structure [190]. On the basis of those calculations, an assignment of each Raman and far IR band was made, which was consistent with the observed Raman intensities. However, a unique assignment could not be made for the intramolecular Raman bands.

A molecular dynamics simulation study of the ordered and disordered phases of crystalline F_2 calculated several macroscopic and microscopic equilibrium properties at different temperatures, including orientational probability functions of molecules in both crystalline phases [191]. Dynamical properties were analyzed by calculating several auto- and cross-correlation functions at different temperatures and their characteristic times were given in comparison with several other theoretical models. Similar molecular dynamics simulation techniques were then applied to study the monoclinic and cubic phases of crystalline F_2 [192].

2.13 Optical, Electrical, and Magnetic Properties of Liquid Fluorine

Optical properties can be used to determine the purity of fluorine samples. Absorption spectra provide information on the energy levels and bonding states in the molecule.

2.13.1 Absorption, Emission, and Fluorescence Spectra of Liquid Fluorine

2.13.1.1 UV/Visible Absorption Spectra of Fluorine

The visible and UV absorption spectrum of fluorine gas was determined over the range 2100 to 800 Å [193]. A single broad absorption peak was observed with a maximum molar absorptivity of $6.0 \text{ L mol}^{-1} \text{ cm}^{-1}$ at a wave length of 2845 Å. Beer's law was obeyed over a pressure range of 10 to 100 kPa (80 to 760 mm Hg) pressure. Increasing the temperature to 373 K (100 °C) caused only a slight decrease in the absorption, which was within the experimental error arising from more rapid etching of the cell windows. The absorption at 2845 Å appears to be consistent with the pale yellow color of fluorine, and it falls into place in the trend of the colors of the halogens in the periodic table of elements.

The continuous absorption spectrum of molecular fluorine and the Raman displacement for the $0 \rightarrow 1$ vibrational transition have been used to compute the potential energy curve for the repulsive $^1\Pi_u$ state dissociating to two normal fluorine atoms [147]. This curve was consistent with a value of $37.1 \pm 0.85 \text{ kcal/mol}$ for the dissociation energy of the ground state. A weak absorption, attributed on the grounds of location and intensity to $^3\Pi_0^+ \leftarrow ^1\Sigma_g^+$, has been shown to occur in the long wavelength region of the main absorption and a segment of the potential energy curve for $^3\Pi_0^+$ has been deduced. Absorption curves, calculated from the potential energy curves and the ground-state anharmonic eigenfunctions, matched the observed data satisfactorily.

The absorption spectrum of F_2 has been observed in the vacuum-UV region using a special windowless absorption apparatus and a Lyman discharge light source in combination with a 1-m normal incidence spectrograph [149]. A Rydberg series established the photoionization potential of F_2 as 15.7 eV. From a progression of bands at 874 Å, one can deduce the dissociation energy of fluorine as $156.9 \pm 8.4 \text{ kJ/mol} =$

37.5 ± 2 kcal/mol. The binding energy of F_2^+ is 3.3 eV. The low value of the ionization potential was consistent with the observed low value of the dissociation energy. See also Bresler and Shtilerman [194].

The vacuum-UV absorption spectrum of molecular difluorine has been observed at wavelengths below 1500 Å, at a dispersion of 3.75 Å/mm [144]. Spectra have been observed at pressures from 80 to 600 μm Hg and at temperatures both somewhat below 293 K = 20 °C and at approximately 373 K = 100 °C. Previously observed spectra in the vacuum-UV region have been re-interpreted and extended to a wider range. The spectroscopic determination of the fluorine dissociation energy based on a previously identified progression of bands at 877 Å was used to fix a minimum value for the F_2 dissociation energy of 138.3 kJ/mol = 33.05 kcal/mol. Rydberg series converging to the first ionization potential of F_2 have been established and the current data were compared with those of previous studies in the UV region and data from photoelectron spectroscopy to reinterpret data on F_2^+ . Looking at the binding energies of the “ π ” molecular orbitals, some evidence suggested that participation of the “ π ” molecular orbitals may actually be more important than previously acknowledged.

The absorption spectra of liquid F_2 , NF_3 , N_2F_4 , CF_4 , BF_3 , and SF_6 have been measured at low temperatures in the near UV region of the spectrum [195]. It was shown that the liquid-phase absorption spectra did not differ much from the spectra in the gaseous phase. Therefore, the elementary absorption event was characterized by the cross section of photon absorption by an individual molecule. The absorption cross sections of these molecules were represented in the liquid phase, which did not differ significantly from absorption cross sections of these molecules in the gaseous phase. The dependence of the absorption cross sections of liquid fluorine on its concentrations in solutions in LN_2 , Ar, NF_3 , or LOX at 77 K = -196 °C has been studied.

When the absorption spectrum of molecular difluorine in the spectral range between 200 and 400 nm was re-measured, excellent agreement with the published spectrum above 250 nm was found, but below that wavelength the observed absorption was less than in the earlier measurements [196].

2.13.1.2 Infrared Absorption Spectra of Fluorine

Far IR and Raman spectra of crystalline fluorine have been obtained in both solid phases [197]. As expected for the disordered higher temperature form, only the Raman-active stretching fundamental was observed for β - F_2 . Near ~20 K α - F_2 exhibited the following spectral features (in cm^{-1}): Raman $\nu(1-0)$ 985; $\nu(2-0)$ 1764; ν (libration) 44, 55, 77, (93?); Infrared ν (translation) 28, 42.5, 80. The predictions of a preliminary calculation of the optically active lattice frequencies for the low-temperature phase were in poor agreement with the observed lattice frequencies, suggesting that an improved model might be required to help to distinguish the correct α - F_2 crystal structure. Solid fluorine more closely resembled solid oxygen than it did the other solid halogens. In particular, the intermolecular forces were extremely weak, as exemplified by the small shifts of the internal frequencies from their gas phase values, the absence of observ-

able factor group splitting of the fundamental and the overtone, and the relatively low values of the external (lattice) frequencies.

2.13.1.3 Raman Fluorescence Spectra of Fluorine

The rotational constants of the F_2 molecule in the electronic ground state were determined from the rotational and vibrational Raman spectra of gaseous fluorine at 1 atm [198]:

$$\begin{aligned} B_0 &= 0.8828 \text{ cm}^{-1} \\ r_0 &= 1.4177 \pm 0.001 \text{ \AA} \\ \Delta G_{1/2} &= 891.85 \pm 0.4 \text{ cm}^{-1} \end{aligned}$$

The intensity alternation in the rotational spectrum showed that the nuclear spin of fluorine was $1/2\hbar/2\pi$ and that the ^{19}F nuclei followed Fermi statistics.

The depolarization factors in Raman spectra of gaseous fluorine were measured with laser excitation [199]. The optical systems were able to produce a laser beam free of unwanted emission lines and focus scattered light on the slit and on the detector. The rotational spectrum of gaseous F_2 has been used as an example to determine a rotational constant of $B_0 = 0.8841 \pm 0.0006 \text{ cm}^{-1}$, corresponding to $r_0 = 1.4168 \pm 0.0005 \text{ \AA}$.

A band shape study of the Raman diffusion by liquid fluorine over the temperature range 75–100 K offered an explanation of the molecular reorientation process [200, 201].

The pure rotational Raman spectrum of $^{19}\text{F}_2$ has been recorded photographically with a reciprocal linear dispersion of $1.4 \text{ cm}^{-1} \text{ mm}^{-1}$ and analyzed to yield: $B_0 = 0.88331 \pm 0.00004 \text{ cm}^{-1}$; 10^6 , $D_0 = 3.48 \pm 0.06 \text{ cm}^{-1}$; $r_0 = 1.41744 \pm 0.00006 \text{ \AA}$ [202]. Assuming from earlier work, $B_1 = 0.872 \pm 0.002 \text{ cm}^{-1}$, the following equilibrium constants were obtained: $B_e = 0.889 \pm 0.001 \text{ cm}^{-1}$; $r_e = 1.4131 \pm 0.0008 \text{ \AA}$. These were the most precise values reported for B_0, D_0, r_0, r_e of $^{19}\text{F}_2$ up to that time. The experimentally determined D_0 value was in good agreement with the value calculated from B_0 and ω_0 .

The Raman spectra and phase diagram of fluorine were studied in a diamond-anvil cell at extremely high pressures up to 6 GPa over the temperature range 10–300 K [203]. The sample slowly reacted with the diamond anvils to form CF_4 . The vibron frequencies in $\alpha\text{-F}_2$ and $\beta\text{-F}_2$, as well as the lattice modes in $\alpha\text{-F}_2$, were determined as a function of pressure. No new phases were discovered at the high pressure. The $\alpha\text{-}\beta$ phase boundary could be fit with an equation of the Simon form:

$$P \text{ } \alpha\beta \text{ (GPa)} = -0.385 + 4.80 \times 10^{-4} T_{\alpha\beta}^{1.75} \text{ (K)}.$$

The melting curve was established to lie between limiting curves:

$$P \text{ upper melt (GPa)} = -0.107 + 1.01 \times 10^{-4} T^{1.75} \text{ melt (K)}$$

and

$$P \text{ lower melt (GPa)} = -0.140 + 1.32 \times 10^{-4} T^{1.75} \text{ melt (K)}.$$

2.13.1.4 Photoelectron and X-ray Photoelectron Spectra of Fluorine

Threshold photoelectron spectra and photoionization thresholds of HF, DF, and F₂ were investigated using a simple threshold photoelectron energy selector in the source of a conventional photoionization mass spectrometer [204]. A number of vibronic levels of the HF⁺ and DF⁺ ions, not previously observed by HeI photoelectron spectroscopy, have been detected, from which spectroscopic constants of the molecular ions could be inferred for comparison with recent emission spectroscopy data. The threshold photoelectron spectra showed some complicated structure associated with resonant autoionization of molecular Rydberg states belonging to series converging to the various vibronic levels of the ions.

Diatomic halogens including difluorine were studied with UV photoelectron spectroscopy using new techniques to preserve high resolution even for reactive species [205]. Vibrational structure was observed on the ²Π_{u,i} (*i* = 1/2, 3/2) states of F₂⁺ and Cl₂⁺ and the ²Σ_g⁺ states of F₂⁺ and Cl₂⁺. On the ²Π_{u,i} states (F₂⁺, Cl₂⁺, Br₂⁺) spin-orbit splitting was resolved. Indications for a small potential barrier on the F₂⁺(²Π_{u,i}) state for large internuclear distances were found. The complementary nature of optical emission and photoelectron spectroscopy for small ions was demonstrated, leading to a more complete picture of the F₂⁺(²Π_{u,i}) and Cl₂⁺(²Π_{u,i}) ionic states.

2.13.2 Index of Refraction of Liquid Fluorine

The refractive index (“index of refraction”) of liquid and gaseous fluorine is summarized in Table 30.

Table 30: Refractive index of fluorine.

Physical state	Temperature, K	Refractive index	Wavelength, nm
Liquid fluorine	at normal boiling point	1.20	Na _D
Gaseous fluorine	273	1.000214	589
For comparison:			
Gaseous oxygen	273	1.000403	589
Gaseous nitrogen	273	1.000298	589
Gaseous hydrogen	273	1.000139	589

Data source: [206]

Elementary fluorine possesses the lowest polarizability after He, Ne, and H₂. This indicates a very dense packing of electrons in the shell. These data can also be used to calculate the dielectric constant of liquid fluorine.

2.13.3 Dielectric Constant of Liquid Fluorine

The dielectric constant ϵ can be calculated from the ratio of the capacitance of a filled capacitor cell to that of an evacuated cell. The dielectric constants and molar polarizability of saturated liquid fluorine and compressed liquid fluorine were measured at the NBS in a capacitance cell at 5 kHz and temperatures ranging from the triple point (53.48 K) to the critical point (144.31 K) and pressures up to 21 MN/m² (3045 psia) [207]. Dielectric constant ϵ and molar polarizability P are connected through the Clausius–Mossotti equation where

$$P = [(\epsilon - 1)/(\epsilon + 2)] \times \rho^{-1}$$

is nearly independent of density ρ . The molar polarizability is found to increase initially with density and then decrease. Current theories of the dielectric constant are thought to give satisfactory qualitative interpretation of the density dependence of the molar polarizability, but lack quantitative accuracy. Measurement of the molar polarizability offers a convenient method for determining the density of propellants in the laboratory as well as in the tanks of flight vehicles. The dielectric constant drops off very steeply as the temperature approaches the critical point (Table 31 and Figure 15).

Table 31: Dielectric constant of saturated liquid fluorine.

Temperature			Dielectric constant	Molar polarizability cm ³ /mol
K	°C	°F		
53.48	-219.62	-363	1.4913	3.1363
70	-203	-333	1.4577	3.1385
80	-193	-315	1.4362	3.1389
90	-183	-297	1.4136	3.1397
100	-173	-279	1.3895	3.1408
110	-163	-261	1.3631	3.1423
120	-153	-243	1.333	3.1442
130	-143	-225	1.2959	3.1461
140	-133	-207	1.2398	3.1473
141	-132	-206	1.2311	3.148
142	-131	-204	1.2208	3.1484
143	-130	-202	1.2073	3.15
144.31	-128.84	-200	1.1498	3.1500 (extrapolated)

Data source: [207]

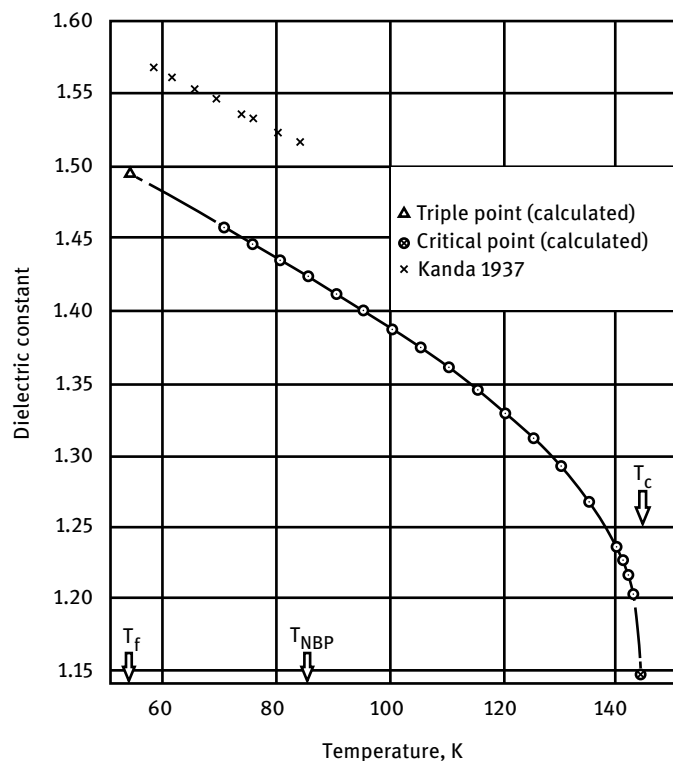


Figure 15: Dielectric constant of saturated liquid fluorine. (Reprinted and modified from [207], with the permission of © 1972 AIP Publishing; permission conveyed through RightsLink.)

The data are lower, but much more accurate than those reported earlier by [170]. The data by Kanda were eliminated from the current book.

The molecular polarizability of liquid fluorine is $1.242 \pm 0.001 \text{ \AA}^3$. The dielectric constant of liquid fluorine at its normal boiling point was calculated from gaseous fluorine refractive index data as $\epsilon = 1.43$, compared with $\epsilon = 1.48$ for liquid oxygen or $\epsilon = 1.45$ for liquid nitrogen [206].

2.13.4 Magnetic Properties of Liquid Fluorine

2.13.4.1 NMR Spectra of Fluorine

Direct comparisons between ^{19}F nuclear magnetic resonance (NMR) spectra of liquid and gaseous F_2 , OF_2 , and NF_3 had not been reported prior to 1966 [208]. Previous publications listed the chemical shift of F_2 gas as -414 ppm (in relation to CFCl_3) and -422 ppm (in relation to SF_6). The chemical shifts of liquid and gaseous F_2 , OF_2 , and NF_3 are listed in Table 32.

Table 32: ^{19}F NMR shifts in liquid and gaseous F_2 , OF_2 , and NF_3 .

	^{19}F NMR Shifts ^a		
	F_2 (ppm)	OF_2 (ppm)	NF_3 (ppm)
Liquid at 77 K	-422 ± 1	-249 ± 1	-142 ± 1
Gas	-419 ± 1	-248 ± 1	-138 ± 1
Difference gas – liquid	3	1	4

^a CFCl_3 reference.

Data source: [208]

As can be seen in Table 32, the chemical shifts for liquid F_2 , OF_2 , and NF_3 were all lower than the corresponding shifts in the gas. This downfield shift due to liquefaction is similar to that observed in the proton magnetic resonance studies of the first-row hydrides.

3 Chemical Properties of Fluorine

Fluorine is a pale yellow, corrosive gas, which reacts vigorously with many organic and inorganic substances. Otherwise inert materials, such as finely divided metals, glass, carbon, and even water, can burn in fluorine with a bright flame. This reactivity makes the selection of materials of construction a very difficult task. The free element has a characteristic pungent odor, detectable in concentrations as low as 20 ppb, which is below the safe working level. The recommended maximum allowable concentration for a daily 8-ho time-weighted exposure is 1 ppm (see Section 8 on the toxicity of fluorine).

The family of fluorine (fluoride) compounds can be categorized by the type of bond. Most fluorides have an ionic bond, whereas all fluoroorganic compounds have covalent C–F bonds. Non-metallic fluorine compounds have transitions between strongly polarized and covalent bonds.

Fluorine is the most reactive of all elements. There are only a few compounds or elements it does not react with. Even with some of the so-called noble gases it forms fluoride compounds, challenging the nobility of these elements. Reactions with sulfur, phosphorus, or selenium start at cryogenic temperatures, whereas oxygen and nitrogen cannot be made to react with fluorine at room temperature and it requires activation by UV irradiation or a glow discharge.

For the production of compounds such as oxygen difluoride OF_2 and nitrogen trifluoride NF_3 , methods are required other than direct synthesis from the elements. Alkali and alkaline earth metals (except magnesium) ignite in fluorine spontaneously and combust with the formation of saline metal fluorides. Fortunately, many metals, in particular those intended as materials of construction for fluorine apparatus, are

protected from further attack by formation of a protective coating of metal fluorides. This is called a passivation film. Inadvertent scratches in the passivating layer or flaking of the protective coating on bending of the metal may be the points of initiation of renewed, sometimes catastrophic reactions of fluorine with the metal. Corrosion by fluorine and recommended methods of passivation and corrosion prevention are discussed in more detail in Section 4.1.

Non-graphitized carbon (activated charcoal), which reacts with chlorine only at elevated temperatures, reacts with fluorine at room temperature in a spectacular display of sparks with a bright flame. This reaction, when conducted in a controlled manner, can be used for the disposal of excess fluorine. Most hydrogen-containing compounds react with fluorine spontaneously and ignite hypergolically, a desirable property for rocket propellant applications. This reactivity is often explained by pointing to the high enthalpy of formation of HF and the high affinity of fluorine to hydrogen. The hydrogen abstraction from hydrocarbons or hydronitrogens is one of the fastest reactions. Other text books try to explain the hypergolicity of difluorine with hydrogen compounds by stating that difluorine readily dissociates into atomic fluorine and that fluorine atoms as free radicals start chain reactions. Even at room temperature there are sufficient free radicals of atomic fluorine in a mixture with fluorine gas to start a chain reaction. Most covalent single bonds of fluorine with other elements are very strong bonds compared with the F–F bond in F₂. The low molecular mass and the high rate of diffusion of difluorine contribute to high global reaction rates. Only few fluorine reactions are kinetically or diffusion limited. Chlorine fluorides such as ClF and ClF₃ are also very reactive with most hydrogen compounds, some even more so than F₂ itself.

Summaries on fluorine chemistry and fluorine compounds such as those listed in Tables 1 and 3, including Haszeldine and Sharpe [42], Simons [43], Slessor and Schram [44], provide additional information, and on the history of fluorine chemistry [41, 209].

3.1 Reactions of Fluorine

Fluorine is one of the most reactive chemicals in the inventory and it reacts with just about everything except element fluorides in their highest state of oxidation. The reactivity of fluorine makes it difficult to find materials of construction that are compatible with fluorine in the liquid and/or the gaseous state. Accidental ignition of materials in fluorine has been the cause of many accidents. Most of the experience in reactions and handling of fluorine was gained in the nuclear industry, where uranium hexafluoride is used for isotope separation, and not in the aerospace industry. Additional experience was gained when fluorine was used in chemical lasers.

Instead of writing a chapter on all the chemicals that react with fluorine, it would be easier to write on the few chemicals that don't react with fluorine.

3.1.1 Reactions of Fluorine with Elements

3.1.1.1 Reactions of Fluorine with Hydrogen

A later set in this series, *Hypergolic Combinations*, will contain a detailed discussion of the reactions of fluorine with hydrogen and deuterium as they are applied to rocket propulsion and chemical lasers.

Apparently early on in the development of fluorine chemistry there was a dispute about the interpretation of reactions of liquid hydrogen with solid fluorine as interpreted by Dewar, Eyring, and eventually, Aoyama and Kanda, and the experiments were repeated with different results [210]. An attempt was made to solve the disagreement between the results of Moissan and Dewar [211], who reported the occurrence of an explosion when a test tube with solid fluorine was immersed in liquid hydrogen and fractured, and the results reported by Wartenberg and Taylor [212] or Eyring and Kassel [213] who failed to reproduce this reaction. With a 10-mm glass tube containing 1 mL of liquid fluorine, a slight explosion occurred, and flames appeared on the surface of the hydrogen. It was suspected that sunlight might initiate the reaction, but that was not confirmed by performing the test under a mercury UV lamp. The results are not in line with earlier suggestions that any explosion results from the presence of organic matter, e. g., rubber. A mixture of the two gases hydrogen and fluorine failed to explode at ordinary temperature either in sunlight or under the influence of a Hg lamp.

3.1.1.2 Reactions of Fluorine with Boron

Once ignited, boron burns in fluorine with a bright green flame, forming boron trifluoride, a gaseous combustion product. Thus, it does not have the same handicap with condensable exhaust species as aluminum combustion in oxygen.

Fluorine/boron combustion experiments were carried out with both single-crystal and polycrystalline boron rods to determine the regression rate of the boron surface. For single-crystal boron fluorination in the 0.1 to 1 mm Hg region, the data indicated a reaction that was independent of fluorine pressure up to about 600 K. At around this temperature there was a change in the rate-limiting process and the rate increased with fluorine pressure [214–216]. Such combinations could be used in a hybrid rocket engine. Rocket propellant performance calculations of fluorine/boron and fluorine/boron hydrides will be presented in future sets of the *Encyclopedia of Rocket Propellants*.

3.1.1.3 Reactions of Fluorine with Aluminum

Once ignited, aluminum burns in fluorine with a bright white flame, forming aluminum trifluoride.

Aluminum particle combustion in fluorine-containing atmospheres is significantly different from aluminum particle oxidation in air or oxygen. The most notable difference between the Al-O and Al-F systems is that the analog to slag-forming

liquid $\text{Al}_2\text{O}_3(\text{L})$, liquid aluminum trifluoride $\text{AlF}_3(\text{L})$, does not exist. AlF_3 is the principal product species of the Al-F system. AlF_3 is solid at room temperature and sublimates to gaseous AlF_3 and its dimer, Al_2F_6 , at 1550K. The heats of formation of $\text{AlF}_3(\text{S})$ and $\text{AlF}_3(\text{G})$ are -361 and -298 kJ/mol respectively. Because most of the heat of combustion is evolved directly by the formation of gaseous AlF_3 , the flame temperature is not limited by the sublimation characteristics of AlF_3 . Owing to the absence of any condensed-phases at temperatures above 1550 K, aluminum particle combustion in fluorine would be similar to fuel droplet combustion. Aluminum particle combustion was studied in SF_6 and mixtures of SF_6/O_2 and SF_6/Ar [217]. Although SF_6 is used more often as a torpedo propellant than as a rocket propellant, some of the metal/fluorine interactions can be studied with this less corrosive and less toxic fluoride.

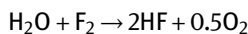
See also Section 4.1.9 on passivation of aluminum metal in gaseous fluorine.

3.1.2 Reactions of Fluorine with Inorganic Compounds

Fluorine bomb calorimetry has developed as a mature technology to determine the heats of formation of a wide range of inorganic and organic compounds [218]. The ultimate products of such calorimeter reactions are HF and CF_4 , besides N_2 and O_2 .

3.1.2.1 Reactions of Fluorine with Water

In looking for chemicals that are in abundant supply and that can be used to destroy and neutralize excess fluorine, the first choice would be water. However, fluorine does not react with water at room temperature. The reaction with water starts only at elevated temperatures and is often inhibited [219]. Once started, the reaction can proceed explosively [220–222]. The reaction of fluorine with water



is highly exothermic. When combining the reactants at 308 K (35°C) and 5.3 kPa (40 mm Hg), the gas phase reaction is very slow and its progress is barely measurable [223]. Studies of diffusion flames and premixed flames of fluorine with hot water vapor (steam) showed that the ignition boundaries of the mixture are at 19 and 95 mol-% F_2 (at an initial temperature of 373 K = 100°C and sea-level atmospheric pressure of 1 atm) [224]. Pure fluorine and steam can be premixed at atmospheric pressure without ignition. The mixture did not autoignite under these conditions, but once ignited, a flame would be sustained in the upward direction. The maximum flame speed was 810 ± 10 cm/s and was obtained with a mixture containing 47.5 mol-% fluorine and 52.5 mol-% steam (Figure 16).

Similar flames are formed with oxygen difluoride and steam [225].

If the electrolyte from which fluorine is made by electrolysis is not kept meticulously dry and free of water, some of the fluorine will evolve as OF_2 instead of F_2 .

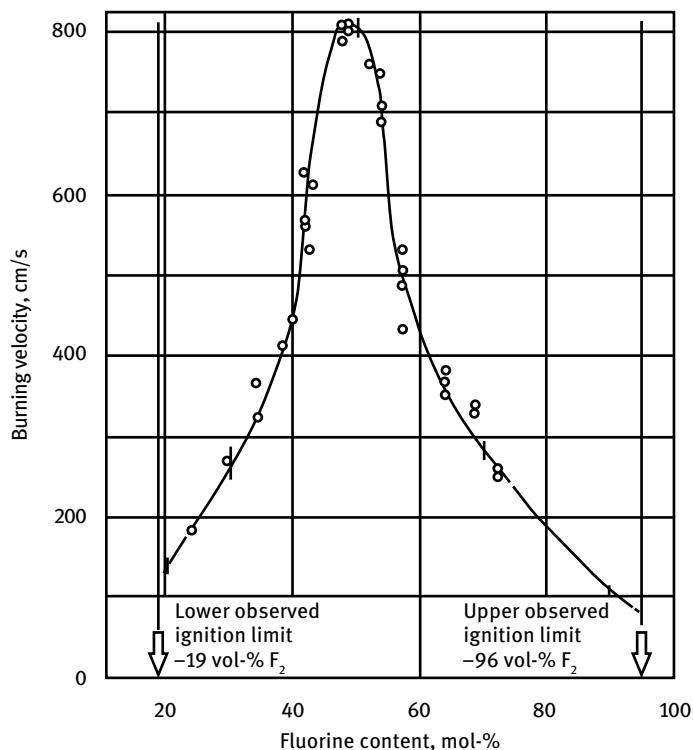
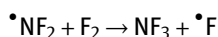


Figure 16: Ignition limits and burning velocity of fluorine-steam flames. (Reprinted and modified from [224], with permission from © 1962 Elsevier; permission conveyed through RightsLink.)

3.1.2.2 Reactions of Fluorine with Tetrafluorohydrazine

The rate of the exothermic free radical reaction



has been directly determined by measuring the disappearance of fluorine and the initial rate of NF_3 formation in the temperature range 1100 to 1600 K by means of a shock tube coupled with a TOF mass spectrometer [226]. The Arrhenius expression

$$k_a = 4.8 \times 10^9 \exp(-14400/RT) \frac{\text{mol}}{\text{s}}$$

was obtained for the rate constant, which, when extrapolated ($\sim 10^7$) to near room temperature, is in reasonable agreement with corrected data. The dissociation of fluorine in neon was also studied in the temperature range 1400 to 2000 K where $k_{\text{F}_2} = 2.0 \times 10^{10} \exp(-35000/RT) \text{ mol/s}$ was an Arrhenius fit to the data.

Fluorine reacts with most other compounds spontaneously at room temperature and those that don't, sometimes need a little help in the form of an electric discharge or UV illumination or high temperature and high pressure. In some cases this may lead to compounds in higher states of oxidation, but in the case of NF_3 it did not work for the synthesis of NF_5 , which would be a desirable rocket propellant if it could be made and stabilized [227].

3.1.2.3 Reactions of Fluorine with Carbon Monoxide and Carbon Dioxide

The reaction between carbon dioxide and fluorine at 303–523 K under various pressure and mixture ratios of both gases forms mixtures of CF_3OF , COF_2 , CF_4 , and $\text{CF}_2(\text{OF})_2$ [228]. The best yield of COF_2 was 11.1% under the reaction condition of $\text{CO}_2/\text{F}_2 = 76 \text{ kPa}/76 \text{ kPa}$ at 498 K for 72 h in a direct reaction.

Attempts to obtain a clean stream of COF_2 by direct fluorination of carbon monoxide with elemental fluorine or by electrochemical fluorination were wrought with problems because the reaction is highly exothermic, difficult to control, and can easily develop into a thermal runaway situation [229]. Under fuel-rich conditions the main product is COF_2 , together with the unreacted carbon monoxide but an excess of fluorine, leads to perfluoro-methyl-hypofluorite (CF_3OF) along with the main product. Performing the reaction in a stainless steel parallel channel microreactor succeeded in controlling the exothermic reaction. Under the same experimental conditions a full-scale reactor suffered serious corrosion that led to nozzle meltdown, lack of selectivity, and frequent plant shutdowns.

3.1.3 Reactions of Fluorine with Organic Compounds

Under uncontrolled conditions, most reactions of fluorine with organic compounds will cause bursting into flames and the final products are tetrafluoromethane and HF. Under carefully controlled conditions, usually working with highly diluted fluorine or at low temperatures, it is possible to fluorinate organic compounds selectively and thus make them more resistant to environmental effects.

Of all the single bonds formed by carbon, the strongest is the one with fluorine, which therefore occupies a special place as a substituent in organic chemistry. Despite this, knowledge of organic fluorine compounds accumulated more slowly in the early years after fluorine discovery than inorganic reactions.

Numerous pharmaceutical medicines carry one or several fluorine atoms in specific locations, thus enhancing their selectivity and healing activity. It has been estimated that 20% of all pharmaceutical drugs and 30% of all agrichemical products on the market contain fluorine. If elemental fluorine was used, the number of fluorine atoms added and their locations would be hard to control. Selective fluorinations are now possible with nucleophilic reagents used to form C–F bonds [230]. These

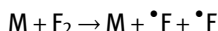
selective fluorination agents include diethylaminosulfur trifluoride, 2,2-difluoro-1,3-dimethylimidazolidine, *N*-fluorobenzenesulfonimide, and bis(2-methoxyethyl) aminosulfur trifluoride. These reagents transform alcohols into monofluorides and carbonyls into *gem*-difluorides. This is an example where military, nuclear, and space technology of fluorine chemistry has resulted in peaceful benefits to humankind at large by allowing the synthesis of more effective medicines [231].

Fluorine gas will react even with perfluorinated organic C_{>2} compounds, leading ultimately to CF₄ as the only stable end product. Attempts to extinguish fluorine-supported fires with a halocarbon-13B or -114B2 fire extinguishant such as those used on electronic equipment and high-value museum pieces would be futile.

Accidental ignition can occur in refrigeration equipment if the leaking refrigerant comes into contact with leaking fluorine. Interactions of coolants CFC-114, cyclo-C₄F₈, or C₄F₁₀ and fluorinating agents such as F₂ or ClF₃ were studied in an effort to determine if a particular mixture can sustain and propagate a flame if ignited, and what the maximum pressure generated by the burning (and possibly exploding) gas mixture might be [232]. Experimental data on such systems are limited, and therefore it was attempted to predict potential detonation pressures and the composition limits of flammability for these systems.

3.2 Pyrolysis of Fluorine

The rate of dissociation of molecular fluorine has been determined in the presence of argon in the temperature range 1300–1600 K by spectrophotometrically observing the disappearance of molecular fluorine behind shock waves in a shock tube [233]. Dissociation rate constants for the reaction



were determined in 5, 10, and 20% F₂ in Ar mixtures. In the 5% mixtures the result may be summarized by

$$\log k_D = 9.85 - \frac{6520}{T}$$

where $\log k_D$ is the rate constant in L mol⁻¹ s⁻¹ and T is the temperature in kelvin, which corresponds to an apparent activation energy of 30 ± 4 kcal/mol. The recombination rate constant calculated from the above value is only about one-tenth as large as the corresponding constant for I₂, Br₂, Cl₂, and H₂, all of which are roughly equal. Fluorine may be somewhat more effective than argon as a third body.

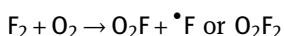
3.3 Photolysis of Fluorine

The reactivity of difluorine is often ascribed to the measurable percentage of fluorine atoms already present at room temperature. Although some reactions of difluorine, such as the reaction with dihydrogen, are inhibited at room temperature, they may get initiated by a flash of short-wavelength light from a flash bulb or a spark discharge [234]. Such initiators are required to get the reactions in a chemical F_2/H_2 or F_2/D_2 laser started. The absorption spectra and the light-induced dissociation are of interest for the participation of F_2 in chemical lasers.

The photolysis of fluorine has been investigated extensively because the photolysis of fluorocarbons in the upper atmosphere is contributing to destruction of the ozone layer. The recombination of fluorine atoms is one of the sinks for fluorine atoms. The reversal of that recombination is the photolysis (photodissociation) of difluorine. The photolysis reaction is also of interest for the reaction kinetics of chemical lasers with fluorine as the oxidizer.

The fluorine photodissociation dynamics in the first absorption band was completely characterized by detection of atomic fluorine using resonantly enhanced multi-photon ionization [235]. Jet-cooled parent molecules were excited into the repulsive $A^1\Pi_u$ state by a $3\sigma_u \leftarrow 1\pi_g$ electronic transition at 234 nm. Different intermediate excited states of atomic fluorine were observed between 126500 and 128500 cm^{-1} in a (3+1) ionization process.

Ultraviolet illumination of mixtures of fluorine with other elements (O_2 , N_2) or compounds (ClF_3) is one method of getting reactions started. The first step in these photochemical reactions is the photodissociation of difluorine, forming fluorine atoms. This is usually done with short wavelength light, but it can also be done in the visible and red spectral range. A search has been made for new, low-energy pathways of the reaction



through excitation of F_2 or O_2 in an oxygen matrix with red and near infrared photons [236]. By monitoring the product yield as a function of laser irradiation frequency, a reaction excitation spectrum of $O_2 + F_2$, which began at 14500 cm^{-1} , was recorded, and extended through the entire red spectral range. It revealed two discrete absorptions $O_2^1\Sigma_g^+, \nu' = 1 \leftarrow {}^3\Sigma_g^-, \nu'' = 0$ and $(O_2)_2(^1\Delta_g, ^1\Delta_g)0,0 \leftarrow ({}^3\Sigma_g^-, {}^3\Sigma_g^-)0,0$, and a continuous, oxygen-enhanced absorption of F_2 , which was assigned to excitation to the repulsive part of the weakly bound ${}^3\Pi_0^+{}_u$ state. The F_2 absorption detected in this experiment extended more than 200 nm to longer wavelengths than any electronic absorption of molecular fluorine reported so far.

3.4 Analysis of Fluorine

In order to determine the assay of a sample of liquid fluorine, the sample has to be evaporated first and the gas can then be analyzed by several methods. If there is a non-volatile residue (most likely consisting of corrosion products), it has to be analyzed separately.

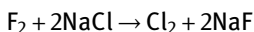
The purity of fluorine that was procured as a rocket propellant for the US Air Force (USAF) was defined by Military Specification MIL-P-27405, which was only circulated as a draft and apparently never formally issued [237]. The proposed F_2 assay was 99 vol.-% min. The maximum allowed sum of CO_2 and CF_4 was 0.2 vol.-% as determined by IR spectrophotometry and the maximum allowed sum of $O_2 + H_2$ was 0.8 vol.-% as determined by gas chromatography. The nuclear industry may have had a different specification.

Additional information on the analysis of fluorine, HF and other fluorine compounds is summarized in [238–240].

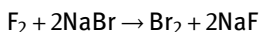
A program was undertaken to develop, evaluate, and deliver a liquid fluorine sampler as a part of a coordinated effort to develop the component technology and ground support equipment required to meet potential requirements for high-energy rocket propulsion systems [241]. The program demonstrated the capability to take liquid fluorine samples, separate particulate from the fluorine sample, using a filter integral with the liquid fluorine sample chamber and provided both volatile and non-volatile particulate samples.

3.4.1 Volumetric Methods for the Analysis of Fluorine

A traditional method for analysis of fluorine mixtures with other gases is to pass the sample over a bed of alkali metal halogenide (other than fluoride) powder to liberate a stoichiometric amount of the other halogen which can then be determined by conventional wet chemistry titrimetric methods [60]:



or



The older halogen conversion analysis method by [60] was quite complicated and time-consuming. It was based upon the reaction of HF with sodium fluoride, the conversion of fluorine to chlorine by reaction with sodium chloride, and analysis of the chlorine for oxygen and inert gases by standard methods. The over-all error in fluorine purity by this method was supposed to be less than 0.4%.

A faster method may be the gasometric assay of fluorine by reaction with mercury. There are two mercury methods in the literature, one with boiling mercury [242] and one operating at room temperature [243] and [244]. The apparatus for the latter method

consists of a 500-mL three-necked round-bottom glass flask with a separatory funnel containing mercury, a glass-covered magnetic stirring bar and a stirring motor with a magnetic coupling. The flask is connected to a sampling train which also carries a U-gauge separated by a shut-off valve, a fluorine inlet valve, an oxygen (or air) inlet valve and a NaCl tube to destroy (convert) excess fluorine. The apparatus must be passivated with dry fluorine gas for at least 16 h prior to its first use. It is difficult to find an inert fluid for the U-gauge manometer. One might use mercury protected by a layer of perfluorinated oil, but it is difficult to keep a clean mercury meniscus. The internal volume of the system must be known very accurately prior to the test. At the beginning of the analysis, one admits fluorine to the apparatus, equilibrates the pressure, shuts of the vent valve, admits 10 mL of mercury to the flask and begins stirring. The stirring is continued until the freshly formed mercury surface remains shiny and the formation of mercury fluoride ceases. The remaining non-reactive gas is admitted to an evacuated manometer system and the residual pressure is determined. The method has also been used for the analysis of oxygen/fluorine mixtures. Oxygen does not react with mercury under the conditions of this test. One can also use a smaller apparatus [169].

3.4.2 Gas-Chromatography Methods for the Analysis of Fluorine Compounds

Nowadays gas analysis can be performed faster and more accurately by gas chromatography. Of course all off-the-shelf GC equipment has to be modified to make it compatible with corrosive gases such as fluorine [245, 246] and other volatile fluorides [247].

Poly(trifluoromonoethylen) oils were used as stationary phases after chemical stabilization [248]. Plasticizing halogenated polymers with halogenated oils created useful stationary phases for column packing [249], and many of those gas chromatography methods involved the separation of reactants in uranium isotope separation plants with UF_6 [250]. In this method, one or several chemical “precolumns” were placed in series with a gas–liquid chromatography (GLC) column. The “precolumn” system retained or destroyed the corrosive compounds (UF_6 , HF, F_2) and the chromatography column separated the components formed.

Another method of analysis of fluorine/oxygen mixtures reacts the gas first with NaCl to form Cl_2 and then analyzes the gas mixture using GLC. It can also be used for the analysis of FLOX [251]. A similar instrument was described in [252]. The electrolysis of wet HF or wet $\text{KF} \cdot \text{HF}$ may produce some ozone as a contaminant in the gas. The ozone concentration in fluorine or oxygen difluoride can be measured by gas chromatography [68]. See also Million et al., [253, 254], Pappas and Million [255], and De Grazio and Auge [256].

The separating efficiency of column packings depends on the viscosity of the stationary phase and its affinity to the fluorides to be analyzed (F_2 , HF, UF_6) [257].

An in-line gas chromatograph made entirely of materials that are corrosion-resistant against fluorine and fluorides has been constructed using two different columns and an automatic sampling system [258]. The separation columns were optimized for a simulated process of gas composition containing N_2 , O_2 , F_2 , and UF_6 , in order to obtain complete peak separation. The column selected for UF_6 analysis was Cu tubing measuring 0.4 cm in diameter, tubing measuring 3 m long packed with 40% poly-trifluoromonochloroethylene oil on poly-tetrafluoroethylene powder. The column for F_2 analysis was a combination of this column with a conversion column packed with KCl powder. Under these conditions, the retention time was 9 and 3 min. for UF_6 and F_2 respectively at a carrier gas flow rate of 100 mL/min. The calibration curves were linear with a zero intercept, and the detection limits were 0.2 and 1 mm Hg in partial pressures of UF_6 and F_2 respectively with a 10-mL sampling volume.

The concentration of F_2 in gas mixtures such as those fed to excimer lasers can be determined by passing the mixed gas through a column packed with an alkali metal oxide or alkaline earth metal oxide, which has no halogens and reacts with F_2 to form a solid fluoride together with molecular O_2 and/or CO_2 and measuring the concentration of O_2 and/or CO_2 in the non-corrosive outflowing fluorine-free gas [259]. If the mixed gas contains molecular O_2 and/or CO_2 to start with, its concentration must be measured separately after fixing F_2 in another column packed with an element, which forms a fluoride. This analyzing method can be used in a feedback closed-loop control system for controlling the concentration of F_2 in the gas fed to an excimer laser during operation of the laser to stabilize the laser output power.

For continuous monitoring of the fluorine purity, a gas chromatographic method with series parallel connection of nine columns with two temperature-conditioned ovens was developed [260]. The corrosion problems have been solved. The fluorine purity and the concentrations of impurities in the fluorine gas can be measured accurately by this method.

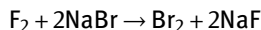
Fluorine produced by electrolysis usually contains impurities such as nitrogen, HF, and carbon tetrafluoride. The carbon tetrafluoride content can be determined by GLC after replacing chlorine in sodium chloride using fluorine and absorbing the chlorine in aqueous NaOH solution [261].

3.4.3 Spectrophotometric and Colorimetric Methods for the Analysis of Fluorine Mixtures

Other methods for instantaneous analysis of gaseous fluorine/oxygen mixtures, such as those formed by evaporation of FLOX, are based on UV-spectrophotometric analysis of the gas mixture flowing through a Teflon[®]-coated flow-through absorption cell from stainless steel with CaF_2 windows. The instrument was light-weight and portable and was intended to be used right at the rocket test site. Prior to the first use, a calibration series had to be run with a series of gas mixtures with known fluorine content. This

instrument was developed by the Astronautics Division of the General Dynamics Corporation.

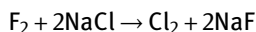
Another continuous spectrophotometric analysis instrument was based on the reaction of fluorine with sodium bromide at 503 K (230 °C) [262],



converting fluorine into a stoichiometric amount of bromine. The gases were then passed over a bed of NaF, which was intended to absorb HF, which otherwise would etch and opacify the windows of the spectrophotometer cell in which the bromine concentration was measured by light absorption at 435 nm. The accuracy in the range from 30 to 40 vol.-% fluorine was only $\pm 3\%$ relative. In the range from 0 to 30 vol.-% fluorine it was $\pm 1\%$ relative. A similar instrument that operated at 423 K (150 °C) measured the bromine concentration at 425 nm with an accuracy of 0.5% for fluorine contents from 0 to 10% [263].

Although fluorine can be recognized by its pungent odor at very low concentrations (~2 ppm), instrumented air surveillance is necessary at all rocket test sites using fluorine oxidizers in order to detect leaks at an early stage. In consideration of the toxicity, the fire hazard, and the corrosive damage caused by fluorine, it is necessary to analyze the air in and around rocket test sites during and after rocket engine tests for traces of fluorine and HF. Several instruments were developed specifically for this purpose. One was a modification of an existing pump colorimeter called Mini-Adak [264]. The reagent was the intensely colored complex of iron(III) with ferron, which becomes colorless in the presence of fluoride. Ferron is 8-hydroxy-7-iodo-quinoline-5-sulfonic acid. The full range of the instrument was 0.1 to 200 mg fluoride/m³. Similar instruments had been used for the analysis of HF in flue gas of aluminum smelters and phosphate fertilizer plants.

An automatic analyzer has been developed for the continuous determination of elemental fluorine in gas mixtures [265]. As the sample stream is passed through hot sodium chloride, the fluorine quantitatively liberates elemental chlorine according to



the light absorption of which was measured at 360 nm in a pressure-controlled flow colorimeter cell. Some chlorine was adsorbed by sodium chloride below 473 K (200 °C), introducing a response lag and some error. The range of the analyzer, calibrated with standard fluorine/nitrogen mixtures, was 0.05 to 15 mol.-% F₂, using a 10-cm cell at a pressure of 500 mm Hg. The relative standard deviation of the fluorine analyzer was about $\pm 1.5\%$ above 0.8% fluorine, and the standard deviation was about ± 0.04 (absolute) at lower levels. Initial response lag was 6 s, with full response in about 1 min. This method is applicable in the presence of HF and other gases that do not absorb radiation near 360 nm or liberate chlorine from sodium chloride.

A continuous fluorine–HF analyzer was developed that was designed to monitor fluorine gas mixtures containing between 0 and 50% F₂, the best accuracy being in the

range from 4 to 30% F₂ ($\pm 5\%$ relative) [266]. The length of time a given sample could be monitored was less than 5 min.

3.4.4 Gas Detection Tubes and Lapel Monitors for the Detection of Fluorine in Work Room Air

For quick spot checks for fluorine or HF in air one can use colorimetric gas test tubes, such as those offered by Draeger or MSA. The HF tube uses a zirconium–alizarin dye supported on silica gel granules that changes color in the presence of HF. The Draeger fluorine gas detection tubes are sensitive to as little as 0.1 ppm F₂ and can measure up to 2 ppm F₂ with ten strokes (Table 33).

Table 33: Draeger fluorine and hydrogen fluoride gas detection tubes.

Tube designation	Concentration range	Draeger part number
Fluorine 0.1/a	0.1–2 ppm	81 01 491
Hydrogen fluoride 0.5/a	0.5–90 ppm	81 03 251

Data source: <http://www.draeger.com/sites/assets/PublishingImages/Products/tubes-for-short-term-measurements/US/tubes-accuro-pump-pi-us.pdf>

It would be convenient to have lapel-mounted badges that immediately change color if exposed to hazardous fluorine concentrations. Similar badges and portable detectors were evaluated for other volatile fluoride rocket propellants [267].

3.4.5 Electrochemical Methods for the Analysis of Fluorine in Air

In order to analyze fluorine by electrochemical methods, it first has to be converted to fluoride by absorption in alkaline water. An electrochemical fluoride analysis method was developed based on the electrochemical potential of a cell:



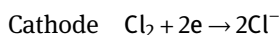
In the presence of fluoride, the concentration of free aluminum ions decreased and the potential across the electrodes changed proportionally [268]. Other instruments were based on the same electrochemical principle.

A portable continuous analyzer for gaseous fluorides in industrial environments responded to all substances that formed fluoride ions in aqueous solution and was specific to fluoride in the presence of common air contaminants [269]. The range of the instrument was 0.1 to 10 mg of fluoride per liter of air, with a higher upper limit available through proper selection of air and solution flows.

The instruments can be miniaturized to fit in a shirt pocket as personnel monitors [270].

These instruments would probably respond to the presence of free elementary fluorine as well, but not in a reproducible manner. Instruments capable of analyzing free fluorine would take advantage of the strong oxidizing power of this element. Most of these would also respond to chlorine or ozone and may thus not be specific to fluorine. Monographs on air pollution contain detailed chapters on analysis of F_2 and HF in the air [271].

Measurements of fluorine dispersion in the atmosphere during a liquid fluorine spill test in a remote area were made using an electrochemical method initially developed for ozone measurement. In this instrument, air containing oxidant (O_3 or F_2) oxidizes the iodide ion in a buffered KI solution in a cell containing platinum and silver electrodes [272]. The iodine formed is reduced at the silver cathode. Insoluble AgI is produced on the cathode so that the iodide is removed from the reaction. This system was made specific to fluorine by substituting LiCl for the KI solution. Atmospheric pollutants do not affect the salt. Fluorine, however, oxidizes the chloride ion, which undergoes the following electrode reactions:



For every molecule of fluorine, two electrons flow through the coulometric circuit and two atoms of chlorine are transferred from solution to cathode. Hence, the current generated may be calculated to be $0.14 \mu A$ times the flow in $mL \min^{-1} ppm^{-1} F_2$ in the atmosphere. This current was easily measured when the flow rate was between 100 and 300 mL/min.

A HF/DF detector was developed to monitor the atmosphere in the vicinity of chemical laser testing to ensure that the scrubbers are working properly and warn adjacent facilities if combustion products or unburnt propellant should escape accidentally [273]. The system uses a continuous impinger and a fluoride ion-selective electrode. The apparatus is portable and it takes only 5 min to set it up in the field and calibrate it.

3.4.6 Other Methods for the Analysis of Fluorine in Air

A prototype detector for atmospheric fluorine and HF using radiochemical exchange of kryptonates was developed and evaluated [274, 275]. The instrument utilized silicon kryptonate for the detection of HF and hydroquinone clathrate for the detection of elemental fluorine. The instrument was capable of simultaneously detecting HF at concentrations of 0–50 ppm by volume and fluorine at 0–10 ppm by volume.

Microchemical methods have been developed for the determination of elemental fluorine in air [276]. A similar micro method was described for the determination of oxygen difluoride in air [277].

Regardless of how fluoride ion is analyzed once it has been captured from the air and is dissolved in water, the most important step in sampling air with an impinger is the completeness of absorption of the analyte in the liquid absorbent solution in the impinger. The efficiency of widely used sodium hydroxide as the impinger absorption solution for analysis of elemental fluorine in air was examined [278]. A recovery of 98% was obtained with a single scrubber in the concentration range 3–4480 ppb. Sodium hydroxide depletion by other acid waste gases from the air is not a factor as long as excess alkalinity is present. Gradual conversion of the NaOH to Na₂CO₃ during sampling periods due to absorption of atmospheric CO₂ did not significantly change the efficiency.

4 Materials of Construction for Fluorine

The selection of the proper materials of construction for fluorine service is a difficult task and must be done with the proper understanding of potential adverse reactions leading to ignition, explosions, leaks, or other failure modes. In addition to the references discussed in detail in this chapter, there are numerous summaries in the literature that may serve as a starting point in the study of this subject (Table 34 contains mostly references that are not discussed in the text). In looking at the dates of publications in this section on materials compatibility, one will notice that most of them date back to the 1950s and 1960s. That is because 1946–1970 is the period when most of the early fluorine materials compatibility work was done, and very little more was done in the interim. Some of the work was already done during the secret Manhattan project during WW-II but was released only after the war.

Table 34: Materials compatibility with fluorine literature summary.

Author(s)	Topic(s)	Date	Pages	References
Brown	Resistance of materials	1946		[279]
Schmidt	Compatibility of metals	1958	16	[280]
Evans	Tankage materials	1960	18	[281]
Schmidt and Rothenberg	Using fluorine in rocket systems	1960	19	[282]
Kleinberg and Tompkins	Compatibility of metals	1962	157	[66]
Cabaniss and Williamson	Corrosion of metal alloys	1963	31	[283]
Cabaniss	Bibliography	1964	84	[9]
Defense Metals Information Center	Compatibility of materials with fluorine	1965		[284]
Schmidt and Harper	Handling and use of fluorine	1967	279	[285]
Anderson	Dynamic compatibility of fluorine with metals	1972	75	[286]

A very thorough collection of literature references on fluorine and fluorine oxygen oxidizers for space applications is Cabaniss [9], with 353 references sorted by subject: materials compatibility, handling, storage, disposal, and safety considerations, physical and chemical properties, propellant oxidizer studies, and vehicle component design studies.

4.1 Metallic Materials of Construction for Fluorine

This section on the compatibility of metallic materials of construction with fluorine is subdivided such that publications dealing with more than one metal, more general overviews, are discussed first. The last several sections deal with specific metals, one at a time.

4.1.1 Metallic Materials of Construction for Fluorine; Multi-Metal Studies and Summaries

A very useful source of materials compatibility information are the Deutsche Gesellschaft für chemisches Apparatewesen (DECHEMA)-Werkstofftabellen [287]. The German-language compendium of corrosion data started as a basic loose-leaf collection in 1953 and since then has been continuously expanded by supplements, which are updated periodically. It describes the corrosion and chemical resistance of all technically important metallic, non-metallic inorganic and organic materials in contact with aggressive media. Parts of the DECHEMA-Werkstofftabellen have been translated into English and published in 13 volumes (second completely revised edition) as the DECHEMA Corrosion Handbook [288].

It is remarkable and difficult to explain that liquid fluorine at the temperature of liquid nitrogen may cause a worse corrosive attack of materials of construction than gaseous fluorine at room temperature. The only materials that are truly resistant to fluoride attack are the fluorides in their highest state of oxidation, but these are mostly brittle, crystalline materials and not useful for any structural load-bearing task.

Under the conditions of slow passivation of new fluorine systems, metals will be coated with a thin protective film of insoluble metal fluorides, which will protect the metal surface from further attack as long as the often brittle protective film is not compromised by scratching or bending. The maximum tolerable operating temperature of a given metal depends on the melting or sublimation point of the protective metal fluoride film. Table 35 gives a summary of melting and sublimation points of some of the fluorides that may form on the surface of metals.

Table 35: Melting and sublimation points of inorganic fluorides.

Below 294 K (21 °C)	294 to 589 K (21 to 316 °C)	589 to 1089 K (316 to 816 °C)	above 1089 K (816 °C)	References
BF ₃	SbF ₅ MoF ₆ NbF ₅	AgF AgF ₂ BiF ₅	CuF ₂ FeF ₂ CdF ₂	[289]
PF ₅	TaF ₅	CrF ₄	CoF ₂	
SF ₆	SnF ₆	PbF ₄	AlF ₃	
SiF ₄	VF ₅	ThF ₄	MgF ₂	[290]
AsF ₅		BeF ₂	NiF ₂	
TeF ₆		MnF ₂	PtF ₆	
SeF ₆		LiF	TiF ₄	[291]
WF ₆		ZnF ₂	ZrF ₄	
UF ₆				[290]

Data source: extracted in part from [292], p. 62

Based on this temperature information one can make a preliminary selection of metals that are potentially useful for fluorine service because the fluoride coating has a high melting point and low volatility. All metals that form volatile fluorides cannot be allowed in alloys for fluorine service, not even at very low concentrations. That applies especially to carbon and silicon, which are common contaminants in steel.

The rate of corrosion of metals and other materials of construction by difluorine depends much on the presence of two contaminants that are sometimes hard to avoid: HF and water. Although carefully dried fluorine does not attack glass, traces of HF or moisture cause glass to lose its transparency in a very short time.

4.1.2 Exposure of Metals to Gaseous Fluorine

The exposure of metals to fluorine has been studied both in an academic setting to better understand the formation of passivating films, as well as in many fluorine conveyance and storage systems as part of developing passivating procedures that would prevent accidental ignition once the metal was exposed to fluorine for the first time. The fluoride film on metals forms during the first few minutes of exposure and the rate of film formation drops sharply after that time. Passivation procedures are discussed in Section 7 under handling precautions.

A study of the rates of corrosion of various metals in gaseous fluorine included stainless steels, iron, copper, aluminum, magnesium, nickel, titanium, and their alloys [292]. Other metals covered were Zr, Ta, Cr, Ag, U, Pt, and Sn. Depending on the particle size and condition of the surface, some of these metals may even autoignite at room temperature in gaseous fluorine.

Kinetic rate studies of this kind are useful for the development and selection of fluorine-resistant materials of construction. The rate of corrosion of 26 different metal

samples in gaseous fluorine was measured [293]. It was noticed that Si-containing Fe alloys are particularly susceptible to fluorine attack in the form of pitting corrosion. Once the samples ignited accidentally in fluorine, the reaction propagated with the intensity of a welding torch as long as the flow of fluorine was maintained.

A summary of the fluorine corrosion literature through 1956 contains data on Ni, Cu, Fe, Al, Mg, and their alloys, supported by numerous references, and is a good starting point for materials compatibility studies [294]. Sparse data are available on the behavior of non-metallic materials (carbon, graphite, asbestos, glass, quartz, ceramics, organic polymers) in fluorine.

As already indicated by the data in Table 35, nickel is very suitable as material of construction for fluorine service at higher temperatures. Table 36 gives additional data on the rate of corrosion of various metals in fluorine gas.

The reactivity of uranium, thorium, aluminum, copper, iron, magnesium, zirconium, and fluorothene [poly(1-chloro-1,2,2-trifluoroethene)] with bromine trifluoride, bromine pentafluoride, chlorine trifluoride, and fluorine was investigated at temperatures ranging from 298 to 683 K (25 to 410 °C) [290, 296].

A study of the corrosion of various metallic and ceramic materials by gaseous fluorine at elevated temperatures (673–1023 K = 400–750 °C) has been made to aid in the selection of materials of construction for the *Fluoride Volatility Process* applied to processing of irradiated plutonium–uranium alloys [297]. The data indicated that nickel and Monel were suitable materials for use in a fluorine atmosphere at temperatures up to 823 K = 550 °C. At higher temperatures, nickel and copper exhibited the lowest corrosion rates. Ceramic materials such as calcium fluoride and alumina were resistant to attack by fluorine even at the highest temperatures, but lack mechanical strength. This report also contains a very good summary of metal corrosion by fluorine gas data gathered from other literature sources.

The physical and chemical adsorption of fluorine on metals was studied using TGA, radioactive tracers, calorimetry, and IR spectrometry [298].

The extent of corrosion by fluorine at low pressure on several cryopanel materials was evaluated for conditions approximating those that might be expected in a space simulation chamber during rocket engine tests with fluorine-containing oxidizers [299]. The chamber pressure was adjusted to 530 Pa (4 mm Hg) of fluorine at room temperature and specimen temperatures were cycled between ambient and 77 K. The chamber was periodically pumped to high vacuums. The total exposure time exceeded 1000 h. CRES 304L, phosphorus-deoxidized copper, and Al-1100 aluminum were tested. Some specimens were welded and some were tested with applied bending stress. No pitting or other microstructural corrosion was detected, but noticeable changes occurred in the surface appearance, especially with aluminum and copper.

The reaction of fluorine with copper and iron was studied within a very wide temperature and pressure range [300]. Under medium fluorine pressures the formation of continuous films was observed. With low fluorine pressures and at relatively high

Table 36: Rate of corrosion of metals in gaseous fluorine.

Material	Corrosion rate, mm/month									
	Temperature, K									
	473	523	573	623	673	723	773	873	973	
Temperature, °C										
200	250	300	350	400	450	500	600	700		
Nickel	—	—	—	—	0.018	0.048	0.13	0.73	0.86	
Monel	—	—	—	—	0.013	0.038	0.051	1.52	3.8	
Inconel	—	—	—	—	0.96	2.44	1.53	4.3	12.9	
Oxygen-free Copper	—	—	—	—	4.07	—	3.2	25.1	73	
Aluminum 2S	—	—	—	—	—	—	0.33	0.45	—	
Magnesium 430	0.0178	—	6.50	1.98	1.98	—	—	—	—	
Magnesium 347	—	3.68	5.42	13.10	20.20	—	—	—	—	
Magnesium 309-Cb	—	—	1.90	11.70	16.90	—	—	—	—	
Magnesium 310	—	—	0.79	9.0	14.23	—	—	—	—	
Armco Iron	—	0.05	0.23	0.20	0.61	7.6	294	—	—	
Leaf Spring Steel (0.007% Si)	—	0.41	0.10	0.05	0.31	7.6	188	—	—	
SAE 1020 (0.22% Si)	0.96	12.2	16.7	—	13.7	38.6	—	—	—	
SAE 1030 (Trace of Si)	0.05	0.20	0.23	—	0.38	13.7	503	—	—	
SAE 1030 (0.18% Si)	—	—	19.0	—	—	—	—	—	—	
SAE 1015 (0.07%Si)	—	—	21.1	—	—	—	—	—	—	

Data source: [295]

temperatures, a process of nucleation and growth of fluorides took place. The presence of traces of oxygen in the gas phase can have a strong influence on the nature of the products formed.

The composition and thickness of fluoride films that formed upon exposure of various metals to F_2/N_2 at room temperature were studied using X-ray photoelectron and Auger electron spectroscopy (AES) [301]. Depth profiles were obtained using AES with argon ion sputtering. The metals studied included low carbon steel, 302 stainless steel, copper, and brass (70% Cu/30% Zn). Samples treated in 0.12% F_2/N_2 displayed small amounts of surface fluorine, primarily in the form of fluorinated hydrocarbons rather than metal fluorides. In contrast, exposure to 25% F_2 produced thicker films, consisting mainly of metal fluorides with some metal oxides. Fluorine did not seem to penetrate beyond the native oxide initially present on the metal foil surface. Iron fluorides formed on low carbon steel and copper fluorides formed on copper. Surprisingly, iron fluorides preferentially formed on stainless steel, and zinc fluorides preferentially formed on brass. These results provided new insight into the passivation of metals by F_2 but also raised new questions.

4.1.2.1 Ignition Temperature of Metals in Fluorine Gas

The ignition temperature of metals in gaseous fluorine was measured in a high-pressure bomb rated for an operating pressure of 20.67 MPa = 204 atm at room temperature [302]. This technique may be suitable as a method for the evaluation of newly developed materials of construction for fluorine service. The attached manifold allowed the bomb to be alternately evacuated, filled with fluorine, or purged with nitrogen. The metal under investigation had to be available in wire form, so that it could be coiled to a spiral and connected to the terminals of an electric feed-through like the filament in a light bulb. The diameter and length of various wire coils are summarized in Table 37, sorted by increasing ignition temperature.

Table 37: Ignition of metals in fluorine gas.

Material tested	Sample diameter	Sample length	Average ignition temperature	
	mm	mm	°C	K
Al	0.25	100	Melted before it ignited	
Mo	0.8	100–125	205	478
W	0.38	50–125	283	556
Monel	0.25	100–150	396	669
Fe	0.35	150–200	672	945
Stainless steel	0.51	150–200	681	954
Cu	0.28	300	692	965
Ni	0.38	150–180	1153	1426

Data source: [302]

The filament was gradually heated by an electric current until ignition took place. After the test the metal wires were coated with black fluoride. If the temperature function of the resistance of the metal under investigation is known, the ignition temperature could be derived from the resistance at the moment of ignition. Following the test, excess fluorine had to be vented into a fluorine neutralization/absorption unit like those described in [303, 304] using the reaction with activated charcoal.

Attempts have been made to correlate the ignition temperature results via an ARRHENIUS function similar to one used for homogeneous gas reactions:

$$\frac{1}{t} = Ae^{-\frac{E_{\text{act}}}{RT}}$$

where t is time to ignition, T is the absolute temperature, and E_{act} is the activation energy.

When the time to ignition was plotted $\log 1/t$ versus $1/T$, a straight line was obtained and the activation energy of the ignition reaction could be derived from the slope of this line. Looking at the results summarized in Table 37, one can see that nickel is very suitable for construction of components that are exposed to fluorine at higher temperatures. Nickel owes this desirable property to the high sublimation temperature of its fluoride. See also Kadri et al. [305].

A study of the ignition of metals in gaseous fluorine used cylindrical samples that were machined to a diameter of 3 mm for a length of 40 mm and heated by passing an electric current through them [306]. When samples were heated by direct passage of an electric current at pressures near 0.2 MPa, it was observed that titanium, molybdenum, tungsten–niobium alloy, nickel, iron, carbon steel, and stainless steel in gaseous fluorine ignited through a thermal explosion mechanism, whereas copper, its alloys, and aluminum ignited when the melting point of the fluoride film was reached. Comparing the ignition temperature data for different metals, it was concluded that compact metallic materials ignite in fluorine by a thermal Semenov–Frank–Kamenetskii mechanism. Another pattern was observed in the ignition of copper and its alloys. The fluoride films formed on the surface of these materials when they are oxidized at high temperatures in fluorine have high protective properties because the process proceeds at a low rate and with a parabolic kinetic dependence. At temperatures below that for ignition, the interaction of steels and nickel with fluorine is characterized by linear oxidation kinetics. The transition from linear to parabolic kinetics is determined by the enrichment of the fluoride film in iron trifluoride and, in the case of nickel, by the coarsening of NiF_2 crystals in the film. The ignition of the refractory metals, nickel, and alloys based on iron in fluorine at pressures near 0.2 MPa proceeds by a thermal Semenov mechanism, whereas copper and its alloys ignite through a Friedman–Macek mechanism.

4.1.3 Exposure of Copper to Gaseous Fluorine

Another metal suitable for fluorine use is copper. The corrosion of copper by fluorine gas at 703 to 923 K (430 to 650 °C) and the rate of fluorine consumption by a freshly cleaned copper foil at a fluorine pressure of 26.7 kPa = 200 mm Hg was measured in order to derive a kinetic rate equation.

The reaction between fluorine gas and copper metal has been studied at 723 K (450 °C) and pressures from 1.3 to 17.3 kPa (10 to 130 mm Hg) [307, 308]. The reaction was pressure dependent and followed the logarithmic law

$$y = K \log(at + c) + C$$

The logarithmic rate constant K varied with pressure according to the equation

$$\log K = m \log P + 6.11439$$

where m is equal to 0.781. Analysis of the corrosion film yielded an F/Cu ratio of 1.11. A reaction mechanism was postulated, and from the evidence presented, it was proposed that fluorine is the migrating species in the diffusion reaction.

It became quickly obvious that this is not a purely chemical reaction, but the global rate is diffusion-limited by the rate of diffusion of fluorine through the CuF_2 layer formed on the surface. When the logarithm of the reaction rate was plotted versus the reciprocal absolute temperature, a change of slope was noticed at 813 K (540 °C), which indicated that two different mechanisms were at work. However, the slope of the curve decreased instead of increasing above 813 K. Other investigators doing similar experiments also had difficulties interpreting their experimental results. The reaction has been investigated under high vacuum conditions between room temperature and 523 K (250 °C), and at pressures between 0.8 and 8 kPa (6 mm and 60 mm Hg) [242]. The equation

$$x = x_0 \log_{10}(1 + at) + b$$

was obeyed, where x is the thickness of the corrosion film at time t , and x_0 , a , and b are constants. The experimental data showed that the reaction cannot be controlled by a simple diffusive process. The most satisfactory interpretation was that it may be due to random cracking of the protective film, but this does not explain the phenomenon precisely.

Copper powder reacted with fluorine at 773 K (500 °C), but the conversion to copper(II) fluoride was only 53% because the fluoride coating prevented further reaction [289].

In preparation for fluorine exposure tests, copper coupons were treated with clean, concentrated nitric acid for 1 s to obtain a bright, shiny surface. The sample exposed at 823 K = 550 °C showed a film that was too thin to measure accurately [297]. Samples of copper exposed at 923 and 1023 K (650 and 750 °C) showed the typical dull, brick-red corrosion layer, which appeared to be fairly adherent. Agreement between the corrosion rates obtained by use of weight change data and those obtained using

film thickness data was surprisingly good considering the uncertainty of the nature of the corrosion product. See also Steindler and Vogel [309].

4.1.4 Exposure of Nickel to Gaseous Fluorine

Looking at the results of time to ignition tests summarized in Table 37, one can see that nickel is very suitable for construction of components that are exposed to fluorine at higher temperatures. Nickel owes this desirable property to the high sublimation temperature of its fluoride.

Similar tests for the reaction between nickel and fluorine were performed using a radioactive tracer technique with radioactive nickel at 873 to 973 K (600 to 700 °C) [310–312]. Again, it was found that the overall rate depends on the rate of diffusion of fluorine through the NiF_2 surface layer. This is in contrast to the growth of oxide films with nickel where it was assumed that nickel ions migrate through the oxide scale to react with more oxygen on the surface.

Nickel difluoride NiF_2 is formed in the fluorination of metallic nickel between 813 and 1083 K (540 and 810 °C) [313]. The kinetics of the formation of the fluoride film within the investigated temperature interval are dominated by a diffusion mechanism. The activation energy of the process of formation of NiF_2 was 247 kJ/mol (59.0 kcal/mol) at medium temperatures (813–873 K = 540–600 °C) and 77.4 kJ/mol (18.5 kcal/mol) at high temperatures (993–1083 K = 720–810 °C). The NiF_2 film was stable to hydrolysis up to temperatures close to 683 K (410 °C). A similar study was done on copper with gaseous fluorine [314].

The film thickness obtained on exposure of nickel to fluorine at 823 K = 550 °C was too small to measure and the data were obtained only from the weight gain of the coupon. Samples exposed at 923 and 1023 K (650 and 750 °C) showed films of measurable thickness and the corrosion rates were calculated from both of these observations [297].

The crystal structures of protective films of FeF_2 and NiF_2 formed on Fe and Ni surfaces in NF_3 and SF_6 at 1473 K (750 °C) were examined by electron diffraction [315]. In NF_3 at 473–573 K (200–300 °C), a phase transformation of $\text{FeF}_2 \rightarrow \text{FeF}_3$ was observed.

The resistance of nickel and its alloys, particularly Monel, against fluorine and HF is fairly good at temperatures up to 900 K [316, 317]. During the attack of nickel–chromium alloys by fluorine between 1000 and 1300 K, an inner fluorination mechanism similarly to the inner oxidation is taking place.

4.1.5 Exposure of Iron to Gaseous Fluorine

Iron is rarely used in the pure state, but it is the main constituent of all steels. The effect of temperature and pressure on the reaction of fluorine gas on solid iron samples was studied at various pressures up to 26.7 kPa (200 mm Hg) over the temperature range of 498 to 798 K (225 to 525 °C) [318, 319]. The reaction was found to follow a logarithmic rate law, and logarithmic rate constants were calculated. The probable mechanism of

film growth is the movement of fluorine through defects in the fluoride film to the iron surface.

The reaction of fluorine with iron has been considered as a method for fluorine removal from waste gas streams [320]. Laboratory tests have been conducted to evaluate the fluorine–iron reaction as a possible method of chemically scrubbing fluorine from waste gas mixtures to be vented to the atmosphere. Iron in the form of coarse steel wool packed into a cylindrical nickel reactor was found to consume nearly all the fluorine from fluorine–oxygen and fluorine–nitrogen mixtures containing from 0.5 to 100% fluorine. External heat to the reactor was required to ensure complete reaction at the lower fluorine concentrations. Gaseous fluorides found in the emitted reaction products ranged from less than 1 to 15 ppm. Gaseous products from the reactions of fluorine–oxygen mixtures with iron were less than 3% of the volume of gases fed into the reactor. The exit gas was essentially nitrogen, which indicated that oxygen had also reacted with the iron. No toxic gaseous products were emitted, and the solid products were non-volatile and totally contained the fluorine for long-term storage or disposal in a landfill.

4.1.6 Exposure of Titanium to Gaseous Fluorine

Titanium powder reacted appreciably with fluorine above $423\text{ K} = 150^\circ\text{C}$, the vigor of the reaction depending on the size of the metal particles [321]. Conversion was complete above $473\text{ K} = 200^\circ\text{C}$. Titanium(IV) fluoride could be synthesized by fluorination of massive titanium, preheated to $523\text{ K} = 350^\circ\text{C}$ in the reactor.

Because titanium may ignite even in liquid oxygen or dinitrogen tetroxide if freshly fractured surfaces are exposed to an oxidizer, this concern about accidental ignition is heightened when exposing titanium and titanium alloys to fluorine (liquid or gas). If titanium tubing or tanks are used for fluorine service, they must not be bent or vibrated while exposed to the oxidizer. Vibrations can be induced externally (launch vibration, road transport vibration) or internally (water hammer, fluttering valves, resonant cavities, combustion instabilities in the rocket chamber).

The resistance of titanium in water-free liquid fluorine at lower temperatures is $<0.3\text{ mm/year}$, which is comparable with that of nickel and Monel [316, 317]. The rate of corrosion of titanium in gaseous fluorine at 377 K is only 0.0082 mm/year .

4.1.7 Exposure of Zinc to Gaseous Fluorine

Zinc is not a metal one would want to use for construction of fluorine equipment, but zinc is a constituent of brass and brass was considered for use with fluorine, although it is not recommended. The reaction between zinc metal and fluorine gas can be described by a parabolic rate law [322]. This reaction is both temperature and pressure dependent. Simple kinetics are complicated by the noticeable vaporization rate for zinc at temperatures above 573 K (300°C).

4.1.8 Exposure of Refractory Metals to Gaseous Fluorine

Fluorine reacted with zirconium powder above $463\text{ K} = 190^\circ\text{C}$. Fluoride coating of metal powder prevented complete conversion to zirconium fluoride. The maximum conversion obtained was about 90% at $693\text{ K} = 420^\circ\text{C}$. At higher temperatures some product was lost owing to sublimation.

In spite of their limited resistance against fluorine and HF, very pure molybdenum and tungsten are employed as construction materials in the design of rocket engines because of their good strength at high temperatures if they are exposed to fluorine–hydrogen or fluorine–hydrazine flames [316, 317]. Lanthanum borides and calcium borides intended as coatings for the inside of combustion chambers were exposed to fluorine–hydrazine flames but were attacked only a little at temperatures between 1400 and 1800 K; they were superior to all special grade alloys.

4.1.9 Exposure of Aluminum to Gaseous Fluorine

Aluminum and duralumin (Al–Cu alloy system, or Al-2000 series) are resistant against fluorine and HF up to 600 and 700 K respectively [316]. The resistance of nickel and its alloys, particularly Monel, against fluorine and HF is fairly good up to 900 and 800 K. During the attack of nickel–chromium alloys by fluorine between 1000 and 1300 K, an inner fluorination appears to take place similar to the inner oxidation by oxygen diffusion.

4.1.10 Exposure of Silver to Gaseous Fluorine

Silver is a constituent of most brazing alloys. It is important to find a brazing alloy that is compatible with fluorine. The effect of temperature and pressure on the kinetics of the reaction of fluorine with silver were studied over a temperature range from 298 to 573 K (25 to 300°C), and the reaction was measured at fluorine pressures of 6.7–80 kPa (50–600 mm Hg) [323, 324]. The reaction was pressure dependent. Three reaction products were identified: silver subfluoride (Ag_2F), silver monofluoride (AgF), and silver difluoride (AgF_2). No simple rate law could describe the growth of film thickness data over the entire time interval of the reaction.

Silver solder may be used to join two or more members. Silver is not very resistive to fluorine attack, but the addition of copper improves its resistance, whereas cadmium or lead lowers the resistance to attack, although the workability of the solder is increased.

4.2 Behavior of Metals in Contact with Liquid Fluorine

In general, all materials that are proven to be compatible with gaseous fluorine are also suitable for service with liquid fluorine. When selecting metals for cryogenic liquid fluorine service, the melting point and volatility of the formed fluoride no longer has the

same importance as when selecting materials for high temperature service. However, the potential solubility of fluorides in liquid fluorine becomes a determining factor. The rates of corrosion of various metals in liquid fluorine were reported ([292]). This section on the compatibility of metallic materials of construction with liquid fluorine is subdivided such that publications dealing with more than one metal, more general overviews, are discussed first. The last several sections deal with specific metals, one at a time.

One must also keep in mind that equipment for handling of liquid fluorine is not always kept at the cryogenic temperatures of liquid fluorine, but may alternate between cryogenic and room temperature, resulting in occasional rapid temperature transients, thermal stresses, and flaking of the protective layer of fluorides. Other materials may be chemically compatible, but become embrittled at cryogenic temperatures (even in the absence of fluorine) and must be eliminated from further consideration. See also [325].

Corrosion tests of 25 metals and alloys by liquid and gaseous fluorine were performed at 77 K (−320 °F) and exposure times ranged from 5 h to 3 days [326]. Exposures to gaseous fluorine were made at approximately 300, 477, 644, and 811 K (80, 400, 700, and 1000 °F). Exposure times were generally 5, 24, and 120 h. Several specimens were also exposed to gaseous fluorine at elevated pressures and temperatures for 24 h. Selected specimens were cross-sectioned and photomicrographs taken to study the passivating fluoride film. Results of the 5-h tests indicated that all tested materials, except tantalum, may be exposed to fluorine at temperatures up to 477 K (400 °F) without exceeding a corrosion rate of 0.0005 in/h. This arbitrarily chosen rate was not intended to signify acceptability. It was equivalent to 4.4 in/year, which is an extremely high corrosion rate under normal circumstances, but not excessive when exposure for only a few hours is required. It must be understood that extrapolation of the results obtained from very short exposures to long time service, such as a year, is not reliable. In general, the corrosion rates tend to decrease as the exposure period is extended. Tests of materials at elevated pressures indicated that corrosion rates were generally higher than specimens exposed to the same temperatures at atmospheric pressure. Microscopic examination of selected specimens showed that materials such as Monel and nickel formed a relatively uniform passivating film at elevated temperatures. Aluminum 1100, however, showed indication of deep, non-uniform penetration.

Studies were made to determine the compatibility and resistance to corrosion of various metals with liquid F_2 at 77 K (−320 °F) [327]. Metals tested included various alloys of Al, stainless and high strength steel, Ti, Cu, Monel, Ni, and Mg. It was found that the total corrosion of Ti that had been exposed to liquid F_2 was independent of time for periods up to 2 weeks. The corrosion of Mg increased up to 1 day, but longer exposures up to 2 weeks produced no further corrosion. Increased corrosion of metals by F_2 contaminated with water does not occur at liquid F_2 temperatures, but takes place in the gas phase while the system is warming. F_2 that had been liquefied in glass cells was found to contain solid material leached from the glass. When new facilities

are placed into service for the first time, pretreatment with F_2 gas is recommended as it can burn off surface contamination, which might prove a dangerous source of ignition during liquid exposure. Abrading metal surfaces under liquid F_2 with wire bristles caused no apparent increase in corrosion rate.

In studies of reactions of liquid fluorine and its contaminants on metal surfaces, the formation of fluoride films was measured during immersion of tensile specimens [66]. A method of preparing contaminant-free fluorine and verifying its purity by IR analysis was developed to ensure that the results are reproducible. No violent liquid phase reactions between fluorine and metals were observed but gas phase reactions occurred during warmup. Small weight changes in metal specimens immersed in liquid fluorine for 15 and 75 min were noted. Exposure of hydrocarbon films on metals to F_2 formed carbon deposits, whereas exposure to ClF_3 or $ClF_3 + F_2$ left fluorocarbon films behind. No detectable fluoride films formed on Al specimens using electron diffraction techniques. At low temperatures gaseous fluorine formed films of less than 200 Å on metal powders with initially rapid film formation tapering off to a negligible rate after 1 day. Metal powders absorbed gaseous fluorine at 100 K (-279°F). Metal tensile specimens exposed to liquid fluorine for 1 year corroded less than one thousandths of an inch. These specimens had essentially the same tensile properties as similar ones exposed to liquid nitrogen.

The rate of penetration of corrosion into material samples immersed in liquid fluorine was measured for durations of up to 1 year [328–330]. The results are summarized in Table 38, but may not be very reliable because they show substantial scatter.

Table 38: Corrosion of passivated metal samples in liquid fluorine.

Metal	Depth of penetration, micrometer, after					
	15 min	75 min	6 h	1 week	2 weeks	1 year ^a
Nickel			0.2		0.2	0.08
Monel			0.5	0.3	0.4	0.08
CRES-304	0.03	0.05	0.05	0.1	0.2	0.08
CRES-430						1.6
Stainless steel 420	0.05		0.2	0.2	0.2	
Steel Armco 15-7PH Mo					0.08	0.03
Copper	0.03	0.05	0.2		0.4	0.08
Magnesium HK31	0.2	0.03	0.5		0.8	17.1
Magnesium AZ31	0.08	0.1	0.5		1.0	8.7
Aluminum 1100	0.03	0.1	1.3	0.03	1.1	5.3
Aluminum 6061	0.03	0.03	0.1	0.2	0.8	4.7
Titanium A 110 AT	1.1	1.0	0.6		1.1	7.1
Titanium C 120 AV			0.3	0.5	1.0	5.8

^a The values after 1 year are unreliable because there may have been contamination by moisture and condensation from ambient air.

Data source: [328]

From Table 38 one can learn that with nickel, Monel, copper, CRES-304, CRES-420, and Armco iron 15-7, the depth of penetration remains below $1\text{ }\mu\text{m}$, even after long-term exposure. For the time frame from 6 h to 2 weeks both passivated and non-passivated specimens gave the same results. Also, mechanically stressed metal coupons did not show a fundamentally different behavior. In another series of tests, the fluorine absorption by metal powders was measured gasometrically and the thickness of the fluoride passivation layer calculated theoretically. In the case of nickel, the predicted thickness was 1.2 nm .

Impurities in the liquid fluorine may affect the rate of corrosion significantly [331]. The presence of HF in fluorine increases corrosion of metals markedly. The HF is usually generated in fluorine systems from the reaction of atmospheric moisture or moisture in the system with fluorine. Contaminants in fluorine other than HF do not present corrosion or safety problems. Cleanliness of a fluorine system must be emphasized because contaminants cannot be removed from the apparatus by passivation procedures. Most corrosion in a liquid fluorine system occurs during the first hour of exposure.

The results discussed here so far covered only the exposure to gaseous or liquid fluorine, whereas in real life the situation may alternate between these two conditions. In a study of the behavior of various metals under more practical conditions of exposure, the samples were exposed in a hermetically closed system alternately for 12 h to liquid nitrogen temperature, causing the fluorine to condense on the samples, and subsequently allowed to thaw and warm to room temperature, where they were kept for another 12 h [332]. Metals tested in this series included Ni, Monel, Al3 S-O, Al52 S-O, CRES-347, CRES-321, as well as a brass with a low lead content (0.96% Pb). The test series was continued for 2.5 to 3.5 months and the weight change of the samples was recorded. It was concluded that all materials tested in this series were suitable for alternating gaseous-liquid fluorine service.

Liquid fluorine is not a very conductive electrolyte. The remaining conductivity is mostly due to contaminants, mainly HF. The galvanic corrosion of eight different metals in contact with each other was measured in liquid fluorine for 21 days at 77 K ($-196\text{ }^{\circ}\text{C}$) [333]. There was evidence of pitting on Al-2014-T6 and silver coupons. The electrode potentials of several metals (Al-1100, soft Cu) versus Pt as a reference electrode were measured and arranged in a sequence of increasing electronegativity.

The mechanisms of corrosion in liquid fluorine and in alternating liquid-gaseous environments are not fundamentally different. In general, all materials proven for liquid fluorine service can also be used for alternating liquid-gaseous conditions. Polished cross-sections of mounted exposed metal specimens were prepared in an attempt to see the thickness of the fluoride layer, such that corrosive action could be examined in cross section, but even at $\times 250$ magnification, the passivation layer could not be seen.

The effect of liquid fluorine immersion on the mechanical properties of several sheet alloys (AM350, ASM6434, Inconel X, AISI 301, AISI 304L, Al-2014-T6, Al-6061-

T6, Al-7075, Ti-6Al-4V) was investigated [334, 335]. The smooth and notched tensile strength and the elongation properties of steel, nickel, aluminum, and titanium alloys were determined in liquid-nitrogen and liquid-fluorine environments at 77 K (-320°F). The smooth specimens were loaded to a stress value equal to 90% of the yield strength of the material at a temperature of 77 K (-320°F = liquid-nitrogen boiling temperature). This load was maintained for 2h. Possible deterioration in the presence of fluorine and high stresses was detected by comparing the properties of alloys exposed to the two fluids at 77 K (-320°F). The as-received fluorine contained contaminants typically found in commercial fluorine. The results of tests in liquid fluorine indicated possible degradation of the mechanical properties of the sheet alloys. Following 2-h exposure, the decrease in tensile strength ranged from negligible to a maximum reduction of approximately 11%. Elongation showed similar trends. The sharp-notch strengths appeared to be unaffected by the liquid fluorine. Variations in test results and surface appearance could have been due to varying amounts of contaminants in the liquid fluorine, fluctuating from one batch to another. There was no evidence of ignition on any of the specimens that were fractured in the liquid fluorine environment. Where high thermal conductivity is essential, Al-6061 is a possible material of construction.

The compatibility of various alloys with liquid fluorine and FLOX under stress [336] and with gaseous FLOX under stress [337] was assessed in static immersion tests [338].

The rates of corrosion of Ti-6Al-4V and Al-2219-T87 in liquid fluorine and Ti-6Al-4V in FLOX (12% F_2) at 77 K were determined by neutron activation analysis, radioactive tracer techniques, and atomic absorption spectroscopy to analyze for leached metals [339, 340]. The rates of corrosion were very dependent on the HF present as a contaminant in fluorine. The results of test durations up to 100 h were used to calculate reaction rate constants and to predict corrosion over a time span of several years.

For a short time, converting a VANGUARD first stage or ATLAS [341–343] or THOR or SATURN S-IC [344] launch vehicle to operation on FLOX instead of LOX was considered, in order to gain more payload capability. In this case, compatibility of FLOX with existing materials of construction was a difficult issue, and that was most likely the main reason why these conversions never got to fly. The results of compatibility testing of ATLAS relief valve, boil-off valve, airborne instrumentation, fill and drain valve, staging valve, and miscellaneous components with 50% FLOX made it obvious that major redesigns would be necessary [345].

In one test series, the following materials in tensile test dog bone coupon shapes were immersed in 20% or 30% FLOX for 200 h and compared with controls immersed in LN_2 for the same duration [346]:

1. stressed CRES-301, plain or spot welded or fusion welded
2. stressed K-Monel, plain or fusion welded
3. stressed fusion butt weld between CRES-321 and nickel A
4. stressed Al-6061-T6

Although the discussion about the safety (or the lack thereof) of launching a Centaur liquid oxygen/liquid hydrogen upper stage as payload from the payload bay of the Space Shuttle has been going on for a long time, only to be eventually canceled, an even more daring launch sequence would have been to fly a fluorine oxidizer upper stage or spacecraft as payload in the Space Shuttle payload bay. The safety and hazards of this project have been thoroughly reviewed, only to suffer the same fate as the Shuttle/Centaur project, being canceled for the sake of safety. The safety implications of Space Shuttle-launched spacecraft using liquid fluorine as the oxidizer for upper stage or spacecraft propulsion were thoroughly investigated. It would be important to always have sufficient liquid nitrogen available to keep the fluorine cold while it is flown to its point of use [347–349]. The feasibility of safe operation was examined and all equipment and procedures necessary to maximize the chance of success were determined. Hazards to the shuttle were found to be similar in kind if not degree to those encountered in the use of dinitrogen tetroxide (also a toxic oxidizer). It was concluded that residual risks from spacecraft using fluorine and nitrogen tetroxide during ground and flight handling can be reduced by isolation of the oxidizer to only its tank. Operation of planetary spacecraft propulsion in the vicinity of the shuttle in earth orbit is not required. The primary hazard to personnel was identified as propellant-loading operations on the ground, which should be accomplished in an area reasonably remote from uninvolved personnel and facilities concentrations. Clearing the pad from all personnel during spacecraft mating with the shuttle orbiter was recommended.

4.2.1 Metals Compatibility with Flowing Liquid Fluorine

Although most compatibility tests were conducted with stagnant propellants, a few were conducted under aggravated conditions with flowing fluorine. The effect of liquid fluorine on metals differs significantly depending on the conditions of exposure, if the metal is exposed to stagnant or flowing fluorine. In a test with liquid fluorine, several candidate metals (nickel, stainless steel, aluminum, brass) were formed into three different test body shapes (capillary tube, a flat bolt, and a triangular sharp-edged wedge behind which turbulent eddies would form) and exposed to flowing liquid fluorine at up to $10.1 \text{ MPa} = 100 \text{ atm} = 1470 \text{ psia}$ and flow velocities up to 120 m/s [350]. All four materials tested were suitable for exposure to liquid fluorine under these conditions, which resembled those in a propellant feed system at a rocket test site [351].

The dynamic compatibility of liquid and gaseous fluorine with metals was examined by exposing 11 metallic materials of construction (301 cryoformed, 304L, 321, and 347 stainless steel; A-286 super alloy steel; 2219, and 6061 aluminum; oxygen-free high thermal conductivity (OFHC) copper; Monel K-500; Inconel 718; and Nickel 200) to flowing fluorine [352]. Six types of tests were used to obtain the data required to establish safe design criteria for fluorine systems: (1) maximum velocity, (2) adiabatic compression (U-tube), (3) liquid impact, (4) flexing/film degradation, (5) vibration/film degradation, (6) liquid phase shock wave. Flow tests with gaseous, preheated

fluorine on heated specimens were conducted with nine metals. The fluorine gas pressure upstream of the test specimen was nominally 689 kPa (100 psia) throughout the investigation. From this type of analysis alone, the threshold temperatures for incipient failure could be defined by the onset of large exotherms. The mechanism of failure was, however, evident only by examination of the “failed” specimen. A “failed” specimen of 304-L stainless steel showed that the ultimate failure was brought about by burning. From all the data available, it was concluded that nickel is the best metal known for containing hot, flowing, gaseous fluorine. In descending order of preference, the other metals studied were ranked as follows: Inconel 718 and Monel K-500 > austenitic stainless steels > copper > aluminum. The results of adiabatic compression tests are summarized in Table 39. Similar tests were conducted for chlorine pentafluoride in parallel with the fluorine tests. The report also contained a very good summary of metals reactivity test results reported by other organizations.

Table 39: Terminal adiabatic compression conditions that result in a 50% probability of fluorine/metal reaction.

Metal	Calculated final temperature		Calculated final density		Extent of resulting reaction
	K	°F	g/cm ³	lb/ft ³	
6061-T6 Aluminum	~994*	~1330 ^a	~0.096	~5.97	Major
A-286 Stainless Steel	978	1300	0.089	5.57	Variable
304-L Stainless Steel	983	1310	0.090	5.64	Slight
304-L Stainless Steel	1089	1500	0.047	2.96	Slight
321 Stainless Steel	1075	1475	0.046	2.9	Variable
347 Stainless Steel	~1191 ^a	~1685 ^a	~0.067 ^a	~4.16 ^a	Major
Inconel 718	~1191 ^a	~1685 ^a	~0.067 ^a	~4.16 ^a	Slight
Monel K-500	~980	~1305	~0.089	~5.55	Variable
Monel K-500	~1164	~1635	~0.061	~3.82	Slight
OFHC Copper	Not Defined				Insignificant
Nickel 200	Not Defined				Insignificant

^a Insufficient positive reaction data points to define reaction probability accurately
Data source: [352]

From the data presented in Table 39, it was concluded that the metals can be ranked in categories in the following descending order of resistance to the effects of fluorine adiabatic compression: (1) Nickel 200 and OFHC copper, (2) Inconel 718, and (3) 304-L, 321 and A-286 stainless steels. The proper ranking of Monel K-500, 6061-T6 aluminum, and 347 stainless steel was uncertain because of insufficient or irregular positive test results.

4.2.2 Copper in Contact with Liquid Fluorine

Pure copper and soft copper alloys have been used for crush gaskets.

4.2.3 Stainless Steel in Contact with Liquid Fluorine

Stainless steels of the 300 series, nickel, Monel, and K-Monel are suitable materials of construction for pumps and propellant feed systems [353]. Bell Aircraft designed a test stand for rocket engine firings with liquid fluorine and FLOX. Between 1956 and 1960, more than 50000 lb of liquid fluorine had been processed at that facility without any accidents. More than 500 test firings with thrust chambers with small and intermediate thrust were performed. The fluorine flow rates were up to 70 lb/s with linear flow velocities of >100 ft/s and feed pressures of 500 psi. On-site stationary storage of LF2 was in a triple-walled storage vessel. The innermost container from 300-series stainless steel held the LF2 and the intermediate surrounding tank contained LN2. All valves had long stem extensions to maintain a safe distance between valve and operator, separated by metal shields. Liquid level gauges could not be incorporated into the tank in order to keep the tank wall penetrations to a minimum, only for a gas inlet and a standpipe outlet.

4.2.4 Titanium in Contact with Liquid Fluorine

Unalloyed titanium and four titanium–base alloys were subjected to a simple preliminary corrosion evaluation in liquid and gaseous fluorine at temperatures between 77 and 378 K (–320 and +220 °F) [291]. All materials exhibited tolerable corrosion resistance under the test conditions. More elaborate experiments would be required to fully establish the utility and safety of titanium in fluorine service.

The compatibility of Ti-6Al-4V with propellant-grade gaseous fluorine and liquid fluorine at 77 K was investigated for up to 3 years [354]. The specimens of Ti-6Al-4V in two heat-treat conditions (annealed, 147 KSI, and heat-treated, 175 KSI) and two surface finishes (16 and 64 RMS) were immersed in liquid fluorine in individual Pyrex capsules and stored under liquid nitrogen for 29 and 39 months. Pre- and post-immersion tests were performed on the propellant and coupons. Tensile properties did not change for either vapor- or liquid-immersed specimens. No significant exposure effects were found by the corrosion mapping, visual, microscopic or scanning electron microscopy (SEM) inspections. Chemical analysis of the off-loaded propellant did not reveal any significant changes due to titanium corrosion. Gravimetric, visual, microscopic, and metallurgical examination with pitting analysis did not reveal gross corrosion of the titanium, although some pitting appeared to be greater after 39 months' exposure. The increase in pit size and the number of pits raised the possibility of unpredictable crack propagation instability. Fracture toughness and stressed coupon tests would be necessary to clear this material for long-term use for pressurized containers.

Titanium alloy 6Al-4V has been investigated for application on a fluorine–hydrazine propulsion system and engineering data were generated for fracture

mechanics, long-term compatibility, ignition and passivation, insulation, and impact sensitivity [355]. The data showed that this alloy should be satisfactory for this application.

The resistance of titanium in water-free liquid fluorine at lower temperatures of <0.3 mm/year is comparable with that of nickel and Monel [316, 317]. However, the corrosion of titanium in gaseous fluorine at 377 K amounts to only 0.0082 mm/year. In spite of their limited resistance against fluorine and HF, very pure molybdenum and tungsten are employed as construction materials in rocket technology because of their great strength at high temperatures if fluorine–hydrogen and fluorine–hydrazine flames are used.

4.2.5 Passivation of Metals in Fluorine

Quite often, passivation of metals can be maintained only if exposure of the metals to air and moisture between fluorine exposures can be avoided. The formation of passivation films with good adherence and minimum sensitivity to air and moisture has been studied extensively for most metals that were qualified for fluorine service.

Tests were conducted to evaluate the effectiveness of cleaning and passivation procedures applied to a valve assembly for fluorine service [356]. The general reaction behavior of fluorine with metal surfaces and contaminants, and cleaning and passivation procedures for systems and components using fluorine-containing oxidizers included: (1) reaction of fluorine system contaminants, (2) impact sensitivity of organic residues left from passivation, (3) corrosive behavior of passivated metal surfaces, (4) gases absorbed on passivated surfaces, and (5) mechanical stability of passivation fluoride films.

Frequently, materials can be eliminated for future use with elemental fluorine by exposing them to HF instead of F_2 . Samples of five different metals were weighed while exposed to 10% HF at 322 K (120 °F) for 300 min.

Fluorination reactions reached completion on stainless steel, nickel, and aluminum alloy surfaces very rapidly [357, 358]. The surface film thickness ranged from 5 to 20 Å and fluoride films grew at the expense of oxide films. The apparent film thickness on copper and Monel surfaces continued to increase slowly over an extended period of time. A study of the composition of passive films formed, and the deleterious effect of atmospheric moisture on passivated surfaces showed that exposure of passive films to a humid atmosphere produced hydrated metal fluorides that caused secondary fluorination reactions upon re-exposure of the surfaces to fluorine. The passive films formed by exposure to chlorine trifluoride and chlorine pentafluoride were comparable in thickness with the films formed by fluorine gas, contained metal chloride species, and were less resistant to humid air attack. Fluorine gas appeared to be the most effective agent for the passivation of metals. Adequate passive films were formed at all pressures within 0.1 to 1.0 atm for a period of 15 to 30 min. A stepwise increase in concentration was unnecessary for the

passivation of metals, and slight deformation of metal surfaces did not destroy the passive films. Most of the passivating procedures developed for elemental fluorine can be equally effectively applied to other non-metallic fluoride oxidizers such as ClF_3 or ClF_5 .

Samples of metal (CRES-316 and Monel 400) powders were first passivated using different techniques under evaluation. Then, 100-g samples of the passivated metal powders under evaluation were placed in a constant-volume bomb, evacuated, and backfilled with fluorine gas. After the apparatus had achieved thermal equilibrium, the pressure decay in the bomb due to fluorine consumption was measured as a function of time for 2–3 h. If a sample did not take up any additional fluorine during this test, it was considered completely passivated [359]. The effects of atmospheric moisture on fluoride films were investigated by making reflection electron diffraction patterns of fluoride films formed on copper before and after exposure to atmospheric moisture.

Even though both liquid fluorine and liquid oxygen are very reactive, most of the common metals are sufficiently resistant for many applications. The compatibility with these oxidizers of alloys of iron, nickel, copper, aluminum, magnesium, titanium, and zirconium was examined and corrosion rate data were compiled from both published and unpublished sources and tabulated [360]. The stimulus required to initiate rapid reactions, or burning of both metals or organic materials by compressive impact, tensile impact, friction, wear, and other mechanisms has to be quantified by experiments. Such experiments can help to identify metals that are less sensitive to impact ignition.

Experience gained over a period of years in the use of metal equipment for the production and handling of fluorine and for the production and shipment of hydrofluoric acid has resulted in construction of durable and reliable production equipment [361]. Unfortunately, none of the common metals or alloys has been found to be universally applicable, and even the nobler metals such as platinum and silver have developed shortcomings under certain conditions. Of the common commercial metals, the nickel–copper alloys such as Monel have been found to be most reliable. However, severe corrosion has been encountered under some conditions. Nickel proved to be excellent for service with fluorine to relatively high temperatures. Mild steel has been used extensively in fluorine cell construction and has proved adequate for the storage and shipment of anhydrous hydrofluoric acid.

4.3 Corrosion of Ceramic Materials in Fluorine

Only a few inorganic compounds that form the base of ceramic materials are resistant toward technical grades of fluorine. Some would be acceptable for use in pure fluorine, but in real life fluorine often contains 0.5 to 1.5% HF, which makes it more corrosive.

α -Alumina is not attacked by fluorine at temperatures up to 1073 K (800°), but finely divided (“activated”) α -alumina does react. Glass can be used for dry and HF-free fluorine; otherwise, it will be etched by HF and opacify. Absolutely HF-free fluorine can be heated in Pyrex glass up to 473 K (200 °C). Asbestos is resistant to fluorine, but only highly purified grades of asbestos can be used.

A summary of the compatibility of other non-metallic materials of construction is provided in Table 11 in [292]. That table also contains some information on organic materials of construction.

At elevated temperatures, even ceramic materials, for instance, mullite-based firebrick, can react with fluorine in a flame reaction. If one aims the flame of a fluorine/hydrogen torch at a firebrick and then turns off the hydrogen supply, the destruction of the brick with fluorine continues as an exothermic reaction [282]. Specialty ceramics manufacturers offer parts made from calcium fluoride that are resistant to fluorine flames up to very high temperatures.

The reactions of ceramics intended as structural materials for chemical lasers with fluorine were studied at very high temperatures and included Al_2O_3 , B_4C , Re, LaB_6 , $\text{LaB}_6\text{-C}$, and $\text{LaB}_6\text{-MoSi}_2$ composites [362, 363]. The mechanisms by which fluorine gasifies solids limit the number of possible fluorine-resistant materials. Alumina gasification reaction kinetics were measured using a low-pressure, transonic microwave discharge flow reactor technique at 2.4 Pa and $1100 < T < 2000$ K. LaB_6 specimens exposed to atmospheric pressure fluorine-rich F_2/H_2 flames reacted with atomic fluorine to form a passivating, white LaF_3 coating. Other ceramics evaluated in a fluorine environment were ZrC and ZrB_2 [364] and HfC and HfB_2 [365].

4.3.1 Corrosion of Ceramic Coatings in Fluorine

Coatings composed of 77 mass-% CaF_2 /23 mass-% LiF fused on IN-750 nickel-based alloy were studied using SEM, X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy and optical microscopic methods [366, 367]. This coating-alloy system had good tribological properties in extreme conditions, such as liquid fluorine. The coating had good adherence and acceptable coating wear life.

4.4 Organic Materials of Construction for the Handling of Fluorine

There are very few organic polymers that are suitable for handling of fluorine. In all these cases, the hydrogen or chlorine in the polymer molecule has to be replaced as completely as possible by fluorine in order to minimize the chance of inadvertent ignition.

4.4.1 Elastomers for Fluorine Service

There are only a few organic polymers that are resistant to fluorine within certain limitations. Hydrogen-containing elastomers, such as polyethylene, polyesters, and phenolic resins, autoignite in gaseous fluorine at room temperature or below. PVC, Plexiglass[®], Neoprene, Viton[®] and a few other materials can be used with limitations. Some of the older literature contains very dubious references, such as the erroneous statement that “red rubber” is compatible with fluorine.

Polytetrafluoroethylene (PTFE; Teflon[®] or Hostaflon-TF[®]) is essentially the only elastomer that is suitable for fluorine service [368]. At sea level pressure, it is compatible with fluorine, but at elevated pressure it may begin to react with fluorine. The upper temperature limit at sea-level pressure is near 473 K (200 °C). Above this temperature, PTFE will be destroyed and converted to gaseous tetrafluoromethane. This reaction can escalate itself to a flame-like reaction. PTFE for fluorine service has to be carefully cleaned and may not contain any contaminants. Already tiny specs of dust or skin grease left behind from a fingerprint are sufficient to cause ignition in fluorine. Friction or rapid compression can also initiate a flame reaction that can be energetic enough to ignite adjacent metal parts. Teflon that has been cleaned with trichloroethylene may absorb and retain some of the solvent, which will then react with fluorine. Teflon containing more than 0.35% trichloroethylene is incompatible with liquid fluorine. Solvent-cleaned Teflon gaskets had to be degassed in a vacuum oven to remove absorbed solvents.

Many fluorine system failures have occurred during flow conditions, although the flow condition itself has not been established as the direct cause of failure in most cases. In one test at NASA Lewis, polytetrafluoroethylene (Teflon) was exposed statically to liquid fluorine at 10.3 MPa (1500 psia) without reaction. The same material when subjected to flow conditions at 345 kPa (50 psia) reacted violently. The fact that Teflon withstood static exposure to liquid fluorine and yet failed in the dynamic test is of particular interest. Metals form a protective fluoride surface film when exposed to fluorine. Teflon, on the other hand, tends to react with fluorine to break down the polymer and form unsaturated low molecular weight fluorocarbons. These fluorocarbons would not adhere to the surface and therefore would be of no value as protective films. It is also possible that a surface impurity could act as a reaction initiator.

Static and dynamic tests were made on the compatibility of gaseous fluorine with various liquids, solid plastics, waxes, and greases at pressures of 10.2 MPa (1500 psig) and room temperature [369]. These tests eliminated many materials from further consideration for use in fluorine systems. Only Teflon and ruby (aluminum oxide) were compatible under the static conditions of the tests at 10.2 MPa. Teflon survived quiescent gaseous fluorine at 10.2 MPa (100 atm) as well as flowing fluorine at 344 kPa (3.4 atm). Further tests under dynamic conditions would be required if the application involves exposure to flowing fluorine. Teflon was resistant to stagnant condition, but flowing fluorine caused rapid decomposition. Besides Teflon, other materials investigated were Kel-F, Fluorolube, and Permatex lubricants and various other elastomers.

Initially, this was only a go/no-go test that did not differentiate between different degrees of reaction and incompatibility. In continuation of this effort, the reactivity of 13 liquids, 11 lubricants, and 20 solids with liquid fluorine was examined at two different pressures [370]. Static tests were made on the compatibility of liquid fluorine with several non-metallic materials at 77 K (–320 °F) and at pressures of 101 kPa and 10.4 MPa (14.7 and 1515 psia). None of the liquids and greases tested was found to be entirely suitable for use in fluorine systems. Polytrifluorochloroethylene and N-43, the formula for which is $(C_4F_9)_3N$, did not react with liquid fluorine at 101 kPa or 10.4 MPa (14.7 or 1515 psia) under static conditions, but they did react when injected into liquid fluorine at 10.4 MPa. They also reacted with gaseous fluorine at 10.4 MPa. Although water did not react with liquid fluorine at 10.4 MPa in this test, it is known to react violently with fluorine under other conditions. The pipe-thread lubricant Q-Seal did not react with liquid fluorine, but did react with gaseous fluorine at 10.4 MPa. The results showed that the compatibility of fluorine with non-metals depends on the state of the fluorine and the system design.

A summary of the results is presented in Table 40, which indicates only whether or not a reaction was observed. Unfortunately, this is insufficient information because the dwell time of the samples was only 10 min. The terms “reaction” and “no reaction”, as they appear in that report were defined as follows: “reaction” means that either a visible explosion or fire took place or that the sample on inspection showed signs of oxidation; “no reaction” means that to the unaided eye, the sample appeared unchanged after exposure to liquid fluorine for approximately 10 min.

Both gaseous and liquid fluorine attacked Teflon more severely when flowing instead of resting. A triangular test sample made of Teflon decomposed rapidly in flowing liquid fluorine and only the pressure drop caused by the inadvertent opening of

Table 40: Resistance of non-metallic materials against gaseous and liquid fluorine.

Material sample	Liquid fluorine at 101 kPa (1 atm)	Fluorine gas at 101 kPa (1 atm)	Liquid fluorine at 10.1 MPa (102 atm)	Fluorine gas at 10.1 MPa (102 atm)
Liquids				
Kel-F Lo No. 10 (Kellogg Co.)	–	–	–	+
Fluorolube HO (Hooker)	–	–	–	+
N 43 (Minnesota Mining Mfg. Co.)	–	–	–	+/-
Tap water	–	–	–	+
Cenco HyVac Oil	O	B	O	O
Glyptal Alkyd Coating	O	B	O	O
Dow Corning 200	E	B	O	O
Waterglass (sodium silicate solution)	O	B	O	O
Dry JP-4 kerosene	O	B	O	O
Tetrachloromethane	O	E	O	O

Table 40: (continued)

Material sample	Liquid fluo- rine at 101 kPa (1 atm)	Fluorine gas at 101 kPa (1 atm)	Liquid fluorine at 10.1 MPa (102 atm)	Fluorine gas at 10.1 MPa (102 atm)
Lubricants				
Kel-F Med. Wax	—	—	+/-	+
Kel-F No.1 Grease	OX	—	OX	OX
Fluorolube LG	OX	—	OX	OX
Fluorolube MG	OX	—	OX	OX
Permatex No.3	—	—	+	+
Q-Seal	—	—	—	+
Blue Goop E (Swagelok)	—	O	+	O
Molylube	E	—	O	+
Plast-O-Seal (Weicon)	B	—	O	+
Permatex No.1	O	B	O	O
Permatex No.2	O	B	O	O
X-Pando Seal Coating	O	B	O	O
Solid Materials				
Rubin (Al_2O_3)	—	—	—	—
Teflon Kel-F	—	—	+/-	+
Kel-F Elastomer 5500	—	—	—	+
Graphitar	—	—	—	+
Graphitar-Powder	O	B	O	O
Neoprene-coated fiberglass	E	—	O	+
Plexiglass	—	—	+	+
Tygon tubing	—	—	+	+
Vynlit	—	—	—	+
Pennsalt PCC	—	—	—	+
Pennsalt PCI	—	—	+/-	+
Dow Corning Elastomer	O	B	O	O
Molykote Z Powder	O	B	O	O

— No Reaction; B burns; + Reaction; E explodes; +/- occasional reaction; O not tested; X same as Kel-F Med. Wax

Data source: [369]

a leak prevented the propagation of the reaction to adjacent metal parts. Judging by the deformation of the sample, the strongly exothermic reaction started over the entire surface of the sample and not only on one of its sharp edges. A few liquid samples were injected into liquid F_2 at 10.4 MPa (1500 psig) pressure. Kel-F 10 and 3M N43 reacted; tap water did not react.

Six soft-seal materials were investigated for compatibility with liquid fluorine under dynamic conditions [371]. For test purposes the materials were divided into two groups. Group 1 consisted of a nitroso-rubber specimen and two commercial glass-filled Teflon samples, Fluorogreen E-600 and Fluorobrown. Group 2 contained

bronze-, copper- and nickel-filled Teflon specimens as well as a plain Teflon control sample. The results indicated that limited application can be made in liquid-fluorine systems of the seals tested. One commercially available rotating-vane flowmeter was also tested. Operation of the meter was satisfactory at liquid-fluorine flow rates up to 1.58 kg/s (3.5 lb/s) and pressures up to 414 kPa (60 psia). A valve design that employed a soft-seal material at the flow shutoff interface was successfully tested with liquid fluorine at flow rates up to 0.9 kg/s (2 lb/s) and inlet pressures up to 669 kPa (97 psia). In support of this valve design, a compatibility investigation under dynamic liquid-fluorine conditions was conducted on six soft-seal materials. The materials tested were mainly fluorinated plastics.

The purpose of additional tests was to investigate the feasibility of using fluorine–oxygen mixtures in rocket-propulsion systems containing some non-metallic materials [372]. These are described in a later section on materials compatibility with FLOX mixtures.

The effects of fluorine gas exposure at between 1 and 2 atm pressure at room temperature and in liquid fluorine at cryogenic temperature on some properties of nitroso rubbers (the $\text{CF}_3\text{NO}/\text{CF}_2=\text{CF}_2$ copolymer and the $\text{CF}_3\text{NO}/\text{CF}_2=\text{CF}_2/\text{ON}(\text{CF}_2)_3\text{COOH}$ terpolymer systems and the compounded terpolymers) were examined for mid-term immersion [373]. These polymeric materials are more elastic than polytetrafluoroethylene and do not cold-flow, but they are less compatible for long-term use.

Because the resistance of hardly any of the commercially available elastomers was satisfactory for fluorine service, it was attempted to custom-synthesize polymers that were supposed to be resistant to attack by fluorine [374, 375].

4.4.2 Lubricants

Several lubricants have been tested for possible reactions on contact with gaseous fluorine [369]. At 101 kPa = 1 atm and room temperature, Kel-F[®] (Medium Wax), Kel-F[®] (No. 1 Grease), Fluorolube[®]-LG, and Fluorolube[®]-MG showed no or only minor changes. At 10 MPa = 100 atm or elevated temperatures they reacted and became unusable. Perfluorinated oils or greases are less compatible than solid polytetrafluoroethylene. Vacuum pumps filled with perfluorinated low-volatility oils can be used to pump fluorine-containing gases, but it is advisable to allow the ballast valve to remain open. Permatex[®] is one of the recommended lubricants for threaded joints.

The fluorine uptake of four fluorocarbon greases was studied in a glass apparatus at 373 K (100 °C) and a fluorine pressure of 13.3 kPa (110 mm Hg) [376]. The reactivity varied with the composition of the greases. The lowest fluorine uptake was observed with a grease formulated with polychlorotrifluoroethylene as the base material and a perfluorocarbon filler. When the same base material was retained but the filler was changed to a silica filler, an unacceptably high fluorine uptake was observed.

4.5 Selection of Materials for the Handling of Fluorine

After reviewing the information presented in the preceding chapters, it becomes apparent that there is no universally usable material of construction for fluorine equipment. Each material must be specifically selected for the component in question and the selection depends on the conditions of operation with gaseous or liquid fluorine and if it involves only stagnant fluorine or if it includes the more severe conditions with flowing fluorine. Table 36 at the beginning of this section has already offered additional information on the selection of materials for fluorine service. Table 41 lists recommended materials for construction of components in contact with fluorine.

Table 41: Recommended materials of construction for fluorine.

	Gaseous fluorine	Liquid fluorine
Storage tanks	CRES-304L, CRES-347, Al-61	Monel®, CRES-304L, CRES-347, Al-61
Tubing, flanges, couplings	Stainless steel, Al, Cu, brass	Monel®, Al-60, Inconel®, CRES-300 series
Valve bodies	Ni, Monel®, bronze, Inconel, brass	Ni, Monel®, CRES-300 series, Inconel®
Valve seats	Ni, Cu, brass, Al	Ni, Cu, Al, brass
Valve stems	Monel®, CRES-300 series	Monel®, CRES-300 series
Gaskets	Soft Al, Teflon®, soft Cu	Soft Al, soft Cu
Valve stem and rotary seal packings	Teflon®, Kel-F®	No recommendations available at this time.

Data source: [282]

5 Components for Fluorine Service

The corrosion of metals by fluorine is stopped or at least retarded by the formation of a passivating fluoride film. As long as the metal is not flexed or scraped, the protective fluoride film remains in place. It is difficult to select materials for components that are designed to be flexed, such as in bellows, which are usually needed to compensate for contraction and expansion of lines during cooling and warming.

Mechanical stability tests were performed to evaluate the metal fluoride stability on metal bellows of CRES-316, Inconel 625, Al-6061-T6, and copper when exposed to various combinations of flexing, cryoshock, gaseous fluorine, and liquid fluorine conditions [377]. Only trace amounts of the passivating coating were susceptible to flaking

by flexing. Most of the particles recovered after the test came from other parts of the system.

A very thorough evaluation of a design for a liquid fluorine feed system was performed by a team at Douglas Aircraft at their test sites at Gypsum Canyon and Antelope Valley [378–380]. These reports contain a complete and detailed description of all components in the system and metallurgical analysis of the locations where some of the components failed during extensive exposure to liquid fluorine at 77 K and gaseous fluorine at ambient temperature. This is one of the best contractor reports we have found in the NASA inventory. It also contains a bibliography of more than 100 related reports and supporting information.

During the period April 1963 to March 1965, the Air Force Rocket Propulsion Laboratory (AFRPL) designed, built, and operated the AFRPL Fluorine Test Facility [381]. The test facility, used to conduct exploratory development investigations of thrust chamber components, had a testing capability up to 44 kN (10000 lb_f) thrust, 10.34 MPa (1500 psia) chamber pressure; and 300 s continuous firing duration. During this development, new insights were gained into materials compatibility, facility design operation problems, control systems, instrumentation, safety considerations, and safe testing approaches. The report described the test facility with block diagrams and control schematics. Results and experience showed that a fluorine test facility can be successfully operated, both safely and economically.

Ground service equipment was designed that was to perform propellant transfer to the upper stage of a launch vehicle operating on liquid fluorine and liquid hydrogen [382] or with fluorine and any other unspecified fuel [383, 384].

In parallel to the development of a liquid fluorine upper-stage vehicle, the problems associated with the launch facility on the ground must be addressed. A paper described the factors that had to be considered in the design and operation of such ground service equipment [385]. Among the factors discussed were general fluorine system requirements, launch facility requirements, safety considerations, and existing facility modification costs. Specific attention was given to storage and transfer, vapor disposal, leak detection, spills, aborts, range safety, and personnel protection.

A liquid fluorine closed flow loop (for component testing) and a rocket engine test stand have been designed, constructed, and operated for extended periods with very few difficulties [386]. Based upon experience with this system, a new attitude toward the handling of fluorine evolved among the operators. Fluorine may now be handled with confidence so long as its peculiar characteristics are considered and respected. More realistic safety, cleaning, passivation, and testing procedures have been developed during that program.

The electrical signal from temperature sensors, liquid level sensors, and other instrumentation that measures properties of fluorine (gas or liquid) under pressure must be conducted through the pressure shell and cryogenic insulation wrapping of the tank. Leak-tight and corrosion-resistant electrical feedthroughs have been developed for use with fluorine and other corrosive fluids [387, 388].

Rocket engines use fluorine as a liquid, but chemical lasers need fluorine as a gas. The on-side storage of the fluorine may be in liquid form. In order to keep the chemical laser supplied with gaseous fluorine, a fluorine vaporizer has to be operated [389]. Using a modified commercial vaporizer, the system vaporized liquid fluorine during eight chemical laser tests with no malfunctions. The nominal operating parameters were 3.79 MPa (550 psig), 40 g/s flow rate and 20 min operating time. Based upon experience with this system, liquid fluorine can be vaporized continuously in a safe, efficient, and environmentally sound manner.

A very detailed fluorine systems design guidebook is Bluhm [390]. This handbook contains criteria for the design of fluorine feed systems and associated components. Two types of information were presented: (1) information defining general methods, and (2) detailed specifications and procedures. Although the major emphasis has been upon criteria for components exposed to elemental fluorine, the information is also applicable to systems utilizing other cryogenic oxidizers such as FLOX, which contain fluorine as a constituent. It also contains a list of components and instrumentation for the design of fluorine systems and a section on the detection and measurement of fluorine concentrations in the air at the workplace. The use of the word “airborne” does not mean that the systems are carried around in an airplane; the word only means to differentiate flight equipment from ground service equipment (which is not covered in this report).

The most complete guide to components and subsystems design, fabrication, and installation considerations for liquid fluorine and FLOX systems is in a NASA Special Publication [391]. It includes sections on properties of fluorine and FLOX mixtures, compatibility of materials, components and subsystems design, fabrication, and installation considerations, facility design criteria, facility preparation and operating procedures, production and transportation, and personnel safety.

A closed-loop components test facility was built specifically for the testing of components for liquid fluorine (LF₂) service. As of 1968, the large-scale 1890-L (500-gallon) liquid fluorine flow facility in the Mojave Desert, CA, had been operational for over 2 years [392, 393]. Constructed from “off-the-shelf” facility hardware, it was capable of instantaneous flow rates up to 113 kg/s (250 lb/s) for simulation of launch site ground service equipment and missile flight conditions. Unique facility features were: 1) largest known capacity single-propellant flow loop for component and subsystem testing; 2) flange and fitting connections instead of welded connections throughout; 3) dual-wall storage and receiver tanks; and 4) gaseous nitrogen blanket maintained at all times other than leak checking and flow operations. Control consoles were used for remotely controlled flow operations. Pressure and temperature instruments (ambient to 77 K = -196 °C = -320 °F) were used to monitor and provide test data. Testing has included valves, seals, quick disconnects, pressurization subsystems, and small combustors. During the first year of operation, 30 different components have been evaluated. Whenever a dead-ended plumbing section or static cavity was opened for component removal, a white, green,

or yellow corrosion product in powder form was encountered and identified as iron, chromium, nickel or aluminum fluoride. The bulk storage tank held 2265 kg (5000 lb) of LF_2 , the low-pressure tank could hold 1631 kg (3600 lb) at 482 kPa (70 psig), and the high-pressure storage tank could hold 679 kg (1500 lb) LF_2 at 5.17 MPa (750 psig). The best gasket was a combination of soft aluminum (Al-2024-T6) sheath surrounding a Teflon gasket, recessed in a groove, and compressed by a serrated flange surface.

The US National Bureau of Standards determined the physical properties of fluorine over a wide range of temperatures and pressures and developed a special fluorine-compatible apparatus for performing PVT measurements [394].

5.1 Valves for Fluorine Service

The selection of materials for fluorine control equipment (shut-off valves, throttling valves, cavitating venturi) is very difficult because the high flow velocities and metal/metal contacts may result in accelerated corrosion or even accidental ignition [395].

Valves for gaseous fluorine service at low pressures can be made of Monel[®] with a seat or plunger of Teflon[®]. For higher pressures the valve body, the seat, and the plunger must be made of Monel. Designs of valves where metal parts rub against each other should be avoided. At the contact point, the protective layer of metal fluorides is scraped off and enhanced corrosion will result. Valves for liquid fluorine service must not only be compatible with fluorine but must also be able to withstand thermal stress caused by the large differences in temperatures as the system cools down. If the valves are externally covered with ice from condensation of moisture from the atmosphere, it may become difficult to operate them. It is recommended to have redundant valves such that the system can be shut off safely if one valve should get stuck open.

Flight-weight axial flow liquid fluorine shutoff valves with a 5-cm (2-in) bore, incorporating bellows-type dynamic seals and poppet and seat combinations, were designed, developed, fabricated, and tested with liquid fluorine [396]. The valve was an all-metal construction utilizing a copper seat and stainless steel poppet. For qualification tests, the coaxial poppet-type valve was cycled under flow conditions of approximately 9 kg/s (20 lb/s) with an upstream pressure of 1.14 MPa (150 psig). This valve had a proof pressure of 1.65 MPa (225 psig = 240 psia), an external leak rate of $<10^{-7} \text{ cm}^3/\text{s}$, an internal leakage of $<100 \text{ cm}^3/\text{h}$ after 1000 LF_2 full flow cycles, valve opening and closing response times of $<500 \text{ ms}$, and a pressure drop of $<34 \text{ kPa}$ differential ($<5 \text{ psid}$) while flowing 29 kg/s (65 lb_m/s) of liquid fluorine [397].

The inlets to propellant valves are usually protected by filters to retain particles that might get lodged on the valve seat and cause the valve to leak when it is commanded shut. The screen material on the filters has to be compatible with the propellant, which in the case of liquid fluorine is a difficult task. The fluoride film growing on the thin metal wires might cause a narrowing of the passages and increase the pressure drop or embrittle the wires. Similar wire mesh is used in surface tension pro-

pellant management devices in propellant tanks for zero-g operation. The long-term effects of propellant immersion on fine micron stainless steel wire cloth were studied for liquid fluorine, chlorine trifluoride, and mixtures of fluorine and oxygen (FLOX) [398]. Historical screen immersion time durations reported in the literature ranged from 3 months to 7 years.

There are many types of valves available for fluorine service. Some of the valves, such as those used for a static rocket engine test with a fluorine/ammonia rocket engine, can be operated by remote control [399].

A pressure relief valve was designed for protecting fluorine–liquid oxygen ATLAS launch vehicle oxidizer tanks against overpressurization [400].

Because it is difficult to design tight packings for rotating or sliding valve stems, bellows-sealed valves are more reliable for fluorine service [401, 402].

5.2 Flowmeters for Fluorine Service

Flowmeters for gaseous fluorine can be built based on the pressure drop through an orifice, with a manometer measuring the pressure differential across the orifice. A flowmeter of this type is described in Straty [403]. Turbine flowmeters are less suitable for fluorine because the rotary parts (shafts and bearings) have friction at metal–metal contacts. Rotameters have been used for low flow rates and low pressures. The float was made of aluminum or steel and the conical glass tube was made from Pyrex[®] [79]. Two precautions must be taken into consideration: The fluorine gas must be free of HF, because otherwise the glass would become opaque, and the float may change its weight or dimensions owing to fluorine corrosion; thus, the rotameter must be calibrated more frequently than with other gases. The wear of metals in a rotameter was measured under various flow conditions [404].

For liquid fluorine, a flowmeter was developed in which a helical swirl was induced in the liquid stream by a multi-hole plate. At a short but wide bulged section of the tubing, the swirl caused a Teflon-coated steel sphere to spin around a race groove in the wall in circles and each passage of the steel ball was recorded on a magnetic pickup on the outside of the tubing. The steel ball was made of CRES-440C. Over an aggregate running time in liquid fluorine of about 1 h with 900 to 1600 RPM, the weight loss of the 1-g ball was less than 0.25% [395]. Other methods of metering F₂ or HF flows are described in Zima and Doescher [405].

A flowmeter for gaseous F₂ using a nickel filament as a sensing element, similar to the katharometer used in thermoconductivity gas chromatography detectors, was calibrated for several gases [406]. The output voltage of the flowmeter was measured for Ar, N₂, O₂, and F₂ for flow rates between 0 and 400 mL/min at filament currents in the range 50–75 mA. The dependence of output on the thermal conductivity of the gas being measured and on the filament current was investigated. The temperature of the filament could be calculated from measured values of the resistance.

5.3 Pumps for Fluorine Service

Low flow rates of fluorine gas can be pumped with membrane pumps, but the repeated flexing of metals shortens the life of the membranes and they have to be replaced very often. In one membrane pump design, the membranes are driven by a hydraulic system, but the (normal, combustible) hydraulic oil is separated from the fluorine by two additional membranes and the interspace is filled with an inert fluid, such as $C_6F_4(CF_3)_2$ (perfluoroxylene) or antimony pentafluoride [407]. Thus, even if one of the membranes should fail, the hydraulic oil and the fluorine would not come into contact with each other.

Pumps for liquid fluorine are not off-the-shelf items and keeping them lubricated is very difficult [408]. In the 1950s, Bell Aerosystems Company developed a liquid fluorine pump that was made from an aluminum alloy and rotated at 30000 RPM [409]. The packings of the rotary seals had to be replaced repeatedly after only 30 min of operation. Some of these pumps are placed in a position where they are referred to as “boost pumps,” such as when liquid fluorine is fed to a vaporizer under pressure. Rocketdyne developed a prototype liquid fluorine pump [410].

A liquid fluorine pump was designed by the stream-filament method and tested for non-cavitating and cavitating performance under different net positive suction head conditions [411]. It was then tested under high RPM conditions and with an inducer tip speed of 57.3 m/s (188 ft/s) [412, 413].

Rotating and reciprocating positive displacement pumps of various types were studied for pumping liquid fluorine for low-thrust, high-performance rocket engines [414]. Included in the analysis were: centrifugal, Pitot, Barske, Tesla, drag, gear, vane, axial piston, radial piston, diaphragm, and helirotor pump concepts. The centrifugal and gear pumps were carried through detailed design and fabrication. After preliminary testing in Freon 12, the centrifugal pump was selected for further testing and development. It was tested in Freon 12 to obtain the hydrodynamic performance. Tests were also conducted in liquid fluorine to demonstrate chemical compatibility.

The design of rapidly rotating dynamic seals in pumps is a difficult task for both cryogenic oxygen and cryogenic fluorine, but highly complicated for liquid fluorine because of the reactivity of fluorine with gasket and seal materials [415]. Friction and wear studies were conducted with four material combinations submerged in liquid oxygen or in liquid fluorine to determine their potential as dynamic seal components for fluorine turbopumps. The friction and wear experiments were conducted with a hemispherically tipped rider with a radius of 3/16 in sliding in a circumferential path on the flat surface of a rotating disk measuring 21 in in diameter. The seals used in this investigation had a flame-sprayed Al_2O_3 nosepiece (0.006 to 0.008 in thick) and were run against a mating disk of TiC cermet or a fused coating of $CaF_2 + LiF-NiF_2$ on Al_2O_3 submerged in liquid fluorine. Results indicated that fluoride films, either as an applied fused coating ($CaF_2 + LiF + NiF_2$) or as a film formed during sliding (NiF_2 on the TiC cermet or possibly AlF_3 on Al_2O_3) in liquid fluorine, were beneficial

in reducing the friction and wear of the Al_2O_3 riders. The seal experiments in liquid fluorine showed that flame-sprayed Al_2O_3 sliding against the TiC cermet or a fused coating of $\text{CaF}_2 + \text{LiF} + \text{NiF}_2$ on Al_2O_3 are potential LF_2 rotary seal materials.

Converting an ATLAS launch vehicle from operation on LOX to operation on FLOX was motivated by the potential gain in payload and terminal velocity capability, but it was a difficult engineering challenge. Compatibility of FLOX with tankage, pumps, and flow control components was extensively investigated before the program was canceled. The most critical part in the conversion project was the oxidizer pump and its rotary seals [416].

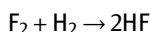
An experimental program was conducted to evaluate and select materials for ball bearings for use in liquid fluorine or FLOX [417]. The ability of three different ball-separator materials, each containing nickel, to form and transfer a nickel fluoride film to provide effective lubrication at the required contact areas of a ball bearing operating in liquid fluorine was evaluated. In addition, solid lubrication of a ball bearing operating in liquid fluorine by either a fused fluoride coating applied to all surfaces of the ball separator, or by fluoride impregnation of porous sintered material ball separators was evaluated. Less bearing wear occurred when tests were conducted in the less reactive FLOX instead of liquid fluorine. Bearings fabricated from any of the materials tested would have only relatively short wear lives and would require frequent replacement in a reusable engine (as opposed to a fly-once-throw-away engine).

Lubricating mechanism, cage design, and design factors of contact seals for liquid fluorine pumps were studied [418].

At a fluorine manufacturing plant, the cylinders to be filled with high-pressure fluorine gas are typically are not pressurized with a compressor, but fluorine is first liquefied into sturdy, pressure-proof cold traps and then allowed to vaporize under its own vapor pressure. This has the advantage that non-volatile contaminants are left behind in the cold trap. However, compressors for gaseous fluorine have been designed for applications where recovered, unreacted gaseous fluorine has to be recycled through a process for another pass through a reactor [419, 420].

5.4 Pressurization Systems for Liquid Fluorine Service

Main tank injection pressurization systems have been tested for several hypergolic propellant combinations. Because fluorine reacts hypergolically with all fuels, fluorine systems would be a good candidate for testing main tank injection pressurization. In the case of



although the reaction takes place mostly on the surface of the liquid propellant, the concern would be about frozen HF particles getting entrained into the lower part of the cryogenic propellant liquid and clogging filters and injection orifices [421–427].

5.5 Pressure Regulators for Fluorine Service

Although a pressurant gas regulator for a pressure-fed rocket using fluorine oxidizer is intended to flow only pressurant gas (helium), fluorine may diffuse back to the regulator membrane and corrode it before it has a chance to fly. A new helium regulator had to be developed for a fluorine propellant system in an upper-stage rocket [428].

5.6 Quick-Disconnect Couplings for Fluorine Service

A prototype “quick-disconnect” coupling for ground-to-vehicle transfer of liquid fluorine was designed, developed, and successfully tested at NASA LRC [371]. Operational features of this hardware included remote positive control of liquid-fluorine flow during the transfer operation, remote connection and separation capabilities, negligible liquid-fluorine spillage upon disconnection of the coupling, and remote reconnection and reuse capability if an abort condition should arise. The design proved satisfactory at flow rates up to 1.13 kg/s (2.5 lb_m/s) and pressure differentials up to 158 kPa differential pressure (23 psid). A commercially available rotating-vane flowmeter was also tested. Operation of the meter was satisfactory at liquid-fluorine flow rates up to 1.58 kg/s (3.5 lb_m/s) and pressures up to 414 kPa (60 psia).

Quick disconnect couplings were developed for use with fluorine and fluorine-containing oxidizers for the ATLAS launch vehicle [429] or a typical upper stage (e.g., NOMAD and for a planned LF₂/LH₂ upper stage) oxidizer fill-and-drain application [430, 431]. Appendix III of van Horn [430] contains a complete summary of materials compatibility with fluorine and chlorine trifluoride.

6 Special Problems During the Use of Fluorine

Like any other hazardous chemical, certain special safety precautions are required for the safe use of fluorine as a rocket or chemical laser propellant [432].

6.1 Controlled Destruction and Disposal of Excess Fluorine

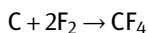
Every once in a while a fluorine user may get stuck with excess fluorine that has been accidentally contaminated or is no longer needed. It is highly unlikely that the supplier would take it back for reprocessing and in most cases the fluorine has to be destroyed at the test site. Contingency planning for a liquid-fluorine test site must assume the worst case scenario where tanks begin leaking and large amounts of fluorine must be destroyed in a controlled and confined manner. In addition, routine transfer of liquid fluorine from one tank to another often requires venting of the receiving tank and the vent gas has to be neutralized. At the end of the transfer, the supply tank has to

be depressurized, venting a mixture of pressurant gas and fluorine. Small amounts of fluorine gas need to be disposed of when new systems are passivated and purged with fluorine. There are only very few geographic locations where fluorine gas can be vented through a tall stack into the atmosphere, as long as a good wind is blowing in the right direction.

Fluorine disposal and destruction processes described here are either dry processes or wet processes. We considered dividing this section into dry, wet, and other processes, but there were several publications that dealt with more than one process that it would be difficult to divide this section by mode of disposal. Instead, it follows the same near-chronological order as most of the other sections in this book.

One method for disposal of excess fluorine (even fluorine contaminated with HF) injected the gas into an air/methane or air/propane ring burner operating on a rich air:fuel ratio [60]. DuPont in Wilmington, DE at one time had a facility of this type that could dispose of 56 kg F₂/h. The burner effluents were first quenched with water in a tower packed with graphite Raschig rings, and then washed with a spray of caustic soda liquid.

The National Advisory Committee for Aeronautics (NACA) Lewis Research Center evaluated several different methods for disposal of excess fluorine [433]. Undesirable fluorine was neutralized by reaction with water, steam, fuel gas or solid absorbents. Many of these earlier methods required continuous control by a well-trained operator, required much floor space, and consumed large quantities of expensive neutralizing chemicals. There was the need for a fluorine disposal method that could operate unattended and would use only readily available, less expensive chemicals. Such a method was found in the reaction of fluorine with activated charcoal that proceeds according to



and quickly leads to tetrafluoromethane without any undesirable by-products. Tetrafluoromethane is not poisonous and can be vented to the atmosphere. It has only a very low ozone depletion potential.

Lignite coal or graphitized coal is not suitable because it may result in the formation of less volatile fluorinated reaction products that may clog the reactor. Graphite reacts with fluorine only above 723 K (450 °C), whereas at lower temperatures it forms an addition (intercalation) product. Activated charcoal must have the necessary porosity and surface area to be reactive with fluorine. The waste gases enter the reaction chamber at the head and leave it at the bottom. The reaction may be so vigorous that it is advisable to dilute pure fluorine with an inert gas so as to extend the useful lifetime of the reactor. The optimal reaction temperature in the reactor depends on the thermal insulation surrounding the reactor and can be controlled by varying the dilution ratio. The reactor has to be kept at a minimum temperature to allow instant destruction of fluorine. The purity and porosity of the activated charcoal determines the ignition temperature. Charcoal (even barbeque briquets)

has a high surface area and absorbs a lot of atmospheric moisture when stored in air in unsealed bags. Excessive moisture content reduces the activity and may delay the start of the reaction. Therefore, it is best to dry the activated charcoal before use. Graphitized carbon reacts only if it is impregnated with an ignition material. While developing the reactor and optimizing the operating conditions, tests were run with fluorine concentrations varying from 0.5 to 100 vol.-%. For instance, when the feed contained 15 vol.-% F_2 , the effluents contained less than 0.003% (30 ppm) residual F_2 . With only 0.5% F_2 in the feed, the conversion was incomplete because the reaction temperature was too low, allowing 138 ppm F_2 to escape unreacted. Adding a little oxygen to the gas feed was recommended to improve the conversion of low fluorine concentrations. For every 5.5 kg fluorine to be destroyed, the reactor will consume 1 kg of activated charcoal. The grain size of the charcoal has to be optimized for the size of the reactor. If the grain size is too small, the pressure drop becomes prohibitively high. On the other hand, small grain size allows more surface area to be exposed to the gas and will result in more complete conversion [303]. The NASA Publication SP-3037, on pages 165–173, shows design examples and a photograph of an actual charcoal fluorine disposal facility [434].

Fluorine disposal reactors have been used extensively at several nuclear reactor fuel processing plants and rocket test sites in the US during the 1960s. The maintenance is relatively simple as one only needs to add more charcoal while the reactor is cold and not in use. If large fluorine flow rates (>10 kg/h) need to be destroyed, several reactors have been operated in parallel. On the other end of the flow rates, a small fluorine disposal unit was developed for laboratory use. It consisted essentially of a Pyrex® glass vessel with a metal screen holding a bed of granular activated charcoal. The progress of the reaction could be observed through the glass wall and the flow rate could be adjusted to keep the flame zone in the upstream part of the bed [304]. Fluorine and fluorine–oxygen and fluorine–nitrogen mixtures containing as little as 6.5 vol.-% fluorine reacted spontaneously with fresh dry charcoal. Fluorine and fluorine–oxygen mixtures were consumed at rates up to 11.3 kg/h (25 lb_m/h) in an experimental portable reactor containing 170 L (6 cubic feet) of charcoal.

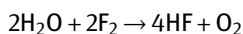
The reaction of fluorine with water was reported to potentially proceed in two ways under otherwise identical conditions, one by a smooth uninhibited burning reaction characterized by a purple flame, and the other by a slower, inhibited reaction in which no flame was observed. Violent explosions took place unpredictably when the inhibited reaction suddenly shifted to the burning reaction mode. The reaction of fluorine with low-temperature steam can also be explosive after a delayed start.

In the literature there are several surveys of various techniques for disposal of excess fluorine. One of the cleanest methods is the reaction of fluorine or diluted fluorine with a 200–500% excess above stoichiometric requirements of superheated steam [219, 435, 436]. Air-diluted fluorine with less than 50% F_2 should be preheated to about 672 K (750 °F) before reacting with superheated steam heated to 533–728 K (500–850 °F).

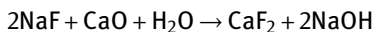
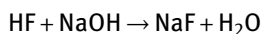
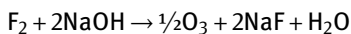
Small reactor units have been designed for fluorine disposal on a laboratory scale [437].

Wood chips, coke, and coconut-shell charcoals were evaluated for fluorine disposal in a reactor [438]. The coconut-shell charcoal produced the smallest amount of solid and liquid reaction products. Efficient removal of fluorine was accomplished by the coconut-shell charcoal in a reactor measuring 12.5 cm (5 in) in diameter with a feed containing 25 vol-% fluorine at flow rates from 2.8 to 11.3 m³/h (100 to 400 scfh) and reactor-wall temperatures of 922 to 1255 K (1200 to 1800 °F).

Carbide & Carbon Chem. Co., then a division of Union Carbide, built a facility for the disposal of large amounts of fluorine, in which fluorine was reacted with a large (2- to 29-fold excess above stoichiometric) amount of superheated steam. In this way, the slow reaction



received the necessary pre-heat to achieve a more rapid and more complete conversion. One must avoid the accumulation of unreacted fluorine and steam because it may result in explosions [224]. Similar reactions take place between oxygen difluoride and steam. High fluorine concentrations in the feed gas may have to be diluted with air to avoid a welding torch-like flame reaction that might melt the apparatus. After complete hydrolysis, the reaction products were quenched in a wash tower with water sprays. The wash tower effluents were collected in a lined holding pond and neutralized with caustic lime. The reactor was made from Monel[®] and the wall temperature was kept at 533 to 673 K (260 to 400 °C). This reactor was more suitable for continuous disposal and required more controls than the activated charcoal reactor. Another facility using sodium hydroxide solution in a counter-flow absorption tower was operating continuously and was capable of destroying 30 kg/day of fluorine, but required complex controls and maintenance and used neutralizing chemicals [439, 440]. In this continuous process, fluorine and HF are absorbed with sodium hydroxide solution (>2% NaOH) and the fluoride-containing nearly exhausted sodium hydroxide solution is reacted with caustic lime slurry (calcium oxide/calcium hydroxide) resulting in insoluble CaF₂, which can settle out in settling ponds and in an NaOH solution, which is pumped back to the F₂/HF absorber



In a similar continuously operating fluorine disposal facility fluorine was reacted with an aqueous solution of 54% NaOH [441, 442]. This design would also be advantageous for treating gases that contain HF in addition to F₂. The fluorine concentration in the effluent was less than 0.02% (still too high for discharge into the air at many locations!). There is also concern that under these conditions, fluorine is only converted

to oxygen difluoride, which is a different problem altogether because it is less reactive than fluorine and more difficult to dispose of.

A review of several candidate methods for disposal of fluorine lists the reaction of fluorine with sodium chloride leading to sodium fluoride and free chlorine [443]. The chlorine can be neutralized as usual with caustic lye and a reducing agent. This avoids the reaction of fluorine with water, which is often inhibited and sometimes starts only explosively after the accumulation of sufficient reactants in a closed vessel. Some investigators did not recommend the charcoal method and alerted their colleagues to the potential formation of graphite fluoride, which can decompose explosively.

There has been no lack of attempts to use anything but the most readily available chemical, water, for the disposal of fluorine, but even if conditions are maintained that allow complete conversion, the question remains about what to do with the dilute HF solutions obtained in this way. See also Houston [10].

Instead of passing the fluorine-containing gas through a packed-bed reactor, it is also possible to pass it through a fluidized-bed reactor [444]. That has the advantage of the suspended solid being continually replaced at the same rate as it is consumed and it avoids hot spots in the reactor. Fluidized bed reactors would only be used for larger installations because they are more complex and are operated continuously.

Alumina, soda lime, and charcoal were evaluated as fluorine disposal media [445]. Plugging of the disposal traps occurred regularly when alumina and soda lime were used. The use of charcoal reduced plugging problems, but a check valve was required to eliminate backflow interference from small pressure surges resulting from the charcoal-fluorine reaction. In a given size trap, charcoal had twice the capacity for fluorine disposal, compared with soda-lime or alumina capacity. Charcoal was selected as the most desirable disposal medium because of its high disposal capacity, gaseous reaction product (CF_4), and freedom from trap plugging. Iron filings and steel wool were tested as a fluorine scavenger [446].

The primary product of the reaction between fluorine and charcoal is CF_4 , with small amounts of higher fluorocarbons. Heated or unheated charcoal traps have been used at several sites for fluorine disposal. Non-activated wood charcoal heated to 398–573 K (125–300 °C) was recommended for fluorine disposal. Explosions were reported with activated charcoals and low fluorine concentrations [447]. The explosions were attributed to the rapid reaction of a large quantity of adsorbed, unreacted fluorine with charcoal after the reaction was initiated by increasing the fluorine concentrations to the ignition point. This hypothesis was confirmed by several observations [448]:

- Non-activated charcoals with low surface areas (and thus lower capacity for fluorine adsorption) did not explode when reacted with fluorine under the same conditions.
- The residual fluorine concentration in unreacted activated charcoal was much higher than that in non-activated charcoal.
- Fluorine adsorbed on activated charcoal could be removed by purging: then the charcoal did not explode when the fluorine concentration was sharply increased.

Published data often do not adequately define trap operating conditions at the time when the problem occurred, such as temperature and fluorine flow, for efficient fluorine disposal. Data for the composition of reaction product gases under various operating conditions are also incomplete. A study was undertaken to clarify these uncertainties. Results indicated that the fluorine–charcoal reaction efficiency increased with temperature. At 5% fluorine in the inlet gas, only 10% of the fluorine reacted with charcoal at 473 K (200 °C). A total flow >25 times higher than in these tests resulted in no fluorine breakthrough at 573 K (300 °C). The effect of charcoal bed depth on F₂ disposal rate needs to be examined. One study demonstrated efficient F₂ disposal with 25% fluorine in a heated charcoal bed, 5 cm (2 in) in diameter and 6.25 cm (2.5 in) deep, at a linear flow speed of 15 m/min (50 ft/min). At 573 K (300 °C), the F₂–charcoal reaction zone was narrow.

A study was performed to determine the best method of disposing of waste fluorine in the effluent from a uranium oxide conversion facility [449]. After reviewing the fluorine disposal literature and upon considering the nuclear safety constraints, it was determined that the two most promising processes were the fluidized alumina bed and the caustic scrubber [450]. To obtain more design data for the latter process, a three-stage, 12.5-cm (5-in) I.D. spray tower was constructed and operated. This unit used a 10% potassium hydroxide solution at scrubbing liquid flows of 5.7 to 11.4 L/min (1.5 to 3 gpm) and achieved a 90% fluorine removal efficiency at fluorine flowrates as high as 15 L/min (4 scfm). However, two toxic by-products, oxygen difluoride and nitroxy fluoride, were detected in the effluent gases. After considering the relative merits of both disposal processes, it was concluded that the fluidized bed is superior, especially if the contaminated waste material (aluminum oxyfluoride) were salable. See also Netzer [451].

6.2 Consequences of Accidental Fluorine Leaks and Spills

Because many materials in and around rocket test sites and rocket launch sites are not designed to be totally compatible with fluorine, a fluorine leak or spill may cause rapid ignition and occasional explosions. Fluorine (both gaseous and liquid) spills have been simulated to obtain a better understanding of the potential consequences of such an accident. This type of testing is an expansion of the materials compatibility tests described earlier. The objective of those tests was to identify materials that are compatible with fluorine in any state (liquid or gaseous) and are designed to be exposed to fluorine for a long time. It is impractical to design the entire test and launch site from such materials; thus, contact with incompatible materials is possible and must be anticipated if static and flight testing with fluorine propellants is conducted. It does not even require an accident; sometimes fluorine has to be vented at the end of a test and those vented gases might come into contact with incompatible materials downwind of the vent stack.

The hypergolicity of cryogenic liquid fluorine or FLOX when spilled in an unconfined manner onto various common materials is of particular interest. Fluorine, FLOX, and their most common byproduct, HF, are all toxic; it is desirable that these gases be inerted or made to rise upward for better dispersion and diffusion into the atmosphere for the safety of personnel and communities downwind of the spill area. An investigation was therefore made to determine the results of such spillages onto various materials. Small quantities (2.2 to 4.5 kg = 5 to 10 lb_m) of liquid (FLOX, fluorine, or oxygen) were spilled from a height of about 51 cm (20 in) upon several common materials that might be found or placed around a test or launch facility [452]. The materials were confined in stainless steel pans (0.9 × 0.9 × 0.3 m = 3 × 3 × 1 ft). Fluorine reacted violently with wet sand or with a puddle of water. The reaction with the water puddle was accompanied by a flash and a loud explosion. When liquid fluorine was spilled upon JP-4, smooth burning occurred, as opposed to the multiple microexplosions with FLOX (Section 10.1.6). From these spill tests, information was obtained in the following areas: (1) The hypergolicity of FLOX and fluorine with various materials upon which they might be spilled; (2) qualitative information on reaction characteristics and combustion propagation by visual observation and high-speed photography; (3) visual, photographic, and cinematographic information on the path of the resultant gas clouds; (4) the feasibility of using charcoal as a reactant for fluorine spills as a means of pollution control. Placing charcoal in areas underneath fluorine pipes where leaks would be suspected is one precaution that can be taken to prevent or mitigate worse disasters.

6.2.1 Neutralization and Treatment of Accidental Fluorine Leaks

6.2.1.1 Evaluation of Neutralization Agents

It is very difficult to deal with fluorine leaks because in many instances the leak is accompanied by a fire within seconds from when it was first detected. There are basically two methods that were tested in various settings: water sprays and dust clouds with sodium carbonate [433, 453]. The various methods were tested in a cubical test chamber that was lined with asbestos, but not hermetically sealed so that overpressure would be vented to the atmosphere. On the ceiling of the chamber was a circular manifold showerhead through which water was sprayed on the leak. Sodium carbonate was blown from a tray along the ceiling with compressed air. There was an array of previously evacuated cylinders into which samples of the atmosphere in the test chamber could be collected at various stages of the experiment to obtain a concentration–time profile. Six tests were conducted with this apparatus, three with gaseous and three with liquid fluorine leaking out. The tests with gaseous fluorine did not produce overpressure or light emission as external signs of a reaction, but liquid fluorine caused overpressure in the chamber and flashes of light. The walls of the chamber were partially destroyed. The results are illustrated in Figure 17 and 18. Figure 17 shows the distribution of fluorine between the absorption media and the surrounding atmosphere.

Figure 18 shows the time profile of the fluorine concentration in the test chamber. One can see that the absorption of gaseous fluorine is less complete than that of liquid fluorine.

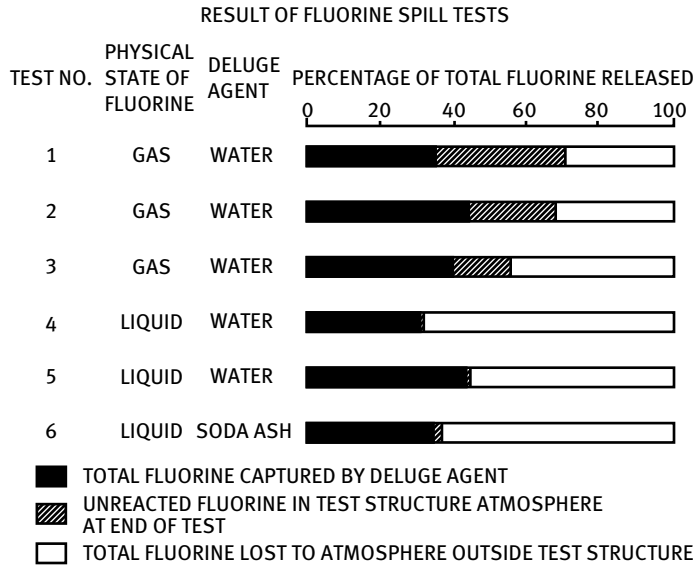


Figure 17: Absorption tests of gaseous and liquid fluorine with water and sodium carbonate. (From [433].)

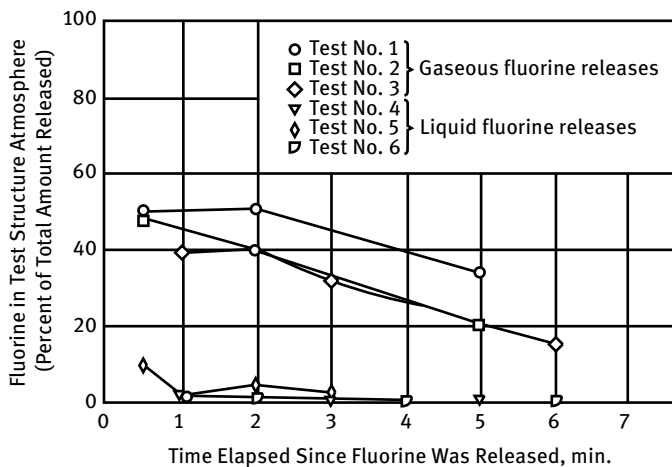


Figure 18: Fluorine concentration in the test chamber atmosphere following the application of water or soda. (From [433].)

In tests with liquid fluorine the concentration was quickly brought down to levels where ignition was no longer a hazard. The application of soda powder was at least as effective as the application of water spray. In a seventh test, liquid fluorine was spilled without any absorbent. The spill ignited and destroyed the test stand. The fluorine vapor cloud extended for several miles downwind.

Water and soda ash were investigated for use as deluge agents to reduce contamination from fluorine spills [454]. Thirty to forty percent of the released fluorine was captured by these agents. The reactions were rapid. However, no damage to the test structure was noted. Fine water sprays were more effective reactants than coarse water sprays.

Thirty-eight different chemicals in addition to water and sodium carbonate were tested for their effectiveness for the neutralization of fluorine spills [453]. The requirements for such chemicals are:

1. large absorption capacity for fluorine
2. fast, but not explosive reaction with fluorine
3. no formation of toxic reaction products
4. no hygroscopy and no tendency to cake during storage.

Three different test methods were used to evaluate the various chemicals. In series A, small quantities of the material were added to 4 mL of liquid fluorine in a test tube. Only $\text{Ca}(\text{OH})_2$, CaCO_3 , NaHCO_3 , Na_2CO_3 , $\text{Na}_2\text{B}_4\text{O}_7$, K_2CO_3 , and KF showed useful absorption properties. In series B, an excess of the materials that passed the requirements of Series A was held in a 250-mL beaker and 6 g liquid fluorine were poured on the pile. In this series, an aqueous suspension of CaCO_3 , solid NaHCO_3 , $\text{Na}_2\text{B}_4\text{O}_7$, Na_2CO_3 , or K_2CO_3 had the best absorption properties. Test series C simulated the conditions of an accidental fluorine leak where the absorbent was dumped on the evaporating fluorine. A fire extinguisher capable of holding 450 kg dry powder was converted for this test and recharged with the powder under test. The fire extinguisher was pressurized with nitrogen to 1414 kPa (14 atm = 205 psia) and capable of applying 360 kg/min. The powder was applied to the leak through a bifurcated manifold that was aimed at the leak from two different sides. The best neutralization was achieved with NaHCO_3 , Na_2CO_3 , and K_2CO_3 . It is assumed that soda was used as the monohydrate $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. Potassium carbonate was less suitable because it is very hygroscopic and may clump together during storage. See also Chamberlain and Siegmund [455, 456].

The USAF conducted fluorine spill neutralization tests on an even grander scale, again using water and soda as the main agents [457]. The objective of these tests was to determine how spilled fluorine in quantities of several hundred kilograms can be neutralized by water or soda and how the unreacted fluorine escapes and spreads in the area. A test site was selected at the boundary of Edwards Air Force Base in the Mojave Desert away from any inhabited areas where open liquid fluorine pools could be dumped with soda powder or sprayed with water sprays. Two tests were conducted,

one with soda and one with water and each used 110 kg of liquid fluorine. The test chamber was less confined than the one used at NASA, such that hot gases could escape more rapidly. In another large-scale test, 730 kg of liquid fluorine were sprayed with 1200 kg of water. The wind speed at the moment of the test was 5 to 7 knots. This was less than desirable, but resulted in gradual dispersion of the downwind plume. Water reacted vigorously with a bright flame with the fluorine, similar to what had already been observed by earlier experimenters. Numerous gas sampling stations were installed at ground level in the downwind area and it was noted that the gases were diluted to non-hazardous concentrations after traveling 1.6 km in downwind direction. The hot HF had substantial buoyancy and rose at the accident site. Groups of white rats were caged and exposed to the plume at 3, 22, 45, 75, and 150 m from the test site. The animals at 3 and 22 m suffered mainly scalding from the heat of reaction and chemical burns were only secondary. Concentrations above ground level were measured by sampling lines dangling from a helicopter, but only in one of the tests. The largest test ever of this kind used 750 kg of liquid fluorine and 6 metric tons of soda. For comparison, a parallel test was conducted with 485 kg of liquid fluorine without any absorbing media applied. In this test, the stainless steel bath tub holding the fluorine ignited and half of it burned, forming yellow fumes (FeF_3).

The cheapest method for neutralizing larger fluorine leaks is without any doubt the use of water sprays. However, it is difficult to reproducibly achieve good absorption of fluorine because the reaction proceeds at different rates, depending on the mixture ratio. If small amounts of fluorine are flooded with water, the gas may only be dissolved, but not reacted.

6.2.1.2 Dispersion of Plumes from Fluorine Spills

The distribution of fluorine gas outside a fluorine spill test chamber, with moistened indicator paper giving a semi-quantitative indication is shown in Figure 19, which gives the fluorine plume shape in the vicinity of a spill test chamber and the different shades indicate the local fluorine concentration in relative units (worst = 100).

Atmospheric diffusion tests were conducted to determine the plume trajectory and downwind 3-D concentration profile for combusting and non-combusting fluorine spills under a variety of atmospheric conditions [458]. The trajectory of a hot conflagration cloud resulting from spills of up to 1360 kg (3000 lb) of a 30% LF_2 /70% LOX FLOX/RP-1 mixture was determined by photographic recording and compared with predictions from a computer model. Two F_2 and two HF atmospheric samplers were placed in strategic locations. In a separate test, the evaporation rate of FLOX from a simulated spill containment system was determined. In another test, the blast overpressure caused by a FLOX/RP-1 deflagration was measured. The rate of dispersal of a toxic vapor cloud would depend on meteorological atmospheric conditions at the accident site [459, 460].

Because of the need to develop contingency planning to manage potential accidents involving the release of either HF or fluorine, dispersion models have been de-

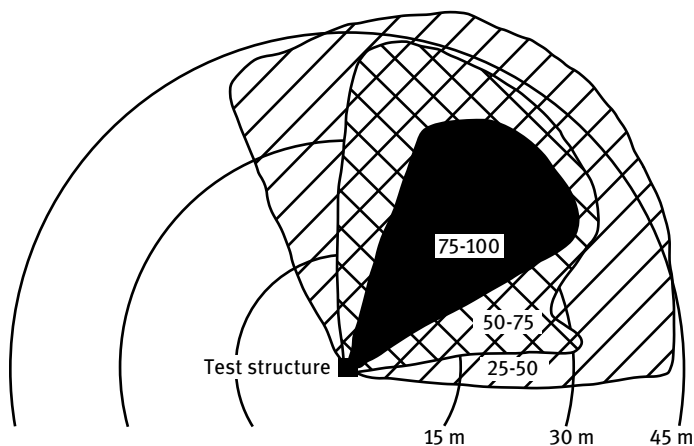


Figure 19: Relative fluorine distribution in the test area following a leak of 3 kg fluorine gas and application of water spray. (From [433].)

Test No. 2. Wind from NNW with 8 to 10 knots

veloped and integrated into the Air Force Dispersion Assessment Model (ADAM) system [461, 462]. The thermodynamic aspects of the HF polymerization reaction and dissociation when mixed with air have been modeled and considered in dispersion calculations. The dispersion results have been compared with test results from the Goldfish Series of field tests. The agreement was good between predicted and measured parameters such as cloud temperature, cloud width, and downwind concentration. The mixing of spilled liquid and evaporated gaseous fluorine with ambient air has been modeled, and dispersion results for fluorine were presented. However, owing to the absence of any field data, no verification of predicted results was possible.

The fireball resulting from a launch mishap of a FLOX/kerosene-fueled rocket would quickly disperse the unreacted fluorine and the thermal updraft from the fire would carry it into the upper atmosphere [463].

6.2.1.3 Extinguishment of Fluorine-Supported Fires

It is illusionary to attempt to extinguish a fire that is supported by fluorine and combustible materials. The extremely exothermic reaction cannot be suppressed by any other chemical. Fires supported by a stream of fluorine cannot be extinguished and the fire-fighting crew cannot approach the source without exposing themselves to extreme danger. In many cases one can only stand by, observe from a safe distance and wait for the end of the reaction. Only then the fire-fighting crew can move in and attack the secondary, air-supported fires ignited by the accident. Some authors warn the fire crew not to apply water to liquid fluorine spills owing to an explosion hazard. The use of carbon tetrachloride in fire extinguishers like those that were at one time used for

electrical fires is not recommended either because it was noted that fluorine can react explosively with CCl_4 (Table XI in [292]), also [369]. Because even fluorine leaks that did not result in a fire are best treated with soda powder dispensers, the same method should continue to be used after a fire has erupted.

6.3 Impact-Ignition Sensitivity of Metals in Liquid Fluorine

The impact sensitivity of titanium in LOX or NTO has been well known, and similar sensitivity exists with titanium (or aluminum) sheared while immersed in liquid fluorine [464]. The impact ignition sensitivity of Ti-6Al-4V in liquid fluorine or liquid chlorine pentafluoride was tested under cryogenic conditions and compared with that in LOX [465].

Certain materials immersed in liquid fluorine or fluorine-containing liquid propellants exploded or ignited when subjected to impact or shock loading. The pressure waves resulting from such impact loading may cause microstructural changes in the interior of materials. Under shock loading, tantalum, columbium, and titanium alloys exhibited discoloration on the specimen surface and dislocation cell structures within crystalline grains throughout the specimen [466]. Commercial polytetrafluorethylene often caused explosive reactions. The shock waves propagating through the PTFE specimen caused pronounced microstructural changes by the formation of microvoids and spherulites. Electron microscopic studies revealed that these spherulites consist of regular arrays of thin (200 to 300 Å) blade-like lamellae containing segments measuring 20 Å wide.

A remotely operated open-cup impact tester for studying impact initiation of reaction of various liquid fluorinating agents with metals and plastics was developed that was similar to an apparatus used to study the impact sensitivity of metals and plastics materials immersed in LOX [467].

It may not always require a strong mechanical impact shock to initiate reactions of fluorine with metals. Sudden gas pressure increases may cause adiabatic heating and ignition. Accidental ignitions have been observed in industrial applications of fluorine or nitrogen trifluoride for cleaning of semiconductor processing equipment [468].

6.4 Absorption of HF Fumes from Rocket Engine Tests with Fluorine Oxidizers

The testing of rocket engines with fluorine-containing oxidizers is substantially complicated by the need to effectively absorb the HF-containing exhaust gases for the safety of the test crew and to meet environmental pollution restrictions. The methods for absorption of HF in the exhaust from rocket engines during static tests on the ground will be discussed in *Encyclopedia of Hypergolic Bipropellant Combinations*.

7 Handling Procedures and Equipment for Fluorine

In my opinion the hazards of work with fluorine and its compounds have been greatly overrated. When treated with the respect which is due to it, fluorine is just another substance.

George Cady, discoverer of nitroxyl fluoride NO_3F , 1947

As a result of its extreme reactivity, strong corrosive power, and extreme toxicity, the handling of fluorine poses unique problems and requires extensive precautions, but it can be done safely with the proper training of personnel and an adequate budget for hazard mitigation.

Since the very first suggestion regarding using fluorine as a rocket propellant, there have been numerous publications calculating the theoretical performance of combinations with fluorine as the oxidizer (also to be discussed in *Encyclopedia of Hypergolic Bipropellant Combinations*). The high specific impulse numbers are intriguing and may justify the extra effort (mostly past effort) to bring this oxidizer to practical application. Authors with industrial experience looked at more realistic questions about how this material should be stored, transported, pumped, analyzed, and disposed of [469]. Even chemical companies who were eager to start selling fluorine for rocket applications in the 1960s would readily admit that the handling of fluorine was not an easy task and they offered assistance to their customers to make sure that this was done safely.

In the 1960s there was a lot of discussion about the pros and cons of using a highly corrosive and extremely toxic propellant such as fluorine in rocket engines. This discussion has somewhat settled down since toward the end of the twentieth century, the drive was more toward environmentally friendly propellants and not so much for extreme specific impulses. It is highly unlikely that NASA in its current mode of operation would consider resuming work with fluorine propellants.

For the initial years after WW-II, the US Government did not seem to be interested in actually testing fluorine as a rocket propellant because in those days the fluorine output was almost exclusively earmarked for UF_6 production and increasing the nation's stockpile of nuclear weapons (or starting commercial nuclear power plants using partially enriched uranium). It seems that some of the first rocket engine tests with fluorine were conducted at Rocketdyne in the early 1950s. The NACA

Lewis Flight Propulsion Center, Cleveland, OH, established a test site for fluorine propellants that was equipped with adequate HF scrubbers to minimize environmental pollution. Bell Aircraft Corp. started development of a fluorine engine in 1956 under a contract from the US Air Force [353]. It was estimated that the three locations had conducted more than 500 engine tests and had consumed 30 metric tons of fluorine between the years 1956 and 1960 without major accidents. Typical feed pressure for these tests was 3400 kPa (34 atm) and the flow rate was of the order of 32 kg/s, with local flow velocities up to 30 m/s, depending on the width of the tubing in the feed

system and injectors. US industry even started on the development of a turbo pump that could pump liquid fluorine at very high pressures and flow rates.

Rocketdyne developed the engine for the NOMAD upper stage using liquid fluorine oxidizer and liquid hydrazine fuel and within 2 years of testing they had consumed 500 metric tons of liquid fluorine [470]. Unfortunately, NOMAD did not get to fly.

In Germany, the Bölkow Company (Ottobrunn) started testing with small liquid fluorine/liquid hydrogen engines in the 1960s [471].

The JPL compiled an excellent summary on the experience with fluorine and its safe use as a propellant, in this case for the planned use of liquid fluorine or storable fluorinated oxidizers for upper stages and/or spacecraft to be launched as payloads from the Space Shuttle payload bay [472]. This detailed report with numerous literature references contained sections on experience gained in handling fluorine for nuclear isotope separation and rocket engine ground testing, materials compatibility, component selection, ground service equipment, handling precautions, toxicity, and recommended operating procedures for loading (and unloading, if necessary) fluorine on the Space Shuttle.

Additional information on the safe handling of fluorine can be found in the references listed in Table 42.

Table 42: References to publications on the safe handling of fluorine.

Author(s)	Topic(s)	Date	Pages	References
Allied Chemical	Product information; technical bulletin	1946		[79]
Gall and Miller	Small-scale production	1947	5	[47]
Landau and Rosen	Industrial handling of fluorine	1947	6	[473]
Landau and Rosen	Industrial handling of fluorine	1951	24	[107]
Slessor and Schram	Technology of fluorine	1951	868	[474]
Anonymous	Experience with fluorine systems	1958		[475]
Gordon and Holloway	Handling gaseous fluorine	1960	2	[476]
Gakle et al.	Ground handling equipment	1960	?	[477]
Cloyd and Murphy	Handling hazardous materials	1965	101	[478]
Schmidt and Harper	Handling and use of fluorine	1967	279	[10]
Siegmund	Handling and shipping of fluorine	1967	5	[73]
Farrar and Barber	Handling of fluorine	1979	45	[479]

In one statement, the company with the most experience in production and handling of liquid fluorine, Allied Chemical Corporation, disagreed with arguments that the hazards of working with fluorine are too high for using it as a rocket propellant. They emphasized that elemental fluorine had been produced at Allied Chemical for almost 18 years and they believed the hazards of working with it were greatly exaggerated

by fluorine foes. They admitted that the use of fluorine and FLOX is not entirely free of problems. However, they also believed that those problems were not insurmountable. Similar problems were faced earlier with other propellants such as dinitrogen tetroxide, and were subsequently solved.

7.1 Personnel Protection Suits for Fluorine Propellant Handlers

Based on 15 years of experience with handling liquid fluorine at rocket test sites, the safety clothing and equipment listed in Table 43 were recommended for different work situations.

Table 43: Recommended protective clothing and safety equipment for fluorine workers.

When the condition is, or is expected to be, one in which:	Recommended safety clothing and equipment
There is no odor of fluorine (less than 0.10 ppm fluorine in air)	Common work clothes
Fluorine can be smelled, but does not irritate the nose (0.10 to 15 ppm fluorine in air)	Easily removable plastic gloves, face shield, cloth head covering, work clothes; avoid staying in the area longer than 1/2 h
Fluorine irritates the nose, but does not affect the skin or hair (15 to 100 ppm fluorine in air)	Filtered-air mask or portable air supply, easily removable plastic gloves, face shield, cloth or plastic head covering, and loose-fitting plastic jacket; minimize time in the area
Fluorine warms the skin and makes body hair sticky (above 100 ppm fluorine in air)	Full safety suit (preferably made of a fluoropolymer) and breathing-air supply
Rescue, standby, or accident surveillance as needed	Full safety suit and breathing-air supply

Data source: [480]

Different types of protective gear would apply to workers in fluorine production factories where the presence of HF and hot electrolyte would add to the inhalation, burn, and skin splash hazards.

A prototype propellant handler's suit for protection against gaseous fluorine and liquid chlorine trifluoride was tested and exposed to the chemicals (without operators in them) [481]. The exposed components of this garment were made of perfluoropolymers and stainless steel. The complete suit and sample components were exposed to both gaseous fluorine and liquid chlorine trifluoride, but the suit reacted with liquid chlorine trifluoride and therefore failed to pass the operational test.

As part of the evaluation of protective clothing for use with fluorine, the following test program was conducted: **(1)** chemical compatibility; **(2)** gaseous permeation;

(3) gaseous impingement; (4) physical property deterioration; (5) liquid impingement [482]. Materials that passed the initial test (chemical compatibility) were subsequently tested for permeability and physical property deterioration. Forty-seven possible protective suit materials were selected for the test. These included neoprenes, cellulose-acetate, Teflon, polyurethanes, butyls, Vitons, and metalized coated laminates of various types. A total of 11 materials were compatible with gaseous fluorine. These sample materials were impinged with liquid fluorine. A total of 24 samples were liquid impinged, and some were re-tested to verify results. The liquid fluorine tests involved impinging the samples, which were mounted on a stainless steel stand, with approximately 50 mL of liquid fluorine per sample, 2.5 cm (1 in) from a 1.5-mm (1/16 in) jet orifice to the surface of the sample, at 344 kPa (50 psig), and exposed for 5–8 s.

For the evaluation of protective clothing for handling fluorine, see [483, 484].

7.2 Accident History with Fluorine

With the high reactivity of fluorine, it was unavoidable that there would be occasional accidents. Unfortunately, these accidents are not well documented in the literature.

An typical incident took place at the JPL, where the standard procedures were not followed in this instance. As a result, liquid fluorine was trapped between two valves and pressure increased (a normal occurrence in any cryogenic system). Technicians nearby first heard sharp cracks. A facility valve and line leaked, spraying fluorine on a flowmeter, and a fire was initiated. Automatic shutoff precluded any extensive damage [472].

Figure 20 shows a section of Monel tubing after an explosion with liquid fluorine.

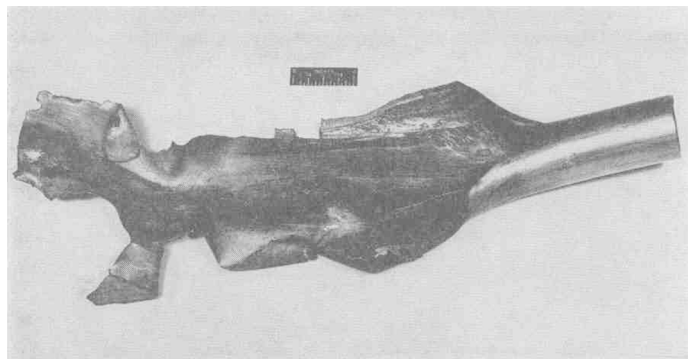


Figure 20: Section of Monel tubing after explosion with liquid fluorine. (From [282].)

7.3 Storage of Gaseous and Liquid Fluorine

The storage of gaseous fluorine in steel cylinders was eventually mastered in the early 1950s and fluorine has been available commercially ever since [485]. At the manufacturing plant, the cylinders are not pressurized with a compressor, but fluorine is first liquefied into sturdy, pressure-proof cold traps and then allowed to vaporize under its own vapor pressure. This has the advantage that non-volatile contaminants are left behind in the cold trap.

For storage of liquid fluorine, double-jacketed, vacuum-jacketed tanks have been developed where the inner chamber can be filled with liquid nitrogen and the outer jacket is evacuated. Similar tanks are used for the transport of liquid fluorine and are described in more detail in the following section. Siting plans for liquid fluorine tanks must consider the distance to populated areas and inhabited buildings. For safety reasons, the cryogenic tanks may be located in underground bunkers or covered areas to minimize heating due to solar radiation.

A unique hazard is the inadvertent formation of mixtures of water ice and liquid fluorine. Such mixtures at 77 K ($-196^{\circ}\text{C} = -320^{\circ}\text{F}$) are shock sensitive and detonable [486]. The ice was tested in two forms: frost crystals and continuous film. No difference in behavior was noted. When liquid fluorine was added to ice at 77 K (-320°F) and then allowed to evaporate, no reaction between the components was observed. The results of the tests indicated that the liquid fluorine/water ice system is very hazardous and must be handled with extreme care. Leakage of moist air or water into a system that contains or will contain liquid fluorine results in the formation of ice and thus an impact-sensitive condition.

A small triple-walled liquid fluorine tank capable of self-pressurizing to 4.1 MPa (600 psia) pressure was made of nickel on the inside and Monel on the outside [395]. As long as the tank was kept dry, there was no corrosion on the nickel tank. Appreciable nickel fluoride deposits, however, resulted when water was not carefully removed. On the basis of that experience, nickel is inferior to Monel as a liquid fluorine container because of its susceptibility to attack by hydrofluoric acid.

7.4 Transportation of Liquid Fluorine

The reactivity of fluorine and the large number of accidents in the early years in handling, storing, and transporting fluorine as a compressed gas have delayed the availability of fluorine as a commercial product. It was not until 1949 that the chemical industry in the UK was confident enough to offer fluorine as a compressed gas in cylinders, and it was predicted that it could be handled with the same ease as elemental chlorine [487].

The largest size cylinder for shipping gaseous fluorine as compressed gas contains only six pounds of the gas at a maximum pressure of 2.7 MPa = 400 psi, which virtually

precluded shipment economically and use in large tonnage quantities at a time when much fluorine was used in the nuclear industry. In 1957, the Interstate Commerce Commission (ICC) in the USA granted a special permit for the shipment of liquid fluorine in an ICC-licensed tank system, making it economically feasible to ship tonnage quantities of fluorine. Since then, in the US, liquid fluorine has been transported by road in tank cars holding 1100, 2300 or 4400 kg fluorine and in railroad tank cars holding 10 to 20 metric tons. These tanks have three walls: the interior wall is made from Monel, and the center and outer walls are made from stainless steel. Liquid nitrogen is filled into the space between the inner two walls in order to keep the hazardous and volatile cargo in the liquid state and at low pressures. The outer chamber is evacuated. For the transport of any cryogenic liquid it is preferred to cool the liquid to below its normal boiling point to minimize vaporization losses during transit. In the case of fluorine, this requirement is much more restrictive, as the tank cannot be vented during transit. Fluorine transport tanks would require an active cooling coil, a reflux condenser, or a cooling jacket filled with a cryogenic, inert liquid that boils below the boiling point of fluorine. The cooling with a jacket of liquid fluorine makes the storage and transport of fluorine independent of mechanical cooling aggregates. The lower boiling point of liquid nitrogen (N_2 : 77.3 K = -195.8°C ; F_2 : 84.8 K = -188.3°C) allows the safe storage and transport of liquid fluorine as long as sufficient liquid nitrogen is available in the outer jacket.

The filling of tank cars can be conducted by personnel that wear only a face shield and rubber clothing, but they do not need to wear a gas mask or respirator at all times (Figure 21). The personnel are trained on how to quickly don gas masks or respirators as soon as the need arises.

The sequence for filling a tank car with liquid fluorine is as follows. First the tank car is checked for leaks and the prior filling status (residual fluorine?) is verified. Then, the inner jacket is filled with liquid nitrogen. This may allow the pressure in the outer vacuum jacket to drop further (which is desirable) as the wall now acts like a cryopanel. In Figure 21, the rear tank car is being filled with liquid nitrogen and the front tank car is being filled with liquid fluorine. The transfer of liquid fluorine from a storage tank into a transport tank and vice versa is achieved by pressurizing with helium. The fleet of tank cars logged 120000 km on public highways in the years from 1956 to 1961 without any severe accidents. At normal (non-desert) ambient temperatures a load of nitrogen will last for 30 days. After this time, the liquid nitrogen has to be refilled or the fluorine overpressure has to be vented, not a pleasant task under any condition. The fluorine tank is hermetically sealed and during normal operation would not be vented to the atmosphere.

A very good summary on handling, transport, and storage of fluorine is contained in [488]. Detailed instructions for unloading a truckload of liquid fluorine are provided in [489].

The inner Monel tank is generally designed for an internal pressure of 485 kPa (4.8 atm) and for an external pressure (from the liquid nitrogen side) of 303 kPa (3 atm).



Figure 21: Filling station for tank cars with liquid fluorine. (Photo courtesy of Allied Chemical.)

The liquid nitrogen jacket is designed for an internal pressure of 303 kPa (3 atm). The outermost tank wall needs to withstand external atmospheric pressure (vacuum on the inside) and is also the attachment for road vibrations and loads created by the mass of the internal tanks. The number of connecting, load-bearing members between the three tank walls has to be minimized as they also act as heat leakage paths.

Over the years (up until 1966), Allied Chemical had designed and built at least three different types of liquid fluorine tanks ([453]). The first two types followed the design described above, with the inner tank and the plumbing made from Monel[®], and the outer tank walls from stainless steel CRES-304. A tank designed later used a carbon-containing steel for the outer wall. All tanks complied with the American Society of Mechanical Engineers pressurized vessel code. The larger transport tank held 2300 kg of liquid fluorine and with a fresh load of liquid nitrogen it could be stored for 25 days without maintenance. The rate of LN₂ evaporation depended on the quality of the vacuum in the outer jacket. The pressure in the vacuum jacket should not exceed $6.6 \text{ Pa} = 5 \times 10^{-2} \text{ mm Hg}$.

If the LN₂ level in the inner jacket should drop to a critical level, a warning signal would sound. If the LN₂ was lost for some unforeseen reason, the inner fluorine tank would remain without noticeable pressure rise for 24 h. It would take another 4 days before the pressure in the fluorine tank reached a critical level. This was considered to be sufficient time to bring in a refill of LN₂ or take other safety precautions. If no new LN₂ can be brought in, the rate of evaporation would be 0.7 kg/h. One would have to evacuate the downwind area. If a leaky vacuum jacket aggravates the problem, the rate

of evaporation can increase to 3.7 kg/h. In the 1960s, tank cars of this type were used by Allied Chemical to transport fluorine from its production facilities at Baton Rouge, LA, and Metropolis, IL, to the rocket test sites of NASA, USAF, and other government and industrial customers. The transports required a special permit from the ICC and were subjected to stringent inspections to make sure that all safety precautions were complied with.

In tests of a portable tank specially designed and constructed under Air Force Contract AF33(616)-2229, liquid fluorine was safely transported and stored [490]. The operation included 82 h of transportation with a total storage time of 2570 h.

Until 1987, USAF transported LF_2 under Department of Transportation (DOT) Exemption DOT E-1479. In later revisions of DOT E-1479 and E-3121, DOT placed several additional requirements upon USAF as a requirement for re-issuance of the exemptions. The new requirements included an emergency response plan, risk assessments, updates for highway routes of movement, and periodic updates of the risk assessments to ensure that routes remain the safest possible.

7.5 Transfer and Pumping of Fluorine

As already mentioned, the most frequently used method for the transfer of liquid fluorine from one tank into another is by pressurization with helium. Additional information can be found in [488]. The tubing is generally made of copper. For larger diameter ($>5\text{ cm} = >2\text{ in.}$) ducts one may use stainless steel. Flanged connections should be avoided as they are prone to leakage. Crush gaskets can be made of aluminum, copper, or annealed nickel. Teflon should be used only as a secondary sealing barrier. Figure 22 gives a plumbing schematic for the transfer of liquid fluorine between two containers using helium gas as the pressurant.

The gas displaced from the tank being filled, a mixture of fluorine and pressurant gas, must be vented from time to time to maintain a pressure differential between the two tanks. The toxic gas is vented into a stack with a propane burner (but that still generates toxic HF). The transfer of a load of 2300 kg of liquid fluorine through a 2.5-cm (1 in) I.D. line with a differential pressure of 100 to 140 kPa may take up to 1 h.

Prior to the first use of a fluorine tankage system, all components need to be thoroughly cleaned and slowly passivated with gaseous fluorine. For proper passivation, the inert gas (nitrogen) in a system is gradually replaced with gaseous fluorine, with 10-min holds programmed in the gradual increase of fluorine partial pressure. After the full fluorine concentration is achieved, the system can be pressurized to the nominal operating pressure and held at that pressure for 12 to 24 h to allow complete passivation to take place. Throughout this procedure the system should be checked for leaks. If the system was not thoroughly cleaned to start with, the combustion of a local contaminant can initiate a metal combustion reaction, which may consume the entire

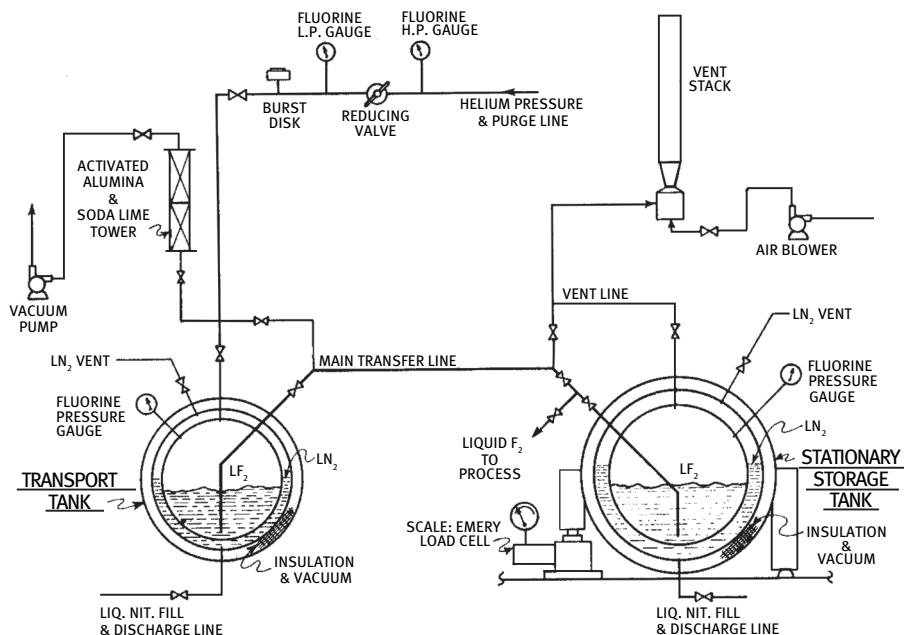


Figure 22: Transfer of liquid fluorine under helium pressure. (Reproduced from [453]; Allied Chemical.)

system and just leave a heap of fluorides and molten metal. This disastrous reaction cannot be stopped by conventional fire extinguishing methods.

When transferring cryogenic fluids from one tank to another, the evaporating liquid used to cool down lines and tank walls of the receiving tank is usually vented to the atmosphere. In the case of fluorine, this may not be an option. Therefore, a no-vent transfer system has been developed for liquid fluorine [491, 492]. The no-vent loading of a propellant tank is basically a non-adiabatic compression of the ullage gas. Initial tests were conducted with liquid nitrogen as an inert substitute in a 113-L (30-gallon) tank, and later tests were performed with liquid fluorine in a 625-L (165-gallon) tank. For a flight weight system, loading time of 15–20 min. and tank pressure of 483 kPa (70 psia) was the nominal condition. Nine test runs were performed with LF_2 with different loading rates and different initial gas compositions in the ullage (helium or helium/fluorine mixtures). Negative pressure in the receiving tank had to be avoided because it might implode and collapse. Loading was terminated when the 5% ullage point was reached.

8 Physiological and Toxic Effects of Fluorine and HF

Traces of fluoride (NOT elemental fluorine) in drinking water or food supplements are essential for the development of healthy teeth. The hydroxyl group in hydroxylapatite, the main constituent of tooth enamel, is readily exchanged for fluoride because this is one of the first known natural ion exchange column packing materials for fluoride analysis. For some industrial applications, the fluoride contained in drinking water has an adverse effect and fluoride has to be removed from drinking water before the water can be used in chemical processes. Hydroxylapatite would be one of the choice materials for this purpose. High-surface area α -alumina has been used as well.

For the fluoridation of drinking water, fluoride is usually added in the form of hexafluorosilicic acid H_2SiF_6 . The fluoridation of drinking water is a controversial subject and the discussion is still raging in many communities as to whether their drinking water should be fluoridated or not. If it seems that the beneficiaries of fluoridation are only children below the age of 13 years, then, why should the drinking water for the entire population be fluoridated? Others claim that the concentration of fluoride in the drinking water required to have a beneficial effect is too close to the concentration of beginning toxic effects. Other scientists point out that the drinking water in many communities naturally already contains sufficient fluoride so that a statistically significant reduction of tooth decay can be proven for periods even before any fluoride was added to the drinking water in other communities. Several periodicals (called “Fluoride” and “Journal of International Society for Fluoride Research”) are devoted exclusively to the health issues surrounding fluorides.

Summaries on fluorine toxicity have been published by other organizations on several occasions [493–495].

A concise account of the clinical and metabolic consequences of chronic endemic and acute exposure to a wide range of inorganic fluorine compounds and a review of adverse effects on humans following exposure, including case histories of established fluorosis, is given in [496]. A useful summary is also presented of the recommendations of various Public Health Authorities relating to maximum permissible levels of fluorides in the atmosphere and in drinking water.

A very comprehensive summary of the physiological and toxic effects of fluorine and fluorine compounds (particularly HF) is available in the monograph by [497]. It deals predominantly with damages caused by the flue gases from aluminum smelters and phosphate fertilizer factories. Anybody who is tasked with the design of fluorine test facilities (rockets or lasers) should familiarize themselves with the possible damages to surrounding populations, animals, and vegetation.

8.1 Olfactory Threshold for Fluorine Gas

Fluorine has a characteristic pungent odor, detectable in concentrations as low as 20 ppb, which is below the safe long-term workplace exposure level. The American Conference of Governmental Industrial Hygienists (ACGIH) recommended maximum allowable concentration for a daily 8-h time-weighted exposure is 1 ppm (see Section 8.2 on the toxicity of fluorine).

Fluorine has such a sharp, penetrating odor that inhalation of toxic quantities is unlikely unless the individual is trapped in a location from which escape is impossible. If the fluorine odor is irritating to the nasal passages, this indicates a sizeable leak and the area should be evacuated immediately. The odor of fluorine becomes annoying or irritating to the nose at about 18 to 27 ppm. As soon as such irritation is noticed, air-pack breathing apparatus should be donned before proceeding. At higher concentrations a full-body protective Self-Contained Atmospheric Protection Ensemble suit, preferably one made from fluoropolymers, is required.

8.2 Maximum Allowable Fluorine Concentrations

The maximum allowable concentration of fluorine at the place of employment has been established by various organizations and may differ from one country to another. The maximum allowable concentration for gases and vapors is usually given in units of “parts per million = ppm,” that is, parts per million by volume, not by weight. Occasionally, one finds maximum allowable concentrations given in other units, such as mg/m^3 . These units are mostly used for dusts and aerosols, but occasionally they are used for gases as well. The advantage of ppm by volume is that this value is independent of the ambient temperature, whereas the mg/m^3 value varies with temperature. The density of fluorine gas has been known to convert one value to the other. The density of fluorine gas at 101 kPa and 273 K is 1.696 g/L; thus, 1.0 ppm by volume corresponds to $1.696 \text{ mg}/\text{m}^3$ at 101 kPa and 273 K.

Maximum allowable concentration values are often listed in comparison to lethal concentration LC50 or lethal dose LD50. The lethal concentration LC50 is the concentration at which 50% of the test animals die within a specified post-exposure observation period as the result of a controlled exposure to the toxic gas for a certain time. One must check the original data for animal tests to see if this was a whole-body exposure or if the hazardous atmosphere was delivered by a breathing mask. Most of the animal tests are conducted with whole-body exposure. For other paths of administration (injection, intubation, ingestion), the lethal dose is often given in relation to the body weight of the animal. The maximum tolerable concentrations for elemental difluorine established by government agencies are closely tied to the limits for HF.

Table 44 is a summary of maximum allowable concentrations of fluorine in air under different conditions and for different populations. Table 45 gives the full-text

meaning of some of the commonly used abbreviations (“alphabet soup”). This table applies not only to fluorine, but to toxicity of all other chemicals in this encyclopedia. This table used to be at the beginning of *Encyclopedia of Oxidizers* before the chapters were rearranged in alphabetical order.

Table 44: Maximum allowable concentrations of fluorine in air.

CAS number	7782-41-4
NIOSH REL	0.1 ppm (0.2 mg/m ³) TWA
OSHA PEL	0.1 ppm (0.2 mg/m ³) TWA
1989 OSHA PEL	Same as current PEL
1993–1994 ACGIH TLV	1 ppm (1.6 mg/m ³) TWA, 2 ppm (3.1 mg/m ³) STEL
Immediately Dangerous to Life or Health (IDLH) Concentrations	
Original (SCP) IDLH ^a	25 ppm
Existing short-term exposure guidelines: National Research Council 1984	
10-min EEGL	15 ppm
30-min EEGL	10 ppm
60-min EEGL	7.5 ppm

Data source: NIOSH <http://www.cdc.gov/niosh/idlh/7782414.html> as of May 1994

^a Basis for original (SCP) IDLH: The chosen IDLH is based on the statement by [498] that “2 men were able to tolerate 25 ppm very briefly but both developed sore throats and chest pains lasting 6 hours; 50 ppm could not be tolerated.”

Table 45: Abbreviations for IDLH documentation.

ACGIH	American Conference of Governmental Industrial Hygienists
EEGL	Emergency Exposure Guidance Level (NRC)
IDLH	Immediately Dangerous to Life or Health concentration value
LC50	Lethal concentration causing death in 50%
LCLo	Lowest lethal concentration causing death
NIOSH	National Institute for Occupational Safety and Health
NRC	National Research Council
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit (OSHA)
REL	Recommended Exposure Limit (NIOSH)
SCP	Standards Completion Program (NIOSH/OSHA)
SPEGL	Short-term Public Emergency Guidance Level (NRC)
STEL	Short-term Exposure Limit
TLV	Threshold Limit Value (ACGIH)
TWA	Time-Weighted Average

Data source: NIOSH <http://www.cdc.gov/niosh/idlh/7782414.html>

Based on a review of literature data, the following exposure limits were recommended in 1970 [495]: Emergency Exposure Limit (EEL): 25.0 ppm for 5 min, Emergency Tolerance Limits (ETLs): 15.0 ppm for 10 min and TLV = 1.0 ppm for 8 h.

Short-term public emergency guidance levels (SPEGLs) for fluorine and other hazardous chemicals were established by Committee on Toxicology, Board on Toxicology and Environmental Health Hazards, Commission on Life Sciences, National Research Council [499]. This document contains a very good summary on fluorine toxicity. A similar document is available from the same publisher for chlorine trifluoride. Exposure limits for fluorine are closely related to exposure limits for HF [500]. Different guidelines may apply for emergency short-term limits for military personnel [501].

8.3 Animal Inhalation Toxicity Exposure Test Results

8.3.1 Acute Toxicity Data

Rats, mice, guinea pigs, rabbits, and dogs were exposed to fluorine for 5, 15, 30, or 60 min. [502, 503]. The LC50s and effects at lower concentrations are summarized in Table 46.

Table 46: Lethal concentration data for animal exposures to fluorine.

Species	LC50 (ppm)	Time	Adjusted 0.5-h LC (CF)	Derived value
Rat	185	1 h	231 ppm (1.25)	23 ppm
Mouse	150	1 h	188 ppm (1.25)	19 ppm
Rabbit	270	30 min	270 ppm (1.0)	27 ppm
Guinea pig	170	1 h	213 ppm (1.25)	21 ppm

Data source: [502]

High concentrations of fluorine caused marked irritation of the eyes and respiratory tract, and damage to the lungs, liver, and kidneys. Exposure at or below 100 ppm for 5 min, 70 ppm for 15 min, 55 ppm for 30 min, or 45 ppm for 60 min caused no apparent effects in the animals. The most pronounced effects of the F₂ exposures observed were irritation of the eyes and respiratory tract. Dyspnea was also observed frequently. Although kidney and liver effects were observed, they occurred only at exposures greater than those producing diffuse congestion of the lung. In rats, mice, guinea pigs, and rabbits, effects observed after exposures at approximately 50% and 25% of the LC50 values were not observed at approximately 12.5% of the LC50 values. The ranges of maximal no-observed-effect concentration for the four species are summarized in Table 47.

Table 47: Ranges of maximal no-observed-effect concentrations in animals.

Duration, min	No-observed-effect concentration, ppm	ppm × min product
5	51–88	260–440
15	49–70	740–1100
30	32–35	960–1100
60	28–38	1500–2300

Data source: [502]

8.3.2 Short-Term Exposure

The effects of intermittent exposure to F₂ were studied by exposing mice, rats, and rabbits four times at weekly intervals for 5, 15, 30, or 60 min at repeat intervals ranging from 24 h to 1 week [504]. Lung damage was the most sensitive index of an adverse effect. Animals were sacrificed immediately after the last exposure, or at 7, 14, 21, or 45 days after the last exposure. Two magnitudes of exposure were used: one that caused slight effects after a single exposure and one that produced marked effects after such an exposure. The results of these studies are summarized in Table 48.

Table 48: Pathology in rodents after single and repeated exposures to fluorine.

Species (Strain) ^a	Time, min	Concentration, ppm	Repeated exposures ^b			Single exposure		
			Lung	Kidney	Liver	Lung	Kidney	Liver
Mouse/Swiss-Webster	5	130	1	N	N	1	P	N
Mouse/Swiss-Webster	5	321	1	P	N	3	P	P
Mouse/Swiss-Webster	30	64	1	N	N	1	P	N
Mouse/Swiss-Webster	30	55	1	N	N	1	P	N
Rat (Osborne Mendel)	5	150	1	N	N	1	P	N
Rat (Osborne Mendel)	5	325	1–2	N	N	3	P	P
Rat (Osborne Mendel)	30	68	1	N	N	1	P	N
Rat (Osborne Mendel)	60	75	1–2	N	N	1	P	N
Rat (Osborne Mendel)	60	140	2–3	N	N	4	P	P
Rabbits (New Zealand)	15	56–73	N	N	N	N	N	N
Rabbits (New Zealand)	30	49–55	N	N	N	N	N	N

Data source: [504]

N = normal or no change; P = some pathology; 1, 2, 3, 4 = degree of gross lung pathological change (1 mildest and 4 most severe).

^a 10 mice or rats per group; number of rabbits per group unspecified.

^b Four exposures at weekly intervals.

It was concluded that four weekly exposures to F₂ caused no more, and in some cases, less, damage than a single exposure at the same concentration. The data suggested the development of a tolerance to F₂ inhalation. It was also shown that the LC50 value for

mice was increased by pre-exposing the test animals to F_2 . This provided additional evidence of the development of tolerance. After four exposures (at weekly intervals) to the same concentration, the lungs had slight changes (grade 1). Livers were normal. Kidneys showed slight changes at 7 and 14 days, but were normal at 21 and 45 days. Four repeated exposures, at concentrations that caused no effect after a single exposure, caused no effect either. Four exposures to fluorine caused no more damage than a single exposure to the same concentration. Repeated exposures were made with different concentrations during each exposure. A low, apparently harmless, level was used first. Then, 4, 24, and 96 h later, the LC50 of fluorine was determined. The LC50s of pre-exposed animals were higher and there was less damage to the lungs than in control animals. Exposures to a low concentration were also repeated every third day (four times). At 1, 3, and 7 days after the last exposure the LC50s were determined. Even at 7 days the pre-exposed animals had higher LC50s and showed less edema in the lungs than animals that were not pretreated by previous exposure to fluorine.

Some of the early fluorine toxicity test results obtained as part of the Manhattan project were published only in internal reports that are difficult to obtain, even after declassification [505, 506].

The lethal effect resulting from the inhalation of air containing relatively high concentrations of fluorine was studied in four animal species: 8 rabbits, 20 guinea pigs, 45 to 50 rats, and 45 to 50 mice were each exposed to concentrations of fluorine approximating 100, 200, 500, 1000, and 10000 ppm, respectively [507]. The duration of exposure ranged from 7 h at 100 ppm to 5 min at 10000 ppm. At a concentration of 10000 ppm all animals died during the 5-min exposure period, with the exception of 1 rabbit, which died within 24 h after exposure. All animals exposed at 1000 and 500 ppm were dead within 6 days after exposure. All animals exposed at 200 ppm, with the exception of 2 guinea pigs, were dead within 14 days after exposure. The 7-h exposure at 100 ppm resulted in the death of 7 of the 8 rabbits, 27 of the 50 rats, and 43 of the 45 mice within 14 days after exposure. No deaths occurred among the guinea pigs exposed at this level. All surviving animals were sacrificed during the 3rd post-exposure week. Death in all cases was apparently caused by respiratory failure resulting from acute pulmonary damage. The animals that survived a 2-week post-exposure period either escaped this damage or were able to withstand its effects until resolution had occurred. Damage to internal organs other than the lung was minor or negligible.

The next test series involved lower fluorine concentrations. The toxic effects arising from the daily inhalation of gaseous fluorine were studied in six animal species: 5 dogs, 30 rabbits, 38 guinea pigs, 46 rats, 50 mice, and 30 hamsters were exposed 6 days a week to a concentration of fluorine approximating 8 mg/m^3 (5 ppm) [508]. The animals were exposed for a total of 160 h apportioned over 29 exposure-days, with the exception of the hamsters, which were exposed for a total of 136 h apportioned over 25 exposure-days. Ten of the rabbits and 12 of the guinea pigs were subjected to head exposure, rather than to the complete body exposure to which the majority of the animals were subjected. Toxicity was evaluated from the study of several independent

factors: mortality, body weight response, changes in cellular elements of the blood, and tissue damage. The inhalation of fluorine produced 100% mortality in dogs after 45 h of exposure, and in fully exposed rabbits after 110 h of exposure. At the termination of the experiment, after 160 h of exposure, 90% of the head-exposed rabbits, 27% of the fully exposed guinea pigs, 20% of the mice, 17% of the head-exposed guinea pigs, and 11% of the rats had died. The hamsters, exposed for the last 136 h of the experiment, miraculously survived.

The next animal exposure test series was run at concentrations that were close to the 8 h/day, 40 h/week recommended TLV for humans in a work environment. Groups consisting of 5 dogs, 30 rabbits, 24 guinea pigs, and 18 rats were exposed for 6 days weekly to a concentration of fluorine approximating 0.8 mg/m^3 (0.5 ppm) [509]. Twelve of the rabbits and 12 of the guinea pigs were subjected to head exposure only. Toxicity was evaluated from the study of several factors: mortality, growth response, and histopathological, hematological, and clinical–chemical changes. No mortality resulting from exposure to fluorine at this concentration was observed. Growth was not noticeably affected by exposure, nor were any significant histopathological or hematological changes produced. Blood calcium and NPN levels of the dog and rabbit remained within normal limits. The excretions of urinary fluorine and amino nitrogen by the rabbit were not significantly altered.

8.4 Human Volunteer Inhalation Tests

It has been reported that two men were able to tolerate 25 ppm very briefly but both developed sore throats and chest pains that lasted 6 h; 50 ppm could not be tolerated [498]. Volunteers tolerated 10 ppm for 15 min with minimal irritation. Toxicity data on short-term animal exposures were compiled, normalized, and correlated with human data [495]. Intermittent exposures to 10 ppm were repeated every 3 to 5 min for 15 min over 2 to 3 h with only slight irritation of the eyes and skin noted. Much irritation of the eyes has been noted at 100 ppm, but with no after effects after only 30 s. It has been observed that exposures up to 30 ppm for 5 to 30 min had no ill effects [510]. Exposure to 1 ppm for 1 h is not expected to cause injury.

At NASA Lewis Research Center, 9 male volunteers were observed during and after exposure to F_2 under controlled conditions [511]. Most of the subjects reported that 15–25 ppm fluorine in air caused some nasal and eye irritation after only two or three breaths. All subjects tolerated repeated short-term (duration unspecified) exposures at up to 10 ppm without discomfort.

Five volunteers (aged 19–50) were exposed to F_2 under a variety of conditions that permitted accurate measurement of F_2 concentrations [502]. Exposure took place under a mask that covered the eyes and nose, but not the mouth. Thus, the effects of F_2 on respiration were not routinely measured (some subjects did inhale and some

Table 49: Irritation caused by fluorine in volunteer human subjects.

Concentration, ppm	Time, min	Effects
10	3	No irritation of eyes and nose
10	5	No irritation of eyes and nose; not uncomfortable
10	15	No irritation of eyes and nose, inhaled without irritation of respiratory tract
23	5	Slight irritation to eyes; could inhale without respiratory difficulty (inhaled intermittently over the 5-min period)
50	3	Irritation of the eyes; slight irritation of the nose
67	1	Irritation of eyes and nose; although exposure was quite irritating, concentration not unbearable
78	1	Irritation of the eyes and nose; (less irritating to eyes than cigarette smoke); face slightly irritated after exposure; inhalation caused coughing
100	1	Very irritating to eyes and nose; eyes burned after exposure; felt like "film" over the eyes after exposure; skin felt sticky and slightly irritated after exposure; subjects did not inhale
100	0.5	Very irritating to eyes and nose; no after-effect

Data source: [502]

data on respiratory effects were obtained). The results of this study are summarized in Table 49.

The authors also noted that, when exposure was repeated weekly, the subjects did not perceive as much irritation as they had on first exposure. The apparent development of tolerance is consistent with that seen in experimental animals. Finally, the authors studied the effects of exposure at 10 ppm for 3–5 min every 15 min for 2 or 3 h. All subjects tolerated such repeated exposures with only slight irritation of the eyes and skin. There was marked irritation of the eyes and nose at 100 ppm.

In 1953, the American Conference of Governmental Industrial Hygienists lowered the recommended threshold of exposure for fluorine from 0.7 ppm, a value that had been based on animal-experiment data, to 0.1 ppm. An experience of 9 years at Union Carbide in Oak Ridge, TN, with personnel working in fluorine concentrations several times the newly recommended threshold led safety managers to believe firmly that concentrations up to at least 1.0 ppm were safe [510]. Subsequently, approval was requested from the US Atomic Energy Commission (AEC) to continue using this limit; with US AEC concurrence, the higher limit was tolerated. The health of workers exposed to higher values than 0.1 ppm as recorded over a 4-year period at the medical department of this plant was correlated with measured fluorine concentrations in the air at the work place. The average fluorine values in air at the fluorine generation unit were compiled for the years 1952–1959 inclusive (Table 50). The air samples were the average of 30-min samples collected at a rate of 1 cu ft/min in giant impingers containing 100 mL of 0.5% sodium hydroxide solution. The fluorine content of the solution

was then determined by the Eriochrome Cyanine R method. Reliable techniques for differentiating between fluorine and HF in air were not available. Sixty-one employees were determined to have been present in the fluorine-contaminated environment for a significant portion of their working time. The group included: (1) Individuals who normally spent 50–60% of their daily work time for periods of 7–9 months in the area, and (2) individuals (repair men) who spent as little as 10% of their daily work time in the area but who did this almost continuously and who, because of the nature of their work, had been present when fluorine concentrations were highest. As the gaseous diffusion process for separating the isotopes of uranium uses the salt, uranium hexafluoride, and involves the use of other fluorides such as HF, these employees were potentially exposed to several fluorides.

Table 50: Historical summary of fluorine concentrations in workroom air at a fluorine generation unit.

Year	Number of samples	Fluorine, ppm			Number of samples at or above 1 ppm
		Average	High	Low	
1952	78	1.4	6.6	0.0	47
1953	70	1.1	10.0	0.1	23
1954	51	0.6	7.4	0.0	9
1955	86	1.0	24.7	0.1	23
1956	80	0.9	6.1	0.1	22
1957	126	0.3	3.8	0.1	4
1958	115	0.5	16.6	<0.1	9
1959	120	1.2	11.5	<0.1	29

Data source: [510]

The toxicity of fluorine is closely related to that of HF. The Canadian Atomic Energy Control Board commissioned an update of a 1984 review on the acute toxicity of HF [512]. The study placed particular emphasis on the effects of inhalation of gaseous HF and was divided into two main parts: a literature review and a lethal concentration estimation. The literature review summarized data under four categories: animal studies, controlled human studies, community exposure, and industrial exposure. Data in these areas were critically reviewed for their relevance to lethal concentrations at LC_{LO} , LC_{10} , and LC_{50} levels that were derived in the 1984 report. In the 10 years prior to 1995, only one additional relevant animal study had been published. No new controlled human studies were found, but one community exposure incident was reported. Three new industrial/accidental exposures had been reported since 1984. Evaluation of new data did not change the lethal concentration estimates made in the 1984 report, but revealed the lack of appropriate models to estimate the lethality of irritant and corrosive gases. Additional information on fluorine toxicity can be found in [513, 514].

8.5 Skin Effects of Fluorine Exposure

Heat release from fluorine exposure to unprotected skin can be felt on the exposed skin of the body (up the sleeve, back of the neck, etc.), which begins to feel warm at concentrations of 90 to 240 ppm. At the same time, the exposed hair on the head and arms feels sticky. If this concentration is observed during maintenance operations, or if monitoring instrumentation indicates fluorine or HF in excess of 90 to 240 ppm, personnel should evacuate the area immediately, and remain clear until the concentration is reduced to a safe level (by natural dissipation or by operation of exhaust systems in enclosed areas). Personnel accidentally exposed to these concentrations (100 to 200 ppm) for more than a few minutes experience minor skin irritation, itching, and subsequently a sunburn effect. To limit this after effect, exposed personnel should immediately flush exposed skin areas with water.

8.6 First Aid in Case of Injury by Fluorine or HF

If a person is accidentally exposed to fluorine, the affected parts of the body should be rinsed thoroughly with water as quickly as possible. Fluorine chemical burns on the skin are similar to HF chemical burns and exposed persons should seek medical care as quickly as possible. First aid treatment for F_2 burns on the skin would be similar to first aid treatment for HF burns. The physician in charge of attending to rocket or laser test site personnel should familiarize him/herself beforehand on how to treat F_2 and HF injuries.

Small injuries can be treated with Calcium Gluconate 2.5% Topical Gel, which is available from various pharmaceutical suppliers or can be mixed as needed from calcium gluconate powder and a water-soluble lubricant [515].

The subcutaneous injection of 5% calcium gluconate solution in the perimeter of HF injuries has been recommended repeatedly. The action principle of this treatment is the precipitation and immobilization of fluoride ion as insoluble calcium fluoride. This may be very painful, but at least it prevents the tissue from becoming necrotic. It has been recommended to bath fresh HF injuries in buttermilk (calcium-rich) if no other first aid treatment is available and until the victim can be transported to medical care. There are several reports in the literature describing fatal accidents caused by splashes of hydrofluoric acid on the skin [516–518]. The rapid depletion of calcium was identified as a major cause of death. Eye injuries should be thoroughly rinsed with water, followed by rinses with dilute boric acid solutions to prevent infection. In all cases the victim needs to be quickly transported to a physician. The literature on the treatment of HF injuries is extensive, though occasionally confusing and often contradictory, with no coherent management policy emerging [519, 520].

The hands are the first place where splash injuries caused by fluorine or hydrofluoric acid are likely to occur [521].

Accidental inhalation of fluorine causes severe damage to the lung tissue. First aid treatment is breathing of oxygen, but not forced ventilation. The inhalation of an aerosol from a calcium acetate solution or 2.5% calcium gluconate in normal saline using a nebulizer has been recommended to treat F_2 or HF inhalation injuries.

Additional information on first aid in cases of accidents with fluorine or HF is contained in [44, 522, 523].

8.7 Environmental Effects of Fluorine or HF

Some living green plants have the ability to accumulate fluoride and/or fluorinated organic compounds in their tissue, in particular in areas downwind of aluminum smelters or phosphate ore processing plants. Livestock grazing on meadows where these plants grow has suffered fluorosis poisoning. All necessary steps have been taken to avoid similar problems in the vicinity of rocket or laser test sites or nuclear fuel processing factories [524, 525].

Although the plan to launch FLOX-powered rockets from Cape Canaveral in Florida never materialized, the concern about the potential impact of HF exhaust on the environment surrounding the launch site arose quickly, as soon as such plans were announced in 1963, and had to be addressed in environmental impact statements [526–528].

9 Mixtures of Fluorine with Other Oxidizers

Mixtures of fluorine with other oxidizers can have certain advantages over pure fluorine and pure oxidizers by themselves. Most of all, this statement applies to mixtures of liquid fluorine with liquid oxygen. The common abbreviation for this mixture is FLOX. This cryogenic oxidizer has been tested as a rocket propellant in combination with many different fuels.

9.1 Fluorine/Oxygen Mixtures

Liquid fluorine is miscible with liquid oxygen over the entire range of compositions [529].

9.1.1 Physical Properties of Fluorine/Oxygen Mixtures

The physical properties of FLOX have been investigated over a wide range of compositions [530–532].

The boiling points of the two cryogenic liquids are very similar. A good summary of the physical properties of FLOX mixtures is provided in a NASA publication [10]. Most of the physical properties of FLOX are readily interpolated from those of the two constituents, assuming additive behavior of the physical properties [533].

The boiling point/composition diagram for FLOX mixtures is shown in Figure 23. A 50 mass-% FLOX mixture boils at approximately 87.42K and the fluorine content of boiloff gas is approximately 63.7 mass-%. The curves were calculated from Raoult's law.

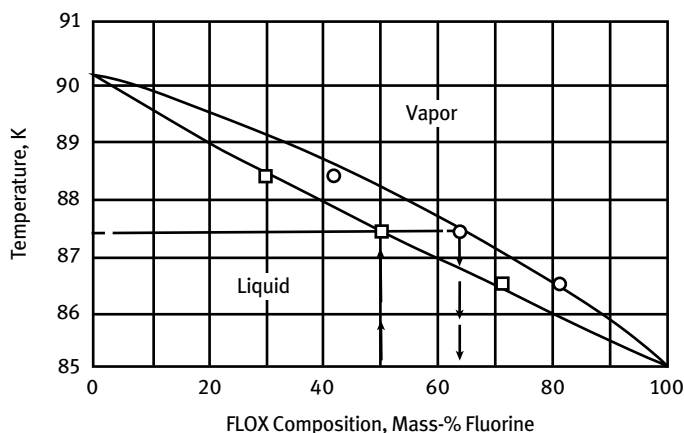


Figure 23: Boiling point/composition diagram for FLOX mixtures. (Reproduced and modified from [10].)

The vapor pressure of a 50% F_2 FLOX mixture is shown in Figure 24, where it was interpolated between the curves for LOX and LF_2 (also shown). The densities of three different FLOX mixtures as a function of temperature are shown in Figure 25. The FLOX density curves fall between those for LOX and LF_2 . The viscosity of a 50% F_2 FLOX mixture as a function of temperature is shown in Figure 26.

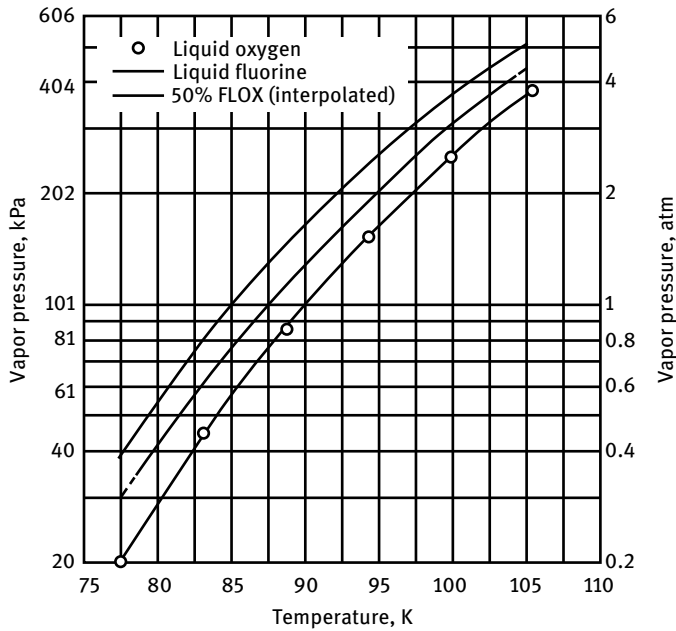


Figure 24: Vapor pressure of a liquid fluorine–liquid oxygen mixture. (Reproduced and modified from [10].)

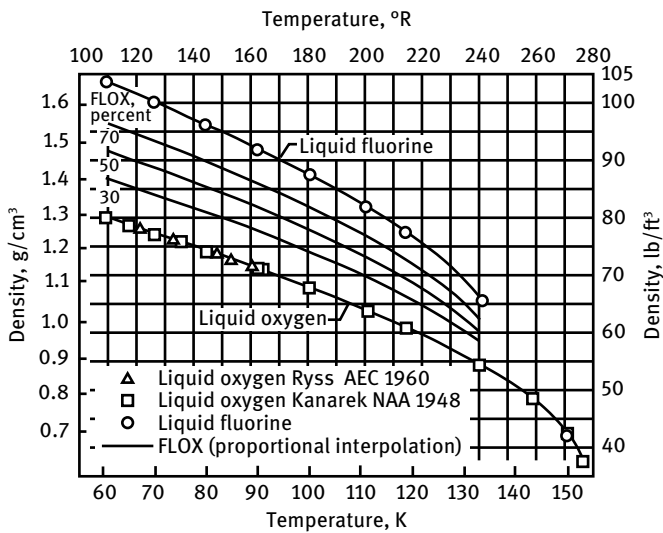


Figure 25: Density of three liquid fluorine–liquid oxygen mixtures. (Reproduced and modified from [10].)

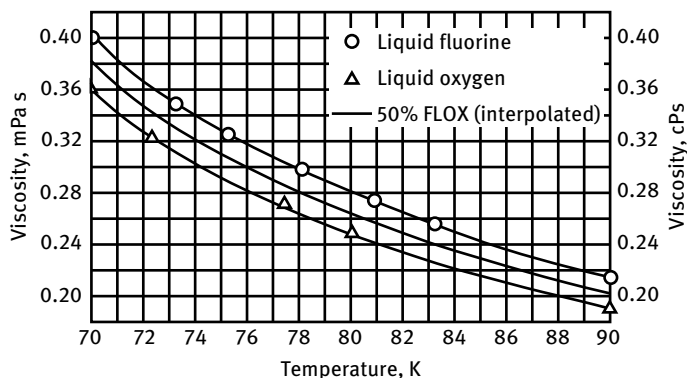


Figure 26: Viscosity of a liquid fluorine–liquid oxygen mixture. (Reproduced and modified from [10].)

9.1.2 Chemistry of Fluorine/Oxygen Mixtures

As long as fluorine and oxygen in FLOX are kept at cryogenic temperatures, one would not expect any reactions to take place between the two oxidizers. It is known that if the gaseous oxygen/fluorine mixtures are subjected to a glow discharge or UV irradiation, then various oxygen fluorides can be formed.

The radiolysis of FLOX under the influence of γ -radiation from a ^{60}Co source did not produce any changes in the cryogenic fluid [534].

9.1.2.1 Analysis of Fluorine/Oxygen Mixtures

The fluorine content of F_2/O_2 gas mixtures can be determined in a 10-cm path length Teflon-coated stainless steel cell with sapphire windows by measuring the direct absorption spectrum of F_2 at 278 nm [535].

Oxygen/fluorine gas mixtures can be analyzed by admitting the mixture to a tightly closed gas vial attached to a pressure gauge, adding mercury metal, allowing the reaction of mercury with fluorine to proceed to completion, and measuring the drop in pressure because the fluorine in the mixture has been consumed [536].

9.1.3 Materials Compatibility with Fluorine/Oxygen Mixtures

The purpose of a series of tests was to investigate the feasibility of using fluorine–oxygen mixtures in rocket-propulsion systems containing some non-metallic materials [372]. The tests were divided into two major areas, static tests and dynamic tests. In the static tests, a number of test samples were exposed to various FLOX mixtures, both gaseous and liquid, at atmospheric pressure and virtually static conditions in order to obtain information on compatibility solely as a function of fluorine concentration. The reactivity of the materials tested with FLOX under static conditions is a function of the concentration of fluorine in the mixture.

In the dynamic tests, selected materials were exposed to fluorine and FLOX at various combinations of concentration and flow velocity. Reactivity profiles were generated for these materials as functions of these two parameters (Figure 27).

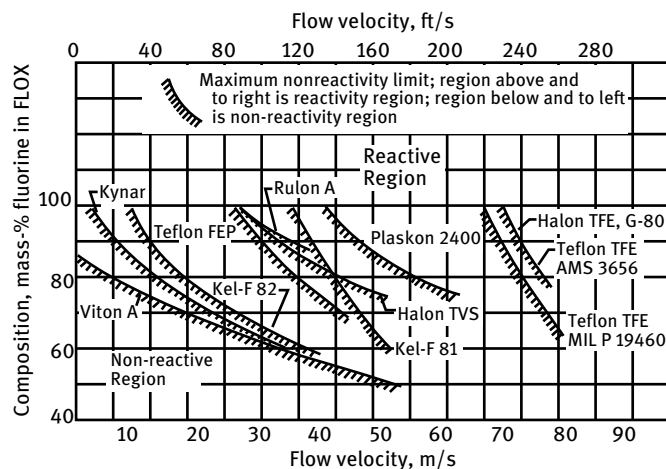


Figure 27: Compatibility profile of elastomers in FLOX. (Reproduced and modified from [372].)

These graphs show the areas of compatibility and non-compatibility of selected materials in a dynamic fluorine or FLOX environment. At any given fluorine concentration, flow velocity was a strongly significant parameter in the reactivity of FLOX with all materials tested. The ferocity of the reactions ranged from smooth burning to explosive burning. Generally, the fluorocarbon polymers, particularly the fully fluorinated, straight-chain polymers, were most compatible with fluorine and with FLOX. In both static and dynamic FLOX tests, a comparison between cryogenic liquid (77 K = -320 °F) and ambient temperature gaseous (271 to 293 K = 30 to 70 °F) test results indicated that the liquid was more reactive at pressures up to 2850 kPa = 400 psig.

9.1.4 Handling of Fluorine/Oxygen Mixtures

The following publications provide information on the handling of FLOX at rocket test sites and the potential benefits of using FLOX instead of LOX. At one time it was planned to convert the ATLAS launch vehicle from LOX to FLOX. This could not be done without a complete re-evaluation of the compatibility of tankage and component materials with the more corrosive oxidizer, even if the pre-launch exposure duration is only a matter of hours [346].

9.1.5 Selection of FLOX Storage Sites

Siting considerations for the selection of FLOX storage sites and FLOX rocket motor test firing facilities include worst-case “what if” scenarios. One US Government contractor sought approval for the siting of facilities for storing 450 kg (1000 lb_m) of liquid fluorine and for the test firing of motors using 1500 kg (3300 lb_m) of FLOX containing 30% fluorine. Recommendations made by the Space Systems Division of the US Air Force were documented, along with the contractor’s rebuttal [537]. Another contractor requested approval for the siting of a FLOX facility extension involving the installation of 378 and 1900 L (100- and 500-gallon) liquid fluorine tanks.

9.1.6 Consequences of Accidental FLOX Leaks and Spills

The consequences of accidental FLOX leaks and spills are not much different from those of fluorine itself. The same precautions must be taken regardless of whether the transported oxidizer is 100% fluorine or 50% FLOX.

The use of liquid FLOX as an oxidizer in a rocket launch or test facility requires knowledge of the reaction characteristics of these liquids in the event of spillage. The hypergolicity of cryogenic FLOX when spilled in an unconfined manner onto various common materials is of particular interest. In addition, the relative hypergolicity of FLOX in comparison to fluorine was uncertain under these spill conditions. An investigation was therefore undertaken to determine the results of such spillages onto various materials. Small quantities (2.2 to 4.5 kg = 5 to 10 lb) of liquid (FLOX, fluorine or oxygen) were spilled from a height of about 51 cm (20 in) upon several common materials that might be found or placed around a test or launch facility [452]. The materials were confined in stainless steel pans ($0.9 \times 0.9 \times 0.3 \text{ m} = 3 \times 3 \times 1 \text{ ft}$). When liquid fluorine was spilled upon JP-4, smooth burning occurred, as opposed to the multiple microexplosions with FLOX (see below). Because of NASA’s historical interest in 30% FLOX (fluorine-oxygen mixture containing 30 mass-% F₂), the majority of spills were made at this concentration. In a spill of FLOX and JP-4, several rapid machine gun-like microexplosions occurred over a period of 1 to 2 s and then a large fireball formed and expanded to 9 m (30 ft) in diameter. FLOX spilled onto water or into a water spray did not start a combustion reaction. When FLOX was spilled onto charcoal, a smooth, large, brilliant flame developed within a few seconds. From these spill tests, information was obtained in the following areas: **(1)** The hypergolicity of FLOX with various materials upon which it might be spilled, including the effect of oxygen as a diluent on hypergolicity; **(2)** qualitative information on reaction characteristics and combustion propagation by visual observation and high-speed photography; **(3)** visual, photographic, and cinematographic information on the path of the resultant gas clouds.

In preparation for the eventual use of FLOX in launch vehicles to be launched from NASA Kennedy Space Center, the meteorology of launch sites on Merritt Island was examined as to the probable path taken by clouds of spilled FLOX propellant or the exhaust plume of a FLOX/RP-1 rocket [459].

9.2 Fluorine/Ozone Mixtures

As will be discussed in detail in a later chapter on ozone properties, the explosion hazards of liquid ozone can be reduced by dilution with liquid fluorine. Liquid fluorine is the ideal diluent for ozone because it increases instead of decreases the specific impulse when this oxidizer is used in combinations with hydrocarbon fuels.

Liquid fluorine and liquid ozone are totally miscible over the entire range of compositions at 74 to 79 K [529, 538]. This is in contrast to oxygen and ozone, which are not totally miscible and have a miscibility gap. In addition to the binary system F_2/O_3 investigations into the ternary system $F_2/O_3/O_2$ were undertaken. As illustrated by Figure 23 in *Encyclopedia of Oxidizers*, chapter “Ozone,” the homogeneous liquid phase range of LOX/LOZ at 77.4 K is widened by the addition of LF_2 . Mixtures containing 14% O_3 , 72% O_2 , and 14% F_2 are a homogeneous liquid, whereas 20% O_3 and 80% O_2 separate into two phases. The physical properties of F_2/O_3 mixtures are summarized in Table 51.

Table 51: Density of fluorine/ozone mixtures.

Temperature		Ozone concentration, mass-%	Density, g/cm ³	
K	°C		Measured	Calculated ^a
90	−183	0	1.472	1.470
90	−183	31.0	1.499	1.502
90	−183	84.6	1.557	1.556
90	−183	100.0	1.571	1.571
77.35	−195.8	0	1.561	1.561
77.35	−195.8	23.0	1.573	1.573
77.35	−195.8	61.8	1.595	1.594
77.35	−195.8	100.0	1.614	1.615

Data source: [539–541]

^a Calculated from Eqs. 1 and 2:

$$\rho \text{ at } 90 \text{ K} = -183^\circ\text{C} = 0.1009 (\text{mass-fraction } O_3) + 1.4704 \quad (1)$$

$$\rho \text{ at } 77.35 \text{ K} = -195.8^\circ\text{C} = 0.0534 (\text{mass-fraction } O_3) + 1.5611 \quad (2)$$

The density of liquid F_2/O_3 mixtures is a linear function of the ozone content. There is no volume contraction during the mixing.

If one plots the logarithm of viscosity against the ozone concentration in mol-%, one obtains a linear curve that facilitates interpolation for in-between concentrations. Liquid ozone at 90 K is ten times as viscous as liquid fluorine. The lowering of viscosity of liquid ozone by the addition of liquid fluorine is very desirable (Table 52).

Table 52: Viscosity of liquid ozone–fluorine mixtures.

Ozone concentration, mol-%	Viscosity, cPs	
	at 90 K = –183 °C	at 77.35 K = –195.8 °C
100	1.55 ± 0.01	4.15 ± 0.04
79.1	0.905 ± 0.01	—
70.5	—	1.95 ± 0.01
30.5	0.343 ± 0.03	—
26.8	—	0.682 ± 0.02
0.0	0.208 ± 0.01	0.344 ± 0.01

Data source: [540]

The surface tension of liquid ozone is three times higher than that of liquid fluorine (Table 53).

Table 53: Surface tension of liquid ozone–fluorine mixtures.

Ozone concentration, mol-%	Surface tension			
	at 90 K = –183 °C		at 77.35 K = –195.8 °C	
	dyn/cm	N/m	dyn/cm	N/m
100.0	39.9	0.0399	43.55	0.04355
79.1	30.2	0.0302	—	—
70.5	—	—	35.6	0.0356
30.5	19.1	0.0191	—	—
26.8	—	—	22.4	0.0224
0.0	12.3	0.0123	15.5	0.0155

Conversion: 10^5 dyn = 1 N; 1 cm = 10^{-2} m; 1 dyn/cm = 10^{-5} N/cm = 10^{-3} N/m

Data source: [540]

If fluorine/ozone mixtures are evaporated, a reaction between fluorine and ozone begins in the vapor phase. The results are influenced by the temperature of the reactants and the absence or intensity of UV radiation.

It has been proposed that the thermal reaction is not one between fluorine and ozone, but a chain reaction between fluorine and ozone decomposition products [542, 543]. The chain reaction is quickly quenched by the wall. For the photochemical reaction, the initiation step is the photolysis of F_2 into two F atoms, which then cause decomposition of ozone in a rapidly propagating chain reaction. This is similar to the photochemical reactions of halocarbons in the upper atmosphere on Earth, causing destruction of the ozone layer. The quantum yield at 293 K is 4600. The end products of both reactions are fluorine and oxygen.

9.3 Fluorine/Oxygen Difluoride Mixtures

The binary system F_2/OF_2 exhibited typical eutectic formation with a probable break in the fluorine-rich liquidus curve due to a solid phase transition at 45 K (Figure 28) [544]. The eutectic temperature is estimated to be 43 ± 0.5 K and the eutectic composition point is at 0.59 ± 0.02 mol-fraction fluorine.

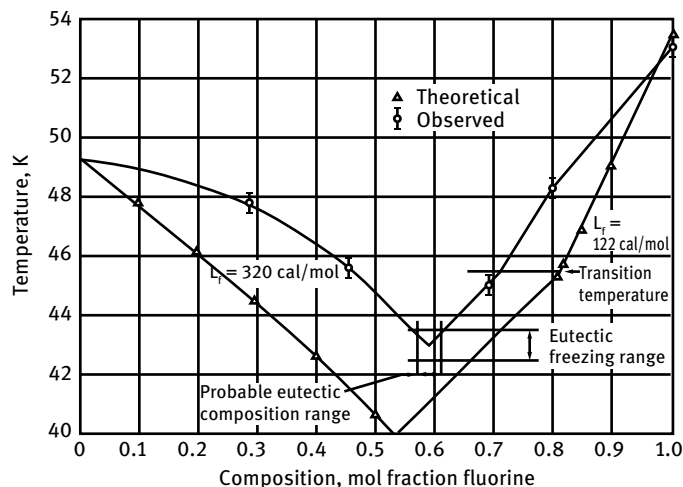


Figure 28: Phase diagram of fluorine/oxygen difluoride mixtures. (Reprinted and modified from [544], with permission from © 1969 American Chemical Society; permission conveyed through RightsLink.)

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Halogen Fluorides

Non-Metallic Fluorides

Besides all the work with elemental fluorine (difluorine) as a rocket propellant discussed in the chapter “Fluorine”, the production and investigation of physical and chemical properties of non-metallic fluorides, all of them gases or liquids, have received intensive study. The advantage of most non-metallic fluorides over elemental fluorine is that they are storable as liquids at room temperature. For the past 70 years, these chemicals have been subjected to rigorous scrutiny with regard to their suitability as rocket propellant oxidizers, but each time the final conclusion drawn was that the gain in performance does not justify the complexity of handling these aggressive and corrosive chemicals [1]. The ultimate in specific impulse with storable propellants is possible with non-metallic fluorides as the oxidizers, coupled with a storable fuel such as hydrazine. In the 1990s the priorities in evaluating rocket propellants shifted away from performance and toward environmental friendliness. This shift was partially caused by insufficient training of propellant handling personnel in the safe handling of hazardous propellants. These propellants can be handled safely, given the right protective equipment and adequate training. Here is a “What if?” question: If one were to imagine a scenario in the near future (not too near future, but inevitable in the distant future) where an asteroid ten to hundred times the size of the Chelyabinsk 15 February 2013 impact were threatening to impact a populated area of Earth and it needed to be diverted on short notice and the only storable rocket propellants capable of providing the necessary specific impulse to reach and divert the wayward asteroid are chlorine pentafluoride and hydrazine, what would your choices be? One would have to see the greater benefit to mankind and neglect the minor environmental impact of using fluorine-based propellants and releasing hydrogen fluoride (HF) into the atmosphere! The main problem in responding to an extraterrestrial threat on short notice would be the readiness of fluorine propellant technology in the US, which has fallen into oblivion since the more competitive days of Sputnik and Star Wars.

At the time when a German book on rocket propellants was published in the 1960s, the area of fluorine and fluorine-based propellants was flourishing and still undergoing active investigation, but in the meantime the interest has waned and the priorities have shifted. Nevertheless, we think it is appropriate to provide here a survey of the physical and chemical properties of non-metallic fluorides and to examine their potential application as rocket propellants. A substantial amount of government funding has gone into developing this technology and the work needs to be documented in a useful format. Some of these non-metal fluorides have also found potential applications as oxidizers in chemical lasers. They can be used as ignition fluid in the form of a hypergolic slug to start up bipropellant rocket engines with non-hypergolic

fuels or solid rocket motors, or to start non-catalytic metalized monopropellant engines (MONEX). All of the non-metal fluorides are capable of forming complex fluoro salts, which are essentially non-metal fluorides in solid form, and open up new applications. They are readily storable and can be made to release the volatile fluoride or elemental fluorine on demand.

Fluorine chemistry as a whole has benefited tremendously from the work done during the Manhattan project in WW-II and following years for the isotope separation using UF_6 . During that time, in addition to UF_6 , many other fluorides, metallic and non-metallic, were synthesized and characterized. The non-metallic fluorides were examined at that time because they may have been unwanted byproducts or they may have been looked at as desirable reactants as substitutes for elemental fluorine in the uranium processing, but with better room-temperature storability.

Many non-metallic fluorides, such as chlorine trifluoride or bromine trifluoride, exhibit the same reactivity that we have come to appreciate and respect (or fear) with elemental fluorine. They ignite hypergolically with most rocket fuels and sometimes, to the surprise of the test stand crew, also with materials of construction. Other non-metallic fluorides have certain advantages over elemental fluorine, such as reduced corrosivity, higher boiling point, or higher density. In spite of this, non-metallic fluorides have not found any flight use as rocket propellants. In some cases, elemental fluorine is needed to produce non-metallic fluorides. Consequently, non-metallic fluorides are more expensive to make than elemental fluorine. Because the exhaust gases from rockets with fluorine and fluorine compounds as oxidizers contain HF, they all share the same environmental problems of toxicity, not only as reactants but also in their exhaust products. If at all, these oxidizers may in the future only be used in upper stages of launch vehicles or in kick stages operating outside the atmosphere. Only the non-metallic fluorides of the lighter elements (oxygen, nitrogen, halogens) are useful as rocket propellants. Fluorides of boron, carbon, or phosphorus are not suitable as rocket propellants. Sulfur hexafluoride is an exception because it is used as an oxidizer in torpedo steam generator propellants. Additional monograph information on non-metallic fluorides (most of them including halogen fluorides, and some of them also including organic fluorine compounds and the infinite number of publications on fluorocarbon polymers) can be found in the publications listed in Table 1. Note that

Table 1: Literature summaries on non-metallic fluorides.

Topic	Author(s)	Year	References
Fluorine and its compounds	Hazeldine and Sharpe	1951	[2]
Fluorine-derived chemicals as liquid propellants	Gall	1957	[3]
Fluorine chemistry and technology	Gall	1959	[4]
Fluorine chemistry	Simons	1950–1964	[5]
Advances in fluorine chemistry	Stacey, Tatlow, and Sharpe	1960–1973	[6]

Table 2 contains a literature summary specifically on halogen fluorides (which would exclude oxygen and nitrogen fluorides).

In addition to monographs on fluorine chemistry, there is a monthly periodical that contains numerous publications on fluorine chemistry, including chemicals that are potentially useful as rocket propellants [7]. A book series *Advances in Fluorine Science* was published in 2006 [8].

There are many comprehensive works on non-metallic fluorides, starting with halogen fluorides, continuing with oxygen and nitrogen fluorides, and many fluoro complex salts. Most of these compounds are potentially useful as oxidizers in rocket propellants.

Three reviews summarized the publications during the period 1955–1967 directed toward the development of energetic oxidizers for use in advanced chemical propellants [9]. The source material for these reviews included over 1200 technical reports and 1150 references. The chapter on inorganic oxidizers included sections on such N-F compounds as NF_3 , N_2F_2 , N_2F_4 , HNF_2 , NF_3O , ClNF_2 , NF ions, NOF , NO_2F , N_3F , and such fluorohalogens as ClF_3 , ClF_5 , ClF ions, ClO_2F , ClO_3F , ClO_3OF , and the fluorides of bromine and iodine; such oxygenated compounds as OF_2 , O_2F_2 , O_3F_2 , NO_2OF , dioxygenyl salts, chlorine oxides, and the perchlorates. A chapter on organic oxygen–fluorine oxidizers described the CFO and CFNO compounds and the fluorinated nitroso, nitro, nitrite, and nitrate compounds.

Because fluorine is a strongly electronegative element and all elements to its left and below in the periodic table of elements are less electronegative, chemical homopolar bonds of fluorine with other non-metals are more or less polarized. Fluorine is always the more electronegative atom in the compound. Going by the chemical convention of naming compounds with the cation first and the anion last, non-metallic fluorides should be named with the central atom first and the fluoride designator last, i.e., oxygen difluoride and not fluorine oxide.

The understanding of the nature of the chemical bond in fluorine compounds was totally revamped when the first noble gas fluorides were detected in the 1960s. In the following decades, a substantial amount of effort was devoted to computational chemistry in an effort to explain the unexpected stability of noble gas fluorides and to predict new, as yet undiscovered fluorides that might also be useful as rocket propellants. Chlorine pentafluoride would be the best example for this type of discovery, but it is the only one that had advanced to the level of actual testing in rocket engines.

The theoretical rocket propellant chemist needs a complete understanding of the bond strength in fluorides and the molecular structure. For instance, the polarity of bonds in fluorides and the symmetry of the molecule determine the physical properties such as freezing points and boiling points.

The following literature on the molecular structure of fluorides [10] and the bond energies of fluorine bonds [11] will be a good starting point for future considerations in the search of even more energetic rocket propellants. The hypervalency of halogen atoms in polyhalogens such as ClF_3 , BrF_5 , IF_7 , ICl_4 , etc., has been described in terms of

sp^3d , sp^3d^2 , or sp^3d^3 hybridization of the valence orbital of the hypervalent atom and the formation of localized electron pair bonds involving hybrid orbitals. The formation of these directed bonds has been argued either from Pauling's principle of maximum overlap or from the "Pauli repulsion" between electrons of the same spin.

In addition to being considered as liquid rocket propellants, many non-metal fluorides have been converted to fluoro-onium cations or fluorometallate salts, which have been evaluated as ingredients for solid rocket propellants and solid gas generants for gaseous difluorine generators from a solid, storable form of fluorine.

Some overly enthusiastic computational chemists claimed that the performance of future more powerful rocket propellants (in particular, oxidizers) can be predicted entirely by quantum mechanical calculations [12]. In spite of advances in computational chemistry, much work remains to be done by chemists in the laboratory. Results of molecular orbital calculations for specific fluorine compounds are discussed in the following sections.

Binary Fluorides

Binary fluorides contain only one element other than fluorine. Fluorides that contain more than one other element are discussed in a later section on ternary fluorides. A literature bibliography dealing specifically with molecular structures and bonding energies in binary fluorides was published in 1976 [13].

The molecular geometries and electronic structures of 14 fluorides were optimized using density functional theory (DFT) and Møller–Plesset perturbation theory methods and an attempt was made to correlate structural and energetic parameters with the acute toxicity (expressed as $-\log LC_{50}$ of fluorides to rats) to establish quantitative structure–activity relationships [14]. The toxic mechanism appears to be controlled mainly by electronic quality factor (the maximum net atomic charge on fluorides). There was some agreement with the experimental values, and the model had good stability and a strong prediction ability.

1 Halogen Fluorides

Halogen fluorides are powerful oxidizers comparable with fluorine itself and ignite hypergolically with many commonly used fuels. They have the advantage over fluorine that they are not cryogenic liquids but can be stored as liquids at room temperature (although some will have substantial vapor pressures). The physical and chemical properties of halogen fluorides have been measured in detail as part of their evaluation as rocket propellants and the most essential data are summarized in this chapter. Halogen fluorides represent a fascinating class of chemical compounds. They generally exhibit amphoteric character and can form complexes with strong Lewis acids and

bases. The central halogen atom in the compounds can have oxidation states ranging from +1 to +7 and coordination numbers from 1 to 8.

Additional summaries on physical and chemical properties of halogen fluorides can be found in references summarized in Table 2 (in chronological order).

Table 2: Literature summary of publications on chemical and physical properties of halogen fluorides.

Topic, abbreviated title	Author	Year	References
Halogen fluorides	Booth and Pinkston	1947	[15]
Volatile inorganic fluorides	Burg	1950	[16]
Interhalogen compounds and polyhalides	Sharpe	1950	[17]
Molecular structures of volatile fluorides	Bauer	1952	[18]
Halogen fluorides	Emeleus	1954	[19]
Halogen fluorides and other covalent fluorides	Clark	1958	[20]
Halogen fluorides	Musgrave	1960	[21]
Structures of interhalogen compounds and polyhalides	Wiebenga	1961	[22]
Interhalogen compounds	Meinert	1967	[23]
Physical and chemical properties of halogen fluorides	Stein	1967	[24]
Inorganic chemistry of the halogens	Sharpe	1967	[25]
Chemistry of halogen fluorides	Nikolaev et al.	1970	[26]
Halogen fluorides	Christe	1973	[27]
Halogen fluorides	Bailey and Woytek	1994	[28]
Halogen fluorides	Bailey and Woytek	2004	[29]
Chemistry of non-aqueous solvents	Martin, Rousson, and Weulersse	2012	[30]

In addition to summary publications in the open literature, there exists a plethora of contractor reports on government-sponsored work on halogen oxidizers that would fill an entire book by themselves if someone made the effort to gather and catalog this work by the type of chemical investigated and the type of rocket propellant data gathered. Most of these reports deal with more than one fluorine-containing chemical at a time. They may deal with liquid and/or solid fluorine-containing compounds. Several of these reports are listed in this book more than once, each time at the chapter of the specific halogen fluoride or other non-metallic fluoride being investigated and described in the report. Some of the reports on high-energy storable rocket propellants may even include work on fuels (intended to be combined later with storable halogen oxidizers), which would be discussed later in a separate chapter of this book. Table 3 may serve as a starting point for a more detailed search of the contractor reports. Many of the reports are now only of historical interest because it is unlikely that fluorine oxidizers will again be used as rocket propellants as long as concerns about environmental pollution and the accidental exposure of propellant handling person-

nel to toxic chemicals persist. In view of the very limited future military utility of any of these toxic chemicals, the distribution limitations on several of these reports should now be relaxed. There may be some commercial uses, e.g., in organic synthesis or batteries and portable energy sources, which would be a late payback for the substantial sums of taxpayer's money spent on this type of work. Those benefits cannot be realized while the information is still kept under lock and key, simply because nobody has made an effort to have it released.

Table 3: Summary of contractor reports on the synthesis of high-energy oxidizers.

Author(s)	Title	Biblio Info	Pages	Date	Contract No.	Accession No.	www. Source
Tannenbaum, S., et al.	Advanced earth storable liquid propellants	Reaction Motors Division, Thiokol Chem. Corp., Denville, NJ, RMD 5036-F, Fin. Eng. Rept.	241 pp.	Feb 1965	NOw 63-0740-c	AD-359324	Not listed in DTIC OnLine; Distr. Stat. C: Distr. Limitation removed
Cain, E. F. C., et al.	Physico-chemical characterization of high energy storable propellants ^a	Rocketdyne, Canoga Park, CA, R-6147, AFRFL-TR-65-125, Fin. Rept.	473 pp.	May 1965	AF 04(611)-9380	AD-364207	
Cain, E. F., et al.	Physico-chemical characterization of high energy storable propellants ^b	Rocketdyne, Canoga Park, CA, R-6737, AFRPL-TR-66-294, Fin. Rept.	404 pp.	Oct 1966	AF04(611)-10544	AD-378773	Declassified, Distr. Limitation removed

^a Quarterly reports on this project, AD-number: 1965-0394,AD-356019; 1965-0392,AD-351424; 1964-0556,AD-348275; 1964-0432,AD-345829

^b Quarterly reports on this project, AD-number: 1967-0082,AD-373918L; 1967-0081,AD-371322; 1966-0912,AD-366525; 1966-0913,AD-368767; 1965-1552,AD-362673

1.1 Physical Properties of Halogen Fluorides

It is interesting to compare the physical properties and thermal stability of halogen fluorides in a table where the column headers are the three core halogens chlorine, bromine, and iodine, and the rows going down list compounds with increasing states of oxidation. Table 4 lists the presently known halogen fluorides, including boiling points and the year of their discovery. As can be seen, all the compounds expected to

exist were synthesized before 1963 and their properties have been summarized previously. The fact that the heptafluoride of chlorine does not exist can be explained by steric arguments (there is just not enough space surrounding the chlorine atom).

Table 4: Known halogen fluoride molecules and their boiling points and year of discovery.

Oxidation State of Central Atom	Chlorine	Bromine	Iodine
+I	ClF −100 °C Ruff (1928)	BrF +20 °C Ruff (1933)	IF Unstable Schmeisser (1960)
+III	ClF ₃ +12 °C Ruff (1930)	BrF ₃ +126 °C Lebeau, Prideaux (1905)	IF ₃ Unstable Schmeisser (1960)
+V	ClF ₅ −140 °C Maya (1962)	BrF ₅ +41 °C Buff (1931)	IF ₅ +98 °C Gore (1871)
+VII			IF ₇ +4.8 °C Ruff (1930)

All of the halogen fluorides listed in Table 4 can be synthesized directly from the elements. Variation of the reaction parameters, such as stoichiometry of the reactants and reaction time and pressure, determine the composition of the product. Many of the prior publications deal with the relatively easy-to-obtain chlorine trifluoride. Bromine and iodine fluorides are less suitable as rocket propellants because the heavy central atom increases the average molecular weight of the exhaust gases and decreases the specific impulse. Iodine has the advantage over chlorine and bromine in that it can form fluorides of heptavalent iodine, containing a higher percentage of fluorine than pentafluorides or trifluorides. The higher fluorine content does not compensate for the disadvantage of the high molecular weight of the exhaust gases, a fact that we try to demonstrate with the data in Table 5.

Table 5: Comparison of fluorine content of halogen fluorides.

	ClF	ClF ₃	ClF ₅	BrF ₃	BrF ₅	IF ₅	IF ₇
Molecular mass, g/mol	54.5	92.5	130.5	137	165	212	260
Fluorine content, mass % F	34.9	61.6	72.8	41.6	51.6	40.1	51.2
Average molecular mass of combustion products with hydrogen as the fuel at the stoichiometric mixture ratio	28.3	24.1	22.7	35.2	28.5	36.3	33.5

Chlorine pentafluoride forms the lowest average molecular mass (22.7) combustion products with hydrogen or other hydrogen-containing fuels of all the halogen fluorides examined here. As far as availability is concerned, chlorine, as the central atom, is much more readily available as a raw material than bromine or iodine. The average molecular weight of combustion products of fuels with chlorine fluorides is lower than that with bromine or iodine fluorides. The reactivity of halogen fluorides with hydrogen-containing fuels can be ranked as follows [20]:



Table 6 is a summary of the physical properties of halogen fluorides.

Table 6: Comparison of physical properties of elemental fluorine, elemental chlorine, and halogen fluorides.

Com- pound	CAS RN	Freezing point			Boiling point			Density, liquid (at __ °C) g/cm ³
		K	°C	°F	K	°C	°F	
F ₂	[7782-41-4]	55.1	-218	-360	85.2	-187.9	-306	1.51 (-188°)
ClF	[7790-89-8]	119.1	-154	-245	172.3	-100.8	-149	1.67 (-108°)
ClF ₃	[7790-91-2]	196.8	-76.32	-105	284.9	+11.75	+53	1.8094 (25°)
ClF ₅	[13637-63-3]	170.2	-103	-153	259.2	-14	+7	1.778 (25°)
Cl ₂	[7782-50-5]	170.7	-102.4	-152	239.2	-34	-29	1.557 (-34°)
BrF	[13863-59-7]	240.2	-33	-27	about 293	about +20	about +68	—
BrF ₃	[7787-71-5]	282.0	+8.8	+48	400.2	+127	+261	2.8030 (25°)
BrF ₅	[7789-30-2]	210.7	-62.5	-81	313.5	+40.3	+105	2.460 (25°)
IF ₅	[7783-66-6]	282.6	+9.43	+49	373.7	+100.5	+213	3.19 (25°)
IF ₇	[16921-96-3]	277.6	+4.5	+40.1	Sublimes at 277.9	Sublimes at +4.77	Sublimes at 40.6	2.75 (25°)

1.2 Reactions of Halogen Fluorides

Halogen fluorides have been evaluated as selective fluorinating agents for the synthesis of organic mono- and poly-fluoro-compounds [31]. The reactivities of halogen monofluorides were compared with those of their stoichiometric equivalents. The mechanisms of the reactions of halogen fluorides and their inorganic complexes with organic compounds still need to be identified.

Highly fluorinated organic compounds can be prepared by fluorination with metal fluorides, electrochemical fluorination, fluorination with elemental fluorine or halo-

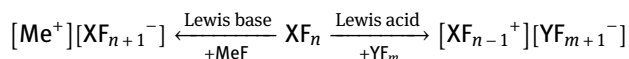
gen fluorides [32]. From Prozac to Teflon, many of the most important products of the chemical and life-science industries rely on organic fluorine chemistry for their useful properties. The semiconductor industry uses non-metallic gaseous fluorides to clean their vacuum deposition chambers.

Halogen fluorides can serve as non-aqueous solvents for a number of fluorination and salt-forming reactions [30].

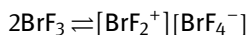
All of the halogen fluorides can be handled safely and are not shock sensitive (as opposed to NCl_3 or NI_3).

Although the last halogen fluoride molecule was discovered in 1962, a large number of halogen fluoride ions (anions and cations) have been discovered since then and their structures established. Essentially, all of the possible binary halogen fluoride molecules and ions have now been synthesized and characterized. Owing to the large number of possible oxidation states, coordination numbers and sterically active free valence electron pairs, this family of compounds is of particular interest from a theoretical structural point of view, but also as a source of high-energy oxidizers.

One of the most significant chemical characteristics of halogen fluorides is their amphoteric nature, i.e., their ability to act as a base toward strong Lewis acids and as an acid toward strong bases. These interactions result in the formation of complex fluoro cations and anions respectively, according to:



where X is another halogen (Cl, Br, I) or a metalloid (B, P, As, Sb). This amphoteric nature of halogen fluorides was first recognized by Woolf and Emeleus. As BrF_3 shows a relatively high electric specific conductance of $8 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$, self-ionization was postulated according to:



Although this assumption is certainly correct for BrF_3 , the specific electric conductances reported for the other halogen fluorides are quite low and often were at the lower limits of the sensitivity of the experimental equipment.

Table 7 summarizes the possibly existing and presently known binary halogen fluoride ions. As can be seen, all ions are known, with the exception of ClF_8^- , ClF_6^- , BrF_8^- , Br_2F^+ , and I_2F^+ .

Table 7: Halogen fluoride ions.

Oxidation state	Cation	Parent molecule	Anion
+1	Cl_2F^+	ClF	ClF_2^-
+3	ClF_2^+	ClF_3	ClF_4^-
+5	ClF_4^+	ClF_5	$\{\text{ClF}_6^-\}$
+7	ClF_6^+	$\{\text{ClF}_7\}$	$\{\text{ClF}_8^-\}$
+1	(Br_2F^+)	BrF	BrF_2^-
+3	(BrF_2^+)	BrF_3	BrF_4^-
+5	(BrF_4^+)	BrF_5	BrF_6^-
+7	(BrF_6^+)	$\{\text{BrF}_7\}$	$\{\text{BrF}_8^-\}$
+1	(I_2F^+)	IF	IF_2^-
+3	(IF_2^+)	IF_3	IF_4^-
+5	(IF_4^+)	IF_5	IF_6^-
+7	(IF_6^+)	IF_7	IF_8^-

Data source: [27]

Note: Compounds listed in {braces} do not exist, those in (parentheses) may exist but have not as yet been prepared.

2 Chlorine Fluorides

Depending on the reaction conditions, the reaction of dichlorine with difluorine can lead to various chlorine fluorides in increasing states of oxidation of the chlorine atom, often in mixtures with each other.

2.1 Chlorine Monofluoride

Under the right conditions, and only under those, a stoichiometric equimolar mixture of chlorine and fluorine reacts to form chlorine monofluoride (chlorine fluoride, ClF, CAS RN [7790-89-8]). The history of the preparation of chlorine monofluoride is remarkable for the number of failed attempts at preparing it. Moissan found no apparent reaction when fluorine and chlorine were mixed at room temperature. Lebeau remarked that one may conclude that fluorine and chlorine react neither directly nor indirectly at room temperature, as fluorine displaced chlorine from chlorides without producing a chlorine fluoride. Lebeau also observed that fluorine dissolved freely in liquid chlorine at 193 K (-80°C), but there was no indication that any definite compound was formed. The solution evolved fluorine when cooled to the freezing point of chlorine. It is unlikely that chlorine fluoride would ever be used as a rocket propellant, as the higher fluorides, chlorine trifluoride, and chlorine pentafluoride have the advantage of better storability and higher fluorine content. Chlorine fluoride is only of interest as an intermediate in the production or decomposition of chlorine trifluo-

ride or chlorine pentafluoride. As an oxidizer in rocket engines, chlorine fluoride does not have any particular advantages as its performance is not any better than that of fluorine or chlorine trifluoride. If one makes storable oxidizers by the fluorination of chlorine, one should continue to do so past the oxidation level of Cl^{1+} and go all the way to trivalent or even pentavalent chlorine.

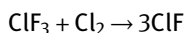
Unlike BrF and IF , ClF shows little tendency to associate or disproportionate but instead exhibits a partial double bond character.

2.1.1 Preparation of Chlorine Monofluoride

Chlorine monofluoride, ClF , forms in a flame-like reaction from the elements [33–35]. Chlorine trifluoride is formed as a byproduct that is left behind owing to its lower volatility. The maximum computed flame temperature was 1409 K at a mixture containing 48.3% fluorine. This reaction can sometimes proceed with explosive violence and it has flammability limits similar to conventional oxidizer/fuel mixtures [36]. The spontaneous explosion limits, the pressure and temperature conditions dividing the explosion region from the non-explosion region for a gaseous mixture in a closed vessel, were found for mixtures of chlorine and fluorine in the 403–473 K (130–200 °C) temperature range. The results showed that the Semenov thermal explosion theory is applicable to the chlorine–fluorine system. The reaction can also be initiated by ultra-violet light.

The kinetics and thermodynamics of these reactions were investigated in efforts to obtain optimal yields of the desired reaction products [37]. The rate of reaction of chlorine with fluorine to form chlorine fluoride was measured in the temperature range 353–401 K (80–128 °C), and the spontaneous ignition limit of the stoichiometric mixture was studied at pressures ranging from 15 to 280 mm Hg and temperatures ranging from 403 to 443 K (130 to 170 °C). The reaction was first order with respect to fluorine and one half order with respect to chlorine. The activation energy obtained from rate studies was 82.8 kJ/mol (19.8 kcal/mol). Neither argon dilution nor the variation of the surface-to-volume ratio affected the observed kinetics. Incipient decomposition of the products often limits the yield of such reactions. The reversal of the formation kinetics is dependent on the decomposition kinetics of ClF_3 and ClF_5 [38].

Although ClF can be prepared directly from the elements, it is generally preferable to employ the reaction of ClF_3 and Cl_2 according to the equation



This reaction was first reported by Schmitz and Schumacher. Reaction conditions were optimized for temperatures between 393 and 453 K (120 and 180 °C) and pressures between 1.1 and 4.6 MPa (160 and 670 psi) and reaction times between 6 and 65 h. Best results (95% yield) were obtained at 423 K (150 °C), 4.27 MPa (620 psi), and 18 h [39]. A trap cooled to 131 K (–142 °C) was used to retain impurities such as Cl_2 , ClF_3 , and FClO_2 , whereas the ClF was condensed in a trap held at 77 K (–196 °C).

2.1.2 Physical Properties of Chlorine Monofluoride

At 173.1 K (−100 °C) chlorine monofluoride condenses to a yellowish liquid, and at 117.6 K (−155.5 °C) it freezes to a white solid. The vapor pressure of liquid chlorine monofluoride can be calculated from

$$\log_{10} P_v = 15.738 - 3109/T + 153800/T^2$$

where P_v is the vapor pressure in mm Hg and T is the temperature in kelvin. A similar Antoine equation from [40] National Institute of Standards and Technology (NIST) Chemistry WebBook valid for the range from 129.7 to 172.6 K is as follows:

$$\log_{10} P_v = 6.03113 - 983.517/(T - 9.791)$$

where P_v is the vapor pressure in bar and T is the temperature in kelvin. The latter equation was used to construct the vapor pressure chart shown in Figure 1.

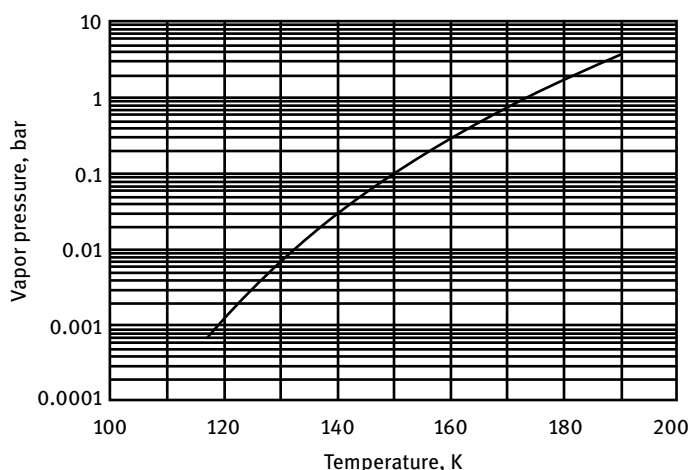


Figure 1: Vapor pressure of chlorine monofluoride. (Chart created by Schmidt 2016 based on data from [40].)

Liquid ClF is completely miscible at a molar ratio of 1 : 1 with OF₂ at 125 K, with ClO₃F at 160 K or with C₃F₈ at 160 K, but forms two separate layers with LOX at 90 K, NF₃ at 150 K, H₂F₂ at 173 K, or ClF₃ at 174 K [41].

2.1.3 Thermodynamic Properties of Chlorine Monofluoride

The heat capacity of gaseous chlorine monofluoride as a function of temperature can be expressed by the Shomate equation

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + E/\tau^2$$

where C_p is the heat capacity in $\text{J mol}^{-1} \text{K}^{-1}$, τ is the temperature in kelvin divided by 1000: $\tau = \text{K}/1000$, and A, B, C, D, and E are constants listed in Table 8 for two temperature ranges.

Table 8: Thermodynamic property polynomial equation coefficients for chlorine monofluoride gas.

Temperature range, K	298–2300	2300–6000
A	33.00963	400.6418
B	7.780901	–226.2720
C	–4.389142	49.98708
D	0.894945	–3.436085
E	–0.258478	–341.4424
F	–61.31694	–626.3866
G	254.2747	327.8775
H	–50.29210	–50.29210

Data source: [40]

The standard enthalpy of formation of the gas is $\Delta H_f^{298} \text{ gas} = -50.29 \text{ kJ/mol}$. The enthalpy of formation of gaseous chlorine monofluoride as a function of temperature can be expressed by the equation

$$H^\circ - H_{298.15}^\circ = A\tau + B\tau^2/2 + C\tau^3/3 + D\tau^4/4 - E/\tau + F - H$$

where H° is the standard enthalpy in J mol^{-1} , τ is the temperature in kelvin divided by 1000: $\tau = \text{K}/1000$, and A, B, C, D, E, F, and H are constants listed in Tables 2–7 and 8 for two temperature ranges. The standard entropy of gaseous chlorine monofluoride as a function of temperature can be expressed by the equation

$$S^\circ = A \times \ln(\tau) + B\tau + C\tau^2/2 + D\tau^3/3 - E/(2\tau^2) + G$$

where S° is the standard entropy in $\text{J mol}^{-1} \text{K}^{-1}$, τ is the temperature in kelvin divided by 1000: $\tau = \text{K}/1000$, and A, B, C, D, E, and G are constants listed in Tables 2–7 and 8 for two temperature ranges. Thermodynamic functions of ClF at 298.16 K were calculated from spectroscopic data and gave the following results for the free energy function $-(F_0 - H_0)/T = 44.904 \text{ cal mol}^{-1} \text{K}^{-1}$, entropy $S_0 = 52.045 \text{ cal mol}^{-1} \text{K}^{-1}$, and the molar heat capacity $C_p = 7.672 \text{ cal mol}^{-1} \text{K}^{-1}$ [42].

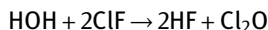
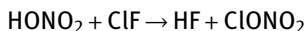
Additional data for thermodynamic properties of ClF are listed in Table 21.

2.1.4 Optical Properties of Chlorine Monofluoride

See Figure 40 in Section 2.3.2.13 “Spectroscopic Data for Chlorine Pentafluoride,” which contains an ultraviolet (UV) absorption spectrum of ClF in comparison with that of other halogen fluorides.

2.1.5 Chemical Properties of Chlorine Monofluoride

Halogen monofluorides can readily be added to C=C double bonds. As the elimination of HF is usually highly exothermic, this type of reaction is often violent and requires careful control of the reaction conditions. With hydroxyl groups the following reactions were observed:



Ultraviolet photolysis of matrix-isolated ClF_3 or a mixture of ClF and F_2 at 16 K resulted in formation of difluorochlorine free radical $\bullet\text{ClF}_2$, which was identified by its infrared (IR) absorption at $\sim 575\text{ cm}^{-1}$ [43, 44]. Much weaker absorptions were observed at 536 and 242 cm^{-1} .

Reactive species often react prematurely in the inlet to a mass spectrometer before a clean mass spectrum can be obtained. Cooling the mass spectrometer inlet will allow the sample to enter the ionization chamber unadulterated. Mass spectra of ClF and several other reactive fluorides were obtained by this method [45]. It will also allow the sample to be examined for dimer association in the vapor phase.

Chlorine fluoride forms the FCl_2^+ cation with strong Lewis acids [46], and the ClF_2^- anion with strong Lewis bases [47, 48].

2.2 Chlorine Trifluoride

Chlorine trifluoride, ClF_3 , CAS RN [7790-91-2], is the most thoroughly studied non-metallic fluoride that was once under evaluation as a rocket propellant. The closest chlorine trifluoride has ever come to being used as a rocket propellant was in the ship-board CONDOR missile under development by the US Navy during the early 1960s, but the program was abandoned in 1967. At room temperature and sea level pressure, ClF_3 is a nearly colorless gas that condenses at $284.9\text{ K} = +11.75^\circ\text{C}$ to form a faintly yellow liquid. In the solid state (below $196\text{ K} = -77^\circ\text{C}$) it is a colorless solid. The odor of ClF_3 is similar to that of fluorine or chlorine and its odor can be detected at very low concentrations in air. There are more reliable instruments than the human nose available for early detection of ClF_3 vapors in the event of a leak.

Chlorine trifluoride was being tested in Germany as early as WW-II as an ignition fluid in flame throwers and rocket engines, but did not find any flight applications at that time. One of the code names for ClF_3 was "N-Stoff." After the war, there were some residual stocks of ClF_3 at Bayer Leverkusen that nobody dared to touch and which were eventually neutralized and disposed of.

In addition to summary reports on non-metal fluorides and halogen fluorides as a group already listed in earlier tables, there are many summary documents specifically on chlorine trifluoride such as those listed in Table 9.

Table 9: Summary reports on chlorine trifluoride.

Topic	Author	Year	Pages	References
Properties	Doescher	1949	73	[49]
Physicochemical properties	Shishkov and Opalovskii	1960	7	[50]
Chlorine trifluoride	Vincent and Gillardeau	1965	45	[51]
Fluorides and oxyfluorides of chlorine	Kourile	1964	11	[52]
Chlorine trifluoride	Steere	1967	1	[53]

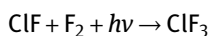
2.2.1 Production of Chlorine Trifluoride

Ruff and Krug, who prepared ClF_3 for the first time, synthesized this compound by total synthesis directly from the elements by mixing chlorine and fluorine in the appropriate volume ratio at $103\text{ K} = -170^\circ\text{C}$ [54].

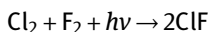
For industrial production, the reaction is better carried out at higher temperatures, at $473\text{ K} = 200^\circ\text{C}$ in a copper reaction vessel. The raw product can be refined by fractionated distillation in a copper apparatus. Large quantities of chlorine trifluoride were first produced in Germany during WW-II and were intended as a hypergolic ignition fluid in rocket engines and artillery shells. In the vicinity of Falkenhagen (Mark Brandenburg), IG Farben established an underground production plant that could produce 5 metric tons of ClF_3 /day. A nearby facility was intended for the production of Sarin (a nerve gas). In the course of the war events, the plant was relocated to Stulln (Bavaria) in the vicinity of a fluorspar mine, but did not resume its production before the end of the war [55–57]. The compound was made by heating the proper proportion of the gaseous elements to 553 K (280°C) in a U-shaped tube. The vapors were condensed at 193 K (-80°C) and passed into iron cylinders, which were vented several times to allow unreacted fluorine, chlorine, and chlorine monofluoride to escape and be recycled. Apparently, the German army intended to use chlorine trifluoride in shells against aircraft and tanks because of its incendiary properties.

Chlorine trifluoride does not have any other large-scale industrial applications and only small quantities are produced at this time. In the 1960s the majority of ClF_3 production capacity in the US resided with Allied Chemical.

Besides thermal reaction, ClF and ClF_3 in addition to ClOF_3 can be produced by photochemical reaction of chlorine/fluorine mixtures. The chemical kinetics of the UV photochemical formations of ClF , ClF_3 , and ClF_3O were investigated experimentally to obtain information relating to optimal conditions for the formation of ClF_3 and the reaction mechanisms involved [58, 59]. The photolysis of ClF_3 was also investigated because it limits the yield. At a wavelength of 365 nm , the quantum yield of the reaction



was found to be about 1 and that of the reaction



was found to be considerably less than 1. This proves that these are not chain reactions.

2.2.2 Physical Properties of Chlorine Trifluoride

The physical properties of chlorine trifluoride were summarized in a very useful company product information brochure once compiled by Allied Chemical in the early 1960s that is no longer available, but from which most of the data in Table 10 were copied and verified by data downloaded later from a NIST web site.

Table 10: Physical properties of chlorine trifluoride.

Property	SI Units	MKS Units	Source
Molecular mass	92.448 g/mol	10.8169 mol/kg	[40]
Melting point	196.84 K	-76.32 °C	Allied Chemical
Melting point	196.94 K	-76.21 °C	[41]
Melting point	196.81 K	-76.34 °C	[60]
Boiling point (b.p.)	284.91 K	11.75 °C	Allied Chemical
Boiling point	285.1 K	11.95 °C	[41]
Boiling point	284.9 K	11.75 °C	[60]
Triple point	196.84 K	-76.31 °C	[61]
Critical temperature	426.7 K	153.54 °C	Allied Chemical
Density, liquid at 285 K	1.8480 g cm ⁻³	0.0667 lb/in. ³ at 53 °F	
Vapor pressure at 294.2 K (21.1 °C)	156.5 kPa	21.5 psia	[62]

2.2.2.1 Density of Chlorine Trifluoride

A corrosion-resistant pycnometer was developed to measure the density of liquid ClF₃ and ClF₃ mixtures at various temperatures [63]. The density of liquid chlorine trifluoride under its own vapor pressure between 268 and 319 K (-5 and +46 °C) can be expressed by the following second-order polynomial equation [64]:

$$\rho_t^4 = 1.8853 - 2.942 \times 10^{-3}t - 3.79 \times 10^{-6}t^2$$

where ρ is the density in g/cm³ and t is the temperature in °C. The density calculated from this equation is illustrated in Figure 2. At 273 K = 0 °C the density is 1.8853 g cm⁻³; at boiling point it is 1.8480 g cm⁻³.

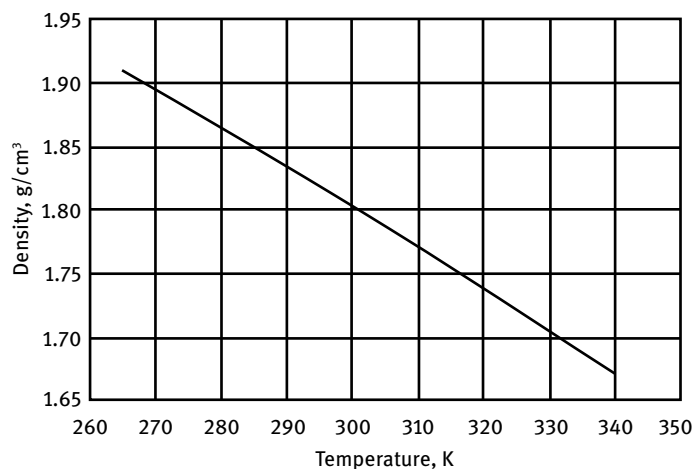


Figure 2: Density of liquid chlorine trifluoride. (Graph created by Schmidt 2018, based on data from [64].)

More recent density measurements are illustrated in Figure 3. The data in Figure 3 for temperatures between 251 and 434 K (−22 to +161 °C) can be expressed by a third-order polynomial formula

$$\rho = 4.924 - 2.517 \times 10^{-2} T + 7.38429 \times 10^{-5} T^2 - 8.215 \times 10^{-8} T^3$$

where ρ is the density in g/cm³ and T is the temperature in K.

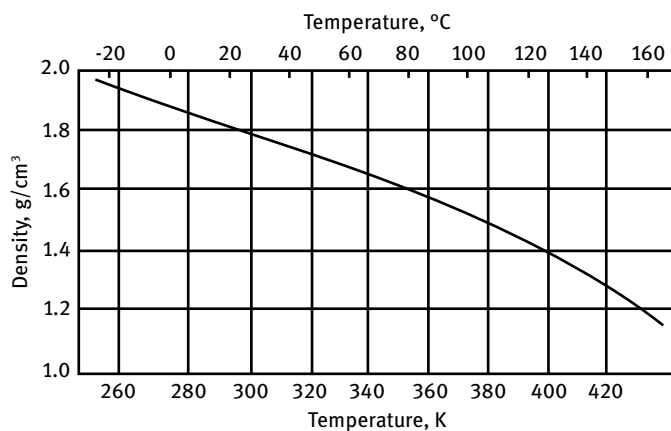


Figure 3: Density of liquid chlorine trifluoride. (Graph created by Schmidt 2018, based on data from [65].)

2.2.2.2 Velocity of Sound in Chlorine Trifluoride

The velocity of sound in liquid chlorine trifluoride was measured over the pressure range from saturation pressure up to 6.88 MPa (1000 psia) and the data are summarized in Table 11 [66]. The sonic velocity increased slightly with pressure but decreased with temperature.

Table 11: Velocity of sound in liquid chlorine trifluoride.

Temperature		Pressure		Sonic velocity	
K	°C	MPa	psia	m/s	ft/s
259	−14.12	Saturation	Saturation	991.9	3254.3
259	−14.12	3.45	500	1002.6	3289.4
259	−14.12	5.52	800	1010.0	3313.6
259	−14.12	6.89	1000	1013.5	3325.1
277.6	+4.43	Saturation	Saturation	923.1	3028.5
277.6	+4.43	3.45	500	933.5	3062.7
277.6	+4.43	5.52	800	939.2	3081.4
277.6	+4.43	6.89	1000	945.1	3100.7

Data source: [66]

The sonic velocity of saturated liquid ClF_3 as a function of temperature is illustrated in Figure 4.

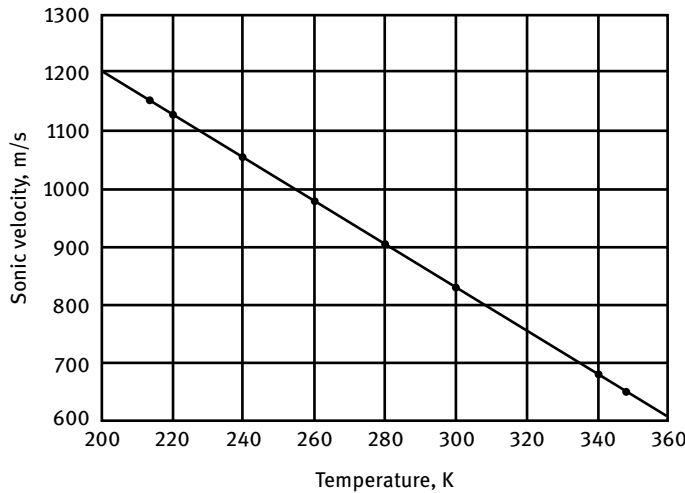


Figure 4: Sonic velocity of saturated liquid ClF_3 as a function of temperature. (Graph created by Schmidt 2018, based on data from [65].)

The sonic velocity for temperatures between 213.4 and 347.6 K (−59.7 to +74.5 °C) in Figure 4 can be expressed by the following linear equation:

$$c = 1951.8 - 3.7508 T$$

where c is the sonic velocity in m/s and T is the temperature in kelvin.

2.2.2.3 Compressibility Coefficient of Liquid Chlorine Trifluoride

The adiabatic compressibility of liquid chlorine trifluoride was curve fitted from experimental data and expressed by the equation

$$\beta = 6.2594 \times 10^{-3} + 6.1059 \times 10^{-5}t + 3.7345 \times 10^{-7}t^2 + 2.6649 \times 10^{-9}t^3 + 2.1283 \times 10^{-11}t^4$$

where β is the compressibility in atm^{-1} and t is the temperature in °C. The data calculated from this curve-fitted equation are shown in Figure 5.

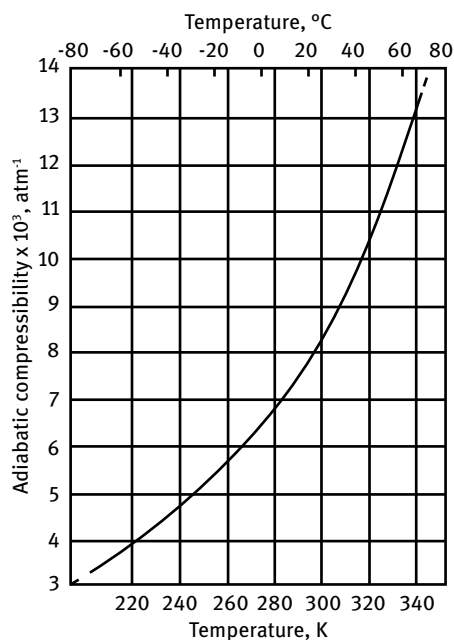


Figure 5: Adiabatic compressibility of liquid chlorine trifluoride. (Reproduced and modified from [65].)

2.2.2.4 Vapor Pressure of Chlorine Trifluoride

The temperature dependence of vapor pressure was measured in support of uranium isotope separation programs [61, 67]. At 273 K = 0 °C the vapor pressure is 60.1 kPa = 0.595 atm = 8.73 psia. At room temperature (298 K = 77 °F) the vapor pressure is

1292 mm Hg = 172.2 kPa = 1.70 atm = 24.99 psia. The data between 226 and 303 K (−47 to +30 °C) can be represented by the following equation:

$$\log_{10} P_v = 7.36711 - 1096.917/(t + 232.75)$$

where P_v is the vapor pressure in mm Hg and t is the temperature in °C.

The vapor pressure of chlorine trifluoride between 192.7 and 284.6 K can be expressed by the following Antoine equation:

$$\log_{10} P_v = 4.31282 - [1182.409/(T - 10.335)]$$

where P_v is the vapor pressure in bar and T is the temperature in kelvin [40]. This equation predicts a normal boiling point of 285 K at sea level pressure. Data in Figure 6 were calculated using this equation.

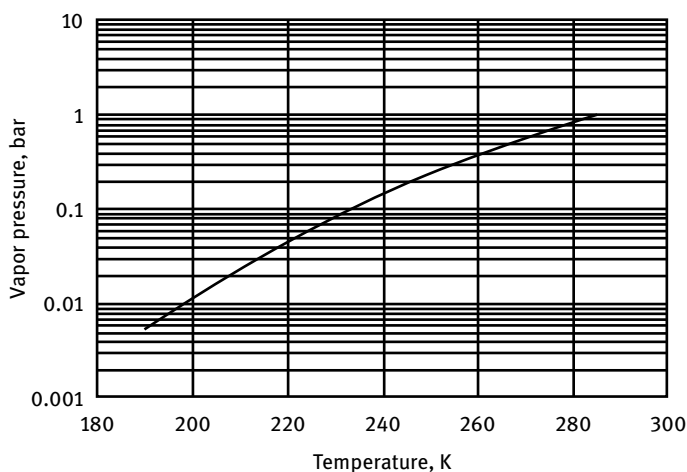


Figure 6: Vapor pressure of chlorine trifluoride. (Graph created by Schmidt 2018, based on data from [40].)

The vapor pressure of ClF_3 in the temperature range from 299 to 422 K (26 to 149 °C), which extends into the critical range, can be expressed by [66]:

$$\log p = 4.8257 - 1363.1/T$$

where p is the vapor pressure in atm and K is the temperature in kelvin. The highest measured vapor pressure point was 3.838 MPa (556.7 psia) at 422 K (148.58 °C). The Trouton constant of ClF_3 is 20.8.

The vapor pressure of chlorine trifluoride was measured by a static-type apparatus over a fairly narrow temperature range at just above room temperature from 300 K to 317 K, with corresponding pressures from 0.1848 MPa to 0.3349 MPa [68]. The vapor pressure at 313.15 K was 0.2947 MPa. The experimental data were correlated in parallel

by both the Antoine and Frost–Kalkwarf equations:

$$\log_{10} P_v = a - b/(T + c) \quad \text{Antoine} \quad (1)$$

$$\ln p = a + b/T + c \ln T + d/T^2 \quad \text{Frost–Kalkwarf} \quad (2)$$

where p is the pressure in MPa and T is the temperature in kelvin. The deviations of both equations were less than $\pm 0.05\%$. For comparison and to make sure that the apparatus was working properly, vapor pressures of *n*-butane were measured in the same apparatus and agreed accurately with literature data. The coefficients for both equations are listed in Table 12.

Table 12: Parameters of vapor pressure equations for chlorine trifluoride in comparison with butane used for calibration of the apparatus.

Substance	Equation	a	b	c	d
<i>n</i> -Butane	1	3.07198	1004.78	−25.4810	
<i>n</i> -Butane	2	37.6216	−3990.58	−4.51131	20090.4
Chlorine trifluoride	1	3.38984	1048.94	−45.5987	
Chlorine trifluoride	2	61.4209	−5574.54	−7.81482	22625.9

Data source: [68]

Figure 7 shows a comparison of Sako’s data and the NIST vapor pressure data. Sako’s measurements showed a substantially lower vapor pressure than the NIST data.

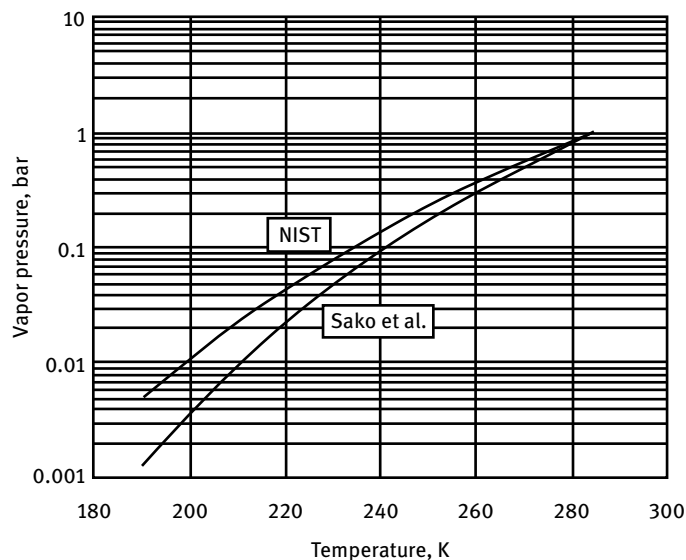


Figure 7: Comparison of Sako’s [68] and NIST [40] vapor pressure data of chlorine trifluoride.

2.2.2.5 Viscosity of Chlorine Trifluoride

Data for the viscosity of liquid ClF₃ are summarized in Table 13.

Table 13: Dynamic viscosity of liquid ClF₃ (interpolated values).

Temperature		Dynamic viscosity η	
K	°C	mPa s	mPs
285	11.75	0.478	4.78
288	15	0.460	4.60
293	20	0.435	4.35
298	25	0.412	4.12
303	30	0.390	3.90
308	35	0.370	3.70
313	40	0.351	3.51
318	45	0.333	3.33
323	50	0.316	3.16

Data source: [69]

The following graph, Figure 8, was generated from these measured data. The data have been curve-fitted and can be expressed by the following equation:

$$\log \eta = -3.83031 + 430.517/T$$

where η is the dynamic viscosity in poise and T is the temperature in kelvin.

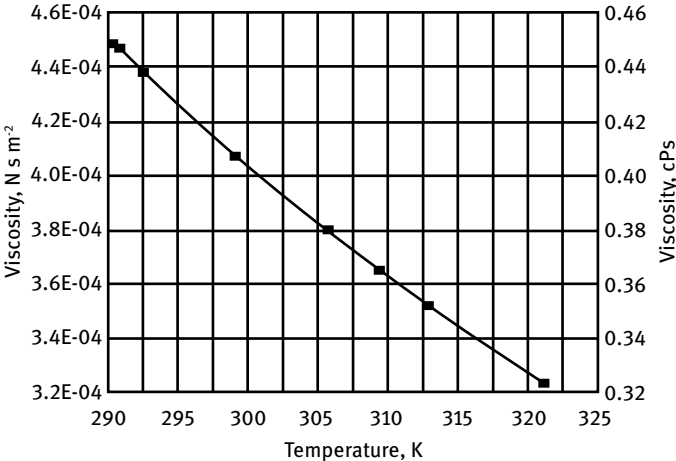


Figure 8: Dynamic viscosity of liquid chlorine trifluoride. (Graph created by Schmidt 2018, based on data from [69].)

Another very similar set of viscosity data for liquid ClF_3 was reported in [50], which seems to include the earlier data above (Table 14 and Figure 9).

Table 14: Viscosity of liquid chlorine trifluoride.

Temperature		Viscosity, η	
°C	K	mPa s	mPs
11.75	284.85	0.478	4.78
15	288.1	0.460	4.60
17.3	290.4	0.448	4.48
17.9	291	0.447	4.47
19.4	292.5	0.438	4.38
20	293.1	0.435	4.35
25	298.1	0.412	4.12
26	299.1	0.407	4.07
30	303.1	0.390	3.90
32.05	305.15	0.380	3.80
35	308.1	0.370	3.70
36.3	309.4	0.365	3.65
39.8	312.9	0.352	3.52
40	313.1	0.351	3.51
48	321.1	0.323	3.23
50	323.1	0.316	3.16

Data: [50]

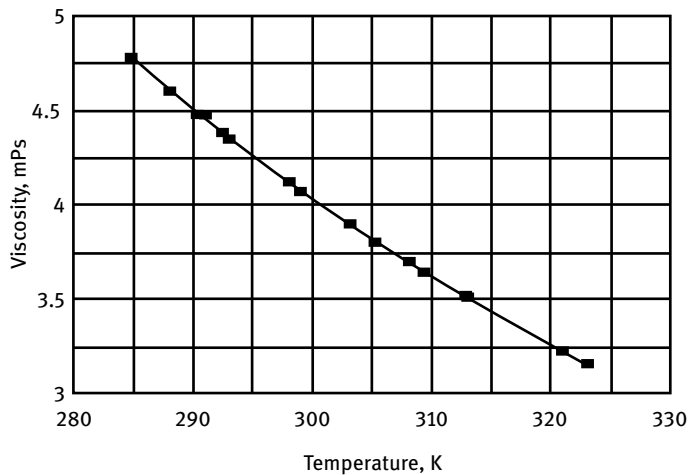


Figure 9: Dynamic viscosity of liquid chlorine trifluoride. (Graph created by Schmidt 2018, based on data from [50].)

The viscosities of gaseous F_2 , ClO_3F , ClF , ClF_3 , ClF_5 , BrF_3 , and BrF_5 were measured over a temperature range from 323 to 423 K (50 to 150 °C) with a corrosion-resistant capillary viscometer [70]. From the experimental data obtained, the parameters σ , (ϵ/k) of the 6–12 Lennard-Jones potential (non-polar gases) and μ , σ , (ϵ/k) of the 3–6–12 Stockmayer potential (polar gases) could be calculated.

2.2.2.6 Surface Tension of Chlorine Trifluoride

The surface tension of ClF_3 between 273 and 323 K (0 and 50 °C) can be expressed by the following equation:

$$\sigma = 26.7 - 0.16t$$

where σ is the surface tension in dyn/cm accurate to within ± 0.2 dyn/cm and t is the temperature in °C. For conversion purposes, $1 \text{ dyn} = 10^{-5} \text{ N}$. From Banks' and Rudge's values (Loc. cit.) for the density of liquid chlorine trifluoride and values of the surface tension calculated from the above equation, the parachor for chlorine trifluoride has been calculated to be 111.5. Table 15 and Figure 10 compare measured and interpolated surface tension data:

Table 15: Comparison of measured and interpolated surface tension data of chlorine trifluoride

Temperature		Surface tension, dyn/cm	
K	°C	Observed	Calculated
273.2	0.0	26.6	26.7
275.7	2.5	26.3	26.3
277.2	4.0	26.0	26.1
282.1	8.9	25.35	25.3
282.2	9.0	25.15	25.3
287.8	14.6	24.3	24.4
291.6	18.4	24.05	23.8
293.8	20.6	23.1	23.4
294.4	21.2	23.3	23.3
298.3	25.1	22.8	22.7
298.7	25.5	22.7	22.6
298.8	25.6	22.8	22.6
304.2	31.0	22.2	21.7
310.8	37.6	20.4	20.7
311.2	38.0	20.3	20.6
313.6	40.4	20.5	20.2
315.2	42.0	20.0	20.0
320.2	47.0	19.1	19.2
323.1	49.9	18.7	18.7

Data source: [69]

Note: For conversion purposes, $1 \text{ dyn} = 10^{-5} \text{ N}$

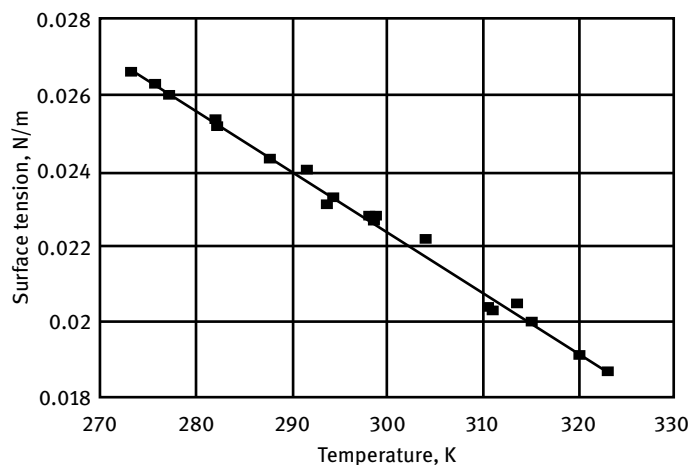


Figure 10: Surface tension of chlorine trifluoride. (Graph created by Schmidt 2018, based on data from [69].)

2.2.2.7 Solubility and Miscibility of Chlorine Trifluoride

Liquid ClF_3 is completely miscible in a molar ratio of 1 : 1 with O_2F_2 at 180 K, with ClO_3F at 195 K or with H_2F_2 at 195 K, but forms two separate layers with NF_3 or OF_2 at 140 K, ClF at 174 K, F_2 at 185 K, or C_3F_8 at 235 K [41].

2.2.2.8 Thermal Conductivity of Liquid Chlorine Trifluoride

The thermal conductivity of chlorine trifluoride is difficult to measure because the surface of the instrument may become fluoridated while the measurement is in progress at higher temperatures. The thermal conductivity of saturated liquid chlorine trifluoride is illustrated in Figure 11. The thermal conductivity of liquid chlorine trifluoride can be calculated from the curve-fitted equation

$$\lambda = 4.74 \times 10^{-4} - 8.7 \times 10^{-7} t$$

where λ is the thermal conductivity in $\text{cal cm}^{-1} \text{s}^{-1} \text{°C}^{-1}$ and t is the temperature in °C .

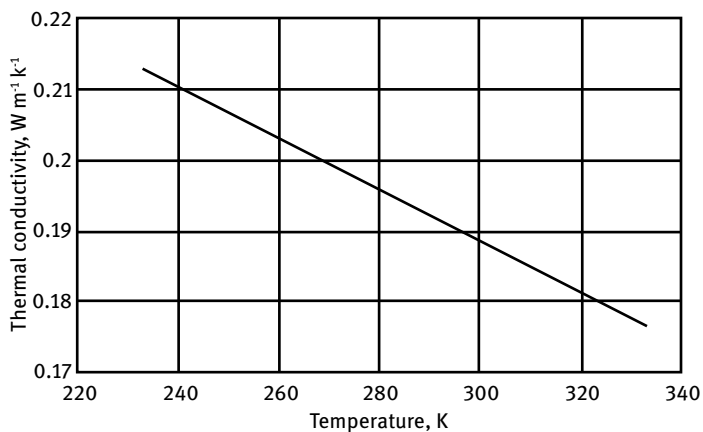


Figure 11: Thermal conductivity of liquid chlorine trifluoride. (Graph created by Schmidt 2018, based on data from [65].)

2.2.2.9 Heat Transfer Properties of Liquid Chlorine Trifluoride

The heat flux of liquid ClF_3 flowing through a tubing at a flow speed of 9.4 m/s (31 ft/s) as a function of the temperature differential is illustrated in Figure 12.

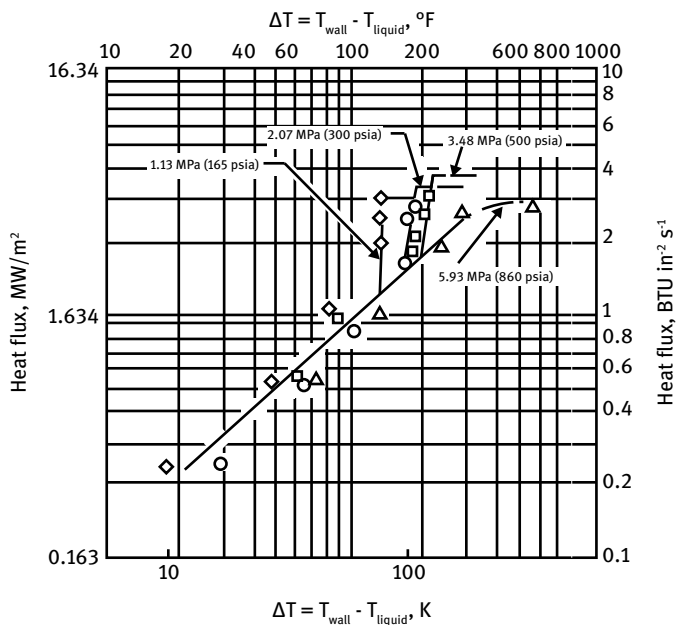


Figure 12: Limiting heat flux of liquid chlorine trifluoride. (Reproduced and modified from [65].)

The heat flux at the upper limit of nucleate boiling for chlorine trifluoride at three different flow velocities and four different bulk temperatures of 258, 308, 333, and 366 K (5, 95, 140, and 200 °F) is illustrated in Figure 13.

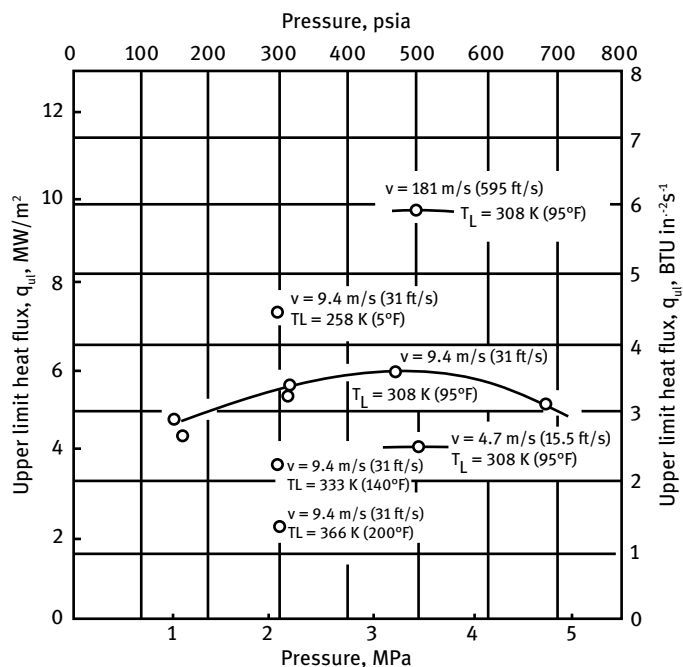


Figure 13: Heat flux of liquid chlorine trifluoride at the upper limit of nucleate boiling. (Reproduced and modified from [65].)

2.2.2.10 Thermodynamic Properties of Chlorine Trifluoride

Thermodynamic properties of chlorine trifluoride are required to calculate the theoretical rocket performance of propellant combinations with this oxidizer. Solid chlorine trifluoride undergoes an isothermal phase transition at 190.50 K that absorbs 1508 J/mol (360.5 cal/mol) [61, 71]. Thermodynamic properties of ClF_3 are summarized in Tables 16 and 17.

The molar heat capacities of liquid ClF_3 based on measurements by [61] are summarized in Table 18.

Table 16: Thermodynamic properties of chlorine trifluoride.

Property	SI Units	MKS Units	Source	Year	References
Heat of vaporization (ΔH) _{vap} (at 11.75 °C)	27.53 kJ/mol	6.580 kcal/mol	Grisard, Bernhardt, and Oliver	1951	[61]
Heat of fusion (ΔH) _{melt} (at -76.32 °C)	7.612 kJ/mol	1.8193 kcal/mol	Grisard, Bernhardt, and Oliver	1951	[61]
Enthalpy of formation (ΔH) ₂₉₈ gaseous	-158.6±4 kJ/mol	-37.9 ± 1.0 kcal/mol	Shishkov and Opalovski	1960	[50]
Enthalpy of formation (ΔH) ₂₉₈ gaseous	-158.87 kJ/mol	-37.97 kcal/mol	NIST Chem Web-Book from Chase	1965	[40]
Enthalpy of formation (ΔH) ₂₉₈ gaseous	-162.3 kJ/mol	-38.79 kcal/mol	Evans, Munson, and Wagman	1955	[72]
Enthalpy of formation (ΔH) ₂₉₈ liquid	-185.8 kJ/mol	-44.4 kcal/mol	Callery Chemical	1961	[73]
Entropy S liquid (at 11.75 °C)	182.7 J K ⁻¹ mol ⁻¹	43.66 ± 0.10 cal °C ⁻¹ mol ⁻¹	Grisard, Bernhardt, and Oliver	1951	[61]
Entropy S gaseous (at 11.75 °C)	279.8 J K ⁻¹ mol ⁻¹	66.87 cal °C ⁻¹ mol ⁻¹	Grisard, Bernhardt, and Oliver	1951	[61]
Entropy $S_{284.9}$ gaseous at boiling point	278.8 J K ⁻¹ mol ⁻¹	66.64 cal °C ⁻¹ mol ⁻¹	Weber and Ferigle	1952	[74]
Entropy S_{298} gaseous	281.59 J K ⁻¹ mol ⁻¹	67.30 cal °C ⁻¹ mol ⁻¹	NIST Chem Web-Book from Chase	1965	[40]

Table 17: Thermodynamic properties of gaseous chlorine trifluoride.

T K	$-(F_0 - E_0)/T$ cal K ⁻¹ mol ⁻¹	S_0 cal K ⁻¹ mol ⁻¹	C_p cal K ⁻¹ mol ⁻¹	$-(F_0 - E_0)/T$ J K ⁻¹ mol ⁻¹	S_0 J K ⁻¹ mol ⁻¹	C_p J K ⁻¹ mol ⁻¹
284.91	56.04	66.9	15.09	234.5	279.9	63.1
298.16	56.54	67.58	15.38	236.6	282.8	64.3
400	59.99	72.32	16.94	251.0	302.6	70.9
600	65.39	79.51	18.36	273.6	332.7	76.8
800	69.63	84.39	18.99	291.3	353.1	79.5
1000	73.16	89.16	19.29	306.1	373.0	80.7
1500	79.92	97.07	19.61	334.4	406.1	82.0

Data source: Allied Chemical Data Sheet

Table 18: Molar heat capacity of liquid chlorine trifluoride.

Temperature		Molar heat capacity C_p	
K	°C	J K ⁻¹ mol ⁻¹	cal K ⁻¹ mol ⁻¹
196.8	-76.3	111.6	26.68
202.8	-70.4	112.0	26.76
204.8	-68.3	112.0	26.78
207.7	-65.5	112.2	26.81
216.5	-56.6	112.7	26.94
219.8	-53.3	112.8	26.96
227.0	-46.2	113.2	27.05
237.8	-35.3	113.9	27.22
248.6	-24.5	114.6	27.38
259.3	-13.8	115.5	27.61
269.9	-3.3	116.5	27.84
278.3	5.1	117.2	28.02

Data source: [61]

The heat capacity and the excess enthalpy of formation of gaseous chlorine trifluoride can be calculated from the following polynomial equations [40]:

$$C_p^\circ = A + B \times \tau + C \times \tau^2 + D \times \tau^3 + E/\tau^2;$$

$$H^\circ - H^\circ_{298.15} = A \times \tau + B \times \tau^2/2 + C \times \tau^3/3 + D \times \tau^4/4 - E/\tau + F - H$$

where the coefficients A through H are listed in Table 19 for two different temperature ranges, and where C_p is the heat capacity in J mol⁻¹ K⁻¹, H° is the standard enthalpy in kJ/mol, and τ is the temperature fraction in (K)/1000.

Table 19: Coefficients for heat capacity and enthalpy polynomial for gaseous chlorine trifluoride.

Temperature range, K	298–1100	1100–6000
A	60.40357	83.01600
B	57.32582	0.072205
C	-54.42296	-0.014656
D	18.19525	0.001015
E	-0.827909	-2.372190
F	-181.7576	-190.8749
G	335.2012	370.5422
H	-158.8661	-158.8661

Data source: [40]

Based on improved microwave spectra, the thermodynamic functions of ClF_3 ideal gas were calculated [75]. Additional data for up to 1500 K are in the original publication; only the lowest temperature data are shown in Table 20.

Table 20: Thermodynamic functions of ClF_3 ideal gas.

Temperature K	Free energy function $-(F_0 - H_0)/T$ $\text{cal mol}^{-1} \text{K}^{-1}$	Entropy S_0 $\text{cal mol}^{-1} \text{K}^{-1}$	Molar heat capacity C_p $\text{cal mol}^{-1} \text{K}^{-1}$
284.91 (b.p.)	56.04	66.90	15.09
298.16	56.54	67.58	15.38

Data source: [75]

In a critical review of the Scheer data, a correction was applied, which changed the entropy of the gas phase at 284.91 K to 66.64 $\text{cal mol}^{-1} \text{K}^{-1}$ [74].

The heat capacity of liquid ClF_3 was measured calorimetrically over a temperature range of 278.5 to 330.4 K (5.4 to 57.3°C) and can be expressed by the following polynomial equation [66]:

$$c_p = 0.4716 - 2.217 \times 10^{-3}T + 8.428 \times 10^{-6}T^2 - 9.453 \times 10^{-9}T^3$$

where c_p is the heat capacity in $\text{cal g}^{-1} \text{K}^{-1}$ and T is the temperature in kelvin. Figure 14 shows the same liquid heat capacity data as in Figure 15, but at a more detailed scale

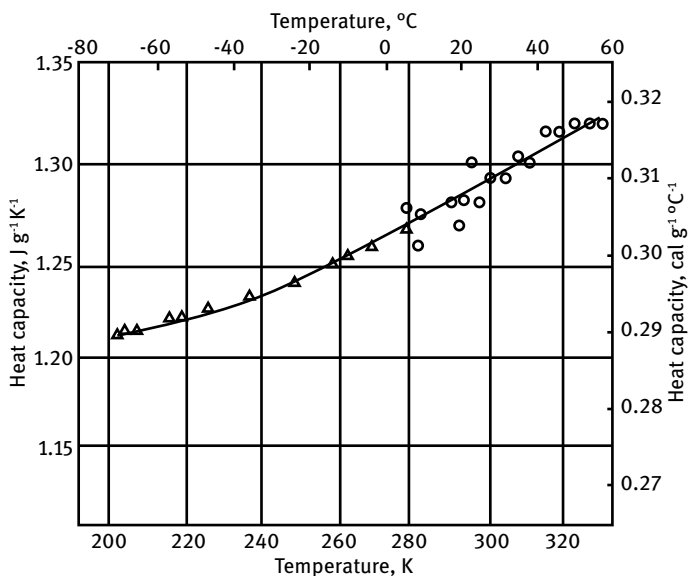


Figure 14: Heat capacity of liquid chlorine trifluoride. (Based on data from [61] and [66].)

expansion and extending the earlier Grisard 1951 [61] measurements to higher temperatures. The solid line in Figure 14 is the result of least square curve fitting and the equation

$$c_p = 0.3025 + 2.43 \times 10^{-4}t + 7.5 \times 10^{-7}t^2$$

where c_p is the heat capacity in $\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$ and t is the temperature in $^\circ\text{C}$. The triangles are the data from [61]. The circles are data obtained by Youel at Rocketdyne [66].

In the same 1967 report, and also shown in the 1969 publication, the heat capacity of solid ClF_3 was measured and curve fitted. The heat capacity of solid ClF_3 at temperatures in the range between 20 and 197 K (-253 and -76 $^\circ\text{C}$) can be expressed by the following equation:

$$c_p = -3.49 \times 10^{-2} + 3.53 \times 10^{-3}T - 3.07 \times 10^{-3}T^2 + 1.47 \times 10^{-7}T^3 - 2.57 \times 10^{-10}T^4$$

where c_p is the heat capacity in $\text{cal g}^{-1} \text{ K}^{-1}$ and T is the temperature in kelvin. The heat capacity of solid and liquid chlorine trifluoride as a function of temperature is illustrated in Figure 15.

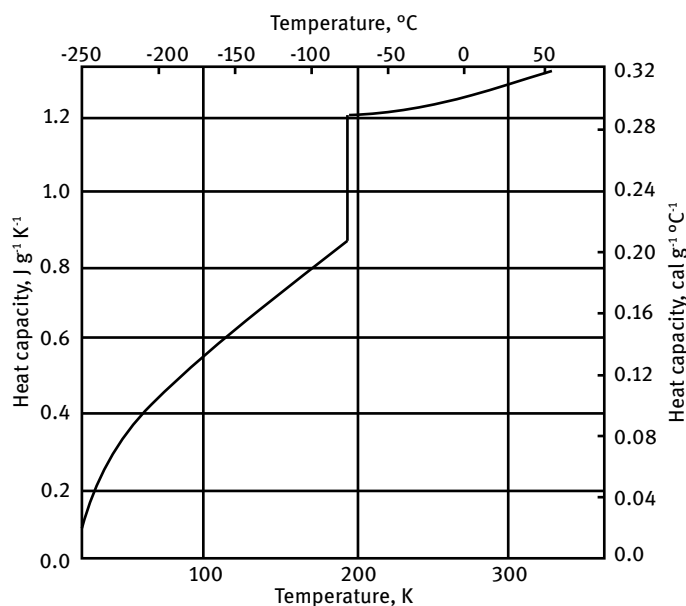


Figure 15: Heat capacity of solid and liquid chlorine trifluoride. (Reproduced and modified from [66].)

Enthalpies of formation have been computed for ClF_n ($n=1-3$) using a density functional theory method [76]. The accuracy of the results was strongly dependent on the basis set quality and it was crucial to add at least one tight d function to the Cl atom. The atomization energies were corrected for scalar relativistic, core-valence, spin-orbit, thermal effects, and zero-point energy. The enthalpies of formation data calculated by this method shown in Table 21 were in very good agreement with experimental values, though suggesting that the Joint Army, Navy, Air Force (JANAF) values from [77] are slightly underestimated.

Table 21: Calculated enthalpies of formation of ideal gas ClF and ClF_3 .

Temperature, K	0	298.16			
Source	[76]	[76]	G2 DFT Method	[77]	[78]
Compound	Enthalpy of formation in kcal/mol				
ClF	-13.1	-13.1	-14.0	-12.0 ± 0.1	-13.3 ± 0.1
ClF_3	-38.2	-39.1	-38.4; -39.6	-38.0 ± 0.7	-39.3 ± 1.2
	Enthalpy of formation in kJ/mol				
ClF	-54.8	-54.9	-58.6	-50.2 ± 0.4	-55.6 ± 0.4
ClF_3	-159.8	-163.6	-160.7; -165.7	-159.0 ± 2.9	164.4 ± 5.0

The enthalpies of formation of ClF, ClF_3 , ClF_5 , ClFO, ClFO_2 , ClFO_3 , ClF_3O_2 , ClF_3O , and ClF_5O have been calculated with the help of atomization reaction, formation reaction, and modified formation reaction at the G3 and G3X levels [79]. The standard thermodynamic functions of the title compounds were evaluated and the results agreed well with the available experimental data. Results showed that ClF, ClF_3 , ClF_5 , and ClF_3O are stable at room temperature, but ClFO_2 , ClF_3O_2 , and ClF_5O may be stable only at a lower temperature. The original publication contained data in 100-K increments from 200 to 800 K, but for our summary we have extracted and are showing only the G3 data at 298 K for comparison in Table 22.

Experimental enthalpies of formation of three different chlorine fluorides measured by combustion reactions in two types of bomb calorimeters (high-frequency spark-ignited bomb and double compartment bomb) were ClF: $-58.1 \text{ kJ/mol} = -13.9 \text{ kcal/mol}$; ClF_3 : $-155.6 \text{ kJ/mol} = -37.2 \text{ kcal/mol}$; ClF_5 : $-239.3 \text{ kJ/mol} = -57.2 \text{ kcal/mol}$ [82].

Table 22: Calculated thermodynamic data of ideal gas chlorine fluorides and oxyfluorides in comparison with experimental data.

Compound	Enthalpy of formation, gas, kJ/mol			Heat capacity, J mol ⁻¹ K ⁻¹		Entropy, J mol ⁻¹ K ⁻¹	
	G3	Experimental	Source	G3	Experimental	G3	Experimental
ClF	-52.0	-56.0±0.4	[80]	31.3	32.1	217.1	217.9
ClF ₃	-149.9	-158.9±2.9	[77]	65.4	63.8	290.2	281.6
ClF ₅	-210.3	-238.5±63	[77]	106.1	97.2	312.2	310.7
ClFO ₂	-416.4	-29.3	[77]	53.7		275.3	
ClFO ₃	-576.4	-21.4±2.9	[77]	63.0	64.9	285.7	279.0
ClF ₃ O			[81]	71.9	77.7	296.7	

Data source: [79]

2.2.2.11 Optical Properties of Chlorine Trifluoride

Infrared Spectra of Chlorine Trifluoride

The IR spectrum of gaseous ClF₃ at five different sample cell pressures is shown in Figure 16.

The Raman and IR spectra of ClF₃ and BrF₃ gave strong support for a planar T-shaped molecule [84]. The fundamental vibrational frequencies of ClF₃ observed for the vapor were 326 (a₁), 364 (b₂), 434 (b₁), 528 (a₁), 703 (b₁), and 752 (a₁) cm⁻¹. The entropy S₀ for ClF₃, calculated statistically at the boiling point, 11.75 °C, was 66.60 cal mol⁻¹ deg⁻¹ compared with a value of 67.04 obtained from a revised calculation of this quantity from available thermal data. See also [85].

Infrared absorption bands observed for gaseous ClF₃ were characterized as follows (wave numbers in cm⁻¹) [86]: 518 s, 535 s, 694 vs, 703 vs, 713 vs, 741 s, 761 s, 957 m, 1022 m, 1223 s, 1273 w, 1451 s, 1466 s, 1488 s, 1505 s. Measurements for solid ClF₃ showed only absorption bands at 499 m, 508 m, 604 vs, 630 vs, 765 m, 770 w.

The IR and Raman spectra of ClF₃ have been studied in the vapor phase and frequencies for the six fundamental vibrations of each molecule have been assigned based on a C_{2v} symmetry [83]. For ClF₃ the frequencies were 752.1, 529.3, and 328 (a₁), 702 and 442 (b₁) and 328 (b₂) cm⁻¹.

The IR spectra of matrix-isolated ClF₃ have been investigated in the region from 800 to 33 cm⁻¹ [87]. All six fundamentals have been observed in Ar and N₂ matrices for ClF₃ and BrF₃, which are planar T-shaped molecules. Both molecules showed only small gas-matrix frequency shifts, and multiplet structure for both molecules suspended in Ar matrices may be understood in terms of isotope and matrix site effects. Several absorption bands found at low matrix-isolation ratios were attributed to dimers and a tentative partial vibrational assignment was presented.

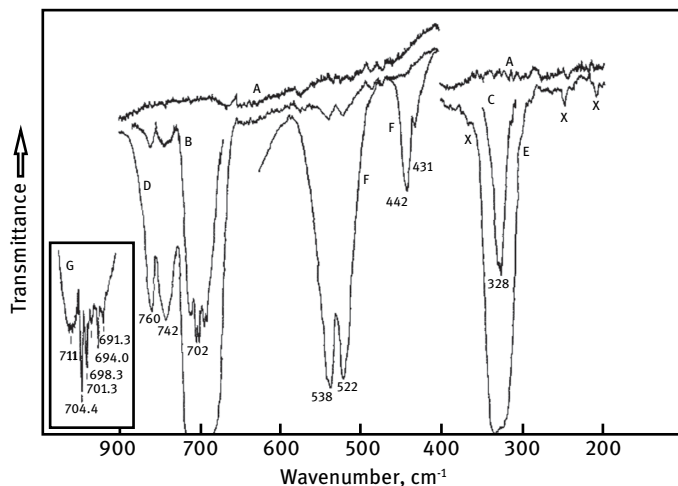


Figure 16: Infrared spectrum of gaseous ClF_3 at five different pressures. (Republished and modified from [83], with permission of © 1970 American Institute of Physics; permission conveyed through Copyright Clearance Center, Inc.)

Legend: A: Baseline, B: 2 mm Hg, C: 10 mm Hg, D: 17 mm Hg, E: 145 mm Hg, F: 450 mm Hg, G: Detail of 700 cm^{-1} peak at 2 mm Hg pressure at higher resolution

Raman laser spectra of ClF_3 have been investigated between 13 and 293 K and IR spectra were recorded and analyzed at liquid nitrogen temperature [88]. The vibrational study of ClF_3 showed an associated state in the liquid and a solid-solid transition at 192.6 K with an intermediate phase covering 5 K. A dynamical model for association was set up to explain both nuclear magnetic resonance (NMR) and Raman spectra. The associated species in the liquid were assumed to be intimately connected with the structure of the intermediate phase; moreover, the splitting of transitions into doublets allowed one to expect molecular interactions. See also [89].

Ultraviolet Spectra of Chlorine Trifluoride

Chlorine trifluoride photolyzes easily with even mild UV irradiation. As a result of this photolysis, one will thus always contain spectra that contain both ClF_3 and the $\bullet\text{ClF}_2$ free radical. UV excitation of ClF_3 in mixture with difluorine and/or other fluorides is a method for the synthesis of other fluorine compounds that are (were) of interest as rocket propellant oxidizers. The UV absorption spectra of these compounds must be known to select the optimal wavelength of the UV source used for the photosynthesis.

Microwave Spectra of Chlorine Trifluoride

A microwave spectrometer designed for the study of the microwave spectra of corrosive fluorine compounds has been used to observe and measure a portion of the microwave spectrum of chlorine trifluoride [90]. A number of transitions were identified, and from these the moments of inertia and quadrupole coupling coefficients of both $^{35}\text{ClF}_3$ and $^{37}\text{ClF}_3$ could be obtained. An intensity alternation was observed showing that the ClF_3 molecule has a C_{2v} axis and is planar. The moments of inertia confirm this and further showed that ClF_3 has a distorted "T" structure with one short (1.598 Å) and two long (1.698 Å) Cl—F bonds. The angle between the two different kinds of Cl—F bonds is $87^\circ 29'$.

The rotational spectrum of the T-shaped ClF_3 molecule was recorded for both ^{35}Cl and ^{37}Cl isotopomers in selected regions between 66 and 581 GHz [91]. The observation of transitions involving J and K_a quantum numbers of up to 82 and 27 respectively permitted the first centrifugal distortion analysis for this molecule. Most of the rotational transitions showed resolved hyperfine splitting due to the ^{35}Cl or ^{37}Cl nucleus yielding, under consideration of previous data, accurate quadrupole coupling constants and, for the first time, nuclear spin-rotation coupling constants. Although the former have been interpreted in terms of ionic bonding of the two different ClF bonds comparable with that in the ClF molecule, the latter were used to calculate nuclear magnetic shielding tensors.

NMR Spectra of Chlorine Trifluoride

Indirect spin-spin coupling tensors, J , are of importance in interpreting NMR spectra. For example, a great deal of experimental and theoretical work has focused on the characterization of J couplings observed across hydrogen bonds. Similar couplings may occur between fluorine bonds and contribute to the association of molecules and the low vapor pressure of ClF_3 and other fluorides. Symmetry properties of indirect nuclear spin-spin coupling tensors can be calculated by a first principles method and results for ClF_3 and OF_2 were shown in Bryce and Wasylishen [92]. Measured J_{iso} (^{35}Cl , ^{19}F) in ClF_3 is ± 260 Hz and J_{iso} ($^{19}\text{F}_{\text{eq}}$, $^{19}\text{F}_{\text{ax}}$) in ClF_3 is ± 403 Hz and the calculated numbers were very close. See Muetterties and Phillips [93, 94].

Gas-phase ^{19}F NMR spectra of ClF_3 at 56.4 MHz over a range of partial pressures (300–1300 mm Hg) were measured, extending to sufficiently low pressures that the shielding and spin-spin coupling constants $(\sigma_A - \sigma_B)/(1 - \sigma_B) = 125.88 \times 10^{-6}$, $|J| = 441 \pm 8$ cps could be regarded as true molecular quantities [95]. Small systematic relaxation effects in the multiplet splitting were identified and eliminated by graphical procedures. NMR data were also given for ClF_3 as a liquid and as a solute in CCl_4 and CCl_3F . Although these spectra were similar enough to that of the gas to indicate that the T-structure persisted in all these phases, there were clear trends in σ_B and J for the sequence: gas, liquid solutions, pure liquid. These trends may result from the existence in the condensed phases of local structure similar to that found in the crystal.

2.2.2.12 Electrical Properties of Chlorine Trifluoride

Electrical Conductivity of Chlorine Trifluoride

Pure ClF_3 at $273\text{ K} = 0^\circ\text{C}$ has a very low specific conductance of $3 \times 10^{-9}\ \Omega^{-1}\text{ cm}^{-1}$, much lower than that of BrF_3 . The electric conductivity of liquid ClF_3 was measured in the temperature range from 261.8 to 143 K (-11.3 to -130°C ; well below freezing point), also in comparison with BrF_3 [96, 97]. The data are illustrated in Figure 17. The two curves shown are from the same sample, one before (Δ) and one after ($\circ$) what was an intended purification cycle, but owing to the longer dwell time in glassware, more contaminants had been leached from the glass walls, allowing the conductivity to go up

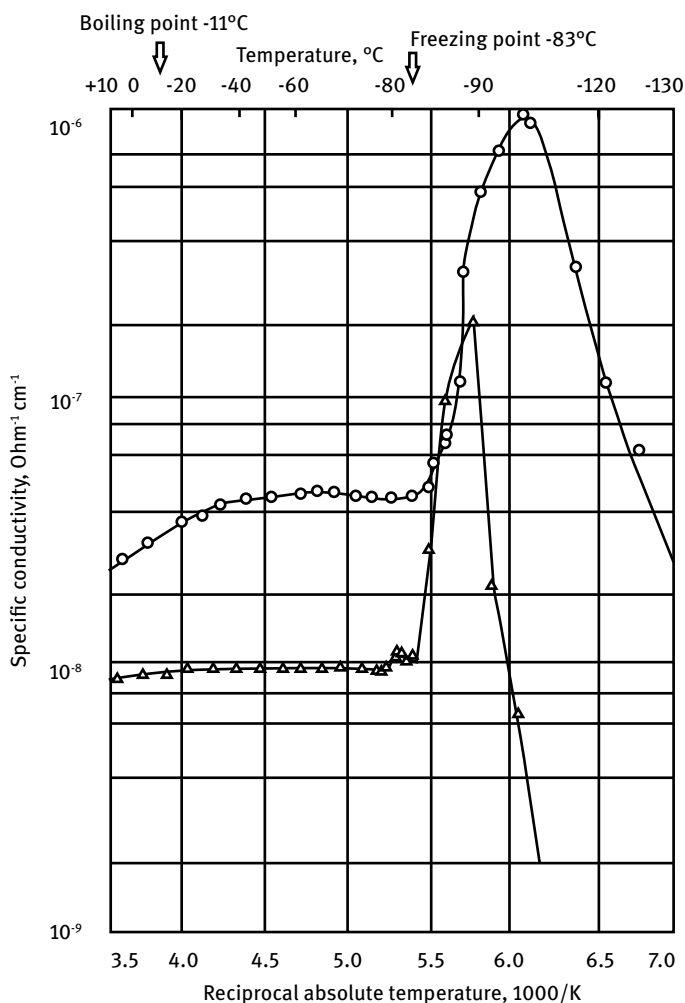


Figure 17: Electrical conductivity of liquid and solid chlorine trifluoride. (Reprinted and adapted from [97], with permission from © 1966 American Chemical Society.)

instead of down as expected. The electrical conductivity underwent steep changes in the area where the sample froze or supercooled. The electrical conductivity of frozen ClF_3 has a negative temperature coefficient.

Dielectric Constant of Chlorine Trifluoride

The dielectric constant of ClF_3 was determined at 9400 MHz by measuring the change in the resonant frequency of a cavity when it is filled with the vapor [98]. Corrections were made for the amount of dimer formed. The monomer molar polarization was best represented by $P = 15,944 + 1882.0/T$, where T is the temperature in K and P is the molar polarization in cm^3 . The dipole moment was 0.554 Debye unit. The average dimer molar polarization was found to be 49.8 cm^3 , assuming no dipole moment.

The dielectric constant of liquid ClF_3 has been measured in the range 273 to 315 K (0 to 42°C) at several frequencies and may be expressed by the equation [99, 100]:

$$\varepsilon = 4.754 - 0.018t$$

for ClF_3 , where ε is the dielectric constant (dimensionless) and t is the temperature in °C. The results indicated that these substances are associated in the liquid state.

The dielectric constants of gaseous ClF_3 (Table 23), BrF_3 , and IF_5 were measured in the vapor phase using a refractivity method [101]. Dielectric constants were measured using the heterodyne beat method. The fixed oscillator was crystal-controlled at 500 kHz. Introduction of the gas into the measuring cell increased the capacitance in the tank circuit of the variable frequency oscillator: the precision capacitor was then adjusted to restore the original beat frequency. The atomic polarizations of ClF_3 and BrF_3 were estimated from the observed molar refractions (10.34 and $15.48 \text{ cm}^3/\text{mol}$) and distortion polarizations (15.94 and $18.98 \text{ cm}^3/\text{mol}$). The atomic polarizations of BrF_3 and IF_5 were assumed to be the same as those of ClF_3 (5.5) and BrF_5 (3.5) respectively.

Table 23: Dielectric constant and molar polarization of gaseous chlorine trifluoride.

Temperature K	Dielectric constant ($1 - \varepsilon$) $\times 10^6$	Molar polarization P_M cm^3/mol
319.3	2825	24.2
351.8	2490	23.6
375.8	2293	23.3
413.3	1929	21.7

Data source: [101]

Dipole Moment of Chlorine Trifluoride

The dipole moment of ClF_3 was calculated from the dielectric constant. The molar refractions, atomic polarizations and average dipole moments (from molar polarizations at three or four temperatures) are shown in Table 24. The dipole moments listed have a probable error of about ± 0.12 D. The average dipole moment of ClF_3 is shown in Table 24 in comparison with dipole moments of BrF_3 and IF_5 .

Table 24: Molar refractions, atomic polarizations, and dipole moments of halogen fluorides.

Compound	Molar refraction M_{RD} , cm^3/mol	Atomic polarization	Dipole moment, D
Chlorine trifluoride	10.34	5.5	0.65
Bromine trifluoride	32.92	5.5	1.19
Iodine pentafluoride	19.17	3.5	2.18

Data source: [101]

Chlorine trifluoride is known to have a planar T-configuration with the central Cl—F bond shorter than the other two by $0.1 \text{ \AA}$ and angles F—Cl—F of about 87° and the small dipole moment agrees with that structure.

2.2.2.13 Magnetic Properties of Chlorine Trifluoride

Chlorine trifluoride and several of the other halogen fluorides examined were all diamagnetic. The specific magnetic susceptibility of chlorine trifluoride was -0.287×10^{-6} c.g.s. units and the molar susceptibility was -26.5×10^{-6} c.g.s. units [102].

2.2.2.14 Molecular Structure of Chlorine Trifluoride

The molecular structure of ClF_3 is planar, in which the three fluorine atoms are grouped asymmetrically around the central atom (Figure 18). It is a curious fact that the dipole moment of 0.554 D found for chlorine trifluoride is less than the moment of 0.881 D found for chlorine monofluoride. It is not clear whether this can be attributed to a fluorine to chlorine electron transfer or if it should be interpreted as a cancellation of the Cl—F₁ moment by chlorine lone electron pair hybrids.

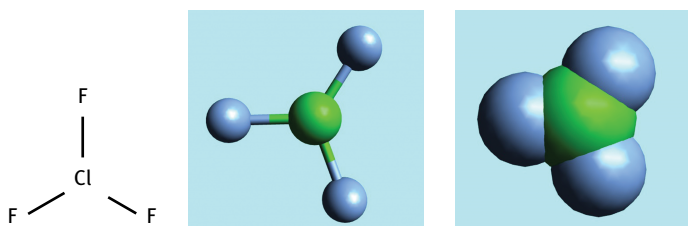


Figure 18: Molecular structure of chlorine trifluoride

The chlorine trifluoride molecule is planar with the point group symmetry mm . The crystal structure of frozen ClF_3 is orthorhombic with the following cell constants: $a = 8.826 \pm 0.01 \text{ \AA}$, $b = 6.09 \pm 0.01 \text{ \AA}$, $c = 4.52 \pm 0.01 \text{ \AA}$. X-ray diffraction (XRD) of frozen ClF_3 at 153 K (-120°C) showed that there is one short Cl—F bond ($1.621 \text{ \AA}$) and two long Cl—F bonds ($1.716 \text{ \AA}$), and the F—Cl—F angle was $86^\circ 59'$ [103]. Similar results were obtained by microwave measurements: the one short Cl—F bond was $1.598 \text{ \AA}$, the two long Cl—F bonds were $1.698 \text{ \AA}$, and the $\angle\text{FCIF}$ angle was $87^\circ 29'$, [90]. A number of transitions have been identified, and from these the moments of inertia and quadrupole coupling coefficients of both $^{35}\text{ClF}_3$ and $^{37}\text{ClF}_3$ were obtained.

Molecular orbital (MO)-Linear Combination of Atomic Orbitals (LCAO)-self-consistent field (SCF) calculations of ClF_3 showed that the T-shaped nuclear configuration can be satisfactorily explained without the use of chlorine 3d orbitals. The calculated charge distribution was found to be similar to that postulated by the Gillespie and Nyholm model but with excess electronic charge on the fluorine atoms [104, 105].

Extended basis set calculations using the CPF method for ClF and ClF_3 were done to clarify discrepancies between experiment and previous computations [106]. Good agreement was found for ClF, but agreement was slightly poorer for ClF_3 , as only the 2dlf basis could be used: $r_{\text{eq}} = 160.7 \text{ pm}$, $r_{\text{ax}} = 171 \text{ pm}$, $\angle\text{FCIF} = 87.1^\circ$. The computation of $\Delta E(\text{ClF}_3 \rightleftharpoons \text{ClF} + \text{F}_2)$ turned out to be difficult: $\Delta E = 59.3 \text{ kJ/mol}$ on the 2dlf level. Various extensions of the basis set led to improvements of a few kJ/mol; the estimate for the 3d2flg basis became $\Delta E \approx 80 \text{ kJ/mol}$. The remaining discrepancy between theory and experiment is attributed to incomplete error cancellation within CPF arising from the very different binding in ClF_3 (three-center-four-electron bonding) compared with ClF and F_2 .

Chlorine trifluoride has a tendency to form dimers. It is believed that the dimer is produced by the formation of bridges from the fluorine atoms between two molecules, the electron pairs from the fluorine atoms occupying 3d orbitals of the chlorine atoms. This configuration can be considered to be derived from the octahedral system, with two electron pairs occupying two axial positions; the dimer therefore has a planar structure. Because of the increased stability of such a configuration, ClF_3 tends to form dimers.

Molecular dynamics computational simulations of liquid ClF_3 at three average temperatures, 217, 260, and 287 K, were conducted in order to explain the temperature variations of its properties in the liquid state [107]. Gas-phase microwave and solid-state XRD studies had already shown that the ClF_3 molecule has a planar distorted “T” structure of C_{2v} symmetry, with the bond lengths and angles $r_{24} = r_{34} = 1.698 \text{ \AA}$, $r_{14} = 1.598 \text{ \AA}$, $r_{45} = 0.36 \text{ \AA}$, and $\angle 142 = \angle 143 = 87^\circ 28'$. On the basis of the results from laser Raman spectroscopic study of ClF_3 , Drifford et al. suggested the presence of dimers in the liquid state. Evidence for dimers existing in the liquid state has also come from the IR spectra of ClF_3 in an argon matrix ([87]). The dimer geometric configuration drawn based on the calculated contact distances was found to be in good agreement

with the results of matrix isolation IR and laser Raman spectroscopic studies. See also [108–110]. The main reason for studying the molecular structure of ClF_3 is to understand the electronic nature of Cl–F bonds and to plan for the synthesis of more highly fluorinated chlorine fluorides such as ClF_5 or ClF_7 .

2.2.3 Chemical Properties of Chlorine Trifluoride

2.2.3.1 Purity Requirements for Chlorine Trifluoride

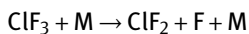
Chlorine trifluoride that was procured by the US Government for nuclear fuel processing or as a rocket propellant had to meet the purity requirements of MIL-P-81399 – Propellant, Chlorine Trifluoride, which required a ClF_3 assay of 99 mass-% minimum, a maximum HF content of <0.4 mass-%, a maximum limit of the sum of $(\text{ClO}_2\text{F} + \text{ClO}_2) < 0.2\%$, and a maximum limit of the sum of $(\text{ClF} + \text{Cl}_2 + \text{F}_2) < 0.4\%$. This specification is no longer maintained.

2.2.3.2 Decomposition of Chlorine Trifluoride

When discussing the decomposition of ClF_3 , one must keep in mind that under certain conditions ClF_3 is associated with a dimer. The dimer would have to dissociate before the monomer starts decomposing. The reversal of the formation kinetics is dependent on the decomposition kinetics of ClF_3 and ClF_5 [38]. The thermal dissociation of ClF_3 behind incident shock waves has been studied in the temperature range 800–1300 K [111]. The course of the dissociation was followed by means of UV absorption spectroscopy centered at 2200 Å. Initial slope measurements gave a value of

$$k_1 = 10^{13.5 \pm 0.4} \exp(28200 \pm 1700)/RT \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for the rate constant of the reaction



where M is a third body or the wall. The collision efficiency of ClF relative to argon was found to be 35 ± 5 to 1. Evidence was presented that favors a heat of formation for ClF_2 of $-19 \pm 2 \text{ kcal/mol}$ at 0 K.

2.2.3.3 Photolysis of Chlorine Trifluoride

Photolysis of chlorine trifluoride, in particular in the presence of excess fluorine, would be a promising first step in the synthesis of higher fluorides such as ClF_5 and ClF_7 .

The dynamics of the 248-nm excimer-laser-induced photodissociation of ClF_3 have been investigated by observation of the Cl atoms by time-resolved laser magnetic resonance [112]. In the presence of Cl_2 , photolytically produced F atoms interacted with Cl_2 to produce Cl atoms. The quantum yields for F and Cl atom formation were 1.85 ± 0.25 and < 0.02 respectively. By examination of the electronic configuration of

the excited state of ClF_3 , the primary photodissociation products are predicted to be $\cdot\text{ClF}_2$ and $\cdot\text{F}$.

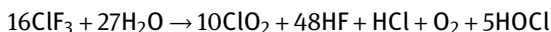
The chemical kinetics of the UV photochemical formation and destruction of ClF_3 were investigated experimentally to obtain information relating to optimal conditions for the formation of ClF_3 and the reaction mechanisms involved [58, 59]. The photolysis of ClF_3 was also investigated because it limits the yield of ClF_3 and ClF_5 production by photochemical methods.

2.2.3.4 Radiolysis of Chlorine Trifluoride

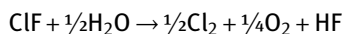
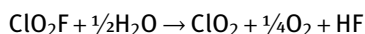
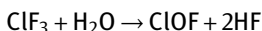
Chlorine trifluoride used to reprocess nuclear reactor fuel rods that are still highly radioactive is potentially subjected to radiolysis by the nuclear radiation. It was explained that thermal decomposition of ClF_3 under the conditions of fuel rod reprocessing would be dominant over radiolytic decomposition [113].

2.2.3.5 Reactions of Chlorine Trifluoride with Inorganic Compounds

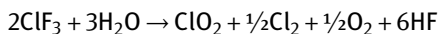
The most probable inorganic compound for chlorine trifluoride to react with is moisture from atmospheric air or water squirted by a HazMat response team on a chlorine trifluoride leak. The reaction of ClF_3 or ClF with H_2O is highly exothermic and can lead to ignition of flammable materials in the vicinity of where the reaction takes place [114–117]. The overall reaction can be expressed by



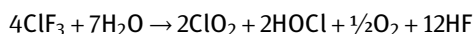
The partial hydrolysis of chlorine trifluoride most likely take place via intermediate formation of chlorosyl fluoride, ClOF [118]. Another of the intermediate reaction products was perchloryl fluoride ClO_2F , which subsequently also hydrolyzed with additional water. Other reaction steps leading to intermediate products are:



Adding these reactions together yields the overall reaction under conditions of excess ClF_3 :



The heat of reaction was calculated to be 243.2 kJ/mol. Under conditions of excess water, the reaction would be

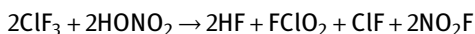


and the heat of reaction for excess H_2O would be 228.0 kJ/mol.

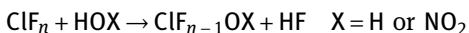
Although some metals such as magnesium, aluminum, and copper form a protective fluoride film that can halt further action, at elevated temperatures these metals combine explosively with chlorine trifluoride.

An investigation of the kinetic rates of four gas-phase reactions involving chlorine monofluoride and chlorine trifluoride showed that radioactive chlorine does not exchange at a measurable rate between Cl_2 and ClF_3 in the liquid phase at 193 K (-80°C) or in the gas phase up to 438 K (165°C) [119]. The reaction of Cl_2 with ClF_3 to form ClF appeared to be essentially homogeneous in the gas phase and proceeded at a conveniently measurable rate in the temperature range 453–523 K (180 – 250°C). It followed a second-order rate expression within experimental error with activation energy of 84.4 kJ/mol (20.18 kcal/mol) and activation entropy of 12.3 e.u. The exchange of radioactive chlorine between ClF_3 and tagged ClF has been followed in the temperature range 476–518 K (203 – 245°C). The exchange appeared to be homogeneous with a rate proportional to the product of the square roots of the reactant concentrations and an activation energy of 66.5 ± 4 kJ/mol (15.9 ± 1.0 kcal/mol).

The reaction of excess ClF_3 with HONO_2 is different from what one might expect. FCIO_2 and ClF were the observed products and not ClFO (which is unstable):



The reactions of ClF , ClF_3 , ClF_5 , and ClO_2F with a monofunctional hydroxyl compound ($\text{HO}-\text{NO}_2$) and a bifunctional hydroxyl compound ($\text{H}-\text{O}-\text{H}$) were studied in systematic series of experiments in an effort to find commonalties and differences between the various reactant pairs [120]. The first step of reactions of chlorine fluorides with a hydroxyl compound is usually the abstraction of HF :



The nature of reaction products depended on which reactant was used in excess. The reactions of chlorine fluorides with HNO_3 are of interest because they might form new solid oxidizers. The reactions with water inevitably occur with atmospheric moisture or they are evaluated as a method for disposal of excess halogen fluorides or as scrubber fluids when venting pressurant gas from pressurized tanks after a test. The reaction products are listed in Table 25. All reactions were very violent and sometimes had to be chilled by dipping the reaction vessel (a U-tube cold trap) into a bath of liquid nitrogen. The partial hydrolysis of chlorine fluorides does not offer a synthetic route toward chlorine oxyfluorides, except for ClO_2F .

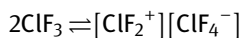
Table 25: Reactions of chlorine fluorides with hydroxyl compounds.

Halide	Hydroxyl compound	
	Nitric acid	Water
ClF	With an excess of ClF, reaction products were ClONO ₂ and HF	With excess water, products were Cl ₂ :ClO ₂ :O ₂ in a mol ratio 2:1:0.25, HF, and some Cl ₂ O
ClF ₃	With an excess of ClF ₃ , reaction products were NO ₂ F, ClO ₂ F, ClF, and HF. With an excess of HNO ₃ , products were ClO ₂ (1.7 mmol), ClONO ₂ (1.7 mmol), HF, N ₂ O ₅ , and O ₂	
ClF ₅	Excess ClF ₅ with HONO ₂ : two layers formed. Products were ClO ₂ F (1.66 mmol), unreacted ClF ₅ (2.4 mmol), NO ₂ F (3.3 mmol), and HF. ClF ₅ with excess HONO ₂ : The reaction products consisted of O ₂ (0.42 mmol), ClO ₂ F (0.55 mmol), ClONO ₂ (0.29 mmol), ClO ₂ (0.36 mmol), N ₂ O ₅ , and HF	Reaction of ClF ₅ with excess HOH: The products consisted of ClO ₂ (1.35 mmol), ClO ₂ F (0.35 mmol), ClO ₃ F (0.18 mmol), O ₂ (<0.5 mmol), and HF
ClO ₂ F	Reaction of ClO ₂ F with excess HONO ₂ : The reaction products were O ₂ (0.25 mmol), ClO ₂ (0.48 mmol), unreacted ClO ₂ F (1.86 mmol), N ₂ O ₅ , unreacted HONO ₂ , and HF	

Data source: [120]

Tetrafluorochloronium(III) and Difluorochlorate(III) Complexes from Reactions of Chlorine(III) Trifluoride with Inorganic Compounds

In parallel with efforts to develop ClF₃ and ClF₅ as oxidizers in liquid rocket propellant combinations, a significant effort has been made to synthesize solid compounds derived from ClF₃ or ClF₅ that could potentially be used as oxidizers in solid rocket propellants or as solid sources of gaseous fluorine in a gas generator formulation. Starting with the known observation that ClF₃ undergoes homolysis (similar to bromine trifluoride)



and knowing that it is an electrolyte [121], it has been observed that electrical conductivity increases substantially when adding Lewis acids such as BF₃, AsF₃, or SbF₅. There is a long series of reports describing the progress in this pioneering work on halogen fluoride chemistry, also including nitrosonium and nitronium salts and salts of the new tetrafluoroammonium cation [NF₄]⁺. The driving force behind this effort spanning more than three decades was the desire to develop a high-energy replacement for ammonium perchlorate as an oxidizer in solid propellants. Some of this series of investigations started at Stauffer Chemical in Richland, CA, and was later continued at Rocketdyne in Canoga Park, CA. The following references give a summary of reports on this effort, but not all this wealth of fluorine chemistry material could be absorbed

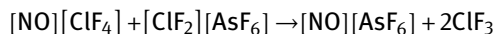
into this book [86, 122–155]. It would require a book of its own to extract from these reports the many different synthetic methods used and the properties of the many new compounds synthesized. Whatever was reported in quarterly progress reports sometimes was superseded in final reports. Quarterly reports contain only preliminary information that may later be superseded and updated in subsequent quarterly or final reports. Sometimes, the Defense Technical Information Center (DTIC) website had only the quarterly reports listed and the bibliographic information on the associated final report could not be found. In those cases we have included quarterly and interim reports in our summary bibliography. In many cases an abstract was not available so one can only guess that the work was on high-energy oxidizers derived from ClF_3 , ClF_5 , and other fluorine compounds, including noble gas fluorides and noble gas oxyfluorides and dioxygenyl salts. Each of these reports deals with at least ten different topics and it would be difficult to separate them and discuss each topic in detail. In some cases the author was not listed and the table shows the author only as “Anonymous.” The list of references above may serve as a starting point for those who intend to follow up on this development of high-energy oxidizers. The continued effort at Rocketdyne in Canoga Park, CA, resulted in the synthesis of many new additional fluoronium and fluorometallate complex salts as candidates for high-energy solid propellant oxidizers. The results were reported both as contractor reports to the sponsoring agency and some of the work was also published in the open periodical literature. In those cases, preprints of the publications were attached as appendices to the annual reports. It would fill an entire book if we tried to summarize all the work that was done on complex fluoride salts. One of the reactions of K_2MnF_6 with SbF_5 led to the first chemical (not electrochemical) synthesis of elementary fluorine, a remarkable discovery that coincided with the centennial of the first discovery of difluorine by Moissan in 1886 [156].

The chemistry of ionic fluoro complexes with chlorine, nitrogen, or oxygen as the central atom of one ion and boron, aluminum, phosphorus, arsenic, or antimony in the other ion is (literally) very complex, and it would be very difficult to give a complete overview here about which salts were synthesized, what their properties are and if they can be used as rocket propellants. We leave this task to other, more qualified chemists. What is needed for an investigator starting to work in this area is a comprehensive survey of the thermal stability of these sometimes very labile salts. Some salts were only stable at low temperatures and only just long enough to have their IR and XRD spectra taken.

Difluorochlorinium Salts

Pure ClF_3 at $273\text{ K} = 0^\circ\text{C}$ has a very low specific conductance of $3 \times 10^{-9}\ \Omega^{-1}\text{ cm}^{-1}$, much lower than that of BrF_3 . If one adds SbF_5 to ClF_3 , making a 0.564-molar solution of $[\text{ClF}_2^+][\text{SbF}_6^-]$, the specific conductance increases to $6.65 \times 10^{-3}\ \Omega^{-1}\text{ cm}^{-1}$. Vapor pressure measurements also indicate compound formation of the type $[\text{ClF}_2^+][\text{AsF}_6^-]$ and

$[\text{ClF}_2^+][\text{BF}_4^-]$. One can even perform “neutralization” reactions with cationic and anionic ClF_3 salts in ClF_3 as the solvent:



If one measures electrical conductivity as a function of reagent addition, the stoichiometric ratio coincides with a sharp minimum of electrical conductivity [157, 158]. Other fluoronium compounds synthesized are $[\text{ClF}_2]_2[\text{SnF}_6]$ and $[\text{ClF}_2]_2[\text{TiF}_6]$. The following fluoronium salts $[\text{ClF}_2][\text{SbF}_6]$, $[\text{ClF}_2][\text{AsF}_6]$, KIF_6 , SbBrF_8 , and AsBrF_8 were patented as oxidizers for rocket propellants [159], but it may be difficult to find a binder that does not prematurely react with these compounds.

^{19}F NMR spectra were measured for HF solutions of ClF_6^+ , ClF_4^+ , ClF_2^+ , ClO_2F_2^+ , and ClF_2O^+ and for NF_2O^+ salts in comparison to chemical shifts for ClF and ClF_3 in order to compare the structures of these cations [160]. Several exchange processes between the cations and anions and the solvent were observed, depending on the temperature and the acidity of the solvent. The acidity of the HF solvent was varied by the addition of AsF_5 . It was shown that ClF_6^+ is octahedral and splitting owing to both $^{35}\text{Cl}-\text{F}$ and $^{37}\text{Cl}-\text{F}$ spin-spin coupling has been observed for the first time.

Solid AsF_5 complexes with various chlorine fluorides were the suspect contaminants that deposited and clogged pipes in a UF_6 isotope separation plant [161]. Their dissociation pressures were measured and methods for removal were tested. See also [162–167].

Tetrafluorochlorate(III) Salts

Tetrafluorochlorate(III) anions form stable salts with Lewis bases [168–170]. See also [171].

A tetramethylammonium salt of the tetrafluorochlorate(III) anion was prepared by metathetical reaction of $[\text{N}(\text{CH}_3)_4]\text{F}$ with CsClF_4 in acetonitrile as the solvent [172]. This salt is thermally stable up to 373 K and, most surprisingly, is not shock sensitive.

Another potential oxidizer is nitrosonium tetrafluorochlorate $\text{NO}^+ \text{ClF}_4^-$ [173]. It can be prepared by reaction of nitrosyl fluoride and chlorine trifluoride at temperatures below 273 K. The compound is a white, crystalline solid and a powerful oxidizer. It ignites hypergolically with many organic fuels. The enthalpy of formation was estimated as $\Delta H_f^{298} = -287 \text{ kJ/mol}$ (-68.6 kcal/mol). Attempts to prepare nitronium tetrafluorochlorate were unsuccessful.

Hexafluorochlorate(V) Salts

Although hexafluorochlorate(V) salts initially could not be obtained in bulk, Raman spectra and ^{18}F isotope exchanges supported the existence of the hexafluorochlorate(V) anion ClF_6^- [174].

The increasing order of oxidizing power from anion to neutral molecule to cation can be used for the synthesis of superoxidizers. This approach is based on the prepa-

ration of high oxidation state transition metal fluoride anions by high-pressure/high-temperature fluorination reactions with elemental fluorine and their conversion into superoxidizing cations by adding strong Lewis acids in anhydrous HF solution, for example, the synthesis of ClF_6^+ and BrF_6^+ from NiF_3^+ [175].

Reactions of Chlorine Trifluoride with Organic Compounds

Chlorine trifluoride is a very strong oxidizer. Organic compounds, even graphite and wood charcoal, react vigorously with chlorine trifluoride and burst into flames. Some of these reactions approach explosive violence. Most organic hydrogen-containing compounds, predominantly all hydrocarbons, will ignite spontaneously with ClF_3 , as will all the hydronitrogens such as ammonia or hydrazine. That makes it of interest as a hypergolic start fluid for bipropellant rocket engines and solid propellant motors. The combustion reactions of chlorine trifluoride with hydrocarbons and other rocket fuels will be discussed in the future *Encyclopedia of Hypergolic Bipropellant Combinations*.

Chlorine trifluoride is thermally stable at room temperature and does not decompose during storage. The main long-term storage problem is contamination by metal fluorides leached from the container walls. Only above 573 K (300 °C) will ClF_3 begin to decompose into chlorine monofluoride and fluorine; above 873 K (600 °C) the decomposition is nearly complete.

2.2.3.6 Analysis of Chlorine Trifluoride

Formerly, when wet chemistry dominated the quality control laboratory, the assay of gaseous ClF_3 was analyzed by reacting a nitrogen-diluted gas sample with potassium iodide solution and titrating the liberated iodine with sodium thiosulfate. However, free chlorine or fluorine present as contaminants in ClF_3 would cause an erroneously high ClF_3 assay. The chlorine interference can be avoided by first reacting the gas with an excess of dry, pulverized sodium chloride, pumping off the residual gas, and then titrating an aliquot of a solution of the salt [176]. In this method, ClF_3 vapor is passed through a known weight of dry sodium chloride, contained in a copper tube. Sodium fluoride is produced and the free chlorine that is liberated is absorbed in sodium hydroxide solution. After decomposition of the sample, chlorine and fluorine are determined in the sodium chloride/fluoride mixture and in the sodium hydroxide solution. From the known weight of sodium chloride used, the chloride contributed by the sample can be calculated. The chloride can be determined by Mohr's volumetric titration method and the fluoride can be titrated with thorium nitrate using alizarin red as indicator.

To avoid wet chemical methods, the analyst will prefer a quick gas chromatographic analysis of chlorine fluorides that can be readily separated from another and from accompanying contaminants, even in the presence of strongly corrosive agents such as HF [177–181]. The methods discussed here for ClF_3 can be equally as well used

for other volatile fluorides, such as ClF_5 , OF_2 , NF_3 , N_2F_4 , and ClO_3F . The column packing used for the gas chromatography (GC) analysis of non-metallic fluorides was Kel-F[®]-oil on Kel-F[®] powder. The GC columns, fittings, and detectors were made mostly of nickel and nickel alloys. Flame ionization detectors are not as suitable for fluorine compounds as they are for chlorine compounds (insecticides), such that thermal conductivity detectors or gas density balances are preferred for this type of work, although the hot filaments may not last very long when exposed to the corrosive gases [182–188]. Gas density bridges are suitable for the analysis of corrosive gases by GC because the hot filament does not come in contact with the sample gas.

The GC determination of trace gaseous impurities in highly reactive fluorine compounds such as ClF_3 presents unique requirements for both equipment and techniques. Analyzing trace gases at the low ppm level requires special equipment such as a custom-designed system with backflush column-switching techniques to protect the columns and detectors. A thermal conductivity detector with nickel filaments was used to determine ppm levels of impurities in ClF_3 [189].

Nuclear magnetic resonance (NMR) is useful for identifying the structures of halogen fluorides, analysis of the mixture ratios in binary mixtures of fluorides, and determination of unwanted impurities (see Furnish [190], Muettterties and Phillips [94], and Williams [191]).

The now obsolete Military Specification MIL-P-81399A recommended a near-IR spectrophotometric method for analysis of HF in ClF_3 . Other volatile contaminants (ClO_2F , ClO_2 , ClF , Cl_2 , F_2) can be determined by gas chromatography.

When attempting to analyze ClF_3 by mass spectrometry, reactive species often react prematurely in the inlet to a mass spectrometer before a clean mass spectrum can be obtained. Cooling the mass spectrometer inlet will allow the sample to enter the ionization chamber unadulterated. Mass spectra of ClF_3 and several other reactive fluorides were obtained using this method [45]. Operating at low temperatures will also allow one to examine the sample for dimer association in the vapor phase.

The ionization of ClF_3 under electron impact leads to the formation of the following ions, at the indicated appearance potentials (eV): ClF_3^+ : 13.0 ± 0.2 ; ClF_2^+ : 12.8 ± 0.3 ; ClF^+ : 12.7 ± 0.3 eV [192]. The ionization potential of ClF_3 , obtained in earlier work, 13.0 ± 0.2 eV, was close to the value of the vertical ionization potential, 12.88 ± 0.01 eV, obtained from photoelectron spectroscopic studies.

Detection of Chlorine Trifluoride in the Air

Chlorine trifluoride and other non-metal fluorides under evaluation as rocket or chemical laser propellants can be detected in trace amounts in the air of working areas to assure the safety of the working personnel and provide warning in case of a leak.

Dosimeter badges and portable detection devices capable of measuring ppm levels of ClF_3 , ClF_5 , NF_3 , N_2F_4 , or OF_2 are needed in work areas where these gases are used. Despite the great energy of reaction released when these compounds act as oxi-

dizers in rocket engines, they are kinetically somewhat inert at room temperature ppm dilutions. Most of the fluoride oxidizers react with Br^- or I^- salts yielding F^- , which can be detected with fluoride-specific reactions. A dosimeter could be constructed by using either the lanthanum-alizarin fluorine blue color reaction or a F^- ion-specific electrode. More expensive techniques for developing a portable detector would be an electron-capture gas chromatograph or a pulsed-leak quadrupole mass spectrometer [193].

Sub-ppm concentrations of ClF_3 in a 1-mL air sample introduced directly into a gas chromatograph without requiring time-consuming concentration procedures could be detected rapidly with an electron capture detector [194]. A linear response was obtained in the range of 0.05 to 1.0 ppm by volume and detectability of less than 0.01 ppm was indicated. A 10-ft $\times$ 1/4-in stainless steel column filled with 5% DC-200 on 60/80 Chromosorb G mesh was used at room temperature. The carrier gas was 95% argon/5% methane at a flow rate of 200 mL/min. An electron capture detector was operated at 50 V RF without purge gas.

2.2.4 Handling of Chlorine Trifluoride

Liquid ClF_3 is considered more reactive than vapor-phase F_2 in all kinds of chemical reactions, as more mols of fluorinating agent are present per unit area of reactant surfaces if liquid ClF_3 is spilled on it. Also, liquid ClF_3 may demonstrate even higher reactivity in certain circumstances than liquid fluorine, as the F_2 liquid temperature is cryogenic, thus reducing its activity potential. See also [195–197].

2.2.4.1 Materials of Construction for Chlorine Trifluoride

Metals. Although chlorine trifluoride is very reactive, many metals with a smooth surface will form a protective fluoride film and become passivated against further attack by dry ClF_3 . Metal powders or samples with a large surface area can autoignite spontaneously in ClF_3 . Similar to the passivation in elemental fluorine, metals such as copper, nickel, bronze, Monel, or stainless steel form a passivating layer of metal fluorides. If the metal parts are subjected to bending or vibration, and the passivation layer flakes off, the same precautions as already discussed with elemental fluorine apply here when in contact with chlorine trifluoride (gaseous or liquid).

In most cases, Monel[®] and nickel would be the preferred materials of construction. Aluminum, copper, magnesium, titanium, niobium (=columbium), and molybdenum and their alloys and several stainless steels have been investigated with regard to their resistance against chlorine trifluoride and perchloryl fluoride [198]. A few aluminum, copper, magnesium alloys, and stainless steel with low carbon content were found to be suitable for ClF_3 service, but only for temperatures up to 303 K (30 °C). In all cases, freshly machined metal surfaces have to be slowly passivated with gaseous ClF_3 before they are placed into service at full pressure. Typical alloys of Al, Cu, Mg,

Ni, low-carbon steel, and stainless steel were resistant to ClF_3 or ClO_3F and their mixtures at 303 K, and even under severe mechanical shock [199]. The metals must be clean and dry, but no special passivation was required. An HNO_3/HF pickling acid cleaning step was recommended for stainless steels and high-Ni alloys. Ti, Nb, Mo, and graphite were rapidly attacked by ClF_3 . Measurements of compatibility and corrosion rates of nine welded alloys of aluminum, nickel, and stainless steel, stressed and unstressed, in ClF_3 , ClO_3F , and 25% $\text{ClO}_3\text{F}/75\% \text{ClF}_3$ at 303 and 339 K (30 and 66 °C) were investigated and showed that corrosion rates at 303 K (30 °C) were all less than 0.1 mil/year (1 mil = 1/1000 in); [200]. At 339 K (66 °C), corrosion in ClF_3 and ClO_3F was less than 0.1 mil/year except for CRES-410 where it was 1–2.2 mil/year. In ClO_3F at 339 K (66 °C) corrosion was normally below 0.5 mil/year, but with moisture present, rates up to 8.3 mil/year were observed. A Teflon orifice in a flow test fixture was attacked by ClF_3 . Liquid impingement jets of ClF_3 and ClO_3F at 30 m/s (100 ft/s) had no effect on these metals, except for a slight pit in aluminum 2014-T6 with ClF_3 . Liquid cavitation of ClF_3 and ClO_3F in an aluminum tube caused no metal change.

The kinetic rates for reaction of ClF_3 with copper were of the same order of magnitude as those observed with elemental fluorine [201]. At atmospheric pressure the coating consisted of copper(II) fluoride and copper(I) chloride.

Chlorine trifluoride by itself or ClF_3/F_2 mixtures can be used for passivating metal surfaces prior to use with either fluorine or chlorine trifluoride, but contamination by organics must be avoided [202, 203].

Titanium, niobium (=columbium), molybdenum, or graphite were strongly attacked by ClF_3 . For the evaluation of candidate materials of construction it is essential to test the compatibility, not only with stagnant but also with flowing ClF_3 . At Reaction Motors, several different metals were tested for ClF_3 resistance in a closed loop with recirculating liquid ClF_3 for later use in tanks for storable missile propellants [204]. Monel, nickel, 300-series stainless steel, brass, and copper were suitable materials of construction even under these operating conditions. Aerosols of suspended particles of boron, boron carbide, and most metal powders suspended and fluidized in a stream of nitrogen, that were candidates for an air/metal or Mars atmosphere (CO_2)/metal ramjet, ignited and burned in chlorine trifluoride [205, 206]. The only exception that failed to ignite was a 200-mesh nickel powder.

For additional information on materials compatibility with chlorine trifluoride, consult [207, 208].

Failures in the weld areas of nickel-plated steel pipe carrying chlorine trifluoride prompted an investigation to determine the effect of weld composition on corrosion by ClF_3 [209]. Monel/steel and nickel/steel alloys of composition to simulate weld overlays were tested to determine their corrosion rates in ClF_3 at 200 °F and 300 °F. For both nickel/steel and Monel/steel, the corrosion rate was higher at the higher temperature. For nickel/steel alloys at compositions up to 50% Fe, which would cover a range considered normal for welding, the corrosion rate would be within acceptable limits.

For Monel/steel alloys, compositions up to 35% Fe had an acceptable corrosion rate. Above this, the corrosion would be greater than a tolerable amount.

A survey of pre-treatment methods for metal surfaces that are to come into contact with ClF_3 and other storable propellants suggested that for most other oxidizers special pre-treatments are not necessary as long as the surfaces are free of contaminants, but in the case of ClF_3 , OF_2 , and FLOX it may be advantageous to practice gradual exposure of metal surfaces to the fluorine compound to ensure deactivation of contaminants that may have resisted the cleaning process [210]. A general procedure for metal systems to be used with ClF_3 , OF_2 , or FLOX proceeds with the following steps: descale, degrease, dry, and control gradual fluorination. The thickness and adherence of fluoride films determines corrosion rates during storage.

Non-metals. Chlorine trifluoride is so reactive that even quartz wool or glass wool can burn in it with a bright flame. Perfluorinated polymers such as polytetrafluoroethylene (PTFE) or poly chlorotrifluoroethylene are compatible with stagnant gaseous or liquid ClF_3 at room temperature, but some precautions against their use in flowing ClF_3 are appropriate. Once ignited, even perfluorinated polymers can burn in ClF_3 with a vigorous flame reaction. Gaskets on flanges or valves can be made from soft copper, aluminum 2S, lead, or PTFE with calcium fluoride as the filler material. Metal-coated polymers, including Teflon[®] and Viton[®], were tested as materials for O-rings and propellant expulsion bladders in propellant tanks in pressure-fed systems [211, 212]. Same as with fluorine systems, it is difficult to find lubricants that are truly compatible with ClF_3 . One of the lubricants tested was Permatex[®] No.2. As a precaution, the first two turns on the inside of a threaded connection should not be lubricated at all.

Of all the perfluorinated greases that were tested for their suitability for use with ClF_3 , only very few were found to be resistant and some ignited.

Poly(tetrafluoroethylene) and poly(chlorotrifluoroethylene) can be used with ClF_3 or ClO_3F and their mixtures at up to 303 K but mechanical shock must be avoided [199]. Both plastics absorb moderate amounts of the oxidizers and can undergo structural changes and embrittlement. These plastics are best used only in the vapor phase with these gases. They should never be used with these oxidizers under heat, shock, or fast flow conditions.

O-ring seals of selected elastomeric and compliant materials were evaluated for resistance to ClF_3 in a simulated end-use test at 296 K (73 °F) [213]. The candidate elastomers were placed under compression in closed cells and exposed to the liquid and vapor of liquid ClF_3 for extended periods of time. Rate of propellant loss through the seal and the change in physical properties of the seal materials were determined.

2.2.4.2 Components for Chlorine Trifluoride Systems

Quick disconnect couplings were developed for use with fluorine and fluorine-containing oxidizers for a typical upper stage (e.g., NOMAD) oxidizer fill-and-drain application [214, 215].

2.2.5 Handling of Chlorine Trifluoride

When preparing a listing of the relative hazards of rocket propellants, ClF_3 was ranked as the most dangerous storable rocket propellant oxidizer [216, 217].

Recommendations for the safe handling of chlorine trifluoride are given in [218–221]. There are several books that summarize recommendations for the safe storage and handling of reactive materials and some include chapters on ClF_3 , for instance, [222].

One of the very best presentations on the hazards of handling ClF_3 was made by representatives of Air Products at the CCPS 2003 Symposium [62]. It is richly illustrated with dramatic images showing the effect of gaseous or liquid ClF_3 on various materials of construction, protective clothing, and flesh (using a dead chicken as a surrogate for human flesh).

It is especially important that all components that come into contact with ClF_3 are thoroughly cleaned prior to use in order to remove grease, dust, stains, oil, or other dirt. Even the smallest contamination can trigger a reaction with ClF_3 that then makes a rapid transition to the bordering metals. New components, such as valves or rotameters, may have to be disassembled before use so that all nooks and crannies can be thoroughly cleaned and degreased. After the system is fully assembled and leak-checked, the slow and controlled passivation can proceed similar to the stepwise method already described in *Encyclopedia of Oxidizers* in the chapter “Fluorine.” The system is first filled with dry nitrogen, and the nitrogen is gradually replaced with chlorine trifluoride, with 1-h hold periods allowed between each successive increase in ClF_3 concentration. Once the desired concentration and full operating pressure is achieved, the system should be left idle under this condition for an hour and after that time the gas can be vented to a scrubber.

If liquid ClF_3 has to be transferred from one tank to another, dry nitrogen gas can be used as the pressurant gas. Storage areas for large ClF_3 tanks must meet certain setback requirements from populated and inhabited areas. When selecting the location for ClF_3 tank farms, the prevailing wind direction needs to be taken into consideration. Storage buildings must be constructed from non-combustible materials and wood, tar paper, and combustible plastics must be avoided.

Potential by-products of hydrolysis of ClF_3 include chlorine oxyfluorides and explosive chlorine oxides [223]. Traces of these contaminants can be found in ClF_3 that was not kept in carefully dried containers and came into contact with atmospheric moisture.

It is very difficult to neutralize a pool of spilled ClF_3 because it reacts with most chemicals that it comes into contact with. If the incorrect neutralization agent is used, instead of neutralizing the spill, it may burst in flames, which aggravates the situation. Damage control procedures for spills of chlorine trifluoride for shipboard firefighting equipment and protective clothing were evaluated, and methods and materials for neutralizing spilled propellants were proposed [224]. Powdered inorganic fluorides may be used as absorbents to prevent spreading of pools of liquid chlorine trifluoride and to facilitate removal of the chlorine trifluoride for disposal. None of the fluorides tested showed any tendency to form compounds with chlorine trifluoride and thus lower its vapor pressure in a closed container. Water spray, as well as finer sprays, is effective in dissipating chlorine trifluoride by controlled chemical reaction. Sodium- and potassium bicarbonate-based dry chemical powder fire extinguishants produced enough heat of reaction that their principal effect was to cause rapid vaporization of pools of chlorine trifluoride.

2.2.5.1 Gelled Chlorine Trifluoride

In an effort to reduce the leakage hazard and rate of evaporation of liquid chlorine trifluoride, a variety of gelling agents have been tested with ClF_3 . Other gelling agents proposed for non-metallic fluoride liquid oxidizers were barium hexafluoroantimonate and barium hexafluorobismuthate [225].

2.2.5.2 Personnel Protection Gear for the Handling of Chlorine Trifluoride

During the transfer of ClF_3 , the personnel in the tank farm or test site must wear protective clothing consisting of fire-proof and acid-proof garments [219, 220]. The recommended protective ensemble consists of a tightly sealed one-piece suit, a gas mask, and neoprene gloves. An oxygen respirator should be kept at the ready on stand-by.

Neoprene and Armalon (woven polytetrafluoroethylene laminated with a continuous sheet of polytetrafluoroethylenepropylene) showed promise as materials for the construction of protective coveralls for ClF_3 handling [226]. It was emphasized that these materials must be kept free of local contamination with substances easily ignited by chlorine trifluoride, such as oil and grease, since, once ignited, the uncontaminated portion may continue to burn, even in dilute chlorine trifluoride vapor. Armalon showed greater resistance to chlorine trifluoride over a wider range of concentrations than neoprene. Butyl rubber-coated cloth and vinyl-coated glass cloth were readily ignited by dilute chlorine trifluoride vapor, and they are unsuitable for protective clothing.

A rocket propellant handlers' suit for protection from chlorine trifluoride and elemental fluorine was developed and operationally tested by the US Air Force (USAF) [227]. The exposed components of this garment were made of perfluoropolymers and stainless steel. The complete suit and sample components were exposed to both

gaseous fluorine and liquid chlorine trifluoride. The suit reacted with liquid chlorine trifluoride and therefore failed to pass the operational test.

Various types of personnel protective gear, including polycarbonate face shields, latex, nitrile rubber, and leather gloves, neoprene, Tyvek[®], and Nomex[®] clean room suits, lab equipment plastics, and building materials were tested for impingement of liquid and (in a separate test) gaseous ClF_3 [62, 228]. Most of the materials ignited instantly as shown by a number of photographs in the presentation. The worst reaction was between a Tyvek polyethylene clean room suit material, that was first wetted with ClF_3 and then had contact with water. The explosive reaction of ClF_3 combined with H_2O tore the suit to pieces.

For protective clothing for the handling of chlorine trifluoride, see also Pharo [229], and Pharo and Nenno [230].

2.2.5.3 Spill Neutralization of Chlorine Trifluoride

Similar to recommended precautions in the handling of elemental fluorine, small leaks of ClF_3 can be neutralized with sodium carbonate powder from a dry powder fire extinguisher. Water helps only if it is applied in great excess. If the rate of water application is insufficient, the exothermic hydrolysis of ClF_3 can aggravate instead of remediate the severity of the situation. Water is so reactive with ClF_3 that it actually worsens the problem situation in the event of a ClF_3 leak. One example of the unique design thinking for ClF_3 equipment is that ClF_3 manufacturers did not recommend installing a water sprinkler inside test facilities for fire mitigation. Chlorine trifluoride is so water reactive that alternative means are necessary for the prevention and mitigation of fires, both internal and external to areas where ClF_3 is used. This position was supported in 1997 by a major industrial insurance company's specific recommendation to prohibit sprinklers in ClF_3 gas cabinets used for the semiconductor industry.

Chlorine oxides are also potential by-products of the hot reaction of ClF_3 with sodium bicarbonate or sodium carbonate, such as that applied with dry chemical fire extinguishers. Besides sodium bicarbonate and sodium carbonate, a large number of other chemicals were tested for neutralization of ClF_3 spills [231].

Instrumented spill tests were conducted using 60 to 800 kg of rocket propellants and the effects on test stand structures, protective clothing, and caged test animals at different distances from the event were studied.

Disposal of Surplus Chlorine Trifluoride

Chlorine trifluoride vapors that are vented from a pressurized tank can be passed through soda lime traps or caustic scrubbers or (in remote areas) flared off in a propane flare stack.

2.2.6 Toxicity of Chlorine Trifluoride

Chlorine trifluoride has been described as the most aggressive, toxic, and dangerous halogen fluoride. It is by one order of magnitude more toxic than HF.

2.2.6.1 Maximum Allowed Exposure Levels of Chlorine Trifluoride

The recommended threshold level (TLV) time-weighted average (TWA) for an 8-h work day is 0.1 ppm with a ceiling notation. In converting ClF_3 concentrations from ppm to mg/m^3 , 1 ppm (vol) is equal to $3.78 \text{ mg}/\text{m}^3$.

The Immediately Dangerous to Life and Health (IDLH) concentration for chlorine trifluoride is 20 ppm, even lower than that of fluorine, which is 25 ppm [232–235].

The 1-h LC₅₀ of chlorine trifluoride is 178 ppm in mice and 230 ppm in monkeys. If a concentration of 50 ppm ClF_3 in air is exceeded for more than 30 to 120 min, the exposure may be immediately fatal. In animal tests the toxic action is obvious after only 3 min at 100 ppm, and immediate at 500 ppm. The symptoms are suffocation, coughing, swelling of the mucous membranes in the eyes and nostrils, and permanent opacity of the cornea.

2.2.6.2 Animal Exposure Tests with Chlorine Trifluoride

Chronic exposure of different groups of test animals to 1.17 ppm, 6 h/days, 5 days/week, resulted in the first fatalities in a group of dogs after 115 days. Under the same conditions, starting with a group of 20 rats, 6 out of 20 rats passed away during a 6-month exposure test [236–239]. The toxicity of ClF_3 is caused primarily by its corrosive effects on surfaces of contact, on the skin, in the eyes, in the nasal passages, and in the lung. The damage caused by ClF_3 is in part a function of its diverse hydrolysis products, which may form in varying proportions in the atmosphere, in pulmonary gases or during decontamination procedures. In the vapor phase, ClF_3 may decompose to ClF , Cl_2 , ClOF , ClO_2F , ClO_3F , ClO_2 , and HF, depending on the availability of water. Of these, Cl_2 , HF, and ClO_2 are probably of greatest significance. Inhalation exposure of rats to 800 ppm ClF_3 for 15 min was always lethal and 13 min of contact was usually survived [240, 241]. Four-hundred ppm was usually lethal after 35 min of exposure. ClF_3 exposures resulted in severe mucosal inflammation and burning of the skin, followed by corneal ulceration. Pulmonary release of $^{14}\text{CO}_2$ from injected [^{14}C]bicarbonate was decreased after ClF_3 inhalation, as was blood pH, indicating pulmonary impairment. Of the principal hydrolysis products considered, ClO_2F decomposes too rapidly in the presence of water vapor for study. In separate tests, ClO_3F was always lethal at exposures of 5000 ppm $\times$ 15 min and 2000 ppm $\times$ 40 min with extensive methemoglobin formation, and essentially non-lethal at 2000 ppm $\times$ 25 min and 1000 ppm $\times$ 60 min. ClO_2 lethality is comparable with that of ClF_3 on a chlorine equivalent basis. ClF_3 lethality is comparable with that of HF, on a fluorine equivalent basis. See also [242].

2.2.6.3 Olfactory Threshold Chlorine Trifluoride

In real life working areas are evacuated as soon as some of the very sensitive instrumented monitors trigger an alarm or as soon as the odor of chlorine trifluoride is detected. The olfactory threshold has not been accurately pinpointed, but it is substantially below the 1 h of exposure to a hazardous concentration.

2.2.6.4 Dermal Effects of Chlorine Trifluoride

Even if working personnel wear full respiratory and eye protection, ClF_3 vapors can cause serious chemical burns on exposed, unprotected skin. The burns are similar to those caused by HF and heal only very slowly. The same first aid measures as outlined in the chapter “Fluorine” should also be taken in case of exposure to ClF_3 . The physician-in-charge of the test area must read up beforehand on the most recent recommended techniques for the treatment of HF burns.

An accident involving chlorine trifluoride occurred on 28 July 2006 in a semiconductor factory in Hsinchu (Taiwan), resulting in a large release of the highly reactive material and causing chemical burn injuries to several workers [243]. ClF_3 is used primarily as an *in situ* cleaning gas in the manufacture of semiconductor silicon-wafer devices. The health hazards of probable decomposition/hydrolysis products from ClF_3 were evaluated based on their basic physicochemical properties and occupational exposure limits. The occupational exposure assessment was further discussed to understand secondary hazards caused by HF and fluorides from the decomposition/hydrolysis products of ClF_3 .

In order to simulate the impingement of a spill of chlorine trifluoride on human skin, a piece of dead chicken (feathers removed, ready for cooking) was used as a surrogate human skin for an impingement test [62, 228]. The spilled liquid ClF_3 ignited instantly as soon as it contacted the skin of the dead chicken (Figure 19).

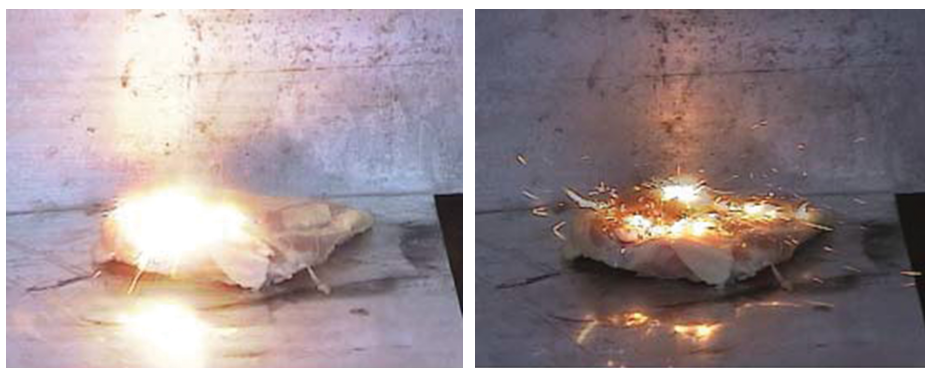


Figure 19: Impingement of liquid chlorine trifluoride on a chicken carcass (reproduced from [228] with permission from ASTM International).

2.2.7 Environmental Effects of Chlorine Trifluoride

If accidentally released into the atmosphere, chlorine trifluoride is not going to persist very long. Gradual hydrolysis will convert it to hydrogen chloride and HF, which are of course also very unpleasant environmental pollutants.

Several volatile inorganic fluorides were reviewed for their chemical, physical, and toxicological properties [244, 245]. The compounds were nitrogen trifluoride; tetrafluorohydrazine; chlorine trifluoride; bromine pentafluoride; oxygen difluoride; HF, and fluorine. Seeds and seedlings of bean, corn, pea, squash, and Sudan grass were exposed to air or water mixture of these compounds. Exposure of dry seeds to less than 500 ppm of either BrF_5 or ClF_3 in air drastically reduced their subsequent germination even when the exposure time was for less than 1 h. Exposures of plant seedlings to gaseous ClF_3 in air at 500 and 2000 ppm for 5 min resulted in extensive destruction of the plants. Plant injury was caused by irrigation of plant seedlings with solutions formed by the reaction of ClF_3 or BrF_5 with water. The exposed seeds and seedlings were analyzed for fluoride content.

Chlorine trifluoride was used in the gaseous diffusion process to fluorinate uranium yellow cake (U_3O_8) on its way to enrich ^{235}U at two plants in the US, one in Portsmouth, OH, and the other in Paducah, KY. ClF_3 was shipped to the two gaseous diffusion plants as compressed liquid in cylinders. These cylinders were stored on-site until they were emptied into large storage tanks that hold about 57 m^3 of ClF_3 liquid under its own vapor pressure. An accidental breach of a ClF_3 storage cylinder or tank would result in a release of ClF_3 vapor to the atmosphere, which is a concern for plant managers and safety engineers because of its extreme toxicity. An atmospheric dispersion model including ClF_3 chemical reactions with water vapor and thermodynamic processes in the atmosphere after an accidental release has been developed [246]. Initial model runs simulated the rapid formation of HF and ClO_2 after an atmospheric release of ClF_3 . At distances beyond the first several meters from the release point, HF and ClO_2 concentrations pose a greater threat to human health than do ClF_3 concentrations. For most of the simulations, ClF_3 concentrations rapidly fell below the IDLH requirement. For releases occurring in ambient conditions with low relative humidity and/or ambient temperature, ClF_3 concentrations exceeded the IDLH requirement by up to almost 500 m.

2.2.8 Accident History of Chlorine Trifluoride

One major incident involving ClF_3 that occurred during the liquid rocket propellant era is relatively famous (infamous) in the industry [62, 228]. In the 1960s, a US chemical company was a major supplier of ClF_3 for US governmental applications. They had an incident at one of their chemical facilities when personnel for the first time loaded a 1-ton steel container with liquid ClF_3 for bulk shipment. The container had been cooled with dry ice to perform the liquid transfer and help to make the product safer to handle, as the ClF_3 vapor pressure would be only about 0.7 kPa (0.1 psia) in the

sub-cooled state. However, the dry ice bath embrittled the steel container wall and, while maneuvering the full container onto a dolly, it split open and instantaneously released 907 kg (2000 lb) of cold ClF_3 liquid onto the building floor. The material “consumed through” (i.e., reacted with) the 30-cm (12-in) thick concrete floor and through about another 90 cm (36 in) of gravel underneath the spill. The fumes that were generated (chlorine trifluoride, HF, chlorine, hydrogen chloride, silicon tetrafluoride, etc.) severely corroded everything that was exposed. One eyewitness described the incident by stating “*The concrete was on fire!*”.

An accident involving chlorine trifluoride occurred on 28 July 2006 at a Hsinchu (Taiwan) semiconductor factory, resulting in a large release of the highly reactive material and causing chemical burns injuries to several workers [243].

2.2.9 Other (Non-rocket) Applications of Chlorine Trifluoride

The first large-scale application of ClF_3 was for military purposes. The Germans produced ClF_3 in tonnage quantities for military use during WW-II to use in flame-throwers based on the liquid’s extreme hypergolic ignition with fuels and as a general incendiary material.

Halogen fluorides have been evaluated as selective fluorinating agents for the synthesis of organic mono- and poly-fluoro-compounds [31].

Chlorine trifluoride instead of elemental fluorine can be used in the processing of uranium oxide (yellow cake) or the reprocessing of spent nuclear reactor fuel elements. The phase diagrams of ClF_3/UF_6 mixtures were therefore determined in order to be able to separate the reactants and reaction products [50, 60].

Chlorine trifluoride can be added to military shaped charges to increase the penetration power of shaped metal jets through steel plates in heavily armored tanks.

In a similar metal-cutting application, jets of hot liquid ClF_3 released at the bottom of oil wells would cut the steel casing tubing wall and/or a jammed drill rod where an extremely rapid and vigorous reaction can cleanly cut the metal in less than 1 s. The tubing or rod could then be withdrawn from the well and recovered.

Chlorine trifluoride is widely used as a non-plasma etching or cleaning gas, especially in semiconductor and microelectromechanical manufacture. Chemical vapor deposition processes require periodic cleaning of the chamber to remove the material that deposits on the walls [247]. *In situ* cleaning of the tool is desirable because the solid residues on the chamber interior are removed from the walls without dismantling the tool or risking personnel exposure to the hazardous residues or cleaning agents. *In situ* cleaning also yields quicker turn-around time for the tool to resume wafer processing. Fluorine atoms readily react with these solid residues to form volatile reaction products that can be purged and evacuated from the system. The primary advantage ClF_3 has over other gaseous fluorine cleaning sources (such as NF_3 , C_2F_6 , or CF_4) is that the high reactivity of ClF_3 allows the operation to be accomplished at relatively low temperatures, without requiring plasma or high temperature heating to disassoci-

ate it for use during the cleaning process. The use of vapor-phase ClF_3 for CVD chamber cleaning has demonstrated the ability to prolong chamber component life through the lack of high temperature or plasma use, and tool dismantling requirements. To minimize the damage to the vapor deposition equipment, the cleaning reagent must be able to react without the need for ion bombardment to create F atoms. Chlorine trifluoride is now widely used to clean semiconductor process tools *in situ*. At least chlorine trifluoride is not an ozone layer-destroying chemical like NF_3 . It would hydrolyze and be rained out before it has a chance to reach the upper atmosphere. Chlorine trifluoride that was used as an etchant and cleaning agent in the semiconductor industry has occasionally caused accidents [243].

2.3 Chlorine Pentafluoride

Chlorine pentafluoride, also known as ClF_5 , CPF, “Compound A”, “Fluoridyne,” CAS RN [13637-63-3] or [53120-06-2] is definitely the chlorine fluoride that would make the best rocket propellant oxidizer. Unfortunately, it is not as readily available as chlorine trifluoride and is more difficult to produce. At one time, it was predicted that for large-scale production, the price of ClF_5 would be not much different from that of ClF_3 or F_2 . When a German book on rocket propellants was written in 1967, chlorine pentafluoride had been discovered only a few years earlier and was still quite sensational. Very little was known about chlorine pentafluoride back in 1967. The code name for chlorine pentafluoride in those days was “Compound A.” It was sometimes only referred to under its confidential code name, Compound A, and the identity of Compound A was not revealed until many years later. Now, this section of properties is 40 pages long and there will be additional sections in future volumes of this book on rocket propellant combinations with ClF_5 as the oxidizer, which would add to this page count. There was a lot of interest in the potential use of ClF_5 as a rocket propellant and some of the early work in the US remained classified confidential for a long time. Only several decades later has some of the information become available to the general public.

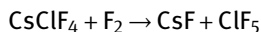
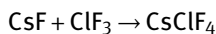
There exist several good summary reports on chlorine pentafluoride that are recommended as a starting point for further in-depth study and that have served as a source for the current book [248–252].

2.3.1 Preparation of Chlorine Pentafluoride

Chlorine pentafluoride can be prepared from fluorine and chlorine trifluoride with thermal [253, 254], ultraviolet at 101 kPa with a 2:1 excess of fluorine [255], or electrical glow discharge activation [256, 257], or by the reaction of platinum hexafluoride with chlorine trifluoride [258]:



or by fluorination of alkali metal tetrafluorochlorate salts [257]

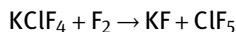
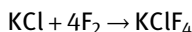


In one experiment, 76 g (0.5 mol) of dry CsF was reacted with 50 g (0.55 mol) of ClF_3 in an autoclave at 353 K (80 °C) for 4 h. After cooling, 15 L (0.67 mol) of fluorine gas was condensed into the autoclave and heated to 423 K (150 °C) for 22 h. After removal of the excess fluorine, 26 g (0.2 mol) of pure ClF_5 could be distilled out of the reactor into a cold trap. The yield was 40% of theory. With KF instead of CsF, the yield was only between 10 and 25%. The thermal, high-pressure process developed by Rocketdyne was scaled up to a pilot-plant scale and Rocketdyne was the main supplier of ClF_5 in the US while the evaluation as a rocket propellant was in full swing in the 1970s and 1980s. Rocketdyne built a pilot plant that was able to produce 12 lb/day in a continuous-flow process. There is a long series of reports covering this work [142, 259–263]. Several of these reports also include work on other oxidizers. From the titles alone, it was not clear if the work was on ClF_5 or ClO_3F , or both. There may be some overlap with information that should have been referenced in the perchloryl fluoride section but the reports were already summarized here.

Chlorine pentafluoride was synthesized by electrolysis from the $\text{HF}/\text{NaF}/\text{Cl}_2$ system [264]. Syntheses were conducted both with and without a gas electrode under various experimental conditions.

The kinetics of photochemical ClF_5 formation from ClF_3 and F_2 were examined at temperatures between 289 and 343 K (16 and 70 °C) using light with a wavelength of 365 μm [265]. The quantum yield of the reaction was always below 1. At 303 K the optimal value was 0.5 molecules of $\text{ClF}_5/h\nu$. ClF_5 formation was not by a chain reaction. Oxygen exerted a strongly inhibiting effect on this reaction.

It had been known for several decades that the reaction of fluorine with alkali metal chlorides would produce alkali metal tetrafluorochlorates, but the remaining gas phase had not been analyzed until it was found that it contained chlorine pentafluoride according to the reactions [266, 267]:



The reaction was conducted with an $\text{F}_2:\text{KCl}$ molar ratio of 5:1 at 473 K (200 °C) for 8 h and gave a yield of 65%. Molar ratios in the range from 12:1 to 3:1, temperatures in the range from 373 to 573 (100 to 300 °C), and reaction durations from 4 to 112 h were investigated but did not improve the yield. The particle size of KCl (75 or 350 μm) had no apparent effect on the yield. If one starts with KBr instead of KCl, similar reactions lead to the formation of bromine pentafluoride. More specifically, potassium chloride (0.25 mol) was placed in a 1-L stainless steel cylinder, 1.25 mol of fluorine was con-

densed at 77 K (−196 °C). When the mixture was allowed to warm to room temperature, a sudden exotherm occurred near room temperature. Then the reactor was heated to 473 K (200 °C) for 8 h. After cooling to an ambient temperature, the cylinder was attached to a vacuum line and cooled to 139 K (−134 °C). The excess fluorine was slowly bled and pumped off through a 139 K (−134 °C) trap into a 77 K (−196 °C) trap. The 139 K (−134 °C) trap and the reaction cylinder were warmed to ambient temperature and their volatile contents were transferred to a stainless steel storage cylinder. The product was identified as chlorine pentafluoride by its infrared bands at 732 and 786 cm^{-1} . No chlorine trifluoride was noted in the infrared spectrum of the majority of the samples. Molecular weight determinations by the vapor density method gave a value of 126 ± 2.5 , which was close to the calculated value, 130.45. The high-resolution ^{18}F NMR spectrum identified the substance as ClF_5 .

Chlorine pentafluoride can also be prepared by an electrolytic process from chlorine or chlorine trifluoride and HF [268, 269]. Electrofluorination of ClF_3 in anhydrous HF as an electrolyte and nickel electrodes resulted in the formation of ClF_5 in a divided or an undivided electrolytic cell. The yields of ClF_5 , based on coulombs in the electrical current, were of the order of 25 and 50% respectively in the undivided and the divided cell. Fluorine, nickel fluoride, and small quantities of chlorine–oxygen–fluorine compounds were also formed at the anode. At the cathode, hydrogen, hydrogen chloride, and chlorine were formed depending on the degree of mixing of anolyte and catholyte. The rate of ClF_5 formation was found to be a function of the concentration of ClF_3 in the electrolyte. From an analysis of polarization data, it was concluded that the mechanism involved the anodic oxidation of fluoride ion to some form of active fluorine, followed by its reaction with ClF_3 to form ClF_5 .

In the thermal autoclave reaction of the elements, the main disadvantage of all these methods is a relatively low space–time yield (quantity of ClF_3 converted into ClF_5 per unit volume in unit time), due to either a relatively low yield of chlorine pentafluoride or to a long reaction time. At higher temperatures, ClF_5 decomposes just as fast as it forms [270]. The space–time yield can be improved by nickel difluoride, which is a very effective catalyst [271]. The highest space–time yield ($143 \text{ g L}^{-1} \text{ h}^{-1}$) was observed at 523 K (250 °C) with a mol ratio $\text{ClF}_3 : \text{F}_2 = 1 : 5$ and an initial pressure of 10.3 MPa (102 atm, measured at 295 K = 22 °C). However, in this case only about 70% of ClF_3 was converted into ClF_5 . Despite the lower space–time yield, for the laboratory scale preparation synthesis at 473 K (200 °C) and a mol ratio 1 : 10 or 1 : 5 seems to be more suitable, because under these conditions the conversion of ClF_3 into ClF_5 is practically complete.

Separation of unreacted chlorine trifluoride from the chlorine pentafluoride product can be achieved by fractionated condensation [272, 273]. According to Smith [253], chlorine pentafluoride was discovered when fluorine and chlorine trifluoride in a molar ratio of 14 : 1 were heated for 1 h to 623 K (350 °C) at 25.2 MPa (250 atm = 3670 psia). Based on mass spectrometric analysis of the reaction product, the product that was separated by fractionated condensation consisted essentially of ClF_5 with small amounts of unreacted ClF_3 . A sample that had undergone additional

purification and contained only very little ClF_3 was a white solid at 77 K (-196°C) and melted to form a colorless to pale yellow liquid at 173 K (-100°C). The vapor pressure of the ClF_5 liquid was 5 to 6 times higher than that of ClF_3 .

Chlorine pentafluoride can be prepared in high purity and good yield by the fluorination of ClF_3 at 195 K (-78°C) with dioxygen difluoride O_2F_2 [274]. The yield of ClF_5 by this method is quantitative. The procedure illustrates the general utility of O_2F_2 in high-valency fluoride synthesis.

A process for the continuous production of ClF_5 on an industrial scale can be carried out by continuously passing fluorine as one reactant and chlorine, chlorine monofluoride, or chlorine trifluoride as the other reactant into a reaction chamber adjacent to the lower end of the chamber, maintaining the temperature and pressure in the reaction chamber sufficiently high to effect a reaction between the reactants to form gaseous chlorine pentafluoride in a mixture with gaseous fluorine ($373\text{--}553\text{ K} = 100\text{--}280^\circ\text{C}$ and $2.27\text{ MPa} = 330\text{ psi}$) [275, 276]. Products are withdrawn from the upper end of the chamber and fed into a collecting chamber near the upper end of the condensing chamber. The temperature in the condensing chamber is kept sufficiently low to achieve condensation of chlorine pentafluoride from the reaction mixture. The condensed chlorine pentafluoride is withdrawn from the condensing chamber as a liquid, and the uncondensed gas is continuously recirculated to the reaction chamber. The yield of ClF_5 can be increased by using excess fluorine, e.g., twice the stoichiometric amount of F_2 .

2.3.2 Physical Properties of Chlorine Pentafluoride

The molecular mass of ClF_5 is 130.44 g/mol. It contains 27.179% Cl and 72.821% F. The discovery of ClF_5 was the most fascinating news for rocket propellant chemists in the 1960s. More detailed summaries of the physical properties of chlorine pentafluoride have been published in the interim. The physical properties of chlorine pentafluoride (Table 26) are no longer shrouded in secrecy and are now widely available.

As of 1968, at the time of the first edition of a German book on rocket propellants, the only detailed publication on properties of chlorine pentafluoride was the paper by Pilipovich et al. [257], but more physical properties were determined and published in the following years.

Table 26: Physical properties of chlorine pentafluoride.

Property	SI Units	MKS Units	References
Melting point	$170 \pm 4\text{ K}$	$-103 \pm 4^\circ\text{C}$	[257]
Boiling point	259 K	-14°C	[257]
	260.2	-12.9°C	[255]
	254	-19°C	[256]
	259.4	-13.7°C	[248]

MKS = meter, kilogram, and second.

2.3.2.1 Density of Liquid Chlorine Pentafluoride

Early reports suggested that the density of liquid chlorine pentafluoride as a function of temperature can be expressed by the following equation [257]:

$$\rho_{\text{liq.}} = 2.696 - 3.08 \times 10^{-8} T$$

where $\rho_{\text{liq.}}$ is the density of liquid ClF_5 in g/cm^3 and T is the temperature in kelvin.

Table 27: Density of chlorine pentafluoride.

Temperature		Density, measured	Density, calculated
°C	K	g/cm^3	g/cm^3
-80.00	193.15	2.100	2.104
-57.00	216.15	2.036	2.030
-23.32	249.83	1.938	1.929
-23.00	250.15	1.922	1.928
-3.05	270.10	1.872	1.869
0.00	273.15	1.863	1.859
8.52	281.67	1.834	1.832
8.75	281.90	1.832	1.831
12.33	285.48	1.818	1.819
17.38	290.53	1.798	1.802
23.28	296.43	1.778	1.781
28.50	301.65	1.759	1.763
34.08	307.23	1.733	1.742
40.45	313.60	1.711	1.717
48.82	321.97	1.677	1.683
55.12	328.27	1.653	1.656
61.50	334.65	1.629	1.627
66.02	339.17	1.615	1.606
67.18	340.33	1.606	1.601
70.75	343.90	1.595	1.583
78.25	351.40	1.548	1.545
83.98	357.13	1.509	1.514
86.25	359.40	1.508	1.501
91.03	364.18	1.480	1.474
97.83	370.98	1.424	1.433
98.90	372.05	1.421	1.427
107.60	380.75	1.263	—
118.90	392.05	1.132	—
123.50	396.65	1.017	—
128.90	402.05	1.160	—
132.10	405.25	0.949	—
139.90	413.05	0.898	—
140.60	413.75	0.769	—
147.30	420.45	0.887	—

Data source: [277]

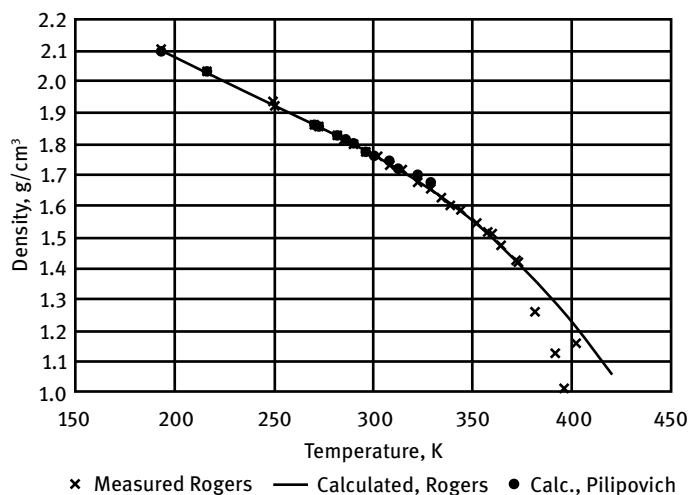


Figure 20: Density of liquid chlorine pentafluoride, comparison of different data sources.

More accurate data are presented in Table 27. The experimental points in Table 27 over the temperature range of 193 to 372 K (−80 to +99 °C) were curve fitted by a least squares computer program and resulted in the following equation:

$$\rho_{\text{liq.}} = 3.553 - 1.396 \times 10^{-2}T + 4.565 \times 10^{-5}T^2 - 6.311 \times 10^{-8}T^3$$

where $\rho_{\text{liq.}}$ is the density of liquid ClF_5 in g/cm^3 and T is the temperature in kelvin. The standard error of estimate of this equation is $\pm 0.0059 \text{ g/cm}^3$. Figure 20 is a comparison of the two density equations. The scatter of data points at the high temperature end of the graph is obvious.

Figure 21, which is based on the same equation, but extends it to higher temperatures, shows a steep drop of density as the temperature approaches the critical point.

2.3.2.2 Velocity of Sound in Liquid Chlorine Pentafluoride

Data from experimental sonic velocity measurements in saturated liquid ClF_5 from 196 to 341 K (−77.1 to +68.7 °C) were curve fitted and resulted in the following equation [248]:

$$c = 1755 + 4.074T + 5.936 \times 10^{-4}T^2$$

where c is the velocity of sound in m/s and T is the temperature in kelvin. A graph derived from this equation is shown in Figure 22.

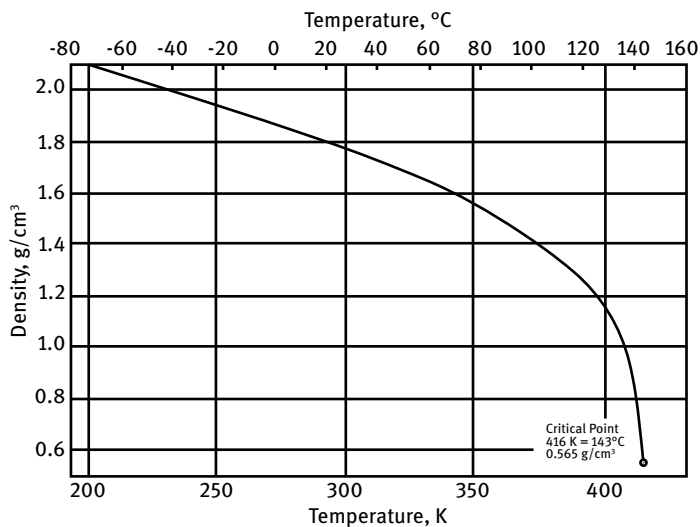


Figure 21: Density of liquid chlorine pentafluoride. (Reproduced and modified from [248].)

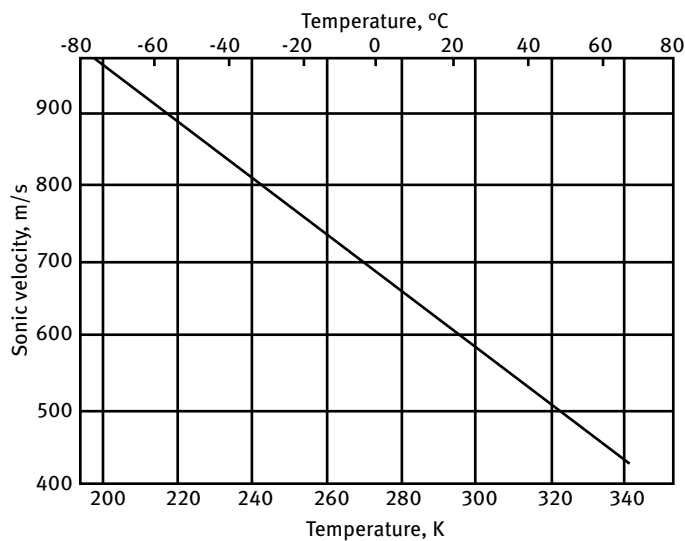


Figure 22: Velocity of sound in liquid chlorine pentafluoride. (Reproduced and modified from [248].)

The velocity of sound in liquid ClF_5 was measured over a range of pressures from saturation pressure at the prevailing temperature up to 6.8 MPa (1000 psia) for five different temperatures [66]. The velocity of sound data are tabulated in Table 28. The velocity of sound increased with pressure and decreased with temperature.

Table 28: Velocity of sound in liquid chlorine pentafluoride.

Temperature		Pressure		Velocity of sound	
K	°C	MPa	psia	m/s	ft/s
258.37	-14.78		Saturation	742.0	2434.4
258.37	-14.78	3.45	500	755.8	2479.7
258.37	-14.78	5.52	800	765.6	2511.8
258.37	-14.78	6.89	1000	770.9	2529.2
275.57	+2.42		Saturation	677.4	2222.4
275.57	+2.42	3.45	500	691.1	2267.4
275.57	+2.42	5.52	800	700.6	2298.5
275.57	+2.42	6.89	1000	707.1	2319.9
296.65	+23.5		Saturation	598.7	1964.2
296.65	+23.5	3.45	500	616.1	2021.3
319.0	+45.88		Saturation	515.7	1691.9
319.0	+45.88	3.45	500	535.0	1755.2
319.0	+45.88	6.89	1000	555.4	1832.0
342.3	+69.2	3.45	500	449.0	1473.1

Data source: [66]

2.3.2.3 Compressibility Coefficient of Liquid Chlorine Pentafluoride

The adiabatic compressibility of liquid ClF₅ was calculated from experimental sonic velocity and density data on the saturated liquid and can be expressed by the following equation [278], as referenced in [279]:

$$\beta_{\text{adiab}} = 1.1565 \times 10^{-4} + 1.3942 \times 10^{-6} T + 1.2708 \times 10^{-8} T^2 + 1.4680 \times 10^{-10} T^3 + 9.6855 \times 10^{-13} T^4$$

where β_{adiab} is the adiabatic compressibility in atm⁻¹ and T is the temperature in kelvin. The resulting curve is shown in Figure 23.

Figure 24 gives the isothermal compressibility of liquid chlorine pentafluoride. This curve is the result of curve-fitting the data from -40 to +30 °C and the equation is

$$\beta_{\text{isoth}} = 2.091 \times 10^{-4} + 3.712 \times 10^{-6} t + 4.238 \times 10^{-8} t^2 + 4.287 \times 10^{-10} t^3 + 2.973 \times 10^{-12} t^4$$

where β_{isoth} is the isothermal compressibility in atm⁻¹ and t is the temperature in °C.

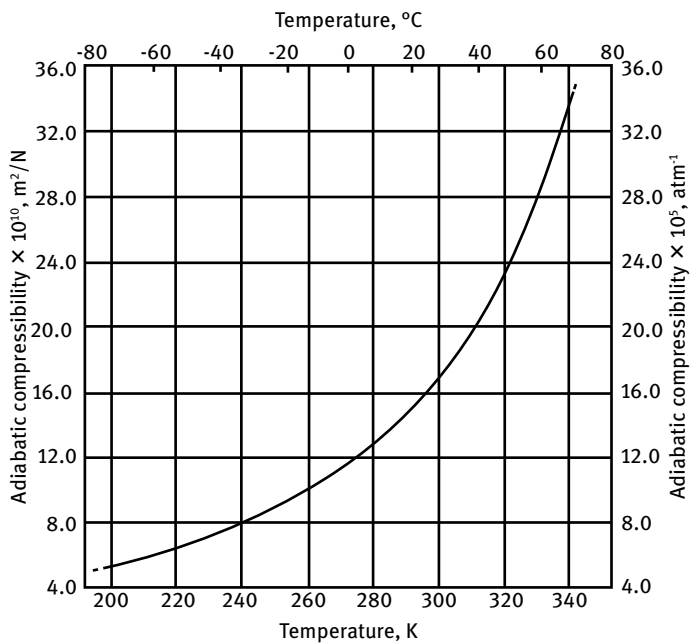


Figure 23: Adiabatic compressibility of liquid chlorine pentafluoride. (Reproduced and modified from [248].)

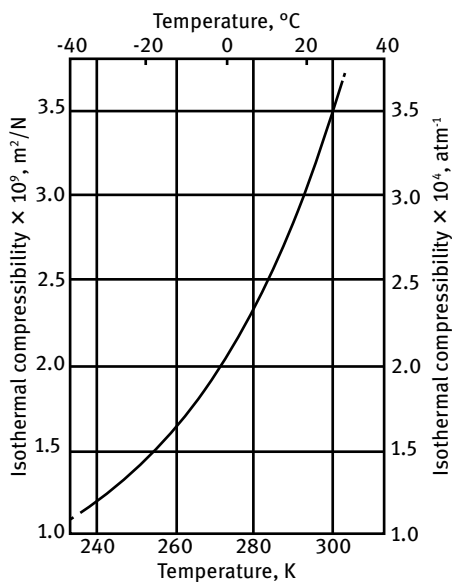


Figure 24: Isothermal compressibility of liquid chlorine pentafluoride. (Reproduced and modified from [248].)

2.3.2.4 Vapor Pressure of Chlorine Pentafluoride

The vapor pressure curve of chlorine pentafluoride can be calculated from the following equation [257]:

$$\log p_v = 7.2683 - (1137.16/T)$$

where p_v is the vapor pressure in mm Hg and T is the temperature in kelvin. Another source gave a slightly different equation [255]:

$$\log p_v = 7.71 - (1257/T)$$

where p_v is the vapor pressure in mm Hg and T is the temperature in kelvin.

A third vapor pressure equation was given as [277, 279]:

$$\log p_v = 4.6029 - (1197/T)$$

where p_v is the vapor pressure in atm and T is the temperature in kelvin. Figure 25 is a comparison of vapor pressure data from two different sources, and Figure 26 uses this equation over a very wide range of temperatures.

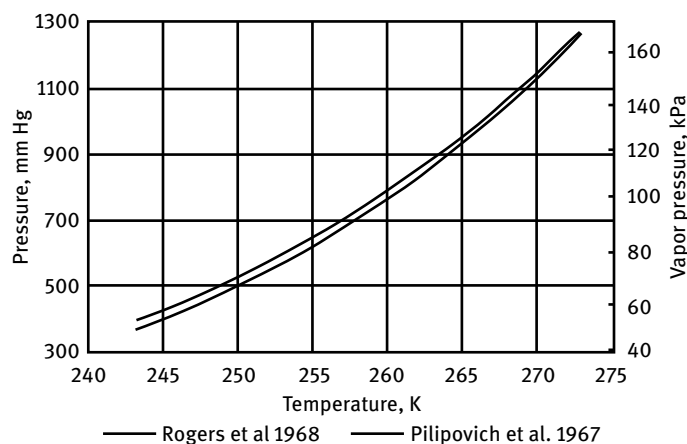


Figure 25: Vapor pressure of chlorine pentafluoride – comparison of data from two different sources.

Vapor pressure data for chlorine pentafluoride over a very wide range, all the way from 228 to the critical point at 416 K (–45 °C to the critical point at +143 °C), are shown in Figure 26, which is on a semilogarithmic scale. Note that data read from the left curve need to be multiplied times 0.1, whereas data read from the right curve can be multiplied times 1.0.

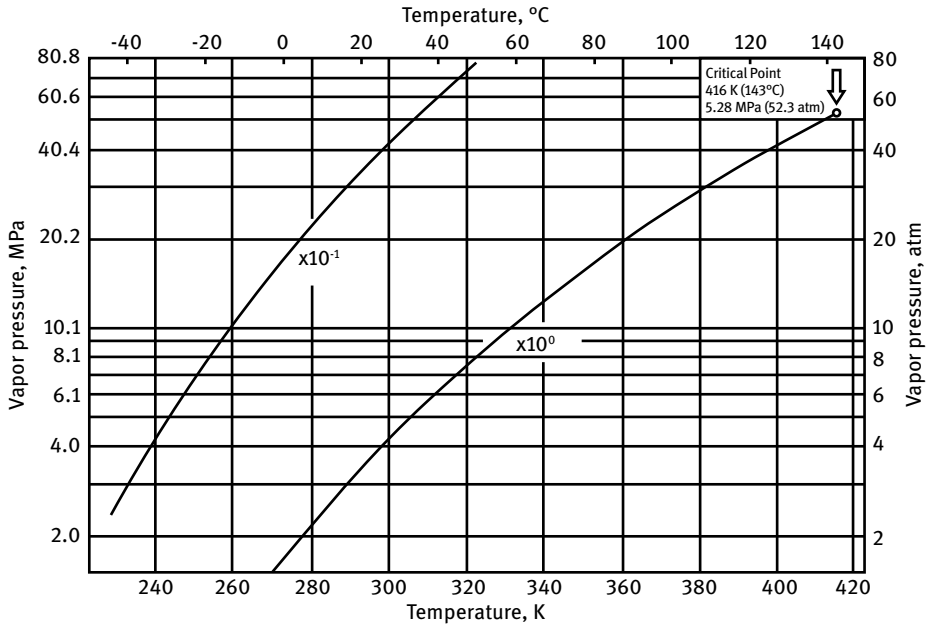


Figure 26: Vapor pressure of chlorine pentafluoride. (Reproduced and modified from [248].)

2.3.2.5 Critical Point of Chlorine Pentafluoride

Critical point data for chlorine pentafluoride are listed in Table 29.

Table 29: Critical point data for chlorine pentafluoride.

Property	SI Units	MKS Units	Reference
Critical temperature	415.7 ± 1 K	142.6 ± 1 °C	[277]
Critical pressure	5242 ± 70 kPa	51.9 ± 0.7 atm	[277]
Critical density	0.565 ± 0.008 kg/m ³	0.565 ± 0.008 g/cm ³	[277]

2.3.2.6 Viscosity of Liquid Chlorine Pentafluoride

The viscosity of saturated liquid ClF₅ under its own vapor pressure can be described by the following equation, which was obtained for the temperature range 183 to 293 K (−90 to +20 °C) [279]:

$$\log \eta = -1.62875 + 335.636/T$$

where η is the viscosity in cPs and T is the temperature in kelvin. The curve for this equation is shown in Figure 27.

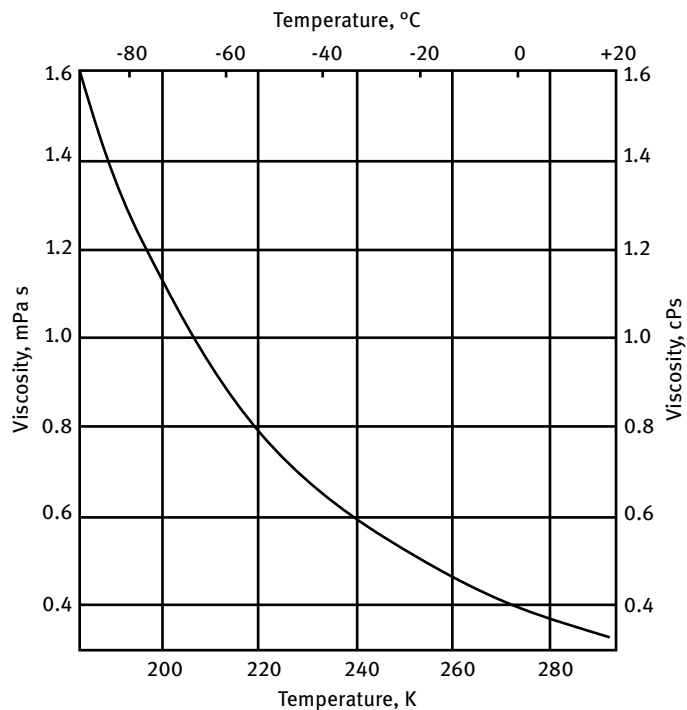


Figure 27: Viscosity of saturated chlorine pentafluoride. (Reproduced and modified from [248].)

Single data points of viscosity reported for saturated liquid ClF₅ under its own vapor pressure are summarized in Table 30.

Table 30: Viscosity of liquid chlorine pentafluoride.

Temperature			Kinematic viscosity		Absolute viscosity	
K	°F	°C	mm ² /s	cSt	mPa s	cPs
297	75	24	0.182	0.182	0.323	0.323
311	100	38	0.164	0.164	0.281	0.281
324	124	51	0.151	0.151	0.252	0.252
341	154	68	0.134	0.134	0.215	0.215
353	176	80	0.121	0.121	0.185	0.185

Data source: [66]

2.3.2.7 Surface Tension of Chlorine Pentafluoride

The surface tension of ClF_5 , which was experimentally determined over a temperature range from 223 to 298 K (-50 to $+25^\circ\text{C}$) is shown in Figure 28. The equation representing these data is

$$\sigma = 57.949 - 0.14463T$$

where σ is the surface tension in dyn/cm and T is the temperature in kelvin.

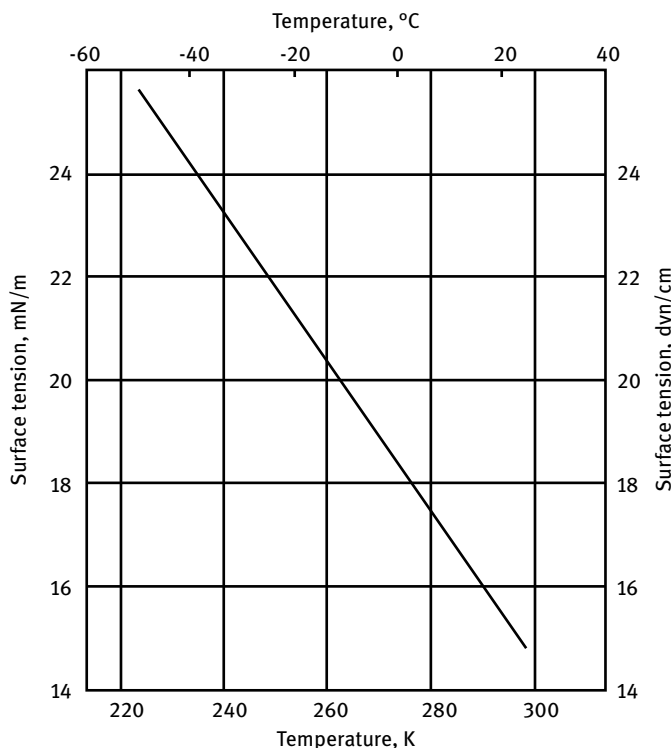


Figure 28: Surface tension of saturated chlorine pentafluoride. (Reproduced and modified from [248].)

2.3.2.8 Solubility/Miscibility of Liquid Chlorine Pentafluoride

In studying the miscibility of ClF_5 with other liquid non-metallic fluorides, the questions were whether these are simple physical mixtures, whether adducts form in specific stoichiometric ratios, or whether the two compounds might even chemically react to form new fluoride compounds, as is the case when reacting ClF_5 with Lewis acids. Fluorides studied as solvents or reaction partners for ClF_5 included ClF_3 , IF_5 , BrF_5 , SbF_5 , and BF_3 .

Binary and ternary mixtures of ClF_5 with a wide range of other fluorides (ClF_3 , BrF_5 , FClO_3 , XeF_2 , XeF_4 , OF_2 , N_2F_4 , ONF_3 , N_2O_4 , $\text{C}(\text{NO}_2)_4$, or $\text{C}(\text{NF}_2)_4$) were described in the ClF_5 Handbook [280]. A 3-to-1 mixture of ClF_5 with HNF_2 detonated within 1 min after mixing at 153 K (-120°C). However, it was also noted that very pure ClF_5 and HNF_2 reacted smoothly at 193 K (-80°C) to form ClNF_2 in good yields. ClF_5 reacts with N_2O_4 and is incompatible with N_2F_4 in the long term. See also [41].

In the binary $\text{ClF}_5/\text{ClF}_3$ system, an adduct $2\text{ClF}_5 \cdot 3\text{ClF}_3$ is formed at 40 mol % ClF_5 [281]. Separated layer formation in the liquid state and phase transitions of pure ClF_5 and the adduct compound were observed by thermal analysis. A peak at 183 K (-90°C) on the heating curve of ClF_5 corresponded to its melting point. At 168 K (-105°C) a phase transition of ClF_5 took place leading to its polymorphous transformation. The binary $\text{ClF}_5/\text{ClF}_3$ system had only limited miscibility. There is a miscibility gap and a bottom layer formed at 63–87 mol % ClF_5 (Figure 29).

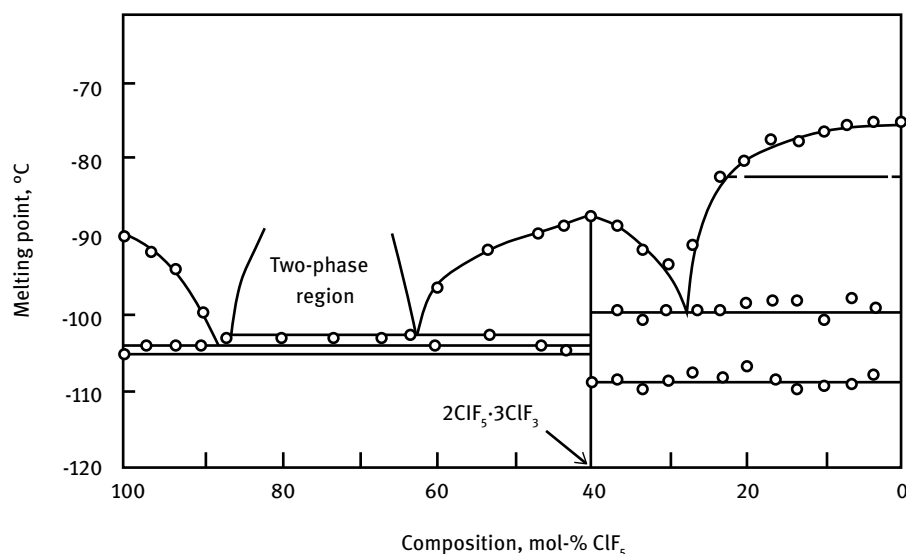


Figure 29: Phase diagram of the $\text{ClF}_5/\text{ClF}_3$ system. (Reproduced and modified from [281].)

Differential thermal analysis (DTA) measurements indicated that the ClF_5/IF_5 system has a degenerate eutectic near 100% ClF_5 and 205 K (-68°C). The phase transition $\beta\text{-ClF}_5 \rightleftharpoons \alpha\text{-ClF}_5$ occurred at 168 K (-105°C) [282].

A DTA study showed that no compounds were formed between BF_3 and either ClF_5 or BrF_5 [283]. The BrF_5/BF_3 system contained a degenerate eutectic at 145 K (-128°) near the BF_3 side of the phase diagram. The ClF_5/BF_3 system exhibited mutual insolubility of the components in both liquid and solid states.

Mixtures of ClF_5 with FClO_3 were found to be completely miscible, compatible and insensitive to shock. The vapor pressures of various mixtures had a slight positive deviation from ideality over a temperature range of 227 to 293 K (-46 to $+20^\circ\text{C}$), but very little vapor pressure deviation was noted in an 80/20 $\text{ClF}_5/\text{FClO}_3$ mixture from 250 to 198 K (-23 to $+25^\circ\text{C}$). Mixtures of 14–40% ClF_5 with FClO_3 have been patented as oxidizers in storable propellant missiles [284]. Thus, a mixture of 39% ClF_5 and 61% ClO_3F has a freezing point of 183 K (-90°C).

$\text{ClF}_5/\text{N}_2\text{F}_4$ mixtures have been extensively studied by Aerojet, Reaction Motors, and Rocketdyne [285, 286] as a primary candidate high-energy storable hypergolic oxidizer formulation. Early studies indicated unwanted reaction between the two compounds above ambient temperatures. Additional laboratory investigations confirmed decomposition of the compounds in various materials over a wide temperature range and suggested that decomposition was both homogeneous and heterogeneous in nature [279]. Addition of 2.5% ClF_5 to N_2F_4 renders the latter hypergolic with hydrazine [287].

It is possible to form completely miscible mixtures of OF_2 and ClF_5 in amounts of approximately 84% by volume OF_2 , 16% ClF_5 , but only at intermediate temperatures above 184.6 K (-78.5°C) [288]. Even a small amount of 16% ClF_5 renders the otherwise unreactive OF_2 hypergolic with most fuels.

2.3.2.9 Solubility of Pressurant Gases in Liquid Chlorine Pentafluoride

Preliminary measurements of the solubility of gaseous nitrogen in liquid ClF_5 indicated a solubility of $\sim 3.0 \times 10^{-5} \text{ gN}_2/\text{gClF}_5 \text{ psi}^{-1}$ at 322 K (120°F ; [289]).

Additional later measurements at three different temperatures (Table 31) showed the solubility of nitrogen in liquid ClF_5 to be about 25% below the earlier measured solubility [66].

Table 31: Solubility of nitrogen gas in liquid chlorine pentafluoride.

Temperature		Vapor pressure		Pressure range		Solubility
K	$^\circ\text{F}$	MPa	psia	MPa	psia	lb N_2 (lb ClF_5) $^{-1}$ psi $^{-1}$
305	90	0.496	72	2.21 to 3.24	320 to 470	1.83×10^{-5}
322	120	0.793	115	4.00 to 4.27	580 to 620	2.25×10^{-5}
339	150	1.21	176	5.10 to 5.38	740 to 780	2.60×10^{-5}

Data source: [66]

The solubilities of oxygen and nitrogen in liquid ClF_5 were determined at 293 K (20°C) and (5×10^5) to (1×10^7) Pa and are listed in Table 32 [290]. Henry's law constants of nitrogen were pressure dependent, but Henry's law constants for oxygen were independent of pressure (Figure 30). The solubilities were relatively high and the oxygen solubility exceeded that in 25 other fluorine-containing organic solvents. The maxi-

Table 32: Solubility of nitrogen and oxygen in liquid chlorine pentachloride under pressure.

Nitrogen		Oxygen	
Pressure, Pa $\times 10^{-5}$	Solubility, vol.-%	Pressure, Pa $\times 10^{-5}$	Solubility, vol.-%
4.9	1.62	20.6	3.84
11.3	2.40	40.3	7.95
22.6	4.41	60.0	10.85
37.2	5.91	79.5	15.40
59.8	7.80	99.0	17.10
79.5	12.40	—	—
88.8	11.80	—	—

Data source: [290]

Note: The table heading in the original publication lists ClF₃(instead of ClF₅), but that is assumed to be a typographic error

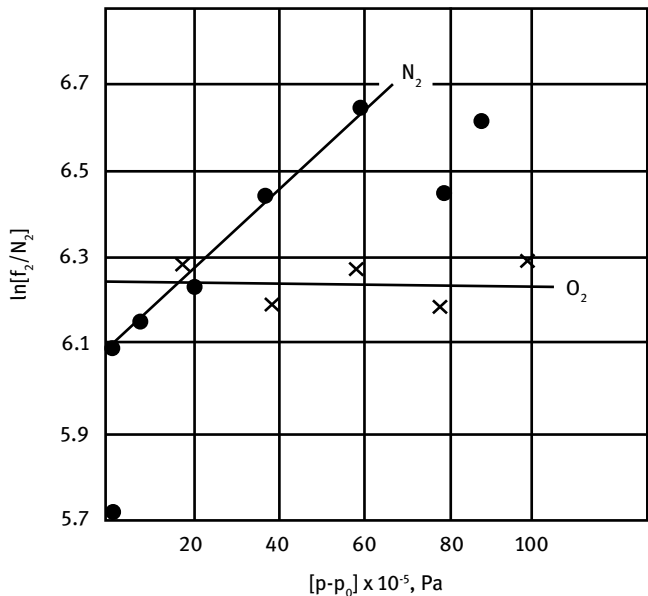


Figure 30: Henry's law constants of solubility of nitrogen and oxygen in chlorine pentafluoride. (Reproduced and modified from [290].)

imum solubilities occurred at much lower pressures than one would expect in relation to the critical temperature of ClF₅ (430.6 K = 157.5 °C).

Helium, nitrogen, argon, or oxygen can be used as the pressurant gas for ClF₅ propellant tanks. Some of the oxygen dissolves in ClF₅ [291].

The solubility of helium in liquid ClF₅ is 117 ppm at 305 K, 2068 kPa or 126 ppm at 283.2K, 2068 kPa. The solubility of helium in liquid ClF₅ is illustrated in Figure 31.

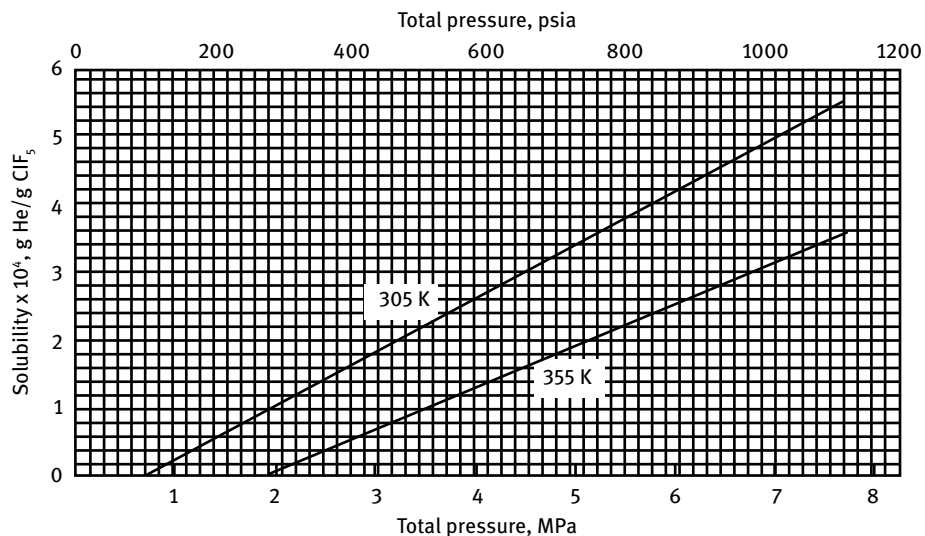


Figure 31: Solubility of helium in liquid ClF₅. (Reproduced and modified from [292].)

The solubility of nitrogen in liquid ClF₅ is illustrated in Figure 32. The solubility of GN₂ in ClF₅ at 283.2 K and 2068 kPa is 2.96×10^{-2} mol/mol. Other sources suggest a solubility of GN₂ in ClF₅ of 0.433×10^{-2} lb/lb at 305 K and 2068 kPa.

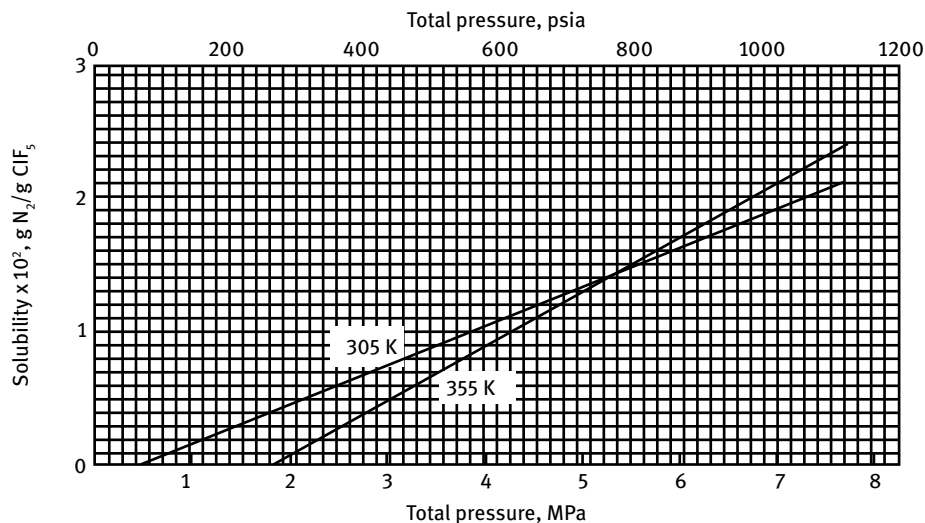


Figure 32: Solubility of nitrogen in liquid ClF₅. (Reproduced and modified from [292].)

2.3.2.10 Thermal Conductivity of Liquid Chlorine Pentafluoride

It was very difficult to measure thermal conductivity and heat transfer properties of a highly reactive fluid such as chlorine pentafluoride. In many cases the equipment and thermocouples were coated with films of metal fluorides, which impeded the flow of heat.

Thermal conductivity measurements were conducted at Rocketdyne on propellant-grade (assay >99.0%) ClF_5 at 293, 313, and 353 K (20, 40, and 80 °C) using the concentric cylinder steady-state thermal conductivity cell [65]. Initial conductivity measurements were made using the concentric cylinder steady-state thermal conductivity cell at 293 K (20 °C) using four different temperature gradients (ranging from 0.18 to 0.58 °C = 0.331 to 1.057 °F) across the cell annulus. The thermal conductivity values obtained ranged from 7.9×10^{-2} to $8.5 \times 10^{-2} \text{ W m}^{-1} \text{ h}^{-1}$ (4.58×10^{-2} to $4.92 \times 10^{-2} \text{ BTU h}^{-1} \text{ ft}^{-1} \text{ °F}^{-1}$), with an average value of $8.2 \times 10^{-2} \text{ W m}^{-1} \text{ h}^{-1}$ ($4.72 \times 10^{-2} \text{ BTU h}^{-1} \text{ ft}^{-1} \text{ °F}^{-1}$). This value was considerably lower than the $0.105 \text{ W m}^{-1} \text{ h}^{-1}$ ($6.08 \times 10^{-2} \text{ BTU h}^{-1} \text{ ft}^{-1} \text{ °F}^{-1}$) obtained in previous measurements (using the same apparatus) under Contract AF04(611)-11407. During subsequent measurements at 40 °C (104 °F), the data varied from 5.4×10^{-2} to $6.9 \times 10^{-2} \text{ W m}^{-1} \text{ h}^{-1}$ (3.13×10^{-2} to $4.0 \times 10^{-2} \text{ BTU h}^{-1} \text{ ft}^{-1} \text{ °F}^{-1}$); a general downward drift in conductivity was noted from measurement to measurement, due to either decomposition of the sample or degradation of the surface of the apparatus. Thermal conductivity measurements were then conducted on saturated liquid ClF_5 using the “hot-wire” apparatus instead. The measurements, which covered the temperature range 237.8 to 327.7 K (−31.7 to +130.2 °F = −35.4 to +54.6 °C), were hindered in the upper temperature regions by the immediate onset of free convection in the ClF_5 and apparent reaction of the oxidizer with the platinum wire. The experimental data were curve-fitted by a least-squares computer program with the following expressions:

$$\lambda = 3.803 \times 10^{-4} + 1.00 \times 10^{-6}t$$

where λ is the thermal conductivity in $\text{cal cm}^{-1} \text{ s}^{-1} \text{ °C}^{-1}$ and t is the temperature in °C. Later reviewers reported the thermal conductivity of liquid ClF_5 as $0.170 \text{ W m}^{-1} \text{ K}^{-1}$ at 298 K ($0.0981 \text{ BTU h}^{-1} \text{ ft}^{-1} \text{ °F}^{-1}$) or $0.191 \text{ W m}^{-1} \text{ K}^{-1}$ at 298 K ($0.456 \times 10^{-3} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ °C}^{-1}$). The thermal conductivity of liquid ClF_5 is illustrated in Figure 33. There appears to be a contradiction in the temperature dependence of the thermal conductivity between theoretical predictions and actual experimental measurements. Although the thermal conductivity of **saturated** liquid ClF_5 calculated from equation

$$\lambda = 8.766 \times 10^{-2} + 1.35 \times 10^{-4}t$$

(where λ is the thermal conductivity in $\text{BTU h}^{-1} \text{ ft}^{-1} \text{ °F}^{-1}$ and t is the temperature in °F) and illustrated in Figure 33 is shown to increase with temperature, the thermal conductivity of liquid ClF_5 from a Weber equation predicted that thermal conductivity would be decreasing with temperature. The Weber equation is a correlation of thermal conductivity, density, molecular mass, and heat capacity. However, measurements

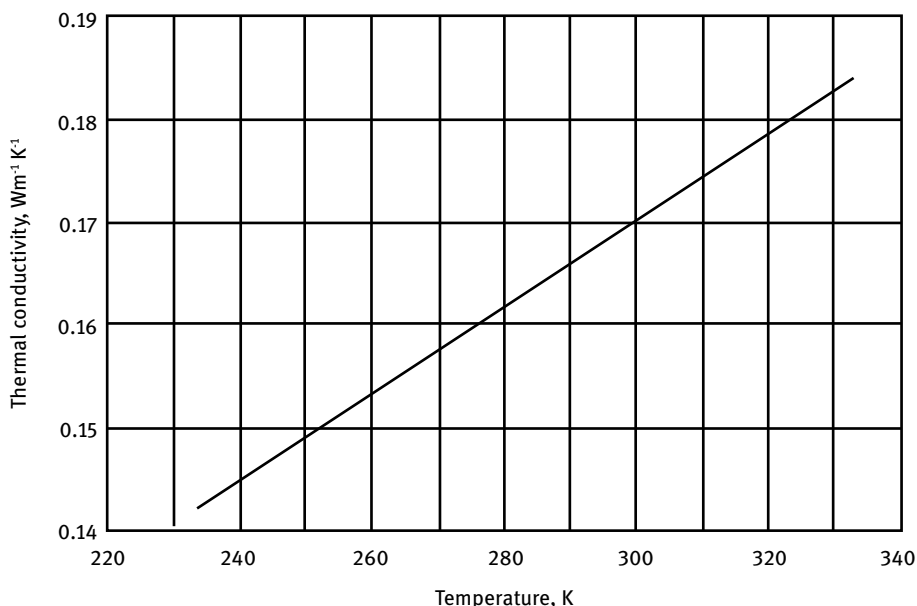


Figure 33: Thermal conductivity of saturated liquid ClF_5 . (Graph created by Schmidt 2018, based on data from [65].)

have shown the opposite to be the case, and thermal conductivity increased with temperature.

2.3.2.11 Heat Transfer Properties of Liquid Chlorine Pentafluoride

Testing with ClF_5 flowing in electrically heated tubes at subcritical and supercritical pressures was done and values of density, specific heat, thermal conductivity, and viscosity were established from existing data for pressures up to 34.5 MPa (5000 psia) and temperatures up to 978 K (1300 °F), and were presented in graphical form. In the course of determining the forced convection heat transfer characteristics of liquid ClF_5 in Monel K-500 tubes, 3 out of 22 tests were terminated by tube burnouts [293, 294]. In two of these tests, wall temperature measurements were available essentially at the time of tube burnout, whereas in the other case, the temperature measurement was lost shortly before burnout. During three initial tests, the results indicated that, although the critical heat flux limits of ClF_5 are relatively low, they were somewhat higher than expected.

2.3.2.12 Thermodynamic Properties of Chlorine Pentafluoride

The thermodynamic properties of chlorine pentafluoride are summarized in Table 33.

Table 33: Thermodynamic properties of chlorine pentafluoride.

Property	SI Units	MKS Units	Source	References
Heat of evaporation (ΔH) _{evap}	24.0 kJ/mol	5.74 kcal/mol	Gatti 1965	[255]
Heat of evaporation at normal boiling point (ΔH) _{evap}	22.92 kJ/mol	5.477 kcal/mol	Rogers et al. 1968	[277]
Heat of evaporation at normal boiling point (ΔH) _{evap}	22.23 kJ/mol	5.313 kcal/mol		
Enthalpy of formation (ΔH) ₅₀₀ (G)	–234 kJ/mol	–56 kcal/mol	Bauer and Shee- han 1967	[270]
	–238.49 kJ/mol	–57.0 kcal/mol	NIST Chem Web- Book 1998	[40]
Enthalpy of formation (ΔH) ₂₉₈ (L)	–254.8 kJ/mol	–60.9 ± 4.5 kcal/mol	Bisbee et al. 1968	[295]
	–253.1 kJ/mol	–60.5 ± 6.0 kcal/mol		[77]
	–253.2 kJ/mol	–464 cal/g = –60.52 kcal/mol		[296]
	–253 kJ/mol	–60.5 kcal/mol		

The molecular mass of ClF₅ is 130.44 g/mol

Heat Capacity of Liquid Chlorine Pentafluoride

The heat capacity of liquid ClF₅ can be expressed by the following polynomial equation [279]:

$$c_p = 1.0847 - 0.9522 \times 10^{-2}T + 0.3595 \times 10^{-4}T^2 - 0.4309 \times 10^{-7}T^3$$

where c_p is the heat capacity in cal g^{–1} °C^{–1} and T is the temperature in kelvin. The results from this equation are illustrated in Figure 34.

The heat capacity of liquid ClF₅ was measured over the temperature range 198 to 241 K (–75 to –32 °C) [297]. The value at 242 K (–31 °C) was 0.283 cal g^{–1} °C^{–1} and was approximately 10% lower than a value reported by Rocketdyne but is higher than the data in Figure 34. The molar heat capacity of gaseous ClF₅ can be calculated from the following equation [40]:

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + E/\tau^2$$

where C_p° is the molar heat capacity in J mol^{–1} K^{–1} and τ is the temperature in kelvin divided by 1000: $\tau = T/1000$ and A, B, C, D, and E are constants listed in Table 34 for two different temperature ranges.

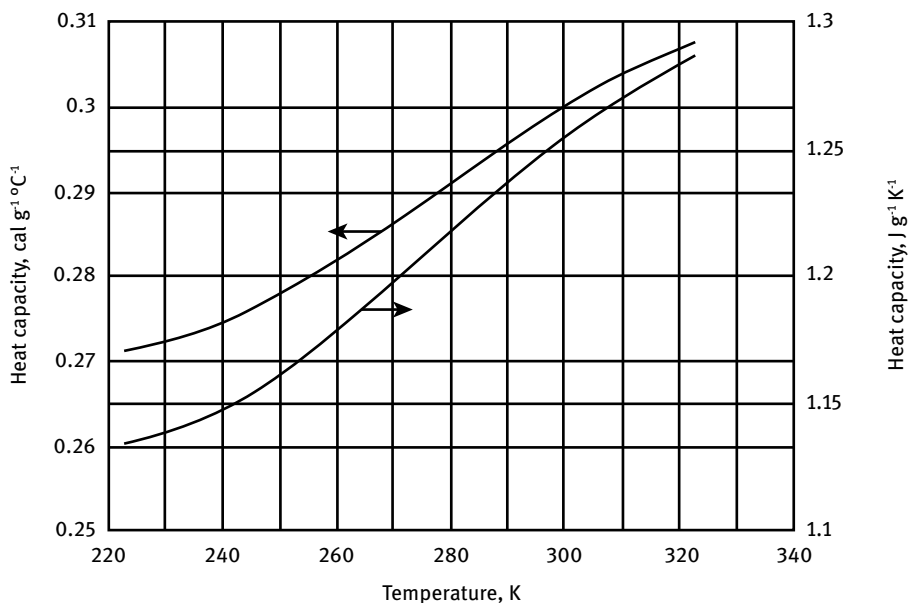


Figure 34: Heat capacity of liquid chlorine pentafluoride (Graph created by Schmidt 2018, based on data from [279].)

Table 34: Coefficients for heat capacity, enthalpy of formation, and entropy of gaseous chlorine pentafluoride.

Temperature, K	298–1000	1000–6000
A	89.15560	132.7721
B	117.0390	0.149737
C	−118.3331	−0.031080
D	42.36216	0.002193
E	−1.556713	−4.258811
F	−274.5344	−291.2512
G	379.8566	450.3658
H	−238.4884	−238.4884

Data source: [40]

Enthalpy of Formation of Gaseous Chlorine Pentafluoride

The enthalpy of formation of gaseous chlorine pentafluoride can be calculated from the following equation:

$$H^{\circ} - H^{\circ}_{298.15} = A\tau + B\tau^2/2 + C\tau^3/3 + D\tau^4/4 - E/\tau + F - H$$

where $H^\circ - H^\circ_{298.15}$ is the excess heat of formation in kJ/mol and τ is the temperature in kelvin divided by 1000: $\tau = T/1000$ and A, B, C, D, E, and H are the constants listed in Tables 2–37 for two different temperature ranges. The standard enthalpy of formation of ClF_5 gas at 1 bar is $\Delta H_f^\circ \text{gas} = -238.49 \text{ kJ/mol}$.

Enthalpy of Formation of Liquid Chlorine Pentafluoride

The enthalpy of formation of liquid chlorine pentafluoride was determined by two independent sets of experiments [295]: In one experiment, the compound was reacted with hydrogen and in the other with ammonia in a calorimetric bomb. At the conditions of reaction, ClF_5 has a vapor pressure of 4.17 atm. The heat of vaporization of ClF_5 is $\Delta H_{\text{evap}} = 20.5 \text{ kJ/mol} = 4.9 \text{ kcal/mol}$ at $301 \text{ K} = 28^\circ\text{C}$. From the measured enthalpies of reaction and the known enthalpies of formation of products and reactants, corrected to their standard states, the standard enthalpy of formation of liquid ClF_5 was derived. The enthalpy of formation calculated on the basis of the hydrogen reaction was $\Delta H_f = -277.8 \pm 28.9 \text{ kJ/mol} = -66.4 \pm 6.9 \text{ kcal/mol}$. Calculated on the basis of the ammonia reaction, it was $\Delta H_f = -250.6 \pm 16.3 \text{ kJ/mol} = -59.9 \pm 3.9 \text{ kcal}$. Assuming that one questionable hydrogen run was invalid, the enthalpy of formation calculated as the average of the data from both sets of experiments was $\Delta H_f = -254.8 \pm 18.8 \text{ kJ/mol} = -60.9 \pm 4.5 \text{ kcal/mol}$.

The heat of reaction due to combustion of ClF_3 or ClF_5 in hydrogen gas was measured in a bomb calorimeter in order to determine the enthalpies of formation of these halides [298]. That of ClF_3 , already fairly well known, was used to standardize the apparatus for measurement concerning ClF_5 , for which no direct data had been available at that time.

The available data on the vibrational and rotational spectra of chlorine, bromine, and iodine pentafluorides have been used to calculate their ideal gas thermodynamic functions, C_p° , $(H^\circ - H^\circ_0)/T$, $(G^\circ - H^\circ_0)/T$, S° , ΔH_f° , ΔG_f° , and $\log K_f$ at 1 atm pressure [299]. For gaseous ClF_5 , a value of 237.2 kJ/mol (-56.7 kcal/mol) has been selected from the literature for the enthalpy of formation at 298.15 K and compared with the calculated data. The enthalpy of vaporization of ClF_5 at 298.15 K was calculated to be 20.9 kJ/mol (5.0 kcal/mol).

Entropy of Gaseous Chlorine Pentafluoride

The standard entropy of gaseous chlorine pentafluoride can be calculated from the following equation:

$$S^\circ = A \ln(\tau) + B\tau + C\tau^2/2 + D\tau^3/3 - E/(2\tau^2) + G$$

where S° is the standard entropy in $\text{J mol}^{-1} \text{ K}^{-1}$ and τ is the temperature in kelvin divided by 1000: $\tau = T/1000$ and A, B, C, D, E, and G are the constants listed in Tables 2–37 for two different temperature ranges. The standard entropy of ClF_5 gas at 1 bar is $310.73 \text{ J mol}^{-1} \text{ K}^{-1}$.

2.3.2.13 Spectroscopic Data for Chlorine Pentafluoride

Infrared Spectra of Chlorine Pentafluoride

The infrared and Raman spectra of XeOF_4 , IF_5 , BrF_5 , and ClF_5 have been recorded and compared and assignments of the fundamental vibration and combination frequencies made on the basis of a square-pyramidal structure for these molecules [300]. Valence force constants, based on estimated molecular parameters, have been calculated for these molecules. Comparisons between the different members of the series showed that the bonding in XeOF_4 was remarkably similar to that in the interhalogen compounds. A square-pyramidal structure of symmetry C_{4v} was assigned to ClF_5 by comparison with the spectra of BrF_5 , IF_5 , and XeOF_4 .

The IR spectrum of gaseous ClF_5 showed eight bands, a very strong one at 732 cm^{-1} , a strong one at 786 cm^{-1} , and four weak ones at 980 , 1216 , 1272 , and 1447 cm^{-1} (Figure 35) [255].

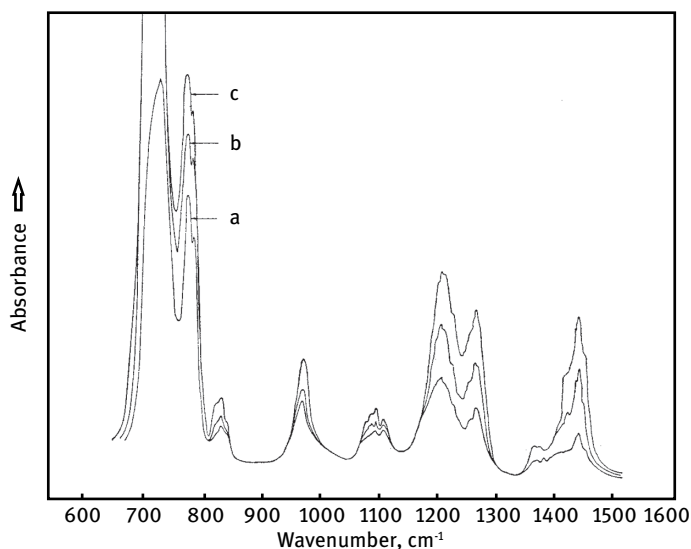


Figure 35: Infrared spectrum of gaseous chlorine pentafluoride. (Republished and modified from [255], with permission of © 1965 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

The IR spectra of solid ClF_5 have been recorded in argon and nitrogen matrices [301]. The previously suggested and very unusual triple coincidence of two deformational and one stretching mode at about 480 cm^{-1} have been experimentally confirmed. The observed $^{35}\text{Cl}/^{37}\text{Cl}$ isotope splitting permitted assignment of the bands to the individual modes of vibration. Spectroscopic evidence was presented for association of ClF_5 in the pure solid and in an Ar matrix at low dilution ratios. Figure 36 shows the infrared spectra of pure ClF_5 in a matrix at different concentrations recorded at 77 K .

Similar spectra are available for frozen ClF_5 at 4 K. In addition to $\nu_7(\text{E})$ at $726/713\text{ cm}^{-1}$, $\nu_3(\text{A}_1)$ at $493/483\text{ cm}^{-1}$, and $\nu_8(\text{E})$ at $482/479\text{ cm}^{-1}$, the following fundamentals were observed in good agreement with the previously published spectrum: $\nu_2(\text{A}_1)$ at 539 cm^{-1} and $\nu_9(\text{E})$ at 299 cm^{-1} .

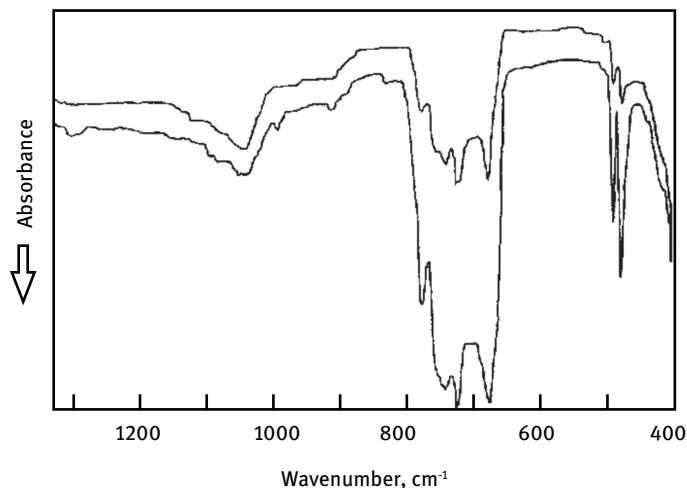


Figure 36: Infrared spectrum of solid ClF_5 at 77 K. (Reprinted and modified from [301], with permission from © 1971 Elsevier; permission conveyed through Copyright Clearance Center Inc.)

The matrix IR and the gas phase Raman spectra of ClF_5 were recorded and all basic vibration frequencies, their isotopic shifts and relative intensities were determined [302]. A semiempirical CNDO/2 calculation of the dipole moment function of ClF_5 was used for analysis of the IR intensities and a comparison with measured data. The wave numbers of IR and Raman lines of ClF_5 as a solid in an Ar matrix, as a liquid, and in the gas phase with their vibration assignments are summarized in Table 35.

The left part of Table 35 contains the frequencies and relative intensities of the IR bands of ClF_3 in an Ar matrix. The band frequencies for the gas phase from Begun and Fletcher 1965 are given for comparison. Isotopic splitting is not observed in the gas phase, and the bands are assigned to the ^{35}Cl isotope, whose natural concentration exceeds that of ^{37}Cl by approximately a factor of two. The vibrations ν_3 , ν_8 , and ν_1 , ν_7 correspond to two pairs of close-lying lines, which cannot be separated in the gas phase, but are well resolved in the matrix. The IR spectrum of ClF_5 in the Ar matrix is similar to that obtained by Christie [301], but was taken with higher resolution. Figure 37 shows a portion of the ClF_5/Ar spectrum in the region of the ν_3 and ν_8 vibrations.

Table 35: Infrared and Raman spectra and vibration assignments of chlorine pentafluoride.

Vibration	IR spectrum		Raman spectrum		
	In Ar matrix	Gas phase ^a	Gas phase	Liquid phase ^b	
ν_1	³⁵ Cl 718.7 (6)	723 (35)	709 (30)		
ν_1	³⁷ Cl	714.2			
ν_2	³⁵ Cl	539 (0.1)	541	545 (12)	538 (10)
ν_3	³⁵ Cl	483.8 (3)	486	487 (100)	480 (100)
ν_3	³⁷ Cl	480.3			
ν_4			498 (30)		
ν_5			317 (0+)		
ν_6			385 (0.5)	375 (10)	
ν_7	³⁵ Cl	725.4 (100)	732	730 (9)	
ν_7	³⁷ Cl	712.7			
ν_8	³⁵ Cl	495.7 (0.7)			
ν_9	³⁵ Cl	299 (0.3)	302	300 (0+)	296 (0+)

^a source: [300]^b Numbers (in parentheses) indicate relative intensity of the spectral bands

Data source: [302]

Figure 38 shows the overlapping bands belonging to the ν_7 and ν_1 vibrations of both isotopic molecules together with their separate contours. It is interesting to note the doublet structure of the ν_7 band, which has a matrix origin.

The IR spectra of ClF₅ were studied in the gas phase and in solutions in liquid Kr ($T=130\text{ K}$) and Xe ($T=180\text{ K}$) under pressure over a wide frequency range (2500–200 cm⁻¹), including the third-order transition region [303]. The frequencies of >50 vibrational bands were measured and identified. The integral absorption coefficient of the $\nu_7(\text{E})$ band of ³⁵ClF₅ was determined in addition to the relative intensities of all observed ClF₅ bands, anharmonicity constants of some vibrations, and isotopic shifts for a series of bands. The different nature of the Cl–F_{axial} and Cl–F_{equatorial} bonds becomes distinct when looking at the IR spectra of ClF₅.

Accidental releases of XF₃ and XF₅ (X=Cl or Br) from industrial operations may be regarded as being among the most dangerous components in the hazardous emissions from electronic or nuclear material manufactures. The Cl and Br fluorides interact quickly with atmospheric moisture resulting in the formation of hydrogen halide, Cl and Br oxyfluorides and oxides, which are transformed into stable adducts (HHal)_x⋯(H₂O)_y, where Hal equals F, Cl, Br; $x+y \geq 2$. Vibrational spectra of the interhalogens were recorded as part of a study into reaction mechanisms with XF₃ and XF₅ compounds, their secondary hydrolysis products and the applicability of the remote laser sensing analytical techniques [304].

The infrared intensities (and wave numbers) for the fundamental vibrations of ClF₅, BrF₅, and IF₅ can be predicted by computational chemistry [305]. Comparison of the calculated intensities with the experimental spectra of XF₅ molecules revealed

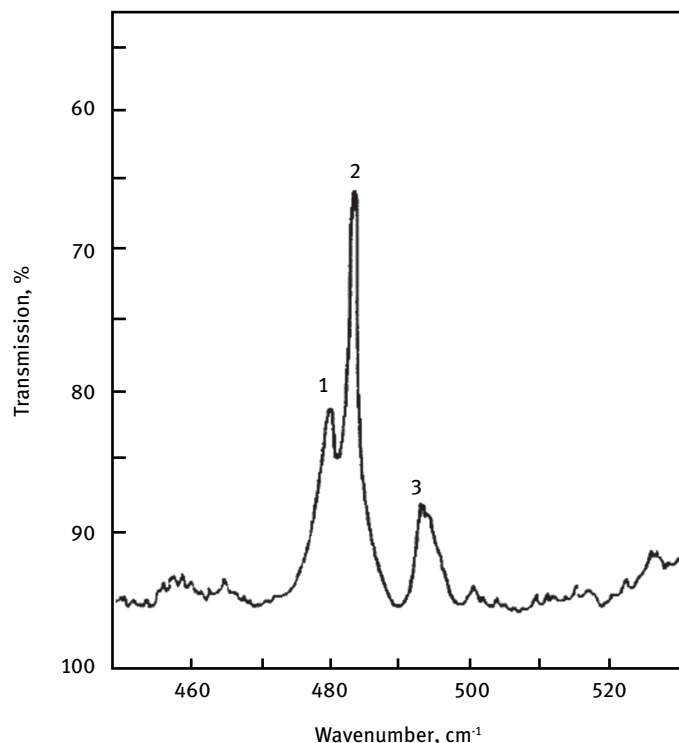


Figure 37: Infrared spectrum of frozen ClF_5 in an argon matrix in the long wavelength range. (Republished and modified from [302], with permission of © 1986 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

that the predicted values were in fairly good agreement with the experimental values. The model and procedure allowed prediction of intensities of binary combination and overtone bands as well as fundamental vibrations.

Raman Spectra of Chlorine Pentafluoride

The Raman spectrum of RbClF_4 confirmed the square-planar structure (D_{4h} symmetry) of ClF_4^- in RbClF_4 [306]. Force constants for ClF_4^- indicated that the bonding in ClF_4^- is best described by the semiempirical molecular orbital model involving mainly two delocalized p -electron pairs of the Cl atom for the formation of two semi-ionic three-center four-electron p - σ bonds. A very unusual occurrence of two bending modes at a frequency higher than that of one of the stretching modes has been observed in the vibrational spectra of ClF_4^- and the approximate square-planar part of the ClF_5 molecule can be compared with ClF_4^- . The assignments of the vibrational modes and force constants reported by Begun, Fletcher, and Smith [300] for ClF_5 were confirmed.

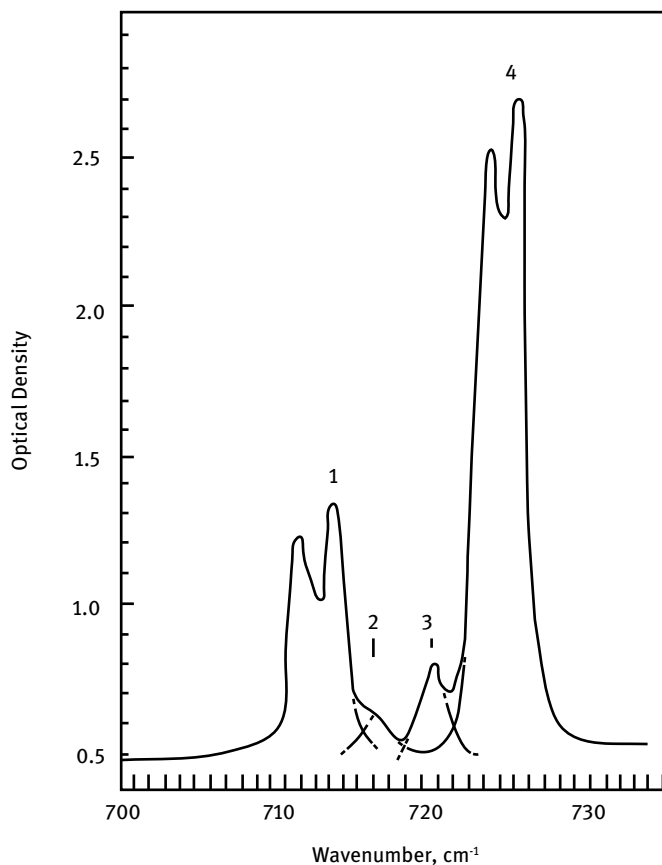


Figure 38: Infrared spectrum of frozen ClF_5 in an argon matrix in the short wavelength range. (Republished and modified from [302], with permission of © 1986 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

Raman spectra of ClF_5 have been investigated in the condensed phases between room temperature and 4 K [307]. XRD and neutron diffraction patterns showed that the three solid phases previously described by NMR measurements are as follows. Solid I ($161\text{ K} < T < 181\text{ K}$), which is a body-centered cubic with $a = 5.7\text{ \AA}$, and its Raman spectrum were quite comparable with that of the liquid. Solid II ($117\text{ K} < T < 161\text{ K}$), which is orthorhombic with $a = 6.17\text{ \AA}$, $b = 7.22\text{ \AA}$, $c = 7.66\text{ \AA}$; according to the Raman spectra its structure seemed to be similar to that of solid BrF_5 . The structure of solid III ($T < 117\text{ K}$) had not been determined. However, the vibrational spectra showed that it was not very different from solid II. The structures of the tri- and pentafluorides of chlorine and bromine are very similar.

Raman spectra of ClF_5 were recorded in the condensed phases between room temperature and 4 K. The reorientation motions in the liquid phase (295 to 180 K) were deduced from Raman band shape analysis [308].

The Raman spectrum of ClF_5 in the gas phase is shown in Figure 39. The frequencies of the fundamental bands are given on the right-hand side of Table 35, where they are compared with frequencies for the liquid phase.

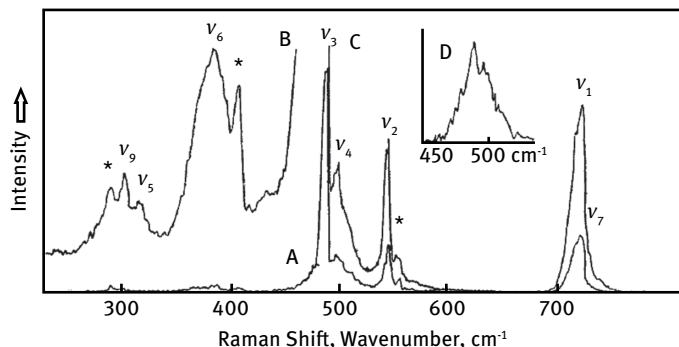


Figure 39: Raman spectrum of ClF_5 gas. (Republished and modified from [302], with permission of © 1986 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

Ultraviolet/Visible Range Spectra of Chlorine Pentafluoride

The UV spectrum of ClF_5 is continuous. The absorption coefficients of ClF , ClF_3 , and ClF_5 were measured using a continuous spectrum source with a resolving power of 0.5 nm in the range from 160 to 300 nm [309]. The UV spectra of ClF_5 and several other halogen fluoride compounds are shown in Figure 40.

Microwave Spectra of Chlorine Pentafluoride

The rotational spectra of $^{35}\text{ClF}_5$ and $^{37}\text{ClF}_5$ were measured in the frequency range from 70 to 140 GHz and the molecular parameters (inertia, bond lengths) were calculated [311]. The $|K| = 2$ type splitting could be identified. A few years later, microwave spectra of ClF_5 were studied at frequencies up to 210 GHz and a new interpretation of the absorption lines gave better determination of the rotational parameters, the molecular structure, and force constants [312].

Several rotational transitions in the ground vibrational state of gaseous $^{35}\text{ClF}_5$ and $^{37}\text{ClF}_5$ were measured in the microwave spectrum [313]. From the frequency data the following constants were derived: $B_0(^{35}\text{ClF}_5) = 3550.272(4)$ MHz; $B_0(^{37}\text{ClF}_5) = 3545.885(4)$ MHz; $D_J = 0.76(9)$ kHz; $D_{JK} = -0.67(15)$ kHz; $eQq(^{35}\text{ClF}_5) = 43.93(8)$ MHz; $eQq(^{37}\text{ClF}_5) = 34.63(6)$ MHz; dipole moment $\mu = 0.586(10)$ D. The bond angle $\text{F}_{\text{axial}}-\text{Cl}-\text{F}_{\text{equatorial}}$ was estimated to be $86.5(1.0)^\circ$.

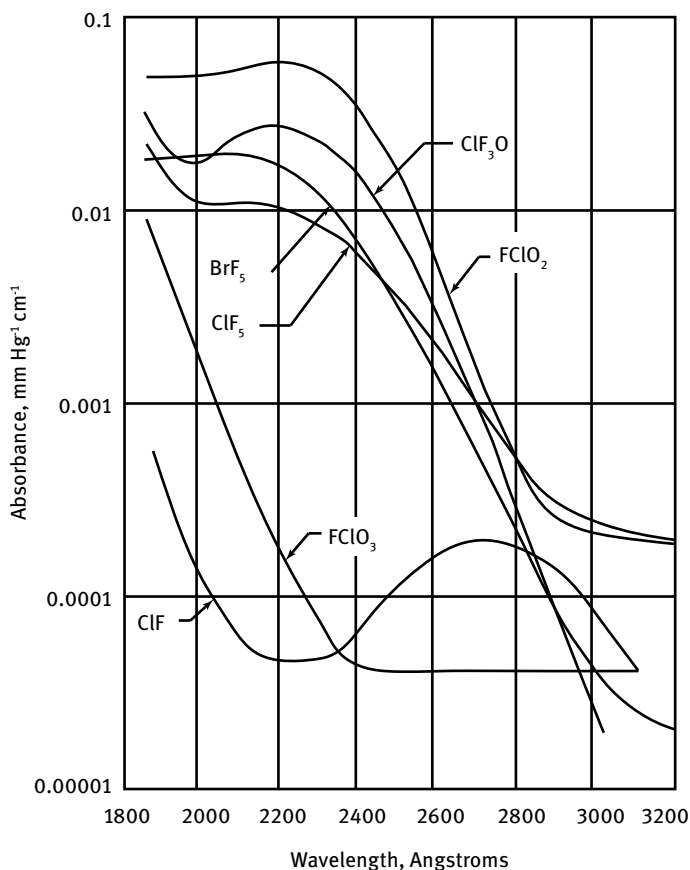


Figure 40: Ultraviolet absorption spectra of chlorine pentafluoride and other halogen fluorides. (Reprinted and modified from [310], with permission from © 1972 American Chemical Society; permission granted through RightLink.)

NMR Spectra of Chlorine Pentafluoride

^{19}F NMR spectra confirmed the tetragonal-pyramidal structure of ClF_5 , which was assumed on the basis of microwave spectra. ClF_5 spectra were found to be composed of a doublet with an intensity ratio 1:1 of hyperfine structure components in a strong field (F atoms at the base of the pyramid), and by a quintet with 1:2:4:2:1 in a weak field (F atom at the top of the pyramid) [314]. Chemical shifts of the doublet and quintet are -337 and 504 ppm, respectively, with a constant of spin-spin interaction of fluorine atoms at the J-level of 131 Hz. The absence of non-equivalent F atom exchange can be concluded from the temperature independence of component intensity and width in the temperature range from 183 to 293 K (-90 to $+20^\circ\text{C}$). A comparison with IF_5 and BrF_5 showed a decrease in F atoms' non-equivalency in going from Cl to I. For the

mixtures of ClF_3 (20 mass-%) and ClF_5 , no complex formation was observed, but the formation of complex compounds was concluded for solutions of ClF_5 (12.7, 16.5, and 25 mol %) in an excess of SbF_5 .

The high-resolution ^{19}F NMR spectrum of ClF_5 consisted of a doublet and quintet with relative intensities of 1:4 (an AB₄ system) [315]. This is consistent with a square pyramidal structure with four F atoms in the base and one non-equivalent F atom at the apex. The quintet was 170 ± 3 ppm downfield from the doublet, which was 280 ± 3 ppm upfield from trifluoroacetic acid (external standard). The coupling constant between the apical and base F atoms was 133 ± 3 Hz. For comparison, the internal chemical shifts for BrF_5 and IF_5 were also measured and found to be 130 ± 3 and 42 ± 3 ppm respectively. A study of the spectra in the temperature range from 183 to 293 K (–90 to +20 °C) showed little effect on line shapes, indicating an extremely slow exchange of the apical F. Temperature broadening was more apparent in BrF_5 and even greater in IF_5 , indicating that a self-ionization mechanism is involved in the exchange process.

Nuclear relaxation time measurements and interpretations of absorption line shape in ClF_5 and ClOF_3 provided molecular structure data for these compounds [316]. Thus, the chemical shift between non-equivalent fluorine atoms in ClOF_3 was equal to 50 ± 2 ppm. The coupling constant chlorine ^{35}Cl –fluorine was 192 Hz for the axial fluorine and less than 20 Hz for the equatorial fluorines. The mean coupling constant chlorine–fluorine in ClOF_3 and ClF_3 was obtained, in addition to other information, such as exchange times between fluorine atoms in ClOF_3 .

The ^{19}F NMR line shape and relaxation in solid ClF_5 were recorded from melting point down to liquid nitrogen temperature [317]. ^{19}F NMR and ^{35}Cl NMR and nuclear quadrupole resonance (NQR) together yielded information about phase transitions and molecular motions in ClF_5 . In particular, a new solid–solid transition was found at 117 K. ^{35}Cl wide-line and ^{19}F high-resolution NMR spectra were obtained in the high temperature phase S I, which turned out to be a plastic phase where molecular reorientations ($\tau_g = 8 \times 10^{-12}$ s) are nearly as fast as in the liquid. In addition to the reorientation, there was a much slower translational diffusion, the main characteristics of which were derived from ^{19}F T_1 and $T_{1\rho}$ measurements. In the low temperature phases S II and S III, the ^{19}F T_1 is due to rotations of the molecules by jumps around their C_4 axis ($\tau_r = 10^{-8}$ s at 110 K).

The ^{35}Cl nuclear quadrupole resonance frequency ν_q was studied as a function of temperature between 4.2 and 135 K [318]. No break was seen on either the $\nu_q(T)$ curve or its derivative, in spite of a phase change observed in the ^{19}F NMR at 117 K. The quadrupole coupling constant can be interpreted in terms of the occupancy of the 3p orbitals on Cl as predicted by MO calculations and compared with the value found by microwave spectroscopy. A value of the lowest libration frequency ($\nu \approx 30 \text{ cm}^{-1}$) was obtained, which was also consistent with the value of the relaxation time, T_1 , of ^{35}Cl nuclei.

A very detailed summary of nuclear relaxation and molecule motions in six different halogen fluorides was published in a French report [319]. The NMR and NQR spectra of solid phases of ClF_3 , BrF_3 , ClF_5 , BrF_5 , IF_3 , and IF_7 were recorded and compared. The relaxation times relate to molecular motion. The three solid phases of ClF_5 and the four solid phases of IF_7 were studied in detail. In both ClF_5 and IF_7 the high temperature phases are plastic phases. At low temperatures along with fast rotations about the molecule's axis a tilting of the axis occurs in ClF_5 and an intermolecular F-exchange was observed in IF_7 .

2.3.2.14 Molecular Structure of Chlorine Pentafluoride

Prior to the actual discovery of ClF_5 , chemists were already speculating about what molecular structure this molecule might have. Chlorine pentafluoride seems to possess the molecular structure of a quadratic bipyramid similar to that of BrF_5 and XeOF_4 (Figure 41).

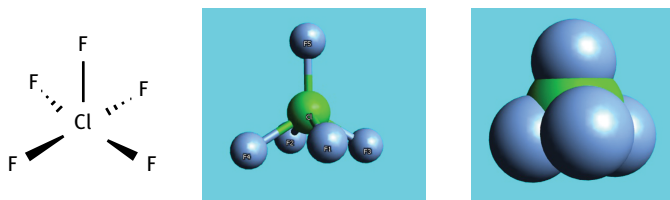


Figure 41: Molecular structure of chlorine pentafluoride

Electron diffraction spectroscopy is an advanced method for identifying the crystalline structure of solid ClF_5 and the structure of the ClF_5 molecule [320]. Electron-diffraction measurements showed that the ClF_5 molecule has a tetragonal pyramid structure (C_{4v}) with the Cl atom and one F atom out of the 4 F-atom plane. The interatomic distances and angles can be determined by this method.

The dielectric constant of ClF_5 gas at 297 K is 1.00279 ± 0.00007 at 10 MHz. The dielectric constant as a function of temperature between 193 and 256 K (−80 and −17 °C) is

$$\epsilon = -0.015t + 3.08$$

where t is the temperature in °C.

Computational Chemistry: Illuminating the Molecular Structure of Chlorine Pentafluoride

Molecular orbital populations of atomic orbitals, and effective charges of atoms in ClF_5 obtained by an MO LCAO self-consistent field method showed that the bond in ClF_5 can be qualitatively described by one axial two-center bond, Cl–F, and by two equatorial

three-center bonds, F—Cl—F, with highly delocalized molecular orbitals [321]. With an increasing number of F atoms, the covalence character of the Cl—F bond increased with a considerable increase of the 3d-atomic orbital contribution.

2.3.2.15 Electrical Properties of Chlorine Pentafluoride

Electrical Conductivity of Chlorine Pentafluoride

The specific electric conductivity of liquid ClF₅ is below $1.3 \times 10^{-9} \text{ Ohm}^{-1} \text{ cm}^{-1}$ over the temperature range from 193 to 256 K (–80 to –17 °C) [277]. Another data point is $0.45 \times 10^{-9} \text{ Ohm}^{-1} \text{ cm}^{-1}$ at 256 K (–17 °C). The values of specific conductivity and dielectric constant of liquid ClF₅ are lower than those of ClF₃ at any given temperature.

Dielectric Constant of Chlorine Pentafluoride

The dielectric constant of liquid ClF₅ as a function of temperature in the temperature range 193–256 K (–80 to –17 °C) is a simple linear function

$$\varepsilon = 3.08 - 0.015t$$

where ε is the dielectric constant and t is the temperature in °C [277]. The dielectric constant of gaseous ClF₅ at room temperature was 1.00279 ± 0.00007 .

Dipole Moment of Chlorine Pentafluoride

Based on rotational transitions in the ground vibrational state of gaseous ³⁵ClF₅ and ³⁷ClF₅ the dipole moment was calculated to be $\mu = 0.586(10) \text{ D}$.

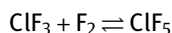
2.3.3 Chemical Properties of Chlorine Pentafluoride

Early observations already indicated that chlorine pentafluoride is not quite as aggressive an oxidizer as fluorine or chlorine trifluoride. This may be partially caused by the symmetry of the molecule. It is still sufficiently reactive to be hypergolic with most fuels, but not quite as corrosive when interacting with materials of construction.

2.3.3.1 Thermal Stability of Chlorine Pentafluoride

Based on theoretical considerations, chlorine pentafluoride should be as stable as xenon tetrafluoride. It appears that chlorine pentafluoride may decompose at elevated temperatures in reversal of its formation from chlorine trifluoride and fluorine. Such a decomposition would be very undesirable if it occurred during long-term storage in a propellant tank as the tank pressure could rise substantially to the point of tank rupture.

Depending on the conditions, the reaction



can proceed in either direction. The equilibrium, which allows the formation of ClF₅, also limits its thermal stability [270]. The progress of the reaction at temperatures be-

tween 484 and 544 K was monitored by measuring the pressure rise with time. The data were fitted to a van't Hoff equation in the form of $\ln K_p = (9175/T) - 21.30$, which gave a heat of reaction of -76.1 ± 3.8 kJ/mol (-18.2 ± 0.9 kcal/mol) and an entropy of reaction of 42.3 ± 1.8 e.u.

The homogeneous gas phase decomposition kinetics of chlorine pentafluoride were determined in the temperature range from 525 to 580 K (252–307°C) using an electrically heated, stirred flow reactor with a retention volume of 91 mL and made from Monel metal, and gave a dissociation energy of 154.8 kJ/mol (37 kcal/mol) [322]. The dissociation energy at 400 K was -77 kJ/mol (-18.5 kcal/mol). A least squares fit of the data to the Arrhenius equation gave

$$k_1 = 10^{13.02} \exp(-36800/RT) \text{ s}^{-1}$$

A non-chain radical mechanism appeared to be most likely. In a similar evaluation [38] Blauer et al. [111] concluded that the thermal dissociation of ClF_5 at elevated temperatures is well described by the statistical theory of unimolecular reaction rates. The activation energy of experimentally observed first-order dissociation in a shock tube was 196.6 ± 8 kJ/mol (47 ± 2 kcal/mol), in agreement with dissociation rate constants derived from statistical theory, but quite different from results in flow reactors or static reactors.

Other investigators made a study of the dissociation of ClF_5 in a flow reactor over the temperature range 525–581 K. The course of the reaction was monitored by means of IR spectroscopy. Empirically, it was found that the reaction is unimolecular and the rate constant was given as

$$k_1 = 10^{18} \exp(-36800/RT) \text{ s}^{-1}$$

The thermal dissociation of ClF_5 was investigated using two different techniques over the temperature range 520 to 1120 K [323]. At temperatures above 800 K the course of the reaction of 0.17–4.5% ClF_5 in argon occurring behind incident shock waves was followed by monitoring of the UV absorption of the reacting system at 2200 Å. ClF_5 has a very large extinction coefficient relative to those for F_2 and ClF at 2200 Å. Although ClF_3 also has a large extinction coefficient at this wavelength, its presence can be accounted for by a correction. The pressure exponent n had a value of 0.7 ± 0.2 . The resulting 1.7th order rate constant had the form

$$k_{11} = 10^{15.8} \exp(-41500 \pm 2500/RT) \text{ mL}^{0.7} \text{ mol}^{-0.7} \text{ s}^{-1}$$

or a first-order rate constant of

$$k_{10} = 0.16 \times 10^{14} \exp(-42403/RT) \text{ s}^{-1}.$$

At lower temperatures the study was conducted with static reactors, which were coupled to a mass spectrometer where the course of the dissociation at low temperatures

was followed by monitoring evolved F_2 at m/e 38 and ClF_4^+ at m/e 111. The rate constant for the static reactor was

$$k_d = 10^{16 \pm 1} \exp(-46300 \pm 2300/RT) \text{ s}^{-1}$$

The unimolecular decomposition rate constants were compared with predictions of a statistical theory. The statistical theory was found to give a good description of the data taken at elevated temperatures; however, it was at great variance with data taken from the static reactor. The difference was attributed to wall effects in the static reactor. The addition of large amounts of NO or ClF to the reacting mixture appeared to have no significant effect on the rate constant.

In a similar study using a 92-mL stirred flow reactor and measuring the disappearance of ClF_5 by measuring the change in its IR absorption at $12.5 \mu\text{m}$, the first-order rate constants obtained over the temperature range 525–580 K (252–307 °C) were expressed by the Arrhenius equation [324]:

$$k_1 = 10^{15.20} \exp(-43034/RT) \text{ s}^{-1}$$

2.3.3.2 Reactions of Chlorine Pentafluoride

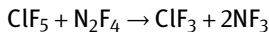
Reactions of ClF_5 with several hundred inorganic and organic chemicals were tested and described in the ClF_5 Handbook [289].

Reactions of Chlorine Pentafluoride with Inorganic Compounds

The binary chlorine fluorides ClF, ClF_3 , and ClF_5 , when used in excess, all undergo facile fluorine–oxygen exchange reactions with the nitrate anion, forming $FClO_2$, unstable $FCIO$, and $ClONO_2$ respectively as the primary products [325]. Whereas $FCIO_3$ does not react with $LiNO_3$ at temperatures as high as 348 K (75 °C), $FCIO_2$ readily reacts with either $LiNO_3$ or N_2O_5 to give $ClONO_2$ and O_3 , probably via the formation of an unstable O_2ClONO_2 intermediate. With an excess of ClF, chlorine nitrate undergoes a slow reaction to give $FCNO_2$ and Cl_2O as the primary products, followed by Cl_2O reacting with ClF to give Cl_2 , ClF, and $FCIO_2$. The alkali–metal fluorides CsF, RbF, and KF catalyze the decomposition of ClF_5 to ClF_3 , and F_2 .

If using an oxygen source other than nitrate ion, the fluorine in ClF_5 can be gradually replaced by oxygen, forming chlorine oxide fluorides while maintaining the state of oxidation of the central chlorine atom. The reaction of potassium dinitramide $KN(NO_2)_2$ with ClF_5 leads to stepwise replacement of two fluorine ligands by a doubly bonded oxygen atom. Thus, $KN(NO_2)_2$ readily reacted with ClF_5 at 260 K (–13 °C) producing an equimolar mixture of $KClOF_4$ and $KClF_4$ [326]. The formation of $KClOF_4$ is remarkable because with most fluorine–oxygen exchange reagents, such as NO_3^- , the exchange process cannot be interrupted at the $ClOF_4$ stage and proceeds all the way to $FCIO_2$ as the only product.

The reaction of ClF_5 with N_2F_4 prevents the use of mixtures of these two very desirable oxidizers. The reaction



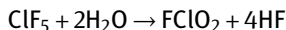
starts to take place at room temperature. It is not facilitated by the ClF_5 first decomposing into ClF_3 and F_2 , but proceeds directly. F_2 is not an intermediate in this reaction [324]. If this reaction proceeds via a direct bimolecular process, then the kinetic rate equation may be

$$k_2 = 10^{12.20} \exp(-25760/RT) \text{ L mol}^{-1} \text{ s}^{-1}$$

Thus, the half-life for a mixture containing 1 atm of N_2F_4 and 1 atm of ClF_5 at 344 K (71 °C) would be approximately 225 days.

Reactions of Chlorine Pentafluoride with Water

In the presence of an excess of ClF_5 and in the absence of catalytic metal, the hydrolysis of ClF_5 can go to an intermediate product of chloryl fluoride



but with an excess of water and in the presence of metals that catalyze the decomposition of FClO_2 , the products are ClO_2 , FClO_3 , and HF:



where one has to remember that ClO_2 is unstable, explosive, and extremely sensitive. The interaction of ClF_5 with water in anhydrous HF solutions was investigated by means of Raman spectroscopy [327]. The reaction between ClF_5 and H_2O yielded only one product (ClO_2F) regardless of the temperature of the process, quantity, and concentration of chemicals. ClOF_3 did not form during interaction of ClF_5 with hydroxides of the following metals: Ni, Mn, Al, and Si. The interaction in the system $\text{H}_3\text{OBF}_4/\text{HF}/\text{ClF}_5$ in the temperature range 293–273 K resulted in a practically quantitative yield of $[\text{ClOF}_2]^+[\text{BF}_4]^-$.

Dinitrogen tetroxide was found to be incompatible with ClF_5 , resulting in a pressure rise in excess of 2.41 MPa (350 psia) after 18 h when samples were mixed and stored in a closed container.

2.3.3.3 Lewis Addition Compound and Complex Salt Formation Reactions with Chlorine Pentafluoride

Chlorine pentafluoride forms stable salts with Lewis acids. These salts have been evaluated as potential solid gas generant oxidizers that would release fluorine or chlorine fluorides on ignition and thus constitute a convenient and safe method of storing fluorine or chlorine fluorides for later use in rocket propellants or lasers.

Chlorine mono-, tri-, and penta-fluoride are quite reactive. Of these, the first two compounds show amphoteric character and form ionic complexes with strong Lewis acids and bases. Thus, ClF forms with strong Lewis acids the FCl_2^+ cation [46], and with strong Lewis bases the ClF_2^- anion. Similarly, the ClF_2^+ cation and ClF_2^- anion have been prepared from ClF_3 . The reactions with ClF_5 were different [328]. ClF_5 and AsF_6 , when mixed at 195 K (-78°C), produced the 1:1 adduct $\text{ClF}_5 \cdot \text{AsF}_5$, a white, crystalline solid. A heat of formation of $[\text{ClF}_4]^+[\text{AsF}_6]^- (\text{S})$, $\Delta H_{298}^\text{f} = -1576 \text{ kJ/mol}$ (-376.8 kcal/mol) was calculated for this compound. The heat of dissociation obtained for $[\text{ClF}_4]^+[\text{AsF}_6]^- (\text{S})$ was 105.6 kJ/mol (25.23 kcal/mol). The 1:1 combining ratio was established by quantitative synthesis and IR measurements of the gas phase above the solid complex. The latter measurements showed that the complex was completely dissociated in the gas phase at 298 K (25°C). Similarly, ClF_5 and SbF_5 , when combined either under pressure or in HF solution, formed the 1:1 adduct. The tendency to form adducts with ClF_5 decreased in the order $\text{SbF}_5 > \text{AsF}_5 > \text{BF}_3$, and was the same as that observed for other halogen fluorides such as ClF_3 or ClF.

Tetrafluorochloronium(V), Hexafluorochloronium(VII), and Hexafluorochlorate(V) Complexes from Reactions of Chlorine Pentafluoride with Inorganic Compounds

In comparing the stability of the various fluoro-chlorine ions among themselves, and comparing it with that of tetrafluoroammonium salts, it is interesting to note that the two most promising energetic oxidizer cations are NF_4^+ and ClF_6^+ . Their central atoms are in their highest oxidation states (N^{+4} and Cl^{+7}) and they possess a high fluorine content. Although the N—F and Cl—F bond energies are relatively low, which make them powerful reactive oxidizers, these bond energies are high enough to give them good stability. Furthermore, these two ions possess outstanding kinetic stability owing to their energetically favorable structures (tetrahedron for NF_4^+ and octahedron for ClF_6^+). This is also reflected by the fact that NF_4^+ and ClF_6^+ are isoelectronic with CF_4 and SF_6 respectively, which are the two most thermally stable covalent inorganic fluorides.

ClF_6PtF_6 , which is useful as an oxidizer for rocket propellants and in the preparation of other oxidizing agents containing chlorine in the +7 valence state, can be prepared by reaction of PtF_6 and ClF_5 at 195–77 K (-78 to -196°C) under UV light in a sapphire reactor [329]. After condensation, the mixture was slowly heated to room temperature, exposed to UV light, and held under vacuum for 5–14 days at $<358 \text{ K}$ ($<85^\circ\text{C}$), during which time ClF_4PtF_6 , the condensation product in the absence of UV, which is formed in about equimolar proportions with ClF_6PtF_6 , decomposed, leaving a solid PtF_4 residue. For example, 1.26 mmol PtF_6 and 3.78 mmol ClF_5 were condensed at 77 K (-196°C) in a sapphire reactor under UV irradiation and the product held under vacuum and irradiation for 8 days at 295–296 K (22 – 23°) to give 0.489 g of a bright-yellow solid containing 81% ClF_6PtF_6 and 19% PtF_4 .

The identity of a stable species having an 890 cm^{-1} infrared absorption as ClF_6^+ was unambiguously established by ^{19}F NMR and vibrational spectroscopy [330]. The vibrational spectrum of ClF_6^+ was compared with that of isoelectronic SF_6 .

The vibrational spectra of $\text{ClF}_4^+\text{AsF}_6^-$, $\text{ClF}_4^+\text{SbF}_6^-$, and $\text{ClF}_4^+\text{PtF}_6^-$ were compared with those of the corresponding BrF_6^+ and IF_6^+ salts [331]. All fundamentals were assigned and a valence force field was computed for ClF_4^+ .

As the techniques that had successfully been used for the synthesis of NF_4^+ salts did not result in ClF_6^+ , other fluorinating agents were investigated. The ClF_6^+ cation was prepared in the form of its PtF_6^- salt from the reactions of PtF_6 with either FCIO_2 , or ClF_3 [332]. A displacement reaction between $\text{ClF}_6^+\text{PtF}_6^-$ and FNO at -78°C yielded only ClF_5 and F_2 , indicating that ClF_7 cannot exist under the given reaction conditions. Attempts were unsuccessful to prepare $\text{ClF}_6^+\text{BF}_4^-$ by low-temperature glow discharge of a $\text{ClF}_5/\text{F}_2/\text{BF}_3$ mixture, to prepare ClF_6^+ salts from ClF_5 , F_2 , and the Lewis acids SbF_5 , AsF_5 , or BF_3 at elevated temperatures and pressures, or to prepare ClF_6^+ salts either from ClF_3O and PtF_6 or from ClF_3O , F_2 , and SbF_5 . Iridium hexafluoride was found to be too weak an oxidizer to produce any heptavalent, chlorine-containing cations from FCIO_3 .

For a long time the only known ClF_6^+ salt was $\text{ClF}_6^+\text{PtF}_6^-$, which could be prepared only as an inseparable mixture with ClF_4PtF_6 . Using KrF_2 as the oxidizer, it was possible to prepare pure $\text{ClF}_6^+\text{AsF}_6^-$ and $\text{ClF}_6^+\text{SbF}_6^-$ [333]. The salts were thoroughly characterized and exhibited very good thermal stability.

In order to increase the energy content of ClF_6^+ salts, the weight of the non-energetic counter ion must be minimized. This goal was achieved by replacing AsF_6^- by BF_4^- using low-temperature metathetical techniques previously developed for NF_4^+ salts [334]. ClF_6BF_4 is a white crystalline solid that is highly soluble in anhydrous HF . It is stable at room temperature and starts to slowly decompose under a dynamic vacuum at about 343 K (70°C) according to



The nature of the decomposition products was established by their IR spectra, which showed only the absorptions characteristic for BF_3 and ClF_5 . The $\text{ClF}_6^+\text{BF}_4^-$ also exhibited good thermal stability and is a potentially useful oxidizer. Attempts to replace the non-energetic BF_4^- anions by the energetic ClO_4^- anion were only partially successful [335]. By analogy with NF_4ClO_4 [336], ClF_6ClO_4 was found to be thermally unstable. However, as with NF_4ClO_4 , the decomposition of ClF_6ClO_4 provided a new, high-yield synthesis of the interesting hypofluorite, FOClO_3 .

Salts of the composition $[\text{ClF}_6^+][\text{BiF}_6^-]\cdot\text{BiF}_5$ and $[\text{ClF}_6^+][\text{Bi}_2\text{F}_{11}^-]$ have been synthesized by high temperature and pressure fluorinations [337, 338]. The products have been characterized by elemental analysis and by comparison of IR, XRD, and NMR spectroscopic data, thermal stability and chemical reactivity behavior with those of the $[\text{ClF}_2^+][\text{BiF}_6^-]$ and $[\text{ClF}_4^+][\text{BiF}_6^-]$ salts.

The synthesis of hexafluorochloronium(VII) hexafluoroplatinate(V), $[\text{ClF}_6^+][\text{PtF}_6^-]$, from the reaction of ClF_5 and PtF_6 was described as an oxidation-reduction reaction. This has been confirmed by elemental analyses, IR and Raman spectroscopy, XRD, and displacement reaction with trifluorochlorine oxide [339]. This was the first example of a perfluorinated heptavalent chlorine cation. Based on preliminary XRD powder pattern, $[\text{ClF}_6^+][\text{PtF}_6^-]$ has a cubic structure.

Vibrational spectra have been recorded for the known adducts $\text{ClF}_5 \bullet \text{AsF}_5$, $\text{ClF}_5 \bullet x\text{SbF}_5$ ($x=1.08$ and 1.36), $\text{BrF}_5 \bullet 2\text{SbF}_5$, and $\text{IF}_5 \bullet \text{SbF}_5$. The spectra of the ClF_5 adduct were consistent with a predominantly ionic structure containing the ClF_4^+ cation [331].

The ClF_4^+ cation was prepared in the form of its PtF_6^- salt from the reactions of PtF_4 with either FCIO_2 or ClF_5 [332]. A displacement reaction between $\text{ClF}_4^+ \text{PtF}_6^-$ and FNO at 195 K (-78°C) yielded only ClF_5 and F_2 , indicating that ClF_7 cannot exist under the given reaction conditions. Attempts to prepare $\text{ClF}_4^+ \text{BF}_4^-$ by low-temperature glow discharge of a $\text{ClF}_5/\text{F}_2/\text{BF}_3$ mixture, to prepare ClF_6^+ salts from ClF_5 , F_2 , and the Lewis acids SbF_5 , AsF_5 , or BF_3 at elevated temperatures and pressures, or to prepare ClF_4O^+ salts either from ClF_2O and PtF_4 or from ClF_3O , F_2 , and SbF_5 were unsuccessful.

Salt formation in the $\text{ClF}_5/\text{SbF}_5$ system was studied by DTA for mixtures with 0–100% SbF_5 [340]. Three compounds, $\text{ClF}_5 \bullet \text{SbF}_5$, $\text{ClF}_5 \bullet 2\text{SbF}_5$, and $\text{ClF}_5 \bullet 4\text{SbF}_5$ were formed congruently with melting points of 393 , 337 , and 335 K (120 , 64 , and 62°C) respectively. These compounds probably consist of endless chains of ClF_4^+ and SbF_6^- , $\text{Sb}_2\text{F}_{11}^-$, or $\text{Sb}_4\text{F}_{21}^-$ ions connected by weak F^- bridges.

The ^{35}Cl , ^{75}As , and ^{181}Ta NQR spectra of $\text{ClF}_x \bullet n\text{SbF}_5$ ($x=3, 5$; $n=1, 2, 4$), $\text{ClF}_5 \bullet \text{TaF}_5$, $\text{ClF}_3 \bullet \text{MF}_5$ ($\text{M} = \text{As}, \text{Nb}, \text{Ta}$), ClF_5 , and CsClF_4 were measured [341]. Based on the ^{35}Cl NQR spectra, the acceptor capacity of anions decreased in the sequence $\text{Sb}_4\text{F}_{21}^- > \text{Sb}_2\text{F}_{11}^- > \text{AsF}_6^- > \text{SbF}_6^- > \text{NbF}_6^- > \text{TaF}_6^-$.

In extending the chemistry of high-fluorine content oxidizers to hypervalent, high-oxidation state fluorides of nitrogen, oxygen, and the halogens, typical target compounds were chlorine pentafluoride oxide, chlorine hexafluoride anion, nitrogen pentafluoride, nitrogen difluoride anion, and combinations of high oxidation state halogen fluoride anions with organic cations [342]. Special experimental techniques, such as low-temperature photolysis and glow-discharge, matrix-isolation spectroscopy, and microwave discharge reactions were explored for the syntheses of these species.

2.3.3.4 Reactions of Chlorine Pentafluoride with Organic Compounds

Chlorine pentafluoride will react hypergolically with most hydrogen-containing organic compounds. Only a few perfluorinated organic compounds are compatible with ClF_5 . Chlorine pentafluoride is compatible with and soluble in Cl_3CF or $\text{Cl}_2\text{FC}-\text{CClF}_2$ at room temperature [343]. If ^{19}F is dissolved in HF , no ^{19}F exchange takes place. Chloroform and carbon tetrachloride both react slowly with ClF_5 at room temperature to form Cl_2 and CFCl_3 . A preliminary experimental characterization of $\text{ClF}_5/\text{C}(\text{NO}_2)_4$

mixtures indicated compatibility between two compounds. Vapor pressure measurements at 271 and 293 K (0 and 20 °C) resulted in vapor pressures very near those of ideal, non-reacting mixtures.

In contrast to limited substitutive fluorination of aromatics with halogen fluorides such as ClF , ClF_3 , BrF_3 , or IF_5 , fluorination is the predominant reaction path with ClF_5 [344]. Under non-catalytic liquid phase conditions, benzene was converted to fluorobenzene (54% yield) and chlorobenzene (37% yield) respectively. One possible fluorination mechanism may involve a transition complex of ClF_5 with benzene. For a heterocyclic substrate, i.e. 2,4,6-trifluoropyrimidine, substitutive fluorination predominated over chlorination. Enhanced exchange fluorination of CCl_4 was effected with ClF_5 ($\text{CF}_2\text{Cl}_2 \gg \text{CFCl}_3 > \text{CF}_3\text{Cl}$) as compared with ClF_3 ($\text{CFCl}_3 \gg \text{CF}_2\text{Cl}_2$).

2.3.3.5 Analysis of Chlorine Pentafluoride

At the time when the USAF still procured ClF_5 for rocket applications, the ClF_5 that was supplied to the Air Force had to be in conformance with Military Specification MIL-P-27413 (tentative). This specification required a ClF_5 assay of at least 99.5 mass-% as determined by GC, and the maximum HF content as determined by IR was 0.2 mass-%.

Glass in a mass spectrometer inlet must be avoided because it creates spurious SiF_4 peaks and all glass in the inlet system of the original apparatus has been replaced with Monel and Teflon. Fluorine gas at 700 mm Hg was used to passivate the inlet manifold. Oxygen difluoride mass spectra displayed rhenium oxyfluorides as the result of sample corrosive interaction with a rhenium filament in the source. Mass spectrometric analysis of ClF_5 (Figure 42) showed that the two strongest peaks were $^{35}\text{ClF}_2^+$ and $^{35}\text{ClF}_4^+$ [345, 346]. There was no neutral $^{35}\text{ClF}_5$ peak. HF, SiF_4 , organofluoride, HBr,

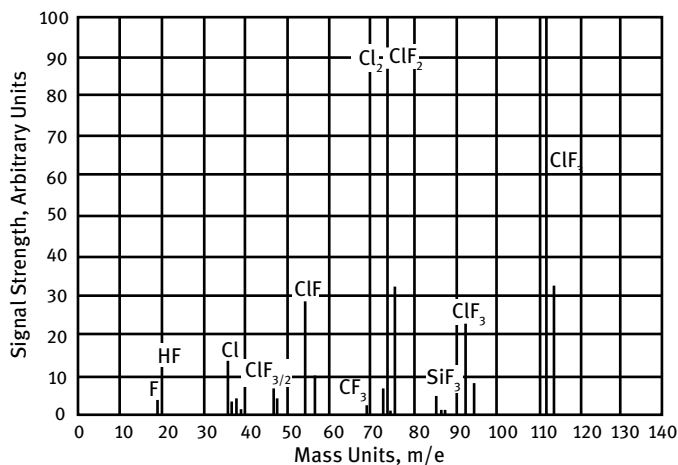


Figure 42: Mass spectrum of chlorine pentafluoride. Ionization Voltage 50 eV. (Reproduced and modified from [346].)

BrF, and HCl were detected as contaminants in the as-received ClF₅. Mass spectra of BrF₅ were made in the same apparatus for comparison.

Low-temperature mass spectrometry of fluorine-containing compounds can be done with a cryogenic inlet system built for a mass spectrometer [347].

The ionization of molecular beams of ClF₅ was investigated by electron-impact mass spectrometry [348]. Appearance potentials and excess kinetic energy of the ions formed were measured. The lowest value of electron affinity of ClF₂ and ClF₃ and the upper limit of the ionization potential of the ClF₄ radical could be derived from these measurements.

2.3.4 Handling of Chlorine Pentafluoride

Detailed instructions on the safe handling of ClF₅ are contained in several of the ClF₅ handbooks and propellant manuals, including *The ClF₅ Handbook* [289]. The handling precautions are similar to those practiced with elemental fluorine or ClF₃. Pressurant gas that is vented from pressurized ClF₅ tanks at the end of a test contains large amounts of ClF₅ and must be passed through a scrubber with a caustic neutralizing solution or (in remote areas) it can be fed into a propane or natural gas torch where it is flared off in a flare stack high above ground (but the combustion products still contain toxic HF). Spill neutralization methods that were developed initially for chlorine trifluoride or liquid fluorine can be applied to ClF₅ spills as well [349].

2.3.5 Materials Compatibility with Chlorine Pentafluoride

A general summary of the results from ClF₅ materials compatibility studies indicated that the behavior of ClF₅ with various structural materials is generally similar to that of ClF₃. The same as with elemental fluorine or chlorine trifluoride, all materials that come in contact with ClF₅ need to be thoroughly cleaned and degreased. Then a slow passivation, initially with ClF₅ diluted with an inert gas, allows a protective passivating fluoride film to form on the metal. The *ClF₅ Handbook* (1966) [289] contains detailed summaries of materials that are compatible with ClF₅ and other materials that are incompatible and must be avoided.

2.3.5.1 Compatibility of Chlorine Pentafluoride with Metals

Most metals that form a protective passivating layer of insoluble fluorides are compatible with ClF₅. Notable exceptions in the metals tested are molybdenum and columbium (niobium), which undergo complete reaction. The compatibility of titanium with ClF₅ is still in doubt because of conflicting results in comparison with ClF₃. The presence of moisture may have a significant detrimental effect on the rate of film formation or corrosion of the metal. Of the metals tested under conditions of moisture contamination, only Hastelloy C and nickel 200 provided complete resistance to attack.

Transition metals (Cr, Mn, Co, Ni, Pd, Pt, Cu, Zn, and Cd), which are least reactive with ClF_5 in studies to 423 K (150 °C), all form fluorides with melting points above 1123 K (850 °C).

Impact sensitivity tests were run on Al2014-T6, 347 stainless steel, nickel 200, and magnesium AZ31B in liquid ClF_5 at 303 K (86 °F) using a pressure type impact tester [350]. The striker was made from 1/8-in sheet point. It was impacted on a 1/8-in-thick base or anvil plate at energy levels from 80 to 96 J (59.4 to 71 ft-lb). For most tests the striker and anvil plate were made from the same metal. A 150-g charge of ClF_5 was used for each test. This was sufficient liquid to cover the base plate to a depth of about 9.5 mm (3/8 in). No signs of ignition were seen for duplicate runs of the four metals in ClF_5 , where the striker and anvil plate were the same metal. There was no sign of ignition of the fresh metal surface that was exposed to the liquid ClF_5 impact. In all other respects, the metals that were impacted in ClF_5 or air were unaffected by the impact exposure. Ignition could not be initiated by impacting Al 2014-T6, magnesium AZ31B, Nickel 200, or CRES-347 in liquid ClF_5 at 303 K (30 °C). Tetrafluoroethylene (TFE) similarly impacted by CRES-410 was completely consumed in a rapid, highly exothermic reaction. The same apparatus and same metals were used for impact tests in liquid fluorine and dinitrogen tetroxide. Immersion in liquid ClF_5 at up to 303 K (30 °C) resulted in moderate weight gains for TFE and Kel-F plastics, complete and rapid reaction of columbium and molybdenum to salts, degradation of blocks of carbon and graphite to powders, and no change in titanium. Corrosion rates of nine other structural metals in liquid ClF_5 at 303 and 339 K (30 and 66 °C) were low (0.2 mil/year) but increased at 339 K (66 °C) for CRES-410 and yellow brass (0.7 mil/year).

Duplicate sets of 34 different materials of construction, exposed to the liquid and vapor phases of ClF_5 for a period of 19 months, exhibited corrosion rates similar to those demonstrated previously in 30-day materials compatibility studies under both ambient-temperature and 344-K (160 °F) conditions [351]. The 34 materials included 10 aluminum alloys, 4 stainless steels, Rene 41, Inconel-X, Hastelloy-C, nickel, Kel-F 81, FEP Teflon, TFE Teflon, PH15-7 Mo, tool steel AM-350, AM-355, 7 Monel alloys, and hard copper. Each container bomb assembly was constructed from a 10-in-long, 1-in-diameter stainless-steel tubing with a stainless-steel bellows-type valve at the top and a threaded plug in the bottom. The tube was lined with Kel-F sheet to prevent galvanic corrosion between the samples and the wall of the bomb. All aluminum alloys tested suffered weight losses in both the liquid-exposed and vapor-exposed specimens. The magnitude of the weight losses, which was similar for each alloy tested, was well within the corrosion resistance rating level (<2.0 mil/year) established as “excellent.” The 300-series stainless steels showed very small weight gains in the liquid-exposed samples and some conflicting results for the vapor-exposed samples. Of the non-austenitic stainless steels tested, the PH 15-7 Mo and AM 350 samples showed slight weight gains. Long-term exposure of the nickel and nickel base alloys to liquid ClF_5 resulted in small weight gains. The copper and Monel alloys, subjected to long-term exposure to ClF_5 , experienced weight gains of relatively slight to moderate

magnitudes. Although all of the Monel surfaces were discolored and dull, evidence for the attack on the two cast Monel alloys, 505 and 507, was demonstrated in the form of surface pitting in the area of the stamped identification markings. Long-term testing of the non-metallic fluorinated ethylene propylene (FEP) Teflon, TFE Teflon, and Kel-F 81, resulted in the expected large weight gains experienced in previous testing. All of the specimens absorbed small amounts of ClF_5 with magnitudes between materials running in the order of Kel – F81 > FEP Teflon > TFE Teflon. In addition to these tests, a selected group of samples was studied in a preliminary 30-day compatibility test with moisture- and air-contaminated ClF_5 at a controlled temperature of $303 \pm 1 \text{ K}$ ($86 \pm 2^\circ \text{F}$). The effects of this closed-system exposure, evaluated on the basis of visual inspection and weight gain/loss analysis, indicated that all the materials were compatible under the test conditions. The propellant storage test bombs were 6.5 in long, 1.5 in in ID, and had a 1/8-in wall thickness. The four bombs and their top flanges were machined from 321 stainless steel, 6061 aluminum, Monel 400 (cold), and oxygen-free copper stock respectively. Each bomb contained 300 g (167 cm^3) of high-purity ClF_5 . Periodic analyses of ClF_5 samples stored at ambient temperature in 321 stainless steel, 6061 aluminum, Monel 400 and oxygen-free copper containers (initial ullage of 20 to 30%) at ambient temperature for a period of 13 months indicated an absence of propellant decomposition and/or reaction.

The results of the 30-day tests were supplemented by the results of 580-day immersion tests with the same materials [352]. The alloys most resistant to attack by ClF_5 under all conditions were Hastelloy-C, nickel 210, René 41, and Inconel X-750. Metallurgy of sectioned and polished specimens when examined under the optical microscope revealed that several of the Monel alloys (Monel 400, R-405, 500, 501, and 507) suffered severe localized attack of second phases of inclusions (stringers). The localized corrosion was severe enough to exclude the use of these alloys from long-term contact with ClF_5 . In most cases, corrosion of alloys began with the formation of a passivation layer, which resulted in weight gain, but when the passivation layer flaked off, the sample would end up with a weight loss. Raising the temperature from ambient to 344 K (160°F) considerably increased the rate of corrosion. The weight change after 30 days at 344 K (160°F) was comparable with the weight change after 580 days at ambient. There was no noticeable attack on Teflon FEP, Teflon TEF, or Kel-F81, but these materials gained a lot of weight.

Eleven metallic materials of construction were included in a program to evaluate the compatibility of liquid and gaseous fluorine and chlorine pentafluoride with metals: 301 (cryoformed), 304L, 321, and 347 stainless steel; A-286 super alloy steel; Al-2219, Al-6061; oxygen-free copper; Monel K-500; Inconel 718; and Nickel 200 [249, 353]. Six different tests were performed to evaluate compatibility of metals with stagnant or flowing gaseous and liquid ClF_5 in comparison with fluorine: (1) maximum velocity, (2) adiabatic compression (U-tube), (3) liquid impact, (4) flexing/film degradation, (5) vibration/film degradation, (6) liquid phase shock wave.

(1) In the maximum allowable flow velocity, sections of heated tubing were tested with gaseous ClF_5 in the stagnant, subsonic, and sonic flow condition. Thermocouples attached to the outside of the tubing would quickly detect incipient ignition and consumption of the tubing wall from the inside until a burn-through occurred. The data showed that velocity had a relatively small influence on the potential failure threshold temperature of any of the metals studied in either F_2 or ClF_5 . Generally, copper, the stainless steels, and Inconel 718 had slightly lower threshold temperatures in the presence of ClF_5 than in F_2 under comparable flow conditions. The threshold temperatures of Monel K-500 and Nickel 200 were lower in the presence of F_2 than in ClF_5 .

(2) Maximum allowable temperature, pressure, and rate of adiabatic compression of propellant vapors tests were conducted in an adiabatic compression test apparatus with 2 to 3 mL of liquid oxidizer condensed in the U-tube. There was only slight erosion but no ignition. U-shaped tubing made from 12 different metals was filled with gaseous ClF_5 and compressed suddenly to 20.7 MPa (3000 psig). Only 3 positive (ignition) results were observed in the 60 tests and these occurred on 301 Cryo and 304-L stainless steels at the maximum pressurization capabilities of the test apparatus (3000 psig driving pressure) and with the ClF_5 vapor at an initial temperature of 373 K (212°F) or higher, whereas many more ignitions happened with gaseous fluorine. Once ignited, the tubes were completely consumed.

(3) The objective of the liquid maximum allowable velocity of impact tests was to determine the maximum temperatures to which the selected metals may be heated without detrimental effects occurring when impacted by liquid streams of fluorine or ClF_5 . The test simulates a situation that may occur during restarts during a heat-soak condition. The temperature of the metal specimens was measured by means of thermocouples attached to the back of the metal strip, which was 0.010 in thick. The metal specimens were placed within 3/16 in of the discharge orifice of the liquid propellant feed system. Two different impact velocities were tested at which the liquid slug would impact the metal specimen at 120 ft/s or 220 ft/s. The threshold temperatures for ignition for a given metal were all very close together, independent of impact velocity and the type of liquid oxidizer (LF_2 or LCIF_5). The results could be arranged in a sequence from the most sensitive metal, Al6061T6, igniting at 755 K (900°F), to the most resistant metal, nickel 200, igniting only above 1422 K (2100°F).

(4) The degradation of the passive film as a result of cyclic loading in liquid ClF_5 tests simulated conditions that are encountered by flexing bellows. Metal specimens were flexed by a reciprocating shaft 0.5 in in either direction at a rate of about 5 flexures per second. The fixture was actuated for 100000 cycles, then vented and dried. None of the samples ignited. The weight gain was 3–4 times higher for flexed specimens than for those in a static test in the same test fixture. The flexing of metal specimens in liquid ClF_5 did not significantly disrupt the passivation film.

(5) The objective of the sonic and ultrasonic vibration film degradation tests was to determine whether the “passivating film” on the selected metals undergoes appreciable degradation when subjected to vibration. The test simulated a situation such as

in pumping, in which cavitation occurs. Samples were immersed in liquid ClF_5 in an ultrasonic cleaning bath which was driven with 400 watts at a frequency of 62.5 kHz. 301 cryoformed stainless steel, Al-6061-T6 aluminum, and Ni-200 were unaffected by the vibration. CRES 347 and A-286 stainless steels and copper suffered slight weight losses in the vibration test.

(6) The effect of a shock wave test simulates the “water hammer effect” in the metallic materials produced during sudden valve closure. Nickel 200 was found to be suitable for use at temperatures up to 1228 K (1750 °F) in gaseous fluorine or chlorine pentafluoride. Inconel 718, under comparable testing, was suitable to 1116 K (1550 °F), whereas Monel K-500 could withstand 1089 K (1500 °F) except when subjected to adiabatic compression. The austenitic stainless steels were suitable at temperatures up to 866 K (1100 °F) except when subjected to adiabatic compression in chlorine pentafluoride. Copper and the aluminum alloys were resistant to attack at temperatures up to only 700 K (800 °F).

A modified Army Ballistic Missile Agency (ABMA) open-cup impact tester was used to measure the impact sensitivity of Al2014-T6 and Ti-6A-4V in liquid ClF_5 at a temperature between 173 K (−100 °C) and its boiling point [354]. The first six drop tests were conducted with the Al2014-T6 alloy at 95 J (70 ft-lb) and a temperature between 173 and 223 K (−100 and −50 °C). Two out of five tests gave faint flashes. A test procedure for bracketing the 50% probability of initiating a reaction was attempted, but only 1 positive reaction occurred at 93 J (69 ft-lb) out of 16 tests. Modified ABMA open-cup impact tests on annealed Ti-6A-4V (extra low interstitials; ELI) were conducted in liquid ClF_5 at boiling point. There were 15 reactions out of 29 tests. The impact energy required for a 50% probability of initiating a reaction in liquid ClF_5 was calculated to be 57.6 J (42.5 ft-lb). See also [208].

2.3.5.2 Compatibility of Chlorine Pentafluoride with Non-metallic Materials

The number and types of non-metallic materials that are compatible with ClF_5 is quite limited. Experimental efforts have shown that Kel-F and Teflon plastics and various fluorocarbon oils are compatible but only under limited conditions (i.e., static application at ambient temperature).

2.3.5.3 Long-Term Tank Storage Tests

Storable Prepackaged Propellant (SPP) systems of a liquid rocket propellant feed system were designed, fabricated, tested, and delivered by General Dynamics Convair for subsequent use in a storability investigation by the Air Force Rocket Propulsion Laboratory (AFRPL) [355]. The propellant tanks were fabricated of Al-2219 and had a volume of approximately 57 L (15 gallons). Each of the 23 delivered systems consisted of a 57-L propellant tank, which contained either a Surface Tension Force Orientation device or a Rolling Diaphragm positive expulsion device, along with one of three different pressurization subsystems, including a Liquid Propellant (hydrazine) Gas Generator, a Solid Propellant LFT-3 (ammonium nitrate composite) Gas Generator (SPGG),

or a Stored Gas Device. Within the gas storage bottle, 90% nitrogen/10% helium gas was contained at 20.79 MPa (3015 psia) by an explosive valve. Each tank was welded closed such that the propellant was contained within an all-metal, welded tank. Metal rupture discs, welded in the tank inlet and outlet, would rupture for propellant discharge when pressurized by the pressurization subsystem. The systems were delivered to AFRPL, hermetically sealed, and loaded with their respective propellants: Mixed Hydrazine Fuel (MHF-5), dinitrogen tetroxide (N_2O_4), or chlorine pentafluoride (ClF_5). In addition, four tanks were delivered empty to AFRPL. One sample of each of the storage subsystems was test fired shortly after being loaded with propellants and the pressure history and propellant flow rate were recorded. This served as a baseline for later comparison when the stored units were to be tested using the same procedure.

An incident happened while one SPP was being packaged for delivery to AFRPL. The system consisted of a rolling diaphragm tank loaded with 69.8 kg (154 lb) of ClF_5 and an SPGG pressurization subsystem. The ClF_5 had been loaded into the tank 20 days previously and the tank had always been maintained in a vertical position. When the tank was laid in a horizontal position to package for shipment, within 10 s after obtaining a horizontal attitude, a reactant noise came from inside the tank. Ninety minutes later the tank ruptured. Post-rupture examination showed that the weld between the liquid bulkhead and the tank cylinder had parted owing to high internal tank pressure. The ClF_5 had leaked through the rolling diaphragm or one of its weld joints and had combined with the silicon rubber to ignite and evolve gas.

The USAF Air Force Research Laboratory at Edwards AFB, CA, conducted tank storage tests with a large number of oxidizer and fuel tanks and published a series of interim progress reports over a period of two decades. The propellants under test were N_2O_4 , ClF_3 , ClF_5 , N_2H_4 , and MHF-5. Tankage materials under test were various alloys of aluminum, steel, and titanium. Tankage was joined by automatic and manual TIG welding, EB welding, and solid-state bonding techniques. There are many areas to consider when selecting tank storage test procedures in providing data to supplement coupon compatibility testing. Storage conditions must be selected that are representative of system operational conditions. Such factors as ambient humidity and temperature play an important role. A detailed propellant chemical analysis before and after testing is required to evaluate the effects of storage on the purity of the propellant. The program was structured as several parallel phases. Phase I used 3×6 -in bomblets from Al-2014-T6 for quick reference tests, one-quart (0.94-L) bomblets made by Alcoa from Al-2014-T6, Al-6061-T6, Al-7007-T6, Al-2219-T81, Al-5456-T6, Al-3003-T6, and Al-X2021-T-6, and cylinders made by Arde from cryoformed CRES-301. Phase II used 57-L (15-gallon) tanks made of Al-2219-T81 and AM350 steel for storability evaluation with N_2O_4 and ClF_5 . Phase III used 57-L (15-gallon) tanks from several aluminum, steel, and titanium alloys. Phase IV used existing tanks from Bullpup and Agena programs. Phase V used prepackaged feed systems built by General Dynamics/Convair, including electron-beam-welded Al-2219-T81 tankage loaded with N_2O_4 , ClF_5 , and MHF-5.

At the date of the first report, a significant number of liquid propellant tanks, fabricated by typical production methods of forming and welding and subjected to the same degree of inspection and quality control documentation as production tankage, had been evaluated in storage testing for nearly 2 years. A number of leaks were encountered in all three types of tankage metals, aluminum, steel, and titanium. In general, the failures were attributed more to quality discrepancies during fabrication and welding than to a lack of compatibility of the metals themselves [356].

Tank storage tests under extreme conditions of relative humidity and temperature (constant 303 K = 85 °F and 85% relative humidity for oxidizer systems and cycling between 294 and 339 K (70 and 150 °F) for fuel systems) in progress for 3–4 years indicated that leakage of propellant can occur as a result of improper weld joint design, inadequate quality control in fabrication, and insufficient acceptance leakage testing. During this period the cause of failure of a total of 12 tanks was analyzed [357]. Twelve Phase II integrated systems were loaded with ClF₅ and approximately 2 weeks later the environment in the oxidizer storage facility was maintained at 303 K (85 °F) and 85% relative humidity. One day, a month later, the storage facility was inspected and no systems were found to be leaking. Two days later, the facility was again inspected and a very large concentration of ClF₅ vapors was found. It was determined that at least two tanks were leaking ClF₅, (one a cryogenically stretch-formed AISI 301 stainless steel container, and one an integrated system with an AM350 steel tank). Numerous other tanks and systems were detanked because of corrosion damage to their external surfaces. The original leak was located in an aluminum tubing weld of a system containing ClF₅. The large concentration of HF (the product of ClF₅ hydrolysis) vapors resulting from the leaks also damaged the building's air conditioning system, which had to be rebuilt.

Later reports contained detailed metallurgical examination of failed tank shells and connecting tubing [358–360]. Stress corrosion cracking susceptibility of the tank material in combination with the propellant and trace quantities of foreign compounds/elements in the propellant can aggravate the situation.

Two chlorine pentafluoride samples that had been off-loaded from 5-year storage tests at AFRL and analyzed at Rocketdyne by GC and IR and showed full compliance with requirements of MIL-P-27413 with regard to ClF₅, ClF₃, HF, and other impurities [361].

Tanks that had held chlorine pentafluoride and had been stored in a controlled storage environment at 303 K (85 °F) and 85% relative humidity for several months were emptied, cleaned, and dissected for metallurgical analysis [362]. The corrosion effects of the stored propellants on the internal metal surfaces were negligible, with no serious degradation of strength or structural integrity occurring. Corrosion was primarily caused by pitting, gas, and liquid phase interactions occurring during storage, manufacturing defects, and at the manifold tubing welds.

2.3.6 Components for Chlorine Pentafluoride Service

2.3.6.1 Valves for Chlorine Pentafluoride Service

A failure analysis of a thrust chamber valve from an attitude control system that had been returned from ClF₅ service examined various failure modes (overstressing of the closures, corrosion, abrasive wear, and impact-initiated reactions) and conducted additional materials compatibility tests to evaluate candidate materials [363]. Corrosion caused by residual water in the valve was one of the most likely failure modes. The modes studied included overstressing of the closures by closing loads, adhesive wear of the closure surfaces/corrosion of the closures by ClF₅, and HF/abrasive wear, corrosive wear, and impact-initiated surface reactions. Equations that relate valve wear to operating and material parameters were developed during the analysis. For all of the normal modes of possible failure investigated, the valve was considered to be adequately designed to withstand any expected level of load or attack as long as it was kept dry.

Tests conducted to select seat and poppet materials and/or sealing concepts for use in ClF₅ attitude control system valves evaluated nickel-, iron-, tungsten-, and zirconium-based materials in the flat-on-flat sealing concept, as well as a sapphire/copper lip-seal concept [364]. Two varieties of tungsten carbide in the flat-on-flat configuration (Kennametal 96 and Kennametal 801) were the only materials that met the leakage requirement of <30 cm³ helium/h after 100000 actuations in ClF₅.

A bipropellant solenoid valve showed extensive finish deterioration of both the poppet and the seat mating surfaces after being operated in ClF₅ [365]. Surface roughness measurements on poppets exposed to ClF₅ revealed that the surface finish deterioration was far more severe in sealing and impact areas than on non-sealing surfaces. A method was developed for determining the mechanism of sealing surface deterioration in halogen fluoride oxidizers.

2.3.6.2 Cleaning of Components for Chlorine Pentafluoride Service

A detergent cleaning technique developed by Aerojet Propulsion Division that eliminates the use of chlorofluorocarbon (CFC) fluids in the cleaning of rocket engine test systems and components (valves, filters, check valves, turbine flow meters, pressure transducers, and tubing) was successfully demonstrated during the construction and operation of a rocket engine test facility that used chlorine pentafluoride and hydrazine propellants during the testing of engine components at thrust levels up to 4448 N (1000 lb_f) [366]. The test stand components had to be cleaned to a particulate level 100 (no particles greater than 100 μm), a non-volatile residue value less than 43.1 mg/m² and a hydrocarbon content less than 10.8 mg/m² of significant surface area. The flow paths were less than 1.27 cm (0.5 in.) in diameter. The facility has been used to successfully conduct over 5500 thruster static hot firings, propellant tank sub-system tests, and a full system hot fire demonstration consisting of three engines, three propellant tanks, and associated propellant delivery and pressurization subsystems.

2.3.7 Toxicity of Chlorine Pentafluoride

Groups of rats, mice, dogs, and monkeys were exposed to various measured concentrations of ClF_5 to determine the 15-, 30-, and 60-min inhalation and whole-body exposure LC50 for each species [367, 368]. All animals were observed for visible symptoms and mortality both during exposure and for 14 days post-exposure. The LC50 values (in ppm) for rats were 257, 194, and 122; for mice 144, 105, and 57; for dogs 298, 156, and 122; and for monkeys 249, 218, and 173, for 15-, 30-, and 60-min exposures respectively. The respiratory tract was the primary target for ClF_5 damage in all four species, and mortality due to ClF_5 exposure was related to its adverse respiratory effects. The LC50 information from this study was compared with LC50s obtained for other fluorinated oxidizers and HF. Chlorine pentafluoride was less toxic than OF_2 , but was more toxic than either ClF_3 or HF. It was also found that mice were the least resistant to ClF_5 exposure. These experiments showed that ClF_5 is extremely toxic to each of the four species tested. See also [235, 369].

2.3.8 Environmental Impact of Chlorine Pentafluoride

Like many fluorocarbon compounds, ClF_5 may have deleterious effects on the ozone layer owing to its release of HF and HCl once it hydrolyzes. However, it is unlikely that any releases of ClF_5 would diffuse all the way to the ozone layer unreacted. Before they got there, they would hydrolyze with atmospheric moisture and be photolyzed by UV in the upper atmosphere.

2.3.8.1 Atmospheric Dispersion of Accidental Chlorine Pentafluoride Releases

An assessment of the launch safety, human toxicity, and environmental impact associated with ClF_5 usage and examination of the hazards resulting from a prelaunch propellant handling and loading accident and from a launch vehicle explosion at the launch site or in-flight was based on known toxicity values for ClF_5 and atmospheric dispersion models [370]. The operational use of ClF_5 may require a more detailed review of personnel safety, industrial hygiene, and handling procedures, especially for transport on public highways. The reactivity of ClF_5 and incompatibility with materials makes it more hazardous than N_2O_4 . For this case of liquid ClF_5 spills, three accident scenarios were considered:

- (1) prelaunch accidents such as during propellant handling and loading leading to an uncombusted cold propellant spill,
- (2) a launch site explosion creating a plume of propellant combustion products settling over the immediate ground area,
- (3) an in-flight explosion dispersing propellant combustion products into the troposphere and stratosphere depending on altitude.

The impact of these accidents is examined in terms of their environmental effects on: (1) human toxicity, (2) animal and plant toxicity, including land and sea life,

(3) atmospheric disturbance in terms of pollution (troposphere) and ozone depletion (stratosphere). Accident scenarios were modeled for cases of ground-based cold and combusted propellant releases and post-launch explosions in the troposphere and stratosphere. Each assessment was supported by a simple worst case model and calculation. More realistic calculations for ClF_5 release and dispersion were then presented based on the Air Force Toxic Chemical Dispersion Model (AFTOX) dispersion model for toxic chemical releases. Ground-based accidents were modeled for a range of weather conditions reported for the most probable sites of accidents at Vandenberg AFB. The effect of ClF_5 on microorganisms, fish, and plants has already been reported [244, 245]. As a group, interhalogens, including ClF_5 , have damaging effects on plants for 10- to 30-ppm exposures of less than 1 h, and are lethal to fish and microorganisms at concentrations of 10–25 mg(F)/L. It was assumed that the ClF_5 is converted mostly to HF within the timescale for expression of toxic effects. A recommended ClF_5 TLV of 2.5 mg(F)/m³ (0.4 ppm) TWA has been adopted by the Occupational Safety and Health Administration (OSHA), the American Conference of Governmental Industrial Hygienists (ACGIH), and the National Institute of Occupational Safety and Health (NIOSH). In the atmosphere ClF_5 most likely hydrolyzes quickly; hence, the toxic and environmental impact should take into consideration the importance of HF. The ACGIH TLV for HF is 2 mg/m³ (3 ppm). A simple calculation was presented for an instantaneous ground-based release that disperses homogeneously and uniformly into a hemisphere centered at the spill site. This model assumes no wind, eddy currents, or vertical convection forces to disperse the plume. No dynamics were included: it was calculated in how large a volume the release must expand to in order for the concentration to fall below some threshold exposure level. The toxic chemical release code AFTOX is used by the Air Force for disaster response and emergency preparedness. AFTOX assumes that gaseous chemicals are carried at wind velocities and that the moving chemical volume spreads out as a Gaussian distribution. The rate of spread or dispersion depends on an atmospheric stability factor determined from wind speed, temperature, sun elevation (computed from location, date, and time), cloud cover and type, and roughness of ground terrain. The model does not allow for changes in wind speed and direction, nor does it treat vertical dispersion by convection from actual thermal gradient information. Vertical dispersion is accounted for solely by the atmospheric stability factor. The AFTOX results show concentration/time profiles along the center axis of the wind vector or in a 2-D plot show equi-concentration lines of the plume shape at different times as a function of wind speed and other parameters. For a release of 2000 kg ClF_5 and a wind speed of 0.5 m/s, the maximum concentration drops below the TLV only after the plume has traveled more than 1 km. The results were compared with two NASA studies that evaluated the short-term acute effects from fluorine propellant accidents [371, 372]. Damaging effects can occur to plants for 10–30 ppm (200 mg/m³) exposures of less than 1 h.

2.3.9 Detonability of Chlorine Pentafluoride

Detonation sensitivity tests proved that ClF_5 is insensitive to initiation and will not propagate a detonation. Impact sensitivity tests with a modified JANAF drop-weight tester in dry nitrogen and dry air at liquid temperatures up to 255 K (0 °F) showed no evidence of detonation up to 100 in-lb, the limit of the tester. A modified cap-in-pipe test in 1/2-in CRES tubing at 255 K (0 °F) resulted in no evidence for propagation of a detonation initiated by a 50-g Compound C charge and blasting cap. Additional adiabatic compression tests with the U-tube apparatus demonstrated the insensitive nature of ClF_5 to adiabatic compression stimulus over a variety of selected “worst conditions” (both air and water contaminated). The insensitive nature of ClF_5 was also confirmed by a standard Trauzl block test [248].

2.4 Chlorine Heptafluoride???

The highest fluorinated form of chlorine so far, ClF_5 , caused quite a stir in the world of chemistry and rocketry when it was first discovered in the 1960s. Now, computational chemists are pushing the limit even higher, all the way to the heretofore unknown chlorine heptafluoride ClF_7 . They argue “*If iodine can amass seven fluorines around it, why not chlorine?*” The fact that the heptafluoride of chlorine does not exist can be explained by steric arguments (there just is not enough space surrounding the chlorine atom).

Several attempts to prepare chlorine heptafluoride, ClF_7 , have been unsuccessful [373]. As part of the same effort, the group also attempted the synthesis of chlorine oxygen pentafluoride, OClF_5 , but without success. Earlier efforts by the same group were aimed at the synthesis of ClF_6SbF_6 as an intermediate to higher halogen oxidation state fluorides [374]. Preliminary IR spectroscopic data on the products of reactions in Monel reactors had been interpreted as showing the probable synthesis of ClF_6^+ . However, subsequent reactions in aluminum reactors established that the compound was not formed unless either copper or nickel was present. The reaction was not catalyzed by a small amount of nickel. Thus, although the possibility that the material was ClF_6SbF_6 could not be completely eliminated, it seemed likely that the product was a complex metal salt formed as a contaminant.

Numerous *ab initio* MO and DFT calculations were made to predict the stability and C—F bond strengths in ClF_7 and its ions in comparison with ClF_5 and ClF_3 stability. Predictions were made for the missing experimental thermochemical data of unknown chlorine fluorides and their ions [375].

Ab initio electronic-structure calculations were performed for the hypervalent chlorine fluorides, ClF_3 , ClF_5 , and ClF_7 , in order to determine their predicted thermodynamic stabilities with respect to dissociation to ClF and F_2 [376]. The calculations included electron correlations and extended basis sets and produced estimated energies of 100.4 and 176 kJ/mol (24 and 42 kcal/mol) for the predicted

stability of ClF_3 and ClF_5 respectively. The more symmetrical molecule was predicted to be more stable than the T-shaped molecule. Calculations on the D_{5h} symmetry structure of ClF_7 indicated that this system is unstable with an energy barrier of only 67 kJ/mol (16 kcal/mol). See also [377].

Gaussian-3 (G3) and Gaussian-3X (G3X) models of theory have been used to calculate the thermochemical data for chlorine fluorides ClF_n , $n = 1-7$, as well as for their singly charged cations and anions and heats of formation (ΔH_f), bond dissociation energies (DEs) of all of the species, ionization energies (IEs), and electron affinities (EAs) of the neutrals, have been tabulated [378]. By comparing well-established experimental data of ClF and ClF_3 with the G3 and G3X results, it was found that the G3X method actually yielded more accurate ΔH_f values. In addition, the G3 values on the IEs and EAs for ClF and ClF_3 were similar to the corresponding G3X results. Predictions were made for the missing experimental thermochemical data of unknown chlorine fluorides and their ions. An alternating pattern of the ΔH_f , DE, IE, and EA values of the ClF_n and their ions with system size n was discovered.

The bonding energies in the ClF_n ($n = 1-7$) series were calculated to further examine the explanatory usefulness of the recoupled-pair bonding model [379]. Optimized structures and energies of the ground and low-lying excited states of the ClF_n molecules were determined by employing high-level *ab initio* calculations with correlation-consistent basis sets. The bond energies for F addition to form ClF_2 , ClF_4 , and ClF_6 were found to be much lower than those leading to ClF , ClF_3 , and ClF_5 . The same type of alternating behavior had been observed in the SF_n series. The differences between ClF_n and SF_n reflect the fact that the $3s^2$ and $3p^2$ electron pairs are more strongly bound in Cl than in S. This behavior and other trends observed in the ClF_n species demonstrated the improved predictive ability of the recoupled-pair bonding model theory over other models for describing hypervalent bonding.

Chlorine heptafluoride, ClF_7 , may not yet exist, but that has not prevented the Chemical Abstract Service from already assigning registry numbers to it: CAS RN [478167-13-4] and [32825-94-8]. So, keep looking.

3 Bromine Fluorides

There are three known bromine fluorides with different states of oxidation (Br^{+1} , Br^{+3} , and Br^{+5}), but only the latter two are thermally stable. Bromine monofluoride decomposes at temperatures as low as near 273 K (0 °C). It would be nice to have a stable bromine heptafluoride, similar to iodine heptafluoride, but that is not the case. As the bromine atom is bigger than the chlorine atom, it might be possible to attach more oxygens in addition to the fluorines to create bromine oxide fluorides, but those compounds have not found any application. Bromine fluorides could be used as fluorinating agents in the synthesis of other high-energy oxidizers.

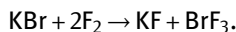
As rocket propellants, bromine fluorides have no advantage over chlorine fluorides. The more than two times heavier atomic mass of the central atom, 79.9 for bromine as opposed to 35.45 for chlorine, results in a higher average molecular mass of the combustion products and a lower exhaust velocity. Bromide minerals are not as readily available from salt mines as chloride minerals.

3.1 Bromine Trifluoride

Bromine trifluoride, BrF_3 , CAS RN [7787-71-5], is a clear, greenish colored liquid. It is not suitable as a rocket propellant because it has an inconveniently high freezing point at 281.9 K (8.8°C). The inconveniently high freezing point can be lowered by mixing with bromine pentafluoride. Bromine trifluoride will not be used as a rocket propellant, but it can be used as an intermediate in the synthesis of other fluoride compounds.

3.1.1 Preparation of Bromine Trifluoride

Bromine trifluoride can be prepared from the elements in an exothermic reaction at room temperature, but the product also contains some of the other bromine fluorides [380]. Moissan, the discoverer of fluorine, already found that fluorine gas combined violently with bromine vapor in the cold with a bright flame. When fluorine was passed through liquid bromine, combination was also immediate but without flame. Bromine trifluoride was also formed when alkaline metal bromides were reacted with fluorine:



One of the manufacturers of bromine fluorides, Allied Chemical, once (in the early 1960s) published product information bulletins that contained a good summary of physical properties of BrF_3 and BrF_5 , but those brochures are no longer available from this source. Most of the data in the following two tables were taken from that historical source. There is currently no domestic source for bromine trifluoride in the USA.

3.1.2 Physical Properties of Bromine Trifluoride

The physical properties of bromine trifluoride are summarized in Table 36. A complete source of physical properties of BrF_3 is the NIST Chemistry WebBook [381].

Table 36: Physical properties of bromine trifluoride.

Property	SI Units	MKS Units	Source	References
Molecular mass	136.899		NIST Chem WebBook	[38]
Freezing point	281.9 K	+8.8 °C	Allied Chemical	
	281.9 K	+8.8 °C	Stein, Vogel, and Ludewig 1954	[382]
Boiling point	400 K	127.6 °C	Allied Chemical	
	398.95 K	125.8 °C	Stein, Vogel, and Ludewig 1954	[382]
	398.85 K	125.7 °C	Air Products & Chemicals MSDS	
Critical temperature	601 K	328 °C	Air Products & Chemicals MSDS	

3.1.2.1 Density of Bromine Trifluoride

The density of liquid BrF_3 as a function of temperature can be calculated from the following linear equation:

$$\rho = 3.623 - 0.00277T$$

where ρ is the density in g/cm^3 and T is the temperature in kelvin. The density of bromine trifluoride at 50 °C was found to be $2.7351 \pm 0.0005 \text{ g/mL}$, and that of bromine pentafluoride at 0 °C was found to be $2.5475 \pm 0.0005 \text{ g/mL}$. The approximate temperature coefficients of density were $-0.00272 \text{ g mL}^{-1} \text{ }^\circ\text{C}^{-1}$ from 23 to 50 °C for the trifluoride and $-0.00348 \text{ g mL}^{-1} \text{ }^\circ\text{C}^{-1}$ from 0 to 25 °C for the pentafluoride [382]. The density of $\text{BrF}_3/\text{BrF}_5$ mixtures at 298 K (25 °C) can be calculated from the equation

$$\rho = 2.8030 - 0.3884M_2 + 0.0641M_2^2 - 0.0183M_2^3$$

where ρ is the density in g/cm^3 and M_2 is the mol fraction of BrF_5 .

3.1.2.2 Vapor Pressure of Bromine Trifluoride

The vapor pressure of BrF_3 can be represented by the following logarithmic equation:

$$\log p_v = 7.74853 - 1685.8/(t + 220.57)$$

where p_v is the vapor pressure in mm Hg and t is the temperature in °C. A different form of the vapor pressure equation is

$$\log p_v = 8.41954 - 2220.2/T$$

where p_v is the vapor pressure in mm Hg and T is the temperature in kelvin.

Early investigators of BrF_3 , Ruff and Braidia (1933) [383] had measured the vapor pressure only over a limited pressure range, 4 to 136 mm Hg. Thirty years later, an investigation extended the vapor pressure data to 2.5 atm on material of high purity. The vapor pressure and heat of vaporization of bromine trifluoride was measured over the

range 312 to 428 (39 to 155 °C) and the following equation was derived by methods of least squares to represent the experimental data [384, 385]:

$$\log_{10} p = 7.74853 - 1685.8/(t + 220.57)$$

where p is the vapor pressure in mm Hg and t is the temperature in °C. A different but very accurate vapor pressure equation for the temperature range from 336 to 453 K (63 to 180 °C) was derived by [386, 387]:

$$\log_{10} p_v = 7.65757 - 1627.5/(t + 215)$$

where p_v is the vapor pressure in mm Hg and t is the temperature in °C.

The vapor phase diagram of BrF₃/BrF₅ mixtures is illustrated in Figure 43. The activity coefficients for these mixtures were tabulated (not shown here).

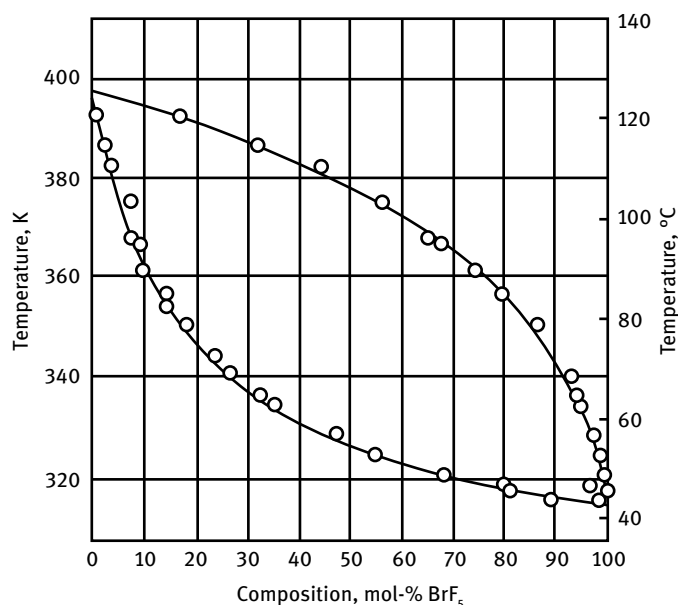


Figure 43: Liquid-vapor diagram of the BrF₃/BrF₅ isobar system, data adjusted to 1 atm. (Reprinted and modified from [387], with permission from © 1958 American Chemical Society.)

3.1.2.3 Optical Properties of Bromine Trifluoride

As the refractive indexes of BrF₃ and BrF₅ are quite different, it should be possible to analyze BrF₃/BrF₅ mixtures as they often are formed during fluorination of bromine by refractive index measurements. At 298 K with the sodium D line, the refractive index of BrF₃ was 1.4536 and the refractive index of BrF₅ was 1.3529 [382]. The IR spectra of

bromine fluorides were studied in an IR cell whereas the bromine was reacting with elemental fluorine or bromine trifluoride [388]. The IR spectra of BrF_3 were compared with those of ClF_3 . The Raman and IR spectra of ClF_3 and BrF_3 gave strong support for a planar T-shaped molecule [83, 84, 87].

In the IR spectrum of matrix-isolated BrF_3 , all six fundamental vibrations expected for a T-shaped molecule of symmetry C_{2v} were observed [389]. Raman spectra of the liquid indicated strong association in the liquid phase through formation of fluorine bridges. A modified valence force field and some thermodynamic properties have been computed for BrF_3 . The differential enthalpy of formation of gaseous (ideal gas at 1 atm) BrF_3 is $(\Delta H_{298} - \Delta H_0) = 14.70 \text{ kJ/mol} = 3.513 \text{ kcal/mol}$.

3.1.2.4 Electric Properties of Bromine Trifluoride

Owing to the autodissociation



bromine trifluoride has a specific conductivity at 288 K (15 °C) of $8.1 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$, which strangely enough decreases as the temperature increases from 288 to 333 K (15 to 60 °C) [121]. Among the four halogen fluorides ClF_3 , BrF_3 , BrF_5 , and IF_5 , BrF_3 has the highest electrical conductivity [390, 391].

Dielectric constants and dipole moments of BrF_3 and IF_5 were already shown in earlier tables in the ClF_3 Section 2.2.2 for comparison. A planar T-configuration for BrF_3 , similar to that now established for ClF_3 , accounted satisfactorily for the dipole moment of this molecule.

3.1.2.5 Thermodynamic Properties of Bromine Trifluoride

A complete source of thermochemical properties of BrF_3 is in the NIST Chemistry Web-Book [381]. Thermodynamic properties of BrF_3 are summarized in Table 37.

The heats of formation of bromine fluorides previously had been derived from spectroscopic and equilibrium data and estimated from bond energy considerations. The following is the first calorimetric measurement of the heat of reaction of $\text{F}_2 + \text{Br}$, which happens to be the same as the heat of formation. The heats of reaction of F_2 with Br were measured with an adiabatic calorimeter in the vicinity of 298 and 378 K (25 and 105 °C) [392]. When excess F_2 was used, BrF_3 and BrF_5 were formed in the 298 K (25 °C) region, and BrF_5 alone was formed in the 378 K (105 °C) region. The standard heats of formation (ΔH_f) of BrF_5 , BrF_3 , and BrF calculated from the measurements were -444.3 , -271.1 , and -74.1 kJ/mol (-106.2 , -64.8 , and -17.7 kcal/mol), respectively (reactants and products in the gaseous state at 298 K = 25 °C). The standard free energies of formation [ΔF_f] were -351.9 , -231.0 , and -75.3 kJ/mol (-84.1 , -55.2 , and -18.0 kcal/mol) respectively.

Table 37: Thermodynamic properties of bromine trifluoride.

Property	SI Units	Other units	Source	References
Enthalpy of formation, gas (ΔH) ₂₉₈ ^f	-255.6 ± 2.9 kJ/mol	-61.1 ± 0.7 kcal/mol	Stein 1962	[392]
Enthalpy of formation, gas (ΔH) ₂₉₈ ^f	-255.59 kJ/mol	-61.087 kcal/mol	NIST WebBook, Chase 1998	[38]
Heat of fusion, at triple point of 281.93 K	12.027 kJ/mol	$2.874.6 \pm 3$ kcal/mol	Oliver and Grisard 1952	[385]
Heat of evaporation (ΔH) _{evap} at the normal boiling point, 398.9 K (125.75 °C)	42.68 kJ/mol	10.2 kcal/mol		
Entropy, liquid BrF ₃ at 298.16 K	178.1 J K ⁻¹ mol ⁻¹	42.57 ± 0.10 cal °C ⁻¹ mol ⁻¹		
Entropy, ideal gas BrF ₃ at 298.16 K	299.4 J K ⁻¹ mol ⁻¹	71.57 cal °C ⁻¹ mol ⁻¹		

The heat of evaporation of BrF₃ was estimated from vapor pressure data by the following equation, which is based upon the Clausius–Clapeyron relation [384]:

$$\Delta H_{\text{vap}} = 7714[(t + 273.16)/(t + 220.57)]^2$$

where ΔH_{vap} is the heat of evaporation in cal/mol and t is the temperature in °C.

3.1.3 Chemical Properties of Bromine Trifluoride

In air, particularly in moist air, the liquid emits white acid fumes. Bromine trifluoride is not as strong an oxidizer as ClF₃ or F₂. Organic materials may not all inflame instantly when coming into contact with BrF₃ and some may require an external source of ignition if this is intended as a rocket propellant. Diethyl ether, benzene, and turpentine ignite instantly with bromine trifluoride.

Similar to chlorine and some iodine fluorides, bromine trifluoride forms fluorobromate(III) and fluorobromonium salts, which are potentially useful as solid propellant oxidizers and fluorinating agents [393–395].

3.1.4 Handling of Bromine Trifluoride

Bromine trifluoride can be handled in all materials of construction that are also acceptable for ClF₃. Similar to the passivation of metals with other reactive fluorides, metals eventually passivate in BrF₃ and be protected from further attack (as long as the film does not dissolve in BrF₃!). In the case of BrF₃, it is a better solvent than F₂

or ClF_3 and it forms many tetrafluorobromates with common metals, such as silver. AgBrF_4 is soluble in BrF_3 .

As far as handling precautions are concerned, BrF_3 is just as toxic as the other halogen fluorides and causes severe skin burns that heal only very slowly. The deep burns will often lead to subsequent complications such as skin edema and necrosis of the surrounding tissue. Additional information on safe handling of BrF_3 can be found in the Safety Data Sheets of former BrF_3 manufacturers, such as Air Products & Chemicals [396].

3.1.5 Toxicity of Bromine Trifluoride

The legal airborne permissible exposure limit (PEL) is 0.1 ppm averaged over an 8-h work shift (OSHA and ACGIH). The recommended airborne exposure limit is 0.1 ppm averaged over a 10-h work shift or 0.3 ppm not to be exceeded during any 15-min work period (NIOSH).

3.1.6 Applications of Bromine Trifluoride

Bromine trifluoride has few other industrial applications and is not particularly suitable as a rocket propellant. It has been tested as an ignition fluid for solid propellants, but does not offer any particular advantages over ClF_3 , other than the lower vapor pressure at room temperature. Chlorine trifluoride, bromine trifluoride, and bromine pentafluoride were evaluated as hypergolic ignition sources for double-base or composite propellants. Chlorine trifluoride was the best ignition fluid [397, 398].

Because BrF_3 is easier to keep as a liquid at room temperature than ClF_3 and has a similar reactivity with metals, it has also been used as a chemical cutting tool in cutting casings and stuck drill strings in oil and gas field drilling applications.

3.2 Bromine Pentafluoride

Bromine pentafluoride, BrF_5 , is a colorless liquid with a pungent, acrid odor, CAS RN [7789-30-2]. Bromine pentafluoride will most likely not be used as a rocket propellant, but it is useful as an intermediate in the synthesis of other fluorine compounds.

3.2.1 Preparation of Bromine Pentafluoride

Bromine pentafluoride can be prepared by reaction of bromine trifluoride with fluorine or by elemental synthesis from the elements themselves. For making bromine pentafluoride, Ruff and Menzel heated bromine trifluoride to 363–373 K (90–100 °C), mixed the bromine trifluoride vapors with fluorine, and then heated the mixture to 473 K (200 °C) in a platinum tube. By fractional condensation of the gaseous products, bromine pentafluoride was separated from the reaction mixture. After an ex-

plosion, however, the two-step process in platinum was abandoned in favor of direct combination of bromine and fluorine to bromine pentafluoride in a copper apparatus at 473 K (200 °C). Purification was accomplished by condensing the entire reaction mixture and then fractionally distilling it in quartz. Bromine pentafluoride also can be prepared by reaction of potassium bromide in an autoclave at high pressures and temperatures with an excess of fluorine [266].

3.2.2 Physical Properties of Bromine Pentafluoride

At room temperature, bromine pentafluoride is a liquid similar to bromine trifluoride. In spite of its higher molecular mass, bromine pentafluoride is more volatile than bromine trifluoride. Among the many non-metallic fluorides, the high density of bromine pentafluoride is remarkable. The physical properties of BrF₅ are summarized in Table 38.

Table 38: Physical properties of bromine pentafluoride.

Property	SI Units	MKS Units	References
Molecular mass	174.896016		[40]
Melting point	210.6 K	−62.5 °C	
	212.6 K	−60.5 ± 0.1 °C	[399]
	211.8 K	−61.3 °C	[382]
Boiling point	313.4 K	40.3 °C	
	313.9 K	40.76 ± 0.05 °C	[399]
	314.4 K	41.3	[382]
Critical temperature	~470 K	~197 °C	
Density at 298 K	2460 kg/m ³	2.4604 g/cm ³	[382]
Refractive index n_D^{25}		1.3529	[382]

The density of bromine pentafluoride as a function of temperature can be calculated from the following linear equation:

$$\rho = 3.496 - 0.00346 T$$

where ρ is the density in g/cm³ and T is the temperature in kelvin. The vapor pressure curve of BrF₅ is represented by the following logarithmic equation, based on old data by Ruff and Menzel:

$$\log p_v = 8.0716 - 1627.7/T$$

where p_v is the vapor pressure in mm Hg and T is the temperature in kelvin.

A slightly different equation was offered by Rogers and Speirs [399]: The vapor pressure as a function of temperature was found to be given by the expression

$$\log p = 7.9727 - 1598.2/T$$

with a probable error of ± 1 mm Hg over the range from 53 to 101 kPa (400 to 760 mm Hg), where p is the vapor pressure in mm Hg and T is the temperature in kelvin. A third equation for the range from 203.8 to 313.5 K was derived by Stull 1947 [400] from data by other investigators:

$$\log_{10} P = 4.79777 - [1411.692 / (T - 19.763)]$$

where P is the vapor pressure in bar and T is the temperature in kelvin. The molar entropy of vaporization calculated from these data is then 23.3 e.u., a reasonable value for a non-associated liquid composed of molecules with a dipole moment of 1.51 D.

Another different vapor pressure equation for BrF_5 for the temperature range from 298 to 419 K (25 to 146 °C) was derived by [387]:

$$\log_{10} p_v = 6.4545 + 0.001101t - 895 / (t + 206)$$

where p_v is the vapor pressure in mmHg and t is the temperature in °C.

The specific electrical conductivity of BrF_5 is much lower than that of BrF_3 . It is only 9.1×10^{-8} Ohm cm.

The molecular structure of BrF_5 was compared with that of BrF_3 and IF_5 [401]. Complete three-dimensional data were recorded at 153 K = -120 °C. The crystal system is orthorhombic, with $a = 6.422$ Å, $b = 7.245$ Å, $c = 7.846$ Å, $Z = 4$, and space group C_{2v} .

3.2.2.1 Thermodynamic Properties of Bromine Pentafluoride

Thermodynamic property data of bromine pentafluoride are summarized in Table 39.

Table 39: Thermodynamic properties of bromine pentafluoride.

Property	SI Units	MKS Units	References
Enthalpy of formation, gas $(\Delta H)^\circ_{298}$	-428.72 kJ/mol	-102.5 kcal/mol	[40]
	-429 $\pm$ 2 kJ/mol	-102.5 $\pm$ 0.5 kcal/mol	[392]
	-519 kJ/mol	-124.0 kcal/mol	[72]
Heat of fusion $(\Delta H)_{\text{melt}}$ (at 211 K = -62 °C)	7.28 kJ/mol	1.74 kcal/mol	
Heat of evaporation $(\Delta H)_{\text{vap}}$ (at 313 K = 40 °C)	30.1 kJ/mol	7.20 kcal/mol	
	30.6 kJ/mol	7.31 kcal/mol	[399]
Entropy of evaporation $(\Delta S)_{\text{vap}}$ (at 313 K = 40 °C)	97.5 J K ⁻¹ mol ⁻¹	23.3 e.u. =	[399]
		23.3 cal °C ⁻¹ mol ⁻¹	

3.2.3 Chemical Properties of Bromine Pentafluoride

Bromine pentafluoride reacts with essentially all known inorganic and organic compounds, with the exception of the other halogen fluorides in their highest state of fluorination. It ignites spontaneously with many other elements and metals. It ignites

spontaneously with all organic compounds with the exception of a few perfluorinated hydrocarbons. This remarkable reactivity makes it suitable as a hypergolic oxidizer.

3.2.3.1 Fluorobromate and Fluorobromonium Salts

Similar to chlorine and some iodine fluorides, bromine trifluoride and bromine pentafluoride form fluorobromate and fluorobromonium salts, which are potentially useful as solid propellant oxidizers or fluorinating agents.

The fluorobromonium salts $\text{BrF}_6^+ \text{AsF}_6^-$ and $\text{BrF}_6^+ \text{Sb}_2\text{F}_{11}^-$ can be synthesized from BrF_5 and the corresponding Lewis acids [402, 403]. In analogy with $\text{IF}_6^+ \text{AsF}_6^-$ crystals, the space group of $\text{BrF}_6^+ \text{AsF}_6^-$ crystals is $Pa\bar{3}$. See also [404].

$\text{BrF}_4^+ \text{AsF}_6^-$ has been prepared from BrF_5 and AsF_5 . It is marginally stable at 178 K (-95°C).

3.2.3.2 Analysis of Bromine Pentafluoride

Mass spectrometric analysis of BrF_5 showed that the strongest peak was $^{79}\text{BrF}_4$ [345]. The $^{79}\text{BrF}_5$ peak was only very weak, 1% of that of the strongest peak. SiF_4 and HBr were detected as contaminants.

3.2.4 Toxicity of Bromine Pentafluoride

The exposure limits for bromine pentafluoride are: 0.1 ppm (0.7 mg/m^3) OSHA TWA; 0.1 ppm ACGIH TWA; 0.1 ppm (0.7 mg/m^3) NIOSH [235].

4 Iodine Fluorides

There are four known iodine fluorides, corresponding to four different states of oxidation of the central iodine atom, I^+ , I^{+3} , I^{+5} , and I^{+7} . The physical properties of the upper two iodine fluorides were included in Tables 2–5 at the beginning of this section on halogen fluorides. At best, the latter two are potentially of interest as rocket propellants because they have a high fluorine content and they have a high density. However, iodine is not as readily available in bulk quantities as chlorine and the advantages of iodine fluorides do not outweigh their disadvantages, the main disadvantage being the high molecular mass of exhaust products and low specific impulse compared with that achieved with chlorine fluorides as the oxidizers. Iodine heptafluoride has such a high freezing point and narrow liquid range that it is not practical as a liquid rocket propellant. The main interest in iodine pentafluoride and iodine heptafluoride is in their molecular structure, to see by analogy of the electronic structure if heptafluorides can be synthesized for bromine and chlorine as well. Once the synthesis of heptafluorides was shown to be feasible for iodine, it was hoped that methods could be found to do the same trick for bromine or even chlorine. As rocket propellants, iodine fluorides have no advantage over chlorine fluorides. The more than three times heav-

ier atomic mass of the central atom, 126.9 for iodine as opposed to 35.45 for chlorine, results in a higher average molecular mass of the combustion products and a lower exhaust velocity. Iodine fluorides would not be used as rocket propellants, but they can be used in the synthesis of other fluorides.

4.1 Iodine Pentafluoride

Iodine pentafluoride, IF_5 , CAS RN [7783-66-6] is a colorless or yellow liquid, depending on the purity of the sample. Iodine pentafluoride will most likely not be used as a rocket propellant, but it is a useful intermediate in the synthesis of other fluorine compounds.

4.1.1 Preparation of Iodine Pentafluoride

The main preparation methods for iodine pentafluoride include: combustion reaction of solid iodine in fluorine gas, combustion reaction of liquid iodine in fluorine gas, or treating alkyl iodides with fluorine gas. The combustion reaction of iodine in fluorine gas is the most commonly used preparation method that has been industrialized [405]. Fluorine gas ignites iodine, burning it with a pale blue flame to yield iodine pentafluoride. The iodine can be in the molten state at high pressure [406] or iodine can be dissolved in iodine pentafluoride and reacted with fluorine to form additional iodine pentafluoride [407]. Iodine pentafluoride can be made by fluorinating iodine pentoxide with carbonyl fluoride [408].

The reaction between I_2O_5 and liquid BrF_3 was found to be a suitable laboratory method for the preparation of IF_5 [409]. The reaction can be performed in a silica flask with no special equipment needed. The yield of the isolated pure IF_5 was 80%.

Likewise, fluorine gas reacts with metallic iodides and hydrogen iodide to produce iodine pentafluoride and the corresponding fluorides. The preparation of small amounts of iodine pentafluoride can be carried out by passing a stream of fluorine over iodine crystals contained in a platinum boat in a glass tube. The iodine pentafluoride can be condensed in a cold trap at the end of the glass tube. At room temperature, iodine pentafluoride is a liquid and iodine heptafluoride is a vapor. Iodine pentafluoride can be distilled at atmospheric pressure without decomposition. When it is heated to approximately 773 K (500 °C), however, iodine vapors are produced.

4.1.2 Physical Properties of Iodine Pentafluoride

The triple point of iodine pentafluoride is $282.553 \pm 0.01 \text{ K}$ [410]. The vapor pressure measured between 283 and 378 K can be represented by the equation:

$$\log_{10} P = -3090.14/T - 6.96834 \log_{10} T + 29.02167$$

where P is the vapor pressure in mm Hg and T is the temperature in kelvin.

For additional information on iodine fluorides and other halogen fluorides, see [411–419].

The enthalpy of formation of liquid iodine pentafluoride as determined calorimetrically by direct reaction of the elements was -882.0 ± 1.6 kJ/mol (-210.81 ± 0.39 kcal/mol) [420]. From the same data an enthalpy of formation for gaseous iodine heptafluoride of -961.5 ± 2.1 kJ/mol (-229.8 ± 0.5 kcal/mol) was derived. Thermodynamic properties of IF_5 and IF_7 are compared in Table 40.

Table 40: Thermodynamic properties of iodine fluorides.

Property	SI Units	MKS Units	References
Iodine Pentafluoride			
Enthalpy of formation, gas (ΔH°_{298})	-847.7 kJ/mol	-202.6 kcal/mol	[72]
	-840.31 kJ/mol	-200.8 kcal/mol	[40]
Enthalpy of formation, liquid (ΔH°_{298})	-882.0 ± 1.6 kJ/mol	-210.81 ± 0.39 kcal/mol	[420]
	-881.99 ± 1.34 kJ/mol	-210.80 ± 0.32 kcal/mol	[410]
Heat of fusion	11.222 ± 0.011 kJ/mol	2.682 ± 0.003 kcal/mol	[410]
Heat of evaporation at 330 K	39.32 kJ/mol	9.39 kcal/mol	[410]
Iodine Heptafluoride			
Enthalpy of formation, gas (ΔH°_{298})	-969 kJ/mol	-231.7 kcal/mol	[72]
	-961.06 kJ/mol	-229.7 kcal/mol	[40]
	-961.5 ± 2.1 kJ/mol	-229.8 ± 0.5 kcal/mol	[420]

Raman spectra of iodine pentafluoride have been measured for the gas as well as for the liquid as a function of temperature [421]. An intense polarized band, which appeared in the room temperature spectra of the liquid at 697 cm^{-1} and a weaker, previously unreported, band at 218 cm^{-1} , were absent both from the gas spectra and from the elevated temperature spectra of the liquid. This indicated that these bands arise from the presence of polymers in the liquid state rather than from Fermi resonance.

The rotational constant, quadrupole coupling constant and C_{4v} symmetry of IF_5 were determined from its microwave spectrum [422].

All halogen fluorides are diamagnetic. The average molar magnetic susceptibility of chlorine trifluoride, bromine trifluoride, bromine pentafluoride, and iodine pentafluoride measured at different field strengths is -26.5×10^{-6} c.g.s. units, -33.9×10^{-6} c.g.s. units, -45.1×10^{-6} c.g.s. units and -58.1×10^{-6} c.g.s. units respectively [102].

The crystal structure of solid iodine pentafluoride is monoclinic with $a = 15.07\text{ \AA}$, $b = 6.836\text{ \AA}$, $c = 18.24\text{ \AA} = 92.96$, $Z = 20$, most probable space group $C2/c$ [423]. The molecular dimensions are $\text{I}-\text{F}_{\text{apical}} = 1.74\text{ \AA}$, $\text{I}-\text{F}_{\text{basal}} = 1.87\text{ \AA}$, and $\angle \text{F}-\text{I}-\text{F} = 81.9^\circ$. The molecular structure of IF_5 was compared with that of BrF_3 and BrF_5 [401]. Complete three-dimensional data were recorded at $153\text{ K} = -120^\circ\text{C}$. The crystal system

is monoclinic with $a = 15.16 \text{ \AA}$, $b = 6.86 \text{ \AA}$, $c = 18.20 \text{ \AA}$, $\beta = 93^\circ 14'$, and space group $C_s^4 = C_c$. The density of solid iodine heptafluoride at $273 \text{ K} = 0^\circ \text{C}$ was reported to be 3.754 g/cm^3 . Liquid iodine pentafluoride has a specific conductivity of 2×10^{-5} to $3 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ at 298 K (25°C) and has a positive temperature coefficient [121]. The dielectric constant of liquid IF_5 has been measured in the range 273 to 315 K (0 to 42°C) at several frequencies and may be expressed by the equation [99, 100]:

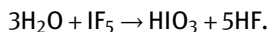
$$\epsilon = 41.09 - 0.198t$$

where ϵ is the dielectric constant (dimensionless) and t is the temperature in $^\circ \text{C}$. The results indicated that these substances are associated in the liquid state.

The dielectric constant of gaseous IF_5 has been measured in the vapor phase using a refractivity method [101]. The large electric moment of IF_5 excludes the trigonal bipyramidal and pentagonal planar structures. This is in satisfactory agreement with a distorted octahedral arrangement in which the iodine atom is probably below the plane of the four fluorine atoms on the side opposite the fifth fluorine atom, and the unshared pair is in the sixth position.

4.1.3 Chemical Properties of Iodine Pentafluoride

Iodine pentafluoride and iodine heptafluoride are both stable at room temperature. Iodine pentafluoride reacts violently with water and with aqueous solutions in general. Apparently, the hydrolysis proceeds as follows:



Iodine pentafluoride and iodine heptafluoride undergo fluorine exchange reactions with iodine pentafluoride oxide [424].

Similar to chlorine and bromine fluorides, iodine trifluoride and iodine pentafluoride form fluoroiodate and fluoroiodonium(V) salts, which are potentially useful as solid propellant oxidizers or as fluorinating agents [425–428]. Single-crystal XRD studies have shown that the $\text{IF}_5 \cdot \text{SbF}_5$ adduct has the predominantly ionic structure $[\text{IF}_4^+][\text{SbF}_6^-]$. Iodine pentafluoride forms adducts with acetonitrile [429].

4.2 Iodine Heptafluoride

Iodine heptafluoride, IF_7 , CAS RN [16921-96-3] forms colorless crystals, which melt at 277.6 K (4.5°C). The liquid range is extremely narrow, with the boiling point at 277.93 K (4.77°C). The vapor has a moldy, acrid odor. On passing fluorine into liquid iodine pentafluoride at room temperature, no appreciable amount of a more volatile fluoride was obtained, but when a mixture of iodine pentafluoride and fluorine was heated under pressure in an autoclave, iodine heptafluoride was produced [430, 431]. Iodine

heptafluoride is of interest because it is the halogen fluoride with the highest state of oxidation of the central atom.

Over the range 373–543 K (100–270 °C), the yield of iodine heptafluoride based on the fluorine used increased with increasing temperature [432]. Because of the corrosive nature of the reactants, a platinum apparatus had to be used for this reaction. Operating at a temperature of 523–543 K (250–270 °C), 83% of the fluorine used was converted to iodine heptafluoride. The iodine heptafluoride was purified by pumping off silicon tetrafluoride contamination at 183 K (–90 °C), followed by fractional distillation of iodine heptafluoride from the iodine pentafluoride. A frequent contaminant in IF_7 is IOF_5 , which forms by hydrolysis with moisture.

Iodine heptafluoride, as one of the interhalogen compounds, is of chemical interest both of a theoretical and practical nature. It is unique in being the only simple binary compound in which sevenfold coordination is observed, and in common with other halogen fluorides, it is a possible substitute for fluorine in certain fluorination reactions [433]. No stable addition compounds of the type $\text{M}[\text{IF}_8]$ could be obtained from the interaction of iodine heptafluoride and alkali metal fluorides.

Free vapor-phase molecules of iodine heptafluoride are pentagonal bipyramids with axial bonds ($1.786 \pm 0.007 \text{ \AA}$) shorter than equatorial bonds ($1.858 \pm 0.004 \text{ \AA}$) [434]. They are deformed from D_{5h} symmetry on average by 7.5° ring displacements and 4.5° axial bend displacements.

Iodine heptafluoride, the most frequently studied prototype of a heptacoordinated molecule, had presented many mysteries concerning its spectroscopic and structural properties. It was shown by *ab initio* calculations and a reexamination of the vibrational spectra and their normal coordinate analysis that most of the previously implied abnormalities were due to incorrect assignments [435]. All the available structural data for IF_7 are consistent with a dynamically distorted pentagonal bipyramidal molecule with D_{5h} symmetry in the ground state.

A potential function consisting of the ordinary valence force terms and central force terms has been adopted for the evaluation of potential constants for iodine heptafluoride [436].

Similar to other halogen fluorides, iodine heptafluoride forms fluoroiodate and fluoroiodonium(VII) salts, which are potentially useful as solid propellant oxidizers or as fluorinating agents [437–439].

5 Ternary Fluorides

By way of definition, we call “binary fluorides” those that contain only one type of atom that is different from fluorine. Examples are ClF_3 and NF_3 . We call “ternary fluorides” those compounds that contain two different atoms other than fluorine. Examples are ClO_3F and NO_2F .

5.1 Chlorine–Oxygen–Fluorides

Several chlorine–oxygen–fluorine ternary fluoride compounds that contain chlorine, oxygen, and fluorine in one and the same molecule are reported in the literature and at least one of these is of interest as an oxidizer in liquid rocket propellants. The chlorine–oxygen–fluorides are: chlorine dioxygen fluoride, ClO_2F , (also called “chloryl fluoride”) chlorine trioxygen fluoride, ClO_3F , (also called “perchloryl fluoride”), chlorine tetraoxygen fluoride (incorrectly also called “fluorine perchlorate”), ClO_4F , and, finally, chlorine oxygen trifluoride, ClOF_3 , and chlorine dioxygen trifluoride, ClO_2F_3 . Summaries of the literature on chlorine–oxygen–fluorine compounds can be found in [52, 223, 440–442].

Halogen oxyfluorides are prepared by forming either halogen–fluorine or halogen–oxygen bonds. One of the published summaries dealt exclusively with the formation of halogen–halogen bonds, and preparative methods for halogen oxyfluorides based on the formation of halogen–oxygen bonds were not included [443].

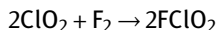
5.1.1 Chlorine Dioxygen Fluoride FClO_2 (also called “Chloryl Fluoride”)

Chloryl fluoride, chlorine dioxygen fluoride, FClO_2 , CAS RN [13637-83-7], is the most common chlorine oxide fluoride and is frequently encountered in the reactions of the binary chlorine fluorides ClF , ClF_3 , and ClF_5 with oxides and hydroxides. Chlorine dioxygen fluoride has no practical use as a rocket propellant. It is often encountered as a contaminant or intermediate in the preparation of other chlorine oxygen fluorides. It might be useful as an intermediate in the synthesis of other high-energy oxidizers. Its relative, chlorine trioxygen fluoride ClO_3F , will be discussed in more detail in Section 5.1.2.

5.1.1.1 Preparation of Chlorine Dioxygen Fluoride

Chloryl fluoride is most conveniently prepared in a high yield by the reaction of stoichiometric amounts of NaClO_3 and ClF , yielding NaF , Cl_2 , O_2 , and FClO_2 . The chlorine fluorides ClF , ClF_3 , and ClF_5 when used in excess, also undergo fluorine oxygen exchange reactions with nitrate anion, forming FClO_2 , unstable FCIO , and ClONO_2 re-

spectively as the primary products. Chlorine dioxygen fluoride is formed by the addition of elemental fluorine to chlorine dioxide:



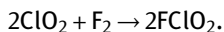
or reaction of gaseous ClO_2 with powdered AgF at 338–343 K (65–70 °C) [444].

The literature methods reported prior to 1975 for the synthesis of FClO_2 were inconvenient, as they either involved the fluorination of shock-sensitive chlorine oxides or, as in the case of the $\text{KClO}_3 + \text{BrF}_3$ reaction, resulted in product mixtures that were difficult to separate. An improved synthesis of FClO_2 from NaClO_3 and ClF_3 is more convenient than the previous literature methods [445]. It is based on the previous observations that gaseous ClF_3 reacts with KClO_3 to produce FClO_2 in a high yield, but it reduces the ClF_3 requirements by 60%. In this method, dry NaClO_3 is combined with approximately an equimolar amount of ClF_3 at 77 K (–196 °C) in a stainless steel cylinder. The mixture is allowed to warm slowly and kept at room temperature for about 1 day. Chloryl fluoride is thus obtained in a high yield according to:



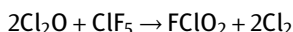
The products condensable at 77 K (–196 °C) can be separated either by fractional distillation or by repeated fractional condensation. The substitution of the previously used KClO_3 by NaClO_3 is significant as KF forms a 1:1 adduct with ClF_3 whereas NaF does not.

Chlorine oxyfluorides can be prepared by the reaction of halogen oxides with elemental fluorine. The interaction of F_2 with chlorine oxides, such as ClO_2 , Cl_2O_6 , or Cl_2O_7 produces FClO_2 . Quantitative yields of FClO_2 are obtained with ClO_2 as a starting material and moderate reaction conditions [446]. Inert solvents, such as CFCl_3 , or diluents, such as air or N_2 , are recommended to avoid hazards due to the explosive nature of the chlorine oxides. For the higher chlorine oxides, the need for elevated temperature and the decreased yields of FClO_2 suggest that the primary step in these reactions might involve the thermal decomposition to ClO_2 , which is then fluorinated. Therefore, all of these reactions are likely to involve the step:

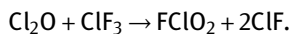


In view of the shock sensitivity of chlorine oxides, none of the above methods is recommended for the large-scale production of FClO_2 , and necessary safety precautions must be used. The recommended method for the preparation of FClO_2 is the reaction of NaClO_3 with ClF_3 .

The risk of explosions in the ClO_2 reactions is reduced when ClO_2 is replaced by the less dangerous Cl_2O . The yield of FClO_2 using this method is 35%. Similarly, Cl_2O can be fluorinated at 195 K (–78 °C) with either ClF_5 :



or ClF_3 :



In these two reactions an unstable FClO molecule is formed as an intermediate, but disproportionates to yield FClO_2 and ClF .

5.1.1.2 Physical Properties of Chlorine Dioxide Fluoride

Chloryl fluoride melts at 158 K (-115°C) and boils at 267 K (-6°C). It is of interest to compare the IR and Raman spectra of the different chlorine-oxygen fluorides, for instance, to compare chloryl fluoride with those of perchloryl fluoride, molecules with different symmetry and bond orders. The IR spectrum of gaseous chloryl fluoride has been examined in detail from 300 to 4000 cm^{-1} and the chlorine and oxygen isotopic structures of many of the fundamental overtone and combination bands have been resolved [447]. The Raman spectrum of liquid chloryl fluoride was also observed from 100 to 1500 cm^{-1} and polarization measurements were taken. All the fundamental frequencies of the molecule were observed and correlated in both the IR and Raman spectra. The strong bands located at 1265, 1104, 627, and 542 cm^{-1} have been assigned to 4 of the 6 fundamental vibrations expected for a pyramidal tetratomic molecule pertaining to the C_8 point group [448].

Additional information on molecular structure and bond constants could be obtained from the microwave spectra of chloryl fluoride [449, 450]. The spectra and kinetics of chloryl fluoride formation and decomposition have been investigated thoroughly because it may play a role in the ozone depletion of the upper atmosphere due to fluorocarbons [451].

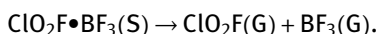
An isomer of chloryl fluoride would be chlorine fluoride peroxide, $\text{F}-\text{O}-\text{O}-\text{Cl}$, which has a CAS RN [177778-93-7] number, but its existence is unlikely.

5.1.1.3 Chemical Properties of Chlorine Dioxide Fluoride

Although FClO_3 does not react with LiNO_3 at temperatures as high as 348 K (75°C), FClO_2 reacts with LiNO_3 or N_2O to give ClONO_2 and O_2 in a high yield. Chlorine nitrate slowly reacts with ClF to give NO_2F and Cl_2O as the primary products and a side reaction of Cl_2O with ClF gives Cl_2 and goes back to more FClO_2 .

Complex Salt Formation with Chlorine Dioxide Fluoride

Salts of the $[\text{ClO}_2^+]$ cation are also called chloronium salts. They may be useful as oxidizers in solid propellants with perfluorinated polymers as binders. The 1:1 adducts $\text{ClO}_2\text{F}\cdot\text{AsF}_5$ and $\text{ClO}_2\text{F}\cdot\text{BF}_3$ have been investigated [452, 453]. Whereas $\text{ClO}_2\text{F}\cdot\text{AsF}_5$ is stable at ambient temperature, the $\text{ClO}_2\text{F}\cdot\text{BF}_3$ adduct showed a dissociation pressure of 30.39 kPa at 298 K (228 mm Hg at 25°C). A pressure-temperature curve gave a heat of reaction of 100.5 kJ/mol (24.0 kcal/mol) for the dissociation process:



The XRD patterns of $\text{ClO}_2\text{F}\bullet\text{AsF}_5$ and $\text{ClF}_3\bullet\text{AsF}_5$ were recorded and indexed. Infrared and Raman measurements showed that $\text{ClO}_2\text{F}\bullet\text{AsF}_5$ and $\text{ClO}_2\text{F}\bullet\text{BF}_3$ have the ionic structures $[\text{ClO}_2^+][\text{AsF}_6^-]$ and $[\text{ClO}_2^+][\text{BF}_4^-]$ respectively in the solid state. All fundamental vibrations were observed and a valence force field was calculated for ClO_2^+ .

The infrared and Raman spectra of chloryl hexafluoroarsenate were obtained [454]. The observed vibrations were interpreted in terms of an ionic compound $[\text{ClO}_2^+][\text{AsF}_6^-]$, where strong cation–anion interaction results in a symmetry lowering of the AsF_6^- ion.

5.1.2 Chlorine Trioxxygen Fluoride ClO_3F (Also Called “Perchloryl Fluoride”)

Next to chlorine trifluoride and chlorine pentafluoride, among all the non-metallic fluorides, perchloryl fluoride (chlorine trioxxygen fluoride) has received the most attention from rocket propellant chemists as a potential high-energy oxidizer for liquid rocket applications. We use the two names for this chemical here interchangeably.

5.1.2.1 Preparation of Chlorine Trioxxygen Fluoride

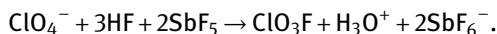
Chlorine trioxxygen fluoride, ClO_3F , perchloryl fluoride (also called “Florox”), CAS RN [7616-94-6], was discovered in 1952 by electrolysis of perchloric acid in H_2F_2 solution [455]. Instead of perchloric acid, similar results are obtained when electrolyzing potassium perchlorate in H_2F_2 [456]. With a formula mass of $M = 102.45 \text{ g/mol}$, it contains 46.85 mass-% O, 34.61 mass-% Cl, and 18.54 mass-% F.

A simple method for making perchloryl fluoride is by reaction of potassium perchlorate with fluorosulfonic acid (fluorosulfuric acid, sulfurofluoridic acid) [457]:

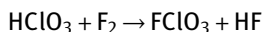


Both reagents are readily available. This method is even suitable for the preparation of small quantities of ClO_3F in the laboratory [458–461].

Perchloryl fluoride can also be made by reaction of perchlorates in H_2F_2 solution with SbF_5 :



Whereas fluorination of halogen oxyacids can result in the formation of the corresponding fluorooxy compounds:



fluorination of the salts of these halogen oxyacids is a more useful method for the synthesis of halogen oxyfluorides [443]. The nature of the halogen oxyfluoride product depends on the starting material and the reaction conditions. Thus, the fluorination of perchlorates is a high-yield synthesis of perchloryl fluoride. Perchloryl fluoride can also be prepared by heating potassium perchlorate with antimony pentafluoride in a high-pressure bomb. Heating of KClO_4 to 973–1473 K (700–1200 °C) in an excess

of SbF_5 produces FClO_3 in a 50% yield [462]. The yield of FClO_3 can be increased to 90% and the reaction temperature can be lowered to 473–773 K (200–500 °C), when a mixture of HF with SbF_5 is used instead. Slightly lower yields are obtained when the HF solvent is replaced by AsF_3 , IF_5 , or BrF_5 .

Most of the commercial processes are based on the use of HOSO_2F as the fluorinating agent for KClO_4 . Evolution of FClO_3 starts at 323 K (50 °C) and goes to completion at 1123–1373 K (850–1100 °C). The yields of FClO_3 vary from 50 to 80% and, if necessary, the HOSO_2F can be regenerated. The addition of certain additives such as 5 to 25% SbF_3 to the HOSO_2F increased the yield of FClO_3 to 90%, but hindered the regeneration of HOSO_2F . Better yields were possible by the addition of BF_3 , SbF_3 , or HF [463]. The addition of HF/ BF_3 increased the FClO_3 yield to 85%, but required elevated pressure. The highest yield of perchloryl fluoride (97%) was achieved with a mixture of fluorosulfonic acid and SbF_5 as fluorinating medium. Potassium, sodium, lithium, magnesium, barium, calcium, and silver perchlorates and perchloric acid itself undergo the reaction, but most of the time KClO_4 is used [464]. See also [465].

Perchloryl fluoride ClO_3F and other halogen trioxygen fluorides can be prepared by a continuous process gas–liquid reaction by passing a mixture of ClF or ClF_3 with F_2 through an aqueous solution of HF, KF, NaF, KOH, NaOH, or K_2CO_3 [466].

5.1.2.2 Physical Properties of Chlorine Trioxygen Fluoride

The physical properties of ClO_3F are summarized in Table 41.

Table 41: Physical properties of chlorine trioxygen fluoride.

Property	SI Units	MKS Units	Authors	Year	References
Molecular mass	102.5				
Melting point	127 ± 2 K	-146 ± 2 °C	Pennsalt	1957	[467]
	127.2 K	-145.9 °C	Streng	1971	[41]
	125.41 K	-147.74 °C	Koehler and Giauque	1958	[468]
Boiling point	226.3 K	-46.8 °C	Pennsalt	1957	[467]
	226.4 K	-46.7 °C	Streng	1971	[41]
	226.48 K	-46.67 °C	Koehler and Giauque	1958	[468]
Density, liquid (at 293 K = 20 °C)	1.434 kg/m ³	1.434 g/cm ³	Jarry (extrapolated)	1957	[469]
Vapor pressure (at 273 K = 0 °C)		5.84 atm	Jarry (interpolated)	1957	[469]
Vapor pressure (at 298 K = 25 °C)		12.0 atm	Jarry (interpolated)	1957	[469]

Table 41: (continued)

Property	SI Units	MKS Units	Authors	Year	References
Vapor pressure (at 323 K = 50 °C)		21.9 atm	Jarry (interpolated)	1957	[469]
t_{crit}	368.32 K	95.17 ± 0.10 °C	Pennsalt	1957	[467]
P_{crit}		53 atm	Pennsalt	1957	[467]
ρ_{crit}	0.637 kg/m ³	0.637 g/cm ³	Pennsalt	1957	[467]
Viscosity at 193 K = –80 °C		0.620 cPs	Simkin and Jarry	1957	[470]
Viscosity at 273 K = 0 °C		0.291 cPs	Simkin and Jarry	1957	[470]
Viscosity at 333 K = 60 °C		0.139 cPs	Simkin and Jarry	1957	[470]
Surface tension at 207.2 K = –75.2 °C		24.05 dyn/cm	Pennsalt	1957	[467]
Surface tension at 204.2 K = –65.9 °C		22.31 dyn/cm	Pennsalt	1957	[467]
Surface tension at 217.4 K = –55.7 °C		21.25 dyn/cm	Pennsalt	1957	[467]
Specific heat at 233 K = –40 °C	$0.958 \text{ J g}^{-1} \text{ K}^{-1}$	$0.229 \text{ cal g}^{-1} \text{ °C}^{-1}$	Pennsalt	1957	[467]
Specific heat at 263 K = –10 °C	$1.021 \text{ J g}^{-1} \text{ K}^{-1}$	$0.244 \text{ cal g}^{-1} \text{ °C}^{-1}$	Pennsalt	1957	[467]
Specific heat at 323 K = + 50 °C	$1.213 \text{ J g}^{-1} \text{ K}^{-1}$	$0.290 \text{ cal g}^{-1} \text{ °C}^{-1}$	Pennsalt	1957	[467]
Standard enthalpy of formation, gas (ΔH) ₂₉₈	–21.42 $\pm 2.84 \text{ kJ/mol}$	–5.12 $\pm 0.68 \text{ kcal/mol}$	Neugebauer and Margrave	1957	[471]
	–21.42 kJ/mol	–5.12 kcal/mol	Cruise	1986	[296]
Adiabatic coefficient C_p/C_v	1.12 ± 0.01	1.12 ± 0.01	Margrave and Wendt	1959	[472]
Heat of evaporation (ΔH) _{vap}	19.25 kJ/mol	4.6 kcal/mol	Pennsalt	1957	[467]
Entropy of evaporation (ΔS) _{vap}	$85.3 \text{ J g}^{-1} \text{ K}^{-1}$	$20.4 \text{ cal °C}^{-1} \text{ mol}^{-1}$	Pennsalt	1957	[467]
Heat of fusion at normal melting point	3.834 kJ/mol	916.3 cal/mol	Koehler and Giauque	1958	[468]
Heat of evaporation at normal boiling point	19.32 kJ/mol	4.619 kcal/mol	Koehler and Giauque	1958	[468]
Entropy, gas S_{298}	$278.3 \text{ J g}^{-1} \text{ K}^{-1}$	$66.51 \text{ cal °C}^{-1} \text{ mol}^{-1}$	Pennsalt	1957	[467]

The density of perchloryl fluoride as a function of temperature can be calculated by the equation [469]:

$$\rho = 2.266 - 1.603 \times 10^{-3} T - 4.080 \times 10^{-6} T^2$$

where ρ is the density in g/cm³ and T is the temperature in kelvin. Data obtained with this equation are illustrated in Figure 44.

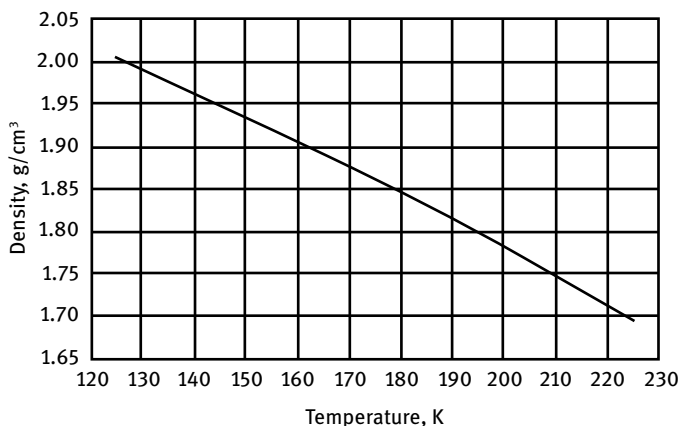


Figure 44: Density of perchloryl fluoride. (Chart created by Schmidt 2016, based on data from [469].)

See also [473]. The heat capacity and several other physical properties of perchloryl fluoride have been measured from 15 to 225 K [468]. The heat of fusion was found to be 3.834 kJ/mol (916.3 cal/mol) at melting point, which was determined as 125.41 K = -147.74°C . The heat of evaporation was determined calorimetrically to be 19.32 kJ/mol (4.619 kcal/mol) at boiling point, which is at 226.48 K = -46.67°C . The vapor pressure was measured and the data are represented by the equation

$$\log P = -1652.37/T - 8.62625 \log T + 0.0046098T + 28.44780$$

where P is the vapor pressure cm Hg (not mm Hg!) and T is the temperature in kelvin. Other investigators found the equation for the vapor pressure curve of ClO_3F to be

$$\log P = 7.683 - 1083.8/T$$

where P is the vapor pressure in mm Hg and T is the temperature in kelvin. A boiling point of 225.6 K = -47.5°C was calculated from this equation.

More accurate vapor pressures can be obtained from the following two equations. One equation is applicable to the temperature range 131 to 234 K (-142 to -39°C) and the other is applicable to the temperature range from the normal boiling point (234 K) to the critical point at 368 K [469]

$$\log P = 18.90112 - 1443.967/T - 4.09566 \log T$$

where P is the vapor pressure in mm Hg and T is the temperature in kelvin and

$$\log P = 4.46862 - 1010.81/T$$

where P is the vapor pressure in atm and T is the temperature in kelvin. A comparison of the Jarry and Koehler/Giauque vapor pressure equations shows that the two curves falls virtually on top of each other and agree totally (Figure 45).

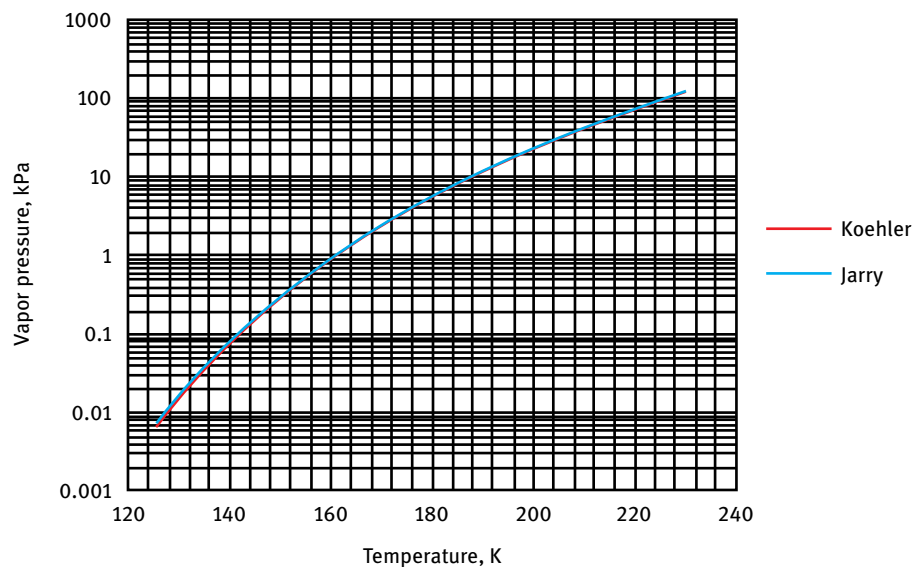


Figure 45: Comparison of perchloryl fluoride vapor pressure data in the low temperature range from two different sources.

The vapor pressure data for the high pressure range from the normal boiling point at 234 K to the critical point at 368 K are illustrated in Figure 46.

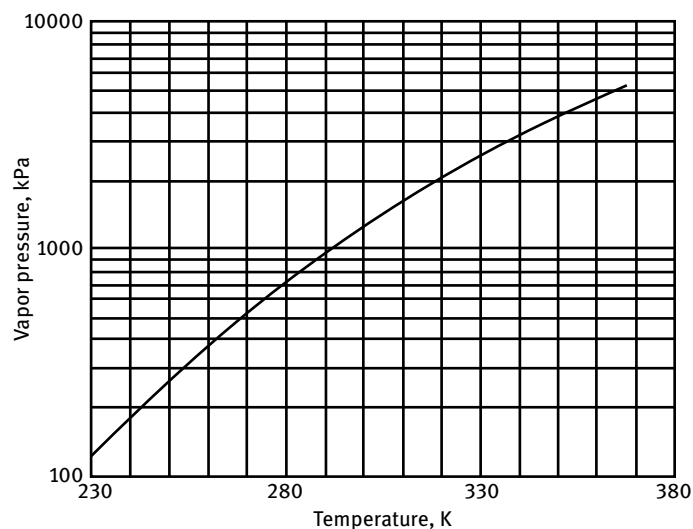


Figure 46: Vapor pressure of perchloryl fluoride for the high pressure range from the normal boiling point to the critical point.

The viscosity of liquid perchloryl fluoride can be calculated from the following equation [470]:

$$\log \eta = 299/T - 1.755$$

where η is the viscosity in centiPoise and T is the temperature in kelvin.

Optical Properties of Chlorine Trioxygen Fluoride

Strong optically pumped laser action has been obtained in perchloryl fluoride, excited by a CO₂ laser [474]. Thirty-four new lines were observed between 16.3 and 17.7 μm , with outputs of up to 4 mJ.

Infrared Spectra of Chlorine Trioxygen Fluoride

Infrared spectra of perchloryl fluoride have been used in determining the molecular structure of the molecule and for quality control to identify contaminants in the product. The IR spectrum of ClO₃F was determined between 525 and 625 cm⁻¹ and supported the structure of a symmetric top-shaped molecule [475].

The IR spectrum of gaseous ClO₃F was obtained over the range 3–43 μm [476]. Satisfactory assignments of absorption bands were achieved on the basis of a C_{3v} model in which the four peripheral atoms are each bonded to the central chlorine (Table 42). The stability of the C_{3v} structure for ClO₃F was compared with that of ClO₄⁻ and similar molecules.

Table 42: Infrared band assignments for gaseous perchloryl fluoride.

Wave number, cm ⁻¹	Species group	Designation	Vibration type
1061	A ₁	ν_1	Cl—O stretching
715	A ₁	ν_2	Cl—F stretching
549	A ₁	ν_3	ClO ₃ bending
1315	E	ν_4	Cl—O stretching
589	E	ν_5	ClO ₃ bending
405	E	ν_6	Rocking

Data source: [476]

The intensities of the IR absorption spectrum of FClO₃ in the gas phase, as shown in Figure 47 and Table 43, have been used to calculate the force field and the bond strengths of the FClO₃ molecule [477]. Possible versions of the force constant matrix and the dependence of the forms of the vibration on the choice of force field have been analyzed. The electron density distribution has been estimated by a semi-empirical quantum-chemical method. The FClO₃ molecule has a dipole moment of 0.023–0.025 D. On the basis of a simple vector model, it is possible to find the ratio between the dipole moments of the bonds 0.024. This corresponds to an unusual situation in

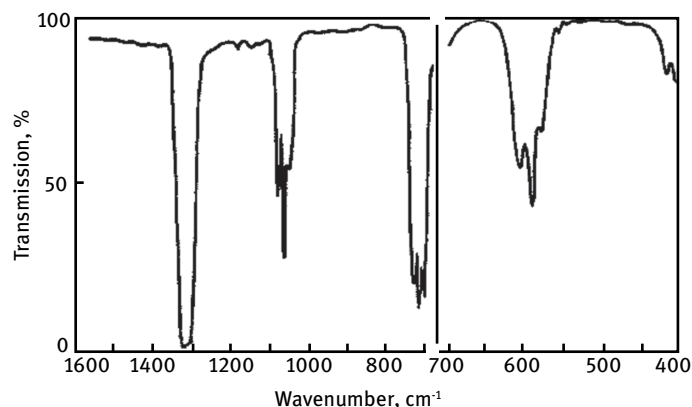


Figure 47: Infrared absorption spectrum of gaseous perchloryl fluoride. (Republished and modified from [477], with permission from © 1970 Springer Nature BV; permission conveyed through Copyright Clearance Center, Inc.)

Table 43: Intensities of the IR absorption bands of perchloryl fluoride.

Band assignment (Species)	Wavenumber, cm^{-1}	Absorption coefficient, $\text{L mol}^{-1} \text{cm}^{-2} \times 10^{-3}$
$\nu_1(\text{A}_1)$	1060	2.05
$\nu'_2(\text{A}_1)$	715 and 705	7.08
$\nu_2(\text{A}_1)$	550	2.3
$\nu_4(\text{E})$	1317	19.4
$\nu_5(\text{E})$	589	2.03
$\nu_6(\text{E})$	405	0.44

Data source: [477]

which the effective charge on the strongly electronegative fluorine atom is less than (or equal to) the effective charge on the oxygen atom. An attempt was made to analyze the electron density distribution from the intensities of the infrared spectra of FClO_3 and by quantum-chemical calculation.

The IR spectrum of isotope-labeled $\text{FCl}^{18}\text{O}_3$ has been recorded in the 610–1170 cm^{-1} range, using a Fourier transform infrared (FTIR) spectrometer with a resolution of 0.0024 cm^{-1} [478]. The ν_1 and ν_2 parallel bands (with band centers at 1011.1 and 708.2 cm^{-1} for the $\text{F}^{35}\text{Cl}^{18}\text{O}_3$ isotopomer and 1007.5 and 699.3 cm^{-1} for the $\text{F}^{37}\text{Cl}^{18}\text{O}_3$ isotopomer) have been studied and their resolved J and K structures have been analyzed. A set of accurate molecular constants has been determined for the ground state and $\nu_1 = 1$ and $\nu_2 = 1$ excited states of both isotopic species, which reproduced approximately 9700 observed lines with a standard deviation of $\approx 1 \times 10^{-4} \text{ cm}^{-1}$.

The high-resolution IR spectra of monoisotopic $\text{F}^{35}\text{Cl}^{18}\text{O}_3$ and $\text{F}^{37}\text{Cl}^{18}\text{O}_3$ have been studied in the region of the ν_4 fundamentals, centered at 1278.3 and 1263.3 cm^{-1} respectively [479]. Large perturbations were observed in both bands owing to a Fermi-type anharmonic resonance with the $\nu_2 + \nu_5$ combination bands, centered at 1270.7 cm^{-1} in $\text{F}^{35}\text{Cl}^{18}\text{O}_3$ and 1257.3 cm^{-1} in $\text{F}^{37}\text{Cl}^{18}\text{O}_3$. A comparison of measured high-resolution FTIR spectra of perchloryl fluoride and predictions using high-level *ab initio* methods gave fairly good agreement [480]. The geometry, dipole moment, and anharmonic force field of the molecule have also been calculated using *ab initio* methods. In continuation of this work, the high-resolution infrared spectra of isotope-labeled monoisotopic $\text{F}^{35}\text{Cl}^{16}\text{O}_3$, $\text{F}^{37}\text{Cl}^{16}\text{O}_3$, $\text{F}^{35}\text{Cl}^{18}\text{O}_3$, and $\text{F}^{37}\text{Cl}^{18}\text{O}_3$ have been studied in the region of the $2\nu_5$ overtones, from 1100 to 1200 cm^{-1} [481]. Both the parallel $2\nu_5^\circ$ and the perpendicular $2\nu_5^{\pm 2}$ components were clearly observed in the spectra, their origins differing by about 0.4 cm^{-1} . In each spectrum about 2000 transitions have been assigned, 35% of them belonging to $2\nu_5^\circ$.

Raman Spectra of Chlorine Trioxxygen Fluoride

Raman spectra of gaseous ClO_3F (Table 44) confirmed the earlier proposed tetrahedral C_{3v} symmetry [482].

Table 44: Raman spectra band assignments of gaseous perchloryl fluoride.

Raman wave numbers, cm^{-1}	Corresponding IR fundamental, cm^{-1}	Vibration	Species group	Assignments
410 m	405	6	E	rocking
549 ms	549	3	A_1	bending
587 m	589	5	E	bending
695–724 m	704	2	A_1	stretching ^{37}ClF
	714	2	A_1	stretching ^{35}ClF
1601 s	1061	1	A_1	Cl–O stretching
1175 w (broad)				2×587 (E) = 1174 ($A_1 + E$)
1312 w (broad)	1315	4	E	Cl–O stretching
1346 w				
1460 (broad)				$1060 + 410 = 1471$ (E)

s = strong, ms = medium strong, m = medium, w = weak

Data source: [482]

In agreement with the earlier assignments, bands at 1062, 716, and 549 cm^{-1} were again assigned to A_1 and the 1314, 573, and 414 cm^{-1} bands were assigned to E for tetrahedral C_{3v} symmetry [483]. In the liquid an unexpectedly broad band was observed between 695 and 724 cm^{-1} , whereas in the gas phase this band was resolved to show the isotope shift.

The contour of the ν_6 (E) Raman band of liquid ClO_3F has been studied over the temperature range 133–350 K [484]. Isotope splitting, vibrational, and instrumental influences on the band shapes were taken into account, and reorientational and angular momentum correlation times were obtained by comparing the corrected Fourier transforms of the band contours with the reorientational correlation functions calculated using the J -diffusion limit of the extended rotational diffusion model. The spinning top shape of the ClO_3F molecule is a good subject for such studies.

Microwave Spectra of Chlorine Trioxxygen Fluoride

As a result of the unsuccessful search for a microwave spectrum, it was concluded that the dipole moment of ClO_3F must be very small, not more than 0.09 D [485].

The millimeter-wave spectrum of natural FClO_3 has been recorded in the 350–400 GHz range, and transitions with $33 \leq J \leq 37$ and $0 \leq K \leq 30$ have been measured [486]. For comparison, the IR spectrum of monoisotopic $\text{F}^{35}\text{ClO}_3$ has been investigated in the 350–800 cm^{-1} region with a resolution of $3\text{--}4 \times 10^{-3} \text{ cm}^{-1}$, and the fundamentals ν_2 , ν_3 , ν_5 , and ν_6 were rotationally resolved. The ground state constants B_0 , DJ_0 , and DJK_0 were obtained by combining microwave and millimeter-wave data and ground-state combination differences determined from the ν_2 and ν_5 infrared bands. Equilibrium rotational constants of $\text{F}^{35}\text{ClO}_3$ were deduced with the help of vibrational corrections and the structure of FClO_3 was determined more accurately than before.

^{18}O -enriched, monolabeled perchloryl fluoride, $^{19}\text{F}^{35/37}\text{Cl}^{16}\text{O}^{18}\text{O}_2$, has been synthesized and its rotational microwave spectrum was recorded in the 4–22 GHz region [487]. For comparison, the spectra of the symmetric isotopomers $^{19}\text{F}^{35/37}\text{Cl}^{16}\text{O}_3$ were reinvestigated. Rotational and centrifugal distortion constants, as well as chlorine nuclear quadrupole and chlorine and fluorine spin–rotation and spin–spin coupling constants were then determined for the ground vibrational state and gave geometrical parameters and harmonic force field data.

Electric Properties of Chlorine Trioxxygen Fluoride

Dipole moments derived from the measurement of non-resonant dielectric loss of perchloryl fluoride gave a very small dipole moment of 0.023 D [488].

Perchloryl fluoride possesses one of the lowest molecular electric dipole moments, yet the solid exhibits appreciable dielectric absorption with maxima at low temperatures (90–110 K) and 500 Hz to 200 kHz frequencies from a Debye relaxation process [489, 490]. The dielectric properties and activation energy of 24.8 kJ/mol for molecular reorientation are somewhat unusual for a rotator solid and were discussed in terms of free-volume theory. In the clathrate hydrate condition there was no apparent dielectric dispersion from orientation of the guest ClO_3F , although the temperature dependence of the dielectric permittivity suggested possible contributions from dipole rotations and lattice vibrations at low temperatures.

The dipole moment of ClO_3F in solution was quite different from that in the vapor phase [491].

Magnetic Properties of Chlorine Trioxxygen Fluoride

When a nucleus of non-zero spin is bonded directly, or with a few intervening atoms, to another nucleus of nonzero spin, coupling of the two nuclear spins occurs via the bonding electrons. If the spin-coupled nuclei are magnetically non-equivalent, the spin coupling manifests by a splitting of the observed nuclear resonance peaks. When a nucleus of spin $1/2$ is coupled with a nucleus with spin greater than $1/2$, spin coupling is not always observed in the resonance spectrum of the nucleus with spin $1/2$. This can be attributed to a rapid relaxation of the nucleus with spin greater than $1/2$ owing to interaction of its quadrupole moment with an unsymmetrical electric field gradient. One would expect to see spin coupling when there is spherical symmetry about the nucleus of spin greater than one half, and this is observed. If the symmetry is less, the individual lines broaden and eventually coalesce into a single sharp line when the relaxation is rapid. Prior to this work, no examples had been reported of observable spin coupling of nuclei with chlorine, but sharp single peaks were observed. Both chlorine-35 and chlorine-37 have spin $3/2$ and appreciable quadrupole moments. As chlorine is quite electronegative, unsymmetrical bonds are to be expected in most of its compounds and rapid relaxation of the chlorine nuclear spin should occur. The first instance of observable spin–spin coupling with a chlorine nucleus was found in the fluorine resonance of perchloryl fluoride [492]. The lines of perchloryl fluoride had a width of 430 cycles, whereas at the same sweep rate the resonance of trifluoroacetic acid was immeasurably narrow. Therefore, considerable broadening of the fluorine resonance is occurring owing to rapid relaxation of the chlorine nuclear spin, which needed to be explained.

Pulsed ^{19}F NMR studies of spin–lattice relaxation times of solid ClO_3F gave a single reorientational correlation time with an activation energy of 28.9 kJ/mol (6.9 kcal/mol), an energy so high as to suggest that the residual entropy is due to the “freezing-in” of orientational disorder [493]. The low-temperature ^{19}F line shape yielded a chemical shift anisotropy of 570 ± 20 ppm.

Molecular Structure of Chlorine Trioxxygen Fluoride

Chlorine trioxxygen fluoride is thermally stable up to $\sim 723\text{ K}$ ($\sim 450^\circ\text{C}$). The thermal stability is believed to be due to the high symmetry of the molecule. Chlorine trioxxygen fluoride has a tetrahedral structure with the chlorine atom in the center and the oxygens and the fluorine at the corners of the tetrahedron (Figure 48). The fluorine atom is bonded directly to the central chlorine atom and does not attach to an $-\text{O}-\text{F}$ linkage.

The bond lengths are: $\text{F}-\text{Cl}$ 1.63 Å, $\text{O}-\text{Cl}$ 1.48 Å, $\angle\text{F}-\text{Cl}-\text{O}$ $95^\circ 10'$, $\angle\text{O}-\text{Cl}-\text{O}$ $119^\circ 12'$. The XRD powder diffraction pattern and the density of solid ClO_3F have been determined at liquid air temperatures [494]. From the powder data it appears that crystalline ClO_3F is tetragonal.

In several studies the FClO_3 molecule had been used as a model compound to test the validity of bond strength and force field calculations. The IR spectra of frozen FClO_3 in Ne, N_2 , and Ar matrices were recorded and the ^{35}Cl – ^{37}Cl isotopic shifts were

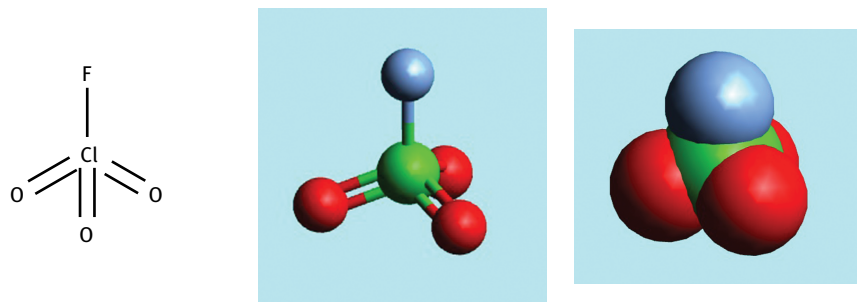


Figure 48: Molecular structures of chlorine trioxxygen fluoride.

measured to calculate bond strengths and force fields [495]. The Coriolis constants of the E-species vibrations were redetermined and, together with the isotopic data, used for the computation of a general valence force field. The A_1 block, for which only isotopic frequencies were available, was fixed with the help of *ab initio* force constant calculations. It was shown that ν_2 and ν_3 would best be described as an anti-symmetric and a symmetric combination respectively of the Cl—F stretching and the ClO_3 bending motions. Comparison with 13 previously published force fields demonstrated the inadequacy of undetermined force fields for strongly coupled systems, such as FCIO_3 . The ClO and ClF stretching force constants were found to be 9.76 and 3.49 mdyne $\text{\AA}^{-1}$ respectively, in good agreement with those expected for mainly covalent Cl—F single and Cl=O double bonds.

Miscibility of Chlorine Trioxxygen Fluoride

Liquid ClO_3F in a molar ratio of 1:1 is completely miscible with O_2F_2 at 127 K, ClF at 160 K, or ClF_3 at 195 K, but forms two separate layers with LOX at 90 K [41].

Thermodynamic Properties of Chlorine Trioxxygen Fluoride

A standard enthalpy of formation for perchloryl fluoride of -22.6 ± 1.0 kJ/mol was determined from its heat of alkaline hydrolysis measured in a calorimeter, which compared well with a previously obtained value of -26.5 ± 2.9 kJ/mol from the heat of hydrogenation [496]. The thermochemistry of hydrolysis and bond fission of perchloryl fluoride helps to explain its reactivity.

The NIST Chemistry WebBook lists the enthalpy and entropy of formation of the gas as $\Delta H_f^\circ_{\text{gas}} = -21.42$ kJ/mol and $S^\circ_{\text{gas}, 1 \text{ bar}} = 278.97$ J $\text{mol}^{-1} \text{K}^{-1}$ [40]. The JANAF Tables list the enthalpy of formation of the gas as $\Delta H_f^\circ_{\text{gas}} = -5.12 \pm 0.68$ kcal/mol ($= -21.42 \pm 2.84$ kJ/mol) [77]. The gas phase heat capacity of ClO_3F can be expressed by a Shomate equation

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + E/\tau^2$$

where C_p is the heat capacity in $\text{J mol}^{-1} \text{K}^{-1}$ and τ is the absolute temperature in kelvin divided by 1000. The constants A through E are listed in Table 45 for two temperature ranges and are also used to calculate the enthalpy and entropy.

Table 45: Constants for heat capacity, enthalpy, and entropy of chlorine trioxide fluoride vapor.

Temperature range, K	298–1200	1200–6000
A	36.66519	107.0485
B	152.4842	0.561539
C	-125.8631	-0.110696
D	37.21241	0.007508
E	-0.625788	-7.743538
F	-40.19443	-74.34382
G	279.6280	377.5227
H	-21.42204	-21.42204

Data source: [40]

The differential enthalpy of formation of gaseous ClO_3F can be expressed by a polynomial equation

$$H^\circ - H^\circ_{298.15} = A\tau + B\tau^2/2 + C\tau^3/3 + D\tau^4/4 - E/\tau + F - H$$

where $H^\circ - H^\circ_{298.15}$ is the differential enthalpy of formation in kilojoules per mol and τ is the absolute temperature in kelvin divided by 1000. The constants A through H are listed in Table 45 for two temperature ranges and are also used to calculate the heat capacity and entropy.

The entropy of formation of gaseous ClO_3F can be expressed by a polynomial equation

$$S^\circ = A \ln(\tau) + B\tau + C\tau^2/2 + D\tau^3/3 - E/(2\tau^2) + G$$

where S° is the entropy in $\text{J mol}^{-1} \text{K}^{-1}$ and τ is the absolute temperature in kelvin divided by 1000. The constants A through G are listed in Table 45 for two temperature ranges and are also used to calculate the enthalpy and heat capacity.

The heat of formation of gaseous perchloryl fluoride was determined by reacting it with hydrogen in a calorimeter bomb and was calculated as $-21.44 \pm 2.85 \text{ kJ/mol} = -5.12 \pm 0.68 \text{ kcal/mol}$ [471].

The heat capacity of solid perchloryl fluoride was measured over the range $2.7 \text{ K} < T < 23 \text{ K}$ [497]. Analysis of the data showed that only lattice vibrations were contributing to the heat capacity below 12.5 K and that a Schottky anomaly was not present down to 2.7 K. The dielectric constant ϵ of ClO_3F has been measured over the range $4.2 \text{ K} < T < 160 \text{ K}$ with an estimated precision of $\pm 1\%$. A rise in ϵ was observed between 80 K and the melting point at 125.64 K. This behavior may be explained

in terms of molar polarization. A correlation of residual entropy with the Raman spectrum of polycrystalline ClO_3F indicated a partially ordered crystal at 0 K.

Additional physical and thermodynamic data on ClO_3F and other fluorine compounds can be found in [498]. See also [499].

5.1.2.3 Chemical Properties of Chlorine Trioxxygen Fluoride

Thermal Decomposition of Chlorine Trioxxygen Fluoride

Chlorine trioxxygen fluoride is thermally very stable; it decomposes only above 773 K (500 °C) [500–502]. Perchloryl fluoride is thermally stable up to 723 K (450 °C).

Reactions of Chlorine Trioxxygen Fluoride

Reactions with Inorganic Compounds

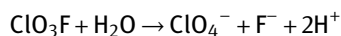
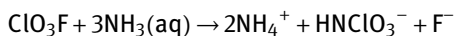
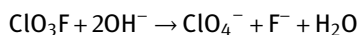
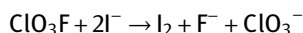
Activated charcoal ignites in ClO_3F even at very low temperatures (195 K = –78 °C).

Chlorine trioxxygen fluoride is highly resistant to hydrolysis because even at 523–573 K (250–300 °C) the reaction is slow. Rapid hydrolysis, however, can be effected by the use of alcoholic potassium hydroxide at 298 K (25 °C) or hot potassium hydroxide aqueous solutions. Indeed, this reaction may be used to determine perchloryl fluoride quantitatively because a quantitative precipitation of potassium perchlorate takes place whereas potassium fluoride remains in solution.

When dissolved in water, perchloryl fluoride reacted only very slowly with the solvent [503]. The solubility in water at 1 atm and temperatures up to 313 K (40 °C) is given by the equation

$$S = 6.387 \times 10^{-8} \exp(6852/RT)$$

where S is the solubility in mol/L solvent, and T is the temperature in kelvin. The following reactions have been studied to learn their rate laws and rate constants:



At temperatures near 273 K (0 °C), perchloryl fluoride and water readily formed a solid clathrate hydrate of variable composition. The observed minimum ratio of H_2O to ClO_3F in the solid was about 7.75.

Perchloryl fluoride oxidized potassium iodide solution to give elemental iodine and chloride and fluoride ions. With anhydrous ammonia, two liquid phases were formed and a slow reaction took place with the formation of a mixture of ammonium fluoride NH_4F and an ammonium salt of the amide of perchloric acid, $[\text{NH}_4^+] \cdot [\text{HNCLO}_3^-]$ [504]. This ammonium salt formed a stable aqueous solution from which the slightly soluble silver or barium salts of the amide can be precipitated.

These salts are explosive, white crystalline solids. Ammonolysis of ClO_3F in liquid NH_3 was greatly accelerated by traces of NaNH_2 (base catalysis).

Perchloryl fluoride was inert toward AsF_5 and SbF_5 , but the analog bromine compound BrO_3F underwent fluoride ion abstraction and O_2 elimination to form $[\text{BrO}_2][\text{SbF}_6]$, rather than simple fluoride ion abstraction to form BrO_3^+ salts. The reaction of FClO_3 with PtF_6 yielded a product containing $[\text{ClO}_2\text{F}_2^+][\text{PtF}_6^-]$. A synthetic method converted this salt into $[\text{ClO}_2\text{F}_2^+][\text{BF}_4^-]$ or $[\text{ClO}_2\text{F}_2^+][\text{AsF}_6^-]$ [505, 506]. All three salts were stable at 298 K (25 °C), reacted violently with water or organic materials and according to their IR, Raman NMR spectra are ionic in both the solid state and HF solution. The PtF_6^- compound was canary yellow, whereas those of AsF_6^- and BF_4^- were white. It is unlikely that any of these salts can be used as rocket propellants, but they add to the large number of fluorine compounds that could potentially give a very high specific impulse.

The reaction of NH_2OH with ClO_3F did not give new difluoroamino compounds (maybe HONF_2 ??), but instead NH_2OH reacted with ClO_3F to form $(\text{NH}_3\text{OH})\text{F}$ and unstable $(\text{NH}_3\text{OH})\text{ClO}_3$. $(\text{NH}_3\text{OH})\text{ClO}_3$ decomposed to $(\text{NH}_3\text{OH})\text{NO}_3$ and ClO_2 [507].

Reactions with Organic Compounds

Chlorine trioxxygen fluoride is a strong oxidizer, but in contrast to chlorine trifluoride it does not ignite common fuels on contact at room temperature. Mixtures of ClO_3F with combustible gases such as propane or hydrogen burn with potentially explosive power once they are ignited by an external source of energy.

The reaction of ClO_3F with guanidine in solution did not give *N*-fluoro or *N,N'*-difluoroguanidine, but instead yielded guanidinium salts $\text{C}(\text{NH}_2)_3^+\text{X}^-$ ($\text{X} = \text{F}, \text{ClO}_4$) [508, 509].

Chlorine trioxxygen fluoride can be used for the selective fluorination or perchlorylation of organic compounds [510]. However, when insufficiently diluted or in a situation where heat accumulates and is not conducted away fast enough, explosions can occur [511].

Surprisingly, perchloryl fluoride can be dissolved in several organic solvents without instant inflammation. The solutions may be detonable, though. The solubility of perchloryl fluoride in several organic solvents was determined at 298 K (25 °C) and 13–101 kPa (100–760 mm Hg) [512]. ClO_3F was gradually fed from the glass reservoir into an ampule immersed in a temperature-controlled bath. After the attainment of equilibrium, the amount of dissolved ClO_3F was estimated as the difference between the amount of ClO_3F brought into the measuring part of the apparatus and the amount of ClO_3F in the gas phase. The solubility of ClO_3F obeyed Henry's law. For the following solvents, the solubilities at 101 kPa (760 mm Hg) in g ClO_3F /L of the solvent and Henry's law coefficients (ClO_3F partial pressure in the gas phase/ ClO_3F concentration in the liquid phase, in mm Hg/mol fraction) were: tetrahydrofuran 52.4, 14760; dimethoxyethane 44.4, 15950; CCl_4 39.3, 18130; Me_2CO 35.1, 22100; diethylene glycol

dimethyl ether 20.6, 27390; 2-methoxyethanol 22.8, 42940; dimethylformamide 19.3, 52910; MeOH 24.7, 65240; acetonitrile 17.9, 73600.

Analysis of Chlorine Trioxxygen Fluoride

Analytical methods are available to analyze traces of perchloryl fluoride in the work-room air and methods for quality control of perchloryl fluoride analyze for assay and contaminants.

Mass Spectrometric Analysis of Chlorine Trioxxygen Fluoride

In the inlet to a mass spectrometer, perchloryl fluoride is ionized and dissociated by electron impact [513]. Mass spectrometry can also be used to identify the decomposition products of perchloryl fluoride [514]. By this method, the bond energies $F-ClO$, $Cl-OF$, $O-ClF$, $O-ClOF$, and $O-ClO_2F$ have been calculated.

5.1.2.4 Handling of Chlorine Trioxxygen Fluoride

Chlorine trioxxygen fluoride is not as reactive as ClF_3 , but nevertheless many safety precautions need to be taken before using large quantities of it as a rocket propellant. Just as with other fluorine oxidizers, contact with organic lubricants or other combustible materials (rubber, paper) must be avoided.

5.1.2.5 Materials of Construction for Chlorine Trioxxygen Fluoride

Although it hydrolyzes only very slowly, in the presence of water perchloryl fluoride becomes more corrosive.

Compatibility of Chlorine Trioxxygen Fluoride with Metals

Some stainless steels and nickel alloys are resistant even toward moist ClO_3F , but it is recommended to subject them to a passivation period with dry ClO_3F before putting the system into service.

In most cases, Monel and nickel would be the preferred materials of construction. Aluminum, copper, magnesium, titanium, niobium (=columbium), and molybdenum and their alloys and several stainless steels have been investigated with regard to their resistance against chlorine trifluoride and perchloryl fluoride. Most metals (aluminum, copper, nickel, steel, brass, bronze, and Monel) are compatible with dry ClO_3F at room temperature. However, in the presence of traces of moisture the rate of corrosion can become troublesome [515]. Materials compatibility studies were carried out for ClF_3 , ClO_3F , and mixtures of these two oxidizers [198]. A few aluminum, copper, magnesium alloys, and stainless steel with low carbon content were found to be suitable for ClF_3/ClO_3F service, but only for temperatures up to 303 K (30 °C). In all cases, freshly machined metal surfaces have to be slowly passivated with gaseous ClF_3 before they are placed into service at full pressure. Typical alloys of Al, Cu, Mg, Ni, low-carbon steel, and stainless steel were resistant to ClF_3 or ClO_3F and their mix-

tures at 303 K and even under severe mechanical shock [199, 200]. The metals must be clean and dry, but no special passivation was required. An HNO_3/HF pickling acid cleaning step was recommended for stainless steels and high-Ni alloys. Ti, Nb, Mo, and graphite were rapidly attacked by ClF_3 , Ti and ClO_3F , although non-reactive under stagnant conditions at room temperature, were shock sensitive.

Compatibility of Chlorine Trioxygen Fluoride with Non-metallic Materials

Only PTFE (Teflon) and similar perhalogenated gasket materials and lubricants (Kel-F, Permatex) can be used for service with ClO_3F .

Poly(tetrafluoroethylene) and poly(chlorotrifluoroethylene) can be used with ClF_3 or ClO_3F and their mixtures at up to 303 K but mechanical shock must be avoided [199, 200]. Both plastics absorb moderate amounts of the oxidizers and can undergo structural changes and embrittlement. These plastics are best used only in the vapor phase with these gases. They should never be used with these oxidizers under heat, shock, or fast flow conditions.

Fluorocarbon plastics and silicone rubber are suitable for use with OF_2 , and Teflon, polyethylene, and ethylene propylene rubber are suitable for use with a perchloryl fluoride/tetrafluorohydrazine mixture [516].

5.1.2.6 Toxic Properties of Chlorine Trioxygen Fluoride

Small concentrations of chlorine trioxygen fluoride in air can be recognized by their pungent odor at concentrations below the maximum allowable concentration. In 1968, the TLV listed for perchloryl fluoride was 10 ppm. The 2005 NIOSH TWA for perchloryl fluoride was 3 ppm with a short-term ceiling of 6 ppm. The OSHA PEL was 3 ppm. As of 2014, the IDLH value established for perchloryl fluoride by NIOSH [517] was 100 ppm, which had been revised downward from a former level of 385 ppm.

Laboratory animals were exposed to perchloryl fluoride gas for 4 h [518]. Exposures of dogs and rodents to concentrations ranging from 220 to 885 ppm and repeated exposures (6 h/day, 5 days/week) of rodents to 185 ppm for 7 weeks caused pulmonary irritation and increased methemoglobin formation and red blood cell destruction. The 4-h LC_{50} for rats was 385 ppm and for mice 630 ppm. These changes were less severe in rodents exposed repeatedly (6 h/day, 5 days/week) to 104 ppm for 5 weeks. Urinary excretion and bone deposition of fluoride were found in rodents exposed repeatedly to the 185 ppm and 104 ppm levels and in rodents and dogs exposed (6 h/day, 5 days/week) to 24 ppm of perchloryl fluoride for 26 weeks. Urinary fluoride levels decreased very rapidly when exposures were terminated. Fluoride deposition occurred in the bones at a decreasing rate; removal from the bones was very slow after exposure.

Human volunteers were used to estimate the median detectable concentration of perchloryl fluoride gas. The concentration detected by 50% of the tested personnel was 41 ppm. This value differed significantly from a previously published value of 10 ppm.

The lethal concentration LC_{50} with mice after a 4-h inhalation period was 630 ppm. This relatively high concentration indicated that ClO_3F was not as toxic as elemental fluorine or chlorine trifluoride. In a long-term test where groups of rats were exposed to 200 ppm ClO_3F for 8 h/day, 5 days/week there were no fatalities, but poisoning symptoms were evident from external observation. Similar tests with only 40 ppm with groups of rats and guinea pigs were extended for 3 months, and produced no externally visible poisoning symptoms. The necropsy of the animals after an observation period showed that spleen and lungs were enlarged, and the red blood cell count indicated damage to the platelets. See also [519].

Some of the acute toxicity data for perchloryl fluoride are summarized in Table 46.

Table 46: Acute toxicity lethal concentration data for perchloryl fluoride.

Species	LC_{50} , ppm	LC_{Lo} , ppm	Time	Adjusted 0.5-h LC (CF)	Derived value	References
Rat	—	2000	40 min	2200 ppm (1.1)	220 ppm	[241]
Rat	385	—	4 h	770 ppm (2.0)	77 ppm	[518]
Mouse	630	—	4 h	1260 ppm (2.0)	126 ppm	[518]
Dog	—	451	4 h	902 ppm (2.0)	90 ppm	[520]

Data source: [521]

5.1.3 Chlorine Tetraoxygen Fluoride (also called “Fluorine Perchlorate”)

Chlorine tetraoxygen fluoride, ClO_4F , chlorine tetraoxyfluoride, ClO_4F , and chlorine dioxygen trifluoride ClO_2F_3 [522, 523] are unstable and cannot be used as rocket propellants.

Chlorine tetraoxygen fluoride, fluorine perchlorate, ClO_4F , ClO_3OF , CAS RN [10049-03-3], is colorless as a gas and a liquid and white as a solid. It was found to be stable at room temperature in either Teflon or passivated steel containers and to be the most stable member of the series ClO_3OF , ClO_3OCl , or ClO_3OBr . Although fluorine is usually the most electron-negative part of a molecule, it seems that under certain conditions fluorine can carry a formal positive charge and in those situations names such as fluorine nitrate or fluorine perchlorate may be justified.

5.1.3.1 Preparation of Chlorine Tetraoxygen Fluoride

Chlorine tetraoxygen fluoride, fluorine perchlorate, ClO_4F can be prepared by the reaction of elemental fluorine with 60% perchloric acid in a trickle column packed with glass chips [524]. Oxygen difluoride was observed as a byproduct in this reaction. It was reported that ClO_3OF consistently exploded when frozen. Fluorine perchlorate can also be prepared by reacting an aqueous solution of an alkali metal perchlorate salt with fluorine [525]. Chlorine tetraoxygen fluoride is extremely sensitive to shock

and contact with grease and often exploded before it could be collected for additional study of its properties.

Repeated explosions were encountered at the attempt to determine its melting point, which was eventually found to be near 105.85 K (−167.3 °C). As a precaution, no sample larger than 4 mL has ever been collected. The molecular mass calculated from the gas density (assuming the molecule is not associated in the gas phase) was 120 (theoretical mass is 118.46).

Very pure ClO_3OF could be obtained by the decomposition of NF_4ClO_4 [526]. The ClO_3OF prepared in this manner could be safely manipulated and frozen without explosions [527].

5.1.3.2 Physical Properties of Chlorine Tetraoxygen Fluoride

In view of its explosive nature, it is not surprising that very few papers dealing with ClO_3OF have been published since it was first discovered. The ^{19}F NMR spectrum of ClO_3OF in CFCl_3 and four infrared absorptions of the gas were reported [528]. The same four infrared bands at 1298, 1049, 885, and 666 cm^{-1} have also been observed in a later study in which the heat of hydrolysis was measured for ClO_3OF .

Infrared spectra of gaseous, solid, and matrix-isolated ClO_4F and Raman spectra of liquid ClO_4F were measured and all 12 fundamental vibrations expected for the covalent perchloric structure of symmetry C_s were observed and assigned [529]. A modified valence force field was computed for ClO_3OF by using the observed ^{35}Cl – ^{37}Cl isotope shifts, symmetry relations between the A' and the A'' block, and the off-diagonal symmetry force constants of the closely related FCLO_3 molecule as constraints. Previous assignments for ClO_3OCl , ClO_3OBr , ClO_3OCF_3 , and Cl_2O_7 had to be revised. The ^{19}F NMR spectrum of ClO_3OF was recorded, and thermodynamic properties were computed in the range 0–2000 K. The relative enthalpy of formation, $(\Delta H_T - \Delta H_0)$ of gaseous ClO_4F was $+15.03\text{ kJ/mol} = +3.592\text{ kcal/mol}$. See also [530, 531].

The heat of formation of fluorine perchlorate, ClO_4F , has been determined to be $+157.3 \pm 37\text{ kJ/mol}$ ($+37.6 \pm 9\text{ kcal/mol}$) from the measured value of the heat of hydrolysis [498]. An essentially corroborating value of $155 \pm 63\text{ kJ/mol}$ ($+37 \pm 15\text{ kcal/mol}$) for the heat of formation was obtained from the heat release from the reaction of fluorine perchlorate with hydrogen in a calorimetric bomb. However, experimental limitations contributed to the great uncertainty associated with this value.

5.1.3.3 Chemical Properties of Chlorine Tetraoxygen Fluoride

Under carefully controlled conditions, similar to earlier work with the addition of ClOClO_3 and BrOClO_3 to olefinic double bonds, fluorine perchlorate was found to add to fluorocarbon olefinic double bonds, such as in tetrafluoroethylene [527].

5.1.4 Chlorine Trifluoride Oxide ClF₃O

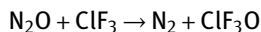
Chlorine trifluoride oxide, also known as chlorine monoxide trifluoride, oxychlorine trifluoride, ClF₃O, CAS RN [30708-80-6], was independently discovered in 1965 at Rocketdyne and in 1970 at Saclay. If it could be produced in larger quantities, it would make a good high-energy rocket propellant oxidizer, a storable version of FLOX.

5.1.4.1 Preparation of Chlorine Trifluoride Oxide

Chlorine trifluoride oxide has been prepared by either direct fluorination of Cl₂O, NaClO₂ or ClONO₂, or by glow discharge of F₂ in the presence of solid Cl₂O [532]. Chlorine trifluoride oxide can be synthesized by way of several gaseous reactions using UV activation at 213 K (−60 °C). The fluorination of both ClO₂F or ClO₃F, using ClF₅ or F₂ as fluorinating agents, gave excellent yields of ClF₃O [310]. Chlorine trifluoride oxide can be prepared by irradiating with UV at 193–283 K (−80 to +10 °C) a mixture of ClO₂F or ClO₃F with a fluorinating agent, such as ClF₃, ClF₅, ClF, OF₂, or F₂ [533]. In addition, the direct photochemical synthesis of ClF₃O from the elements Cl₂, F₂, and O₂ was successfully achieved. Other systems yielding ClF₃O on UV illumination were ClF₃ + O₂ and ClF₃ + IF₅O. All these processes give mixtures of chlorine fluorides and chlorine oxyfluorides that need to be separated before the pure compound can be analyzed any further. The most convenient and practical reaction system for the photochemical synthesis of ClF₃O is obviously the one starting from the elements Cl₂, F₂, and O₂. An intermediate forming first is ClF₃; thus, one might as well skip the first reaction step and start directly with ClF₃, F₂, and O₂.

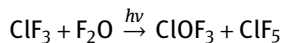
New syntheses of ClF₃O were discovered utilizing UV-initiated reactions of FClO₂ and FClO₃ [534]. In the presence of F₂, ClF₃, or ClF₅, FClO₂ gave ClF₃O in high conversions and high yields. The most effective fluorinating agent was ClF₅. The same techniques were not successful in oxidizing ClF₃O to ClF₅O or BrF₅ to BrF₇. There is some evidence that FClO is an intermediate in the synthesis of ClF₃O by UV activation. Corona discharge activation in the systems FClO₂/F₂ did not result in ClF₃O. In the mass spectrometer, a stable mass cracking pattern for ClF₃O was obtained with the most prominent peaks assignable to ClFO⁺ (100%), ClF₂O⁺ (80.60%), Cl⁺ (29.35%), ClF⁺ (21.23%), and ClO⁺ (14.78%). The ¹⁹F NMR spectrum of gaseous ClF₃O revealed two bands at −276ϕ and −317ϕ with respective ratios of 2 and 1. These bands support the proposed C_s symmetry for ClF₃O.

The use of N₂O as an oxygen source for the synthesis of ClF₃O was successful but offered no advantages over oxygen [535].



Experiments showed that some ClF₃O was indeed formed during the photolysis of N₂O/ClF₃, but no significant advantage over the O₂/ClF₃ reactant system was apparent.

The illumination of a mixture of ClF_3 and F_2O with UV light gives a mixture of ClOF_3 and ClF_5 [536]:



5.1.4.2 Physical Properties of Chlorine Trifluoride Oxide

Pure ClF_3O is colorless as a gas or liquid and white in the solid state. It boils at 302 K (+29 °C) and freezes at 231 K (−42 °C). Vapor pressures were measured over the range 250 to 304 K (−23 to +31 °C) and the data were fitted to the equation

$$\log P_V = 8.433 - 1680/T$$

where P_V is the vapor pressure in mm Hg and T is the temperature in kelvin. The latent heat of evaporation is 32.2 kJ/mol (7.7 kcal/mol). The density at 293 K (20 °C) is 1.865 g/cm³, which is similar to the densities of ClF_3 and ClF_5 .

The IR spectra of gaseous, solid, and matrix-isolated ClF_3O and the Raman spectra of gaseous and liquid ClF_3O showed nine fundamental vibrations, consistent with symmetry C_v . The vibrational spectra of ClF_3O agreed well with a trigonal-bipyramidal model with two fluorine atoms at the apexes and one fluorine atom, one oxygen atom, and one localized free electron pair at the remaining corners [81]. Thermodynamic properties were computed for ClF_3O in the range 0–2000 K. The differential enthalpy of formation of gaseous (ideal gas at 1 atm) ClF_3O is $(\Delta H_{298} - \Delta H_0) = 15.6 \text{ kJ/mol} = 3.732 \text{ kcal/mol}$.

5.1.4.3 Molecular Structure of Chlorine Trifluoride Oxide

Until 1982, no structural data had been published for this compound, except for its vibrational and ^{19}F MR spectra, which were in agreement with a pseudo-trigonal-bipyramidal structure of symmetry C_s . In this structure, two fluorines occupy the axial positions and one fluorine, one oxygen, and one sterically active free valence electron pair occupy the equatorial positions. Based on electron diffraction measurements, chlorine trifluoride oxide is a distorted-trigonal-bipyramidal molecule with three different ligands in the equatorial plane: a single bond, a double bond, and a lone valence electron pair [537]. The angles between the axial bonds and the double bond are larger (by about 7°) than the angles between the axial bonds and the single bond or the lone electron pair; i.e., the axial fluorine atoms are bent away from the double bond into the sector between the single bond and the lone electron pair. The observed bond distances ($\text{Cl}=\text{O} = 1.405 \text{ \AA}$, $\text{Cl}-\text{F}_{\text{eq}} = 1.603 \text{ \AA}$, $\text{Cl}-\text{F}_{\text{ax}} = 1.713 \text{ \AA}$) agreed well with previous estimates. The $\angle \text{F}_{\text{eq}}-\text{Cl}-\text{F}_{\text{ax}}$ angle is 87.9° and the $\angle \text{F}_{\text{ax}}-\text{Cl}-\text{F}_{\text{ax}}$ angle is 170.5°.

Chlorine trifluoride oxide ClF_3O was crystallized from the melt at 231 K (−42 °C) and the crystals were analyzed by XRD to give the cell dimensions as $a = 982.6(2) \text{ pm}$, $b = 1229.5(2) \text{ pm}$, $c = 490.1(1) \text{ pm}$, $\beta = 90.338(4)^\circ$, space group $C_{2/m}$ [538]. The asymmetric unit cell contains two crystallographically non-equivalent, pseudo-trigonal bipyramidal molecules in which two fluorine atoms occupy the axial and one fluorine atom, the oxygen atom and one sterically active, free valence electron pair of chlorine oc-

cupy the three equatorial positions. The structure, vibrational frequencies, isotopic shifts and force field of ClF_3O were calculated by MO methods and were in very good agreement with the observed values.

5.1.4.4 Chemical Properties of Chlorine Trifluoride Oxide

Chlorine trifluoride oxide resembles most chlorine fluorides in its corrosive and oxidizing properties. However, it appears to be somewhat more corrosive than either ClF_3 or ClF_5 .

Reactions of Chlorine Trifluoride Oxide

Chlorine trifluoride oxide, ClF_3O , is a strong oxidizer and ignites hypergolically with many fuels. When ClF_3O was heated to 553 K (280 °C) in a Monel bomblet for 16 h, 70% of the ClF_3O was decomposed to ClF_3 and oxygen.

The reaction of ClF_3O with elemental chlorine does not start at room temperature, but if heated with Cl_2 to 473 K (200 °C) for 16 h it converts to ClF . At ambient temperature, chlorine trifluoride oxide and N_2F_4 do not react. An equimolar mixture of the two was heated in a stainless steel cylinder at 403 K (130 °C) for 15 h before separating the products by fractional condensation. No unreacted N_2F_4 was recovered, the main product was NF_3 . The reaction of ClF_3O with PtF_6 formed a yellow solid identified as $[\text{ClF}_2\text{O}^+][\text{PtF}_6^-]$ and released F_2 gas [539].

Chlorine trifluoride oxide readily hydrolyzes with water. The reaction of chlorine trifluoride oxide with water was studied using DFT [540]. Results showed that the energy barriers of the reaction of chlorine trifluoride oxide and water are very low, and an excess of water produces HF , HClO_2 , and HClO_4 ; however, insufficient water produces HF and ClFO_2 .

Salts Derived from Chlorine Trifluoride Oxide

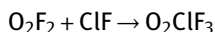
Chlorine trifluoride oxide, ClF_3O , is amphoteric and forms adducts and salts with Lewis acids as well as Lewis bases. The thermal stability of these adducts decreases in the order: $\text{ClF}_3\text{O}\cdot\text{SbF}_5 > \text{ClF}_3\text{O}\cdot\text{AsF}_5 > \text{ClF}_3\text{O}\cdot\text{BF}_3 > (\text{ClF}_3\text{O})_2\cdot\text{SiF}_4$ [541].

The infrared and Raman spectra of $\text{Cs}^+\text{ClF}_4\text{O}^-$ and $\text{Rb}^+\text{ClF}_4\text{O}^-$ were consistent with a C_{4v} structure analogous to that of XeF_4O and ClF_5 [542]. The bonding in ClF_4O^- is best described by a mainly covalent $\text{Cl}=\text{O}$ double bond and two semi-ionic, three-center, four-electron p-p σ $\text{Cl}-\text{F}$ bond pairs.

The vibrational spectra have been recorded for the solid 1:1 Lewis acid adducts with chlorine trifluoride oxide, $\text{ClF}_3\text{O}\cdot\text{BF}_3$, $\text{ClF}_3\text{O}\cdot\text{AsF}_5$, and $\text{ClF}_3\text{O}\cdot\text{SbF}_5$ and for $\text{ClF}_3\text{O}\cdot\text{BF}_3$ in HF solution [543]. These spectra were entirely consistent with the ionic structures, $[\text{ClF}_2\text{O}^+][\text{BF}_4^-]$, $[\text{ClF}_2\text{O}^+][\text{AsF}_6^-]$, and $[\text{ClF}_2\text{O}^+][\text{SbF}_6^-]$ respectively. The structure of ClF_2O^+ can be derived from a tetrahedron with the chlorine atom located at the center and with two fluorine atoms, one oxygen atom, and one free electron pair at the four corners.

5.1.5 Dioxygen Chlorine Trifluoride

Dioxygen difluoride, O_2F_2 , reacts with Cl_2 , ClF , or HCl and under certain conditions forms a deep violet addition product, called dioxygen chlorine trifluoride or chlorine trifluoride dioxide (O_2ClF_3)_n [544–546]. If the reaction between O_2F_2 and ClF is carried out under mild conditions, from just above the melting point of ClF (119 K) up to 130 K, an intense violet-colored intermediate compound of the elementary composition (O_2ClF_3)_n (referred to simply as O_2ClF_3) is formed:



Its color and hue are very similar to those of the organic dye methyl violet. Dioxygen chlorine trifluoride O_2ClF_3 is a solid, thermally stable up to 195 K. At this temperature it can be kept for over a year. It has a vapor pressure of less than 12 microns at 158 K. At this pressure and temperature it sublimates and dissociates into its components, which can be collected on a liquid nitrogen finger (77 K). If the cold finger is warmed up to 119–140 K, the violet compound forms again. The compound is insoluble in LOX at 90 K, in liquid ClO_3F at 140 K, and in liquid NF_3 at 160 K. It is soluble in ClF at 125 K, O_2F_2 at 140 K, and ClF_3 at 190 K. It is readily soluble in anhydrous HF at 190 K, forming a deep violet solution [523]. In the same report, it was also reported that dioxygen chlorine trifluoride can be synthesized from chlorine trifluoride and oxygen under pressure and UV illumination. The color of the ClF_3 solution increased appreciably with time. Dioxygen chlorine trifluoride is a strong oxidizer similar to O_2F_2 but not as powerful. When gaseous NH_3 was admitted to a reaction vessel containing O_2ClF_3 at 90 K, a reaction took place with a flash, forming white solids and some nitrogen-containing gases, whereas the violet color disappeared. Dioxygen chlorine trifluoride did not react with hydrogen or methane at 140 K, but did ignite with ethane or ethylene.

Chlorine trifluoride dioxide was prepared from FNO_2 and $ClO_2F_2PtF_6$, the latter being synthesized from $FClO_3$ and PtF_6 [547, 548]. The NMR spectrum suggested a trigonal–bipyramidal structure of symmetry C_{2v} . Chlorine trifluoride dioxide formed stable adducts with BF_3 and AsF_6 but not with FNO , FNO_2 , or CsF . Pure ClF_3O_2 is colorless as a gas or liquid and white in the solid state. It melts at 191.9 K (–81.2°C). Vapor pressure was measured over the range 177 to 241 K (–96 to –32°C) and the data were fitted by the method of least squares to the equation

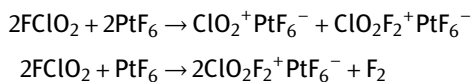
$$\log P = 7.719 - 1217.2/T$$

where P is the vapor pressure in mm Hg and T is the temperature in kelvin. The extrapolated boiling point is 251.57 K (–21.58°C). The latent heat of vaporization of ClF_3O_2 is 23.3 kJ/mol (5.57 kcal/mol). It reacts explosively with organic materials and care must be taken to avoid such combinations.

The IR spectra of gaseous, solid and matrix-isolated ClF_3O_2 and the Raman spectra of gaseous and liquid ClF_3O_2 were measured and 12 fundamental vibrations were observed, consistent with a structure of symmetry C_{2v} . A modified valence force field and thermodynamic properties were computed for ClF_3O_2 [549]. The question

is whether the two oxygen atoms are in axial or in equatorial positions. Proof for a pseudo-trigonal-bipyramidal structure of symmetry C_{2v} was obtained from its ^{19}F NMR spectrum, which showed an AB2 pattern with strong evidence for the two equivalent fluorine atoms occupying the apical positions. The relatively low boiling point (251.6 K = -21.5°C) and Trouton constant (22.13) of ClF_3O_2 imply little association in the liquid phase. The differential enthalpy of formation of gaseous (ideal gas at 1 atm) ClF_3O_2 is $(\Delta H_{298} - \Delta H_0) = 16.9 \text{ kJ/mol} = 4.049 \text{ kcal/mol}$.

The difluoroperchloryl cation, ClO_2F_2^+ , was prepared in the form of its PtF_6^- salt by reacting FClO_2 with PtF_6 in a sapphire reactor at 209 K = 25°C [550]. The following competing reactions were observed:



Cesium difluorochlorate(V), $\text{Cs}^+\text{ClO}_2\text{F}_2^-$, can be prepared from cesium fluoride and chloryl fluoride [551]. The IR and the Raman spectra of $\text{Cs}^+\text{ClO}_2\text{F}_2^-$ were consistent with a ClO_2F_2^- anion of symmetry C_{2v} . The structure can be derived from a trigonal bipyramid, where the two F atoms occupy the axial and the two O atoms and the lone electron occupy the equatorial positions.

5.1.6 Chlorine Pentafluoride Oxide

Chlorine(VII) pentafluoride oxide, also named chlorine(VII) oxygen pentafluoride, chlorine oxopentafluoride, OClF_5 , has not yet been synthesized, and attempts to make it were unsuccessful. Several attempts to prepare chlorine oxygen pentafluoride, OClF_5 have been unsuccessful.

5.2 Bromine Oxygen Fluorides

5.2.1 Bromyl Fluoride

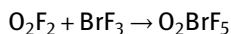
Bromyl fluoride, bromine dioxygen fluoride, BrO_2F , CAS RN [22585-64-4], is not a very powerful oxidizer and will most likely never be used as a rocket propellant. It is included here only for comparison with some of the chlorine oxygen fluorides that contain chlorine instead of bromine [552].

5.2.2 Bromine Trifluoride Oxide

Bromine trifluoride oxide, bromine oxyfluoride, BrF_3O , CAS RN [61519-37-7], will most likely never be used as a rocket propellant. It is of interest mostly as an analog to the more energetic chlorine trifluoride oxide, which would make a good rocket propellant if it became available in larger quantities and if there was no concern about the toxicity of either the propellant and/or the exhaust products.

Bromine trifluoride oxide was prepared from KBrF_4O and O_2AsF_6 by a displacement reaction in BrF_5 . The starting materials KBrF_4O and O_2AsF_6 had to be prepared in the laboratory. On the basis of incomplete vibrational spectra, IR spectra of gaseous, solid, and matrix-isolated BrF_3O and the Raman spectra of solid and liquid BrF_3O and of its HF and FClO_3 solutions, a structure of symmetry C_s was proposed for BrF_3O [553]. A detailed investigation and analysis of the vibrational and ^{19}F NMR spectra confirmed the previously proposed structure of a pseudo-trigonal-bipyramidal structure of symmetry C_s with two fluorine atoms at the apexes and one fluorine, one oxygen, and one localized free electron pair at the remaining corners. The bond lengths and angles were $D(\text{Br}-\text{O}) = 1.56 \text{ \AA}$, $R(\text{Br}-\text{F}') = 1.72 \text{ \AA}$, $r(\text{Br}-\text{F}) = 1.81 \text{ \AA}$, $\angle\alpha(\text{O}-\text{Br}-\text{F}') = 120^\circ$, and $\angle\beta(\text{O}-\text{Br}-\text{F}) = \angle(\text{F}'-\text{Br}-\text{F}) = 90^\circ$. The differential enthalpy of formation ($\Delta H_{298} - \Delta H_0$) of the gas at 298 K is 16.9 kJ/mol (4.050 kcal/mol). See Ellern et al. [538].

A potential high-energy oxidizer is dioxygen bromine pentafluoride, O_2BrF_5 , prepared by reaction of dioxygen difluoride with bromine trifluoride [554]:



Similar compounds are available with iodine instead of bromine as the central atom, but there does not seem to be any practical use for such oxidizers and they are only of academic interest.

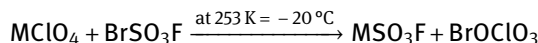
5.3 Iodine Oxygen Fluorides

Iodine oxygen fluorides are only of theoretical interest, in particular when the iodine atom is oxidized to its +7 state of oxidation. They are not likely to be used as rocket propellants, but can serve as intermediates or templates in the synthesis of more powerful oxidizers. A new compound of iodine(VII), IOF_5 , was prepared in pure state in bulk quantities by the reaction of IF_7 with H_2O or SiO_2 , followed by the removal of unreacted IF_7 from the resulting IOF_5 mixture with SbF_5 . IOF_5 was characterized by its IR and ^{19}F NMR spectra [555].

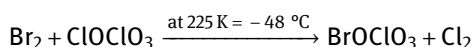
6 Other Halogen Perchlorates

Halogen perchlorates are no fluorine compounds, but closely related to the chlorine oxygen fluorides. Halogen perchlorates are shock sensitive and should be handled with proper safety precautions. Chlorine perchlorate, ClOClO_3 , was synthesized from the action of chlorine fluorosulfate on several perchlorate salts [535]. The low-temperature IR spectrum of solid ClOClO_3 was recorded by condensing the sample on the cold ($77 \text{ K} = -196^\circ\text{C}$) internal AgCl window of a conventional low-temperature cell [556]. From the vibrational spectra the thermodynamic properties

could be calculated. The differential enthalpy of formation of gaseous (ideal gas at 1 atm) ClOClO_3 is $(\Delta H_{298} - \Delta H_0) = +17.4 \text{ kJ/mol} = +4.161 \text{ kcal/mol}$. Similar data were obtained for bromine perchlorate. Bromine perchlorate can be prepared by a method using bromine(I) fluorosulfate [557]



The oxidation of elemental bromine with chlorine perchlorate also forms bromine perchlorate



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Hydrazinium Salt Oxidizers

Hydrazinium salts have the advantage that they do not introduce condensable oxide-forming cations such as sodium or potassium. They share this advantage with ammonium cations, but hydrazinium cations are more energetic than ammonium cations. On the other hand, in both ammonium and hydrazinium salts with oxidizing anions, some of the oxidizing power of the anion is consumed in burning the hydrogen that is carried in with the hydronitrogen cation.

Although ammonium and hydrazinium nitrates and perchlorates can burn by themselves if the decomposition is accelerated by burning rate additives, the mono-solid burning does not offer any advantages over formulations that contain organic binders. The mono-solid burning is done mostly for academic reasons to characterize the ammonium or hydrazinium salt before mixing it in with other ingredients, mainly binders. **Caution:** The strand-burning decomposition of pure hydrazinium salts can spontaneously transition into a detonation.

Even relatively inert salts such as hydrazinium sulfate can explode when heated in concentrated solutions with an open flame to near dryness. During a student preparation of hydrazinium sulfate, using a standard preparative method, the liquid reaction mixture detonated violently [1]. The containing evaporating dish was shattered, and the asbestos gauze was driven down through the opening of the supporting tripod.

This chapter also contains a section on hydrazinium azide (HA), which, although not an oxidizer, is an energetic additive and one of the marginally stable compounds with the highest possible nitrogen content (see Section 5).

1 Hydrazinium(1+) Nitrate

The chemical name “hydrazinium nitrate” is not unambiguous, because there are two hydrazinium nitrates, depending on the degree of protonization of the hydrazine molecule: Hydrazinium ions can exist as mono-protonated hydrazinium(1+) ions and di-protonated hydrazinium(2+) ions. Hydrazinium(2+) salts are formed only with very strong acids, such as perchloric acid. If the (1+) or (2+) designator is missing in a report referring to hydrazinium nitrate, it is safe to assume that the author is writing about the more common hydrazinium(1+) nitrate. Foreign language publications often call this compound “*hydrazonium nitrate*”, but this is not the IUPAC-recommended nomenclature. The term “hydrazine nitrate” is often found in the literature, but is not correct. We would not call ammonium nitrate (AN) ammonia nitrate, would we?

The nomenclature question is if the hydrazinium(2+) salts should be named dianion such as hydrazinium(2+) dinitrate or simply hydrazinium(2+) nitrate. It appears that the (2+) designator should clearly indicate that there must be two nitrate anions in the neutral salt as long as it does not carry any electrical charges.

Hydrazinium nitrate is often abbreviated here as HN. This abbreviation is not to be confused with the diatomic imidogen radical NH. A very detailed summary of the properties of hydrazinium(1+) nitrate and hydrazinium(2+) dinitrate was already published in the author's earlier books on hydrazine: The first edition [2], pages 120 through 272, and the significantly expanded second edition [3], pages 220 through 375, contain information on all hydrazinium salts. Additional information on hydrazinium nitrate is contained in the book by Patil and Rattan [4], pages 37 through 46. The main emphasis in the current chapter is on publications that have appeared in the interim or that were not already included in the two earlier books. For literature searches in the Chemical Abstracts, SciFinder or similar databases it is very useful to have the CAS Registry numbers, which identify the two hydrazinium nitrates with unique numbers:

Hydrazinium(1+) nitrate CAS RN 37836-27-4

Hydrazinium(2+) nitrate CAS RN 13464-98-7

1.1 Production of Hydrazinium(1+) Nitrate

Producing hydrazinium(1+) nitrate by mixing aqueous solutions of hydrazine hydrate and nitric acid would be a simple acid-base neutralization reaction, as long as the reactants are sufficiently diluted and the evolved heat is effectively carried away. What happens if the dilution is not sufficient is called hypergolic ignition and more of this reaction will be discussed in a future volume in this Encyclopedia, *Encyclopedia of Hypergolic Bipropellant Combinations*.

It is also possible to produce HN in non-aqueous media, starting with hydrazinium carbazate. As nitric acid is a stronger acid than carbonic acid, it replaces carbonic acid, carbon dioxide escapes and HN remains in suspension as a salt that is easily dried [5]. In one example, 50 g of hydrazinium carbazate was suspended in chlorofluoroethylene, and treated with 34 g of a fine jet of cold HNO_3 ($\rho = 1.5 \text{ g/cm}^3$) with efficient cooling until a pH of 5.2–5.4 was attained and until the evolution of gas ceased, giving an almost pure powdered HN. The precipitated HN was filtered off with suction and washed with 250 mL MeOH. The yield was 48 g HN.

A similar method avoids or at least minimizes the use of water by working in methylene chloride suspension [6]. For example, 5 g of hydrazine hydrate were mixed with 25 mL CH_2Cl_2 and stirred vigorously. Then, 55 mL of 10.9 vol.-% HNO_3 , cooled to 293–298 K (20–25 °C) was added until a mildly acidic pH was obtained. The precipitate was filtered and 6.2 g of 97% pure HN was obtained. See also [7, 8].

1.2 Physical Properties of Hydrazinium(1+) Nitrate

The physical properties of hydrazinium nitrate are summarized in Table 1.

Table 1: Physical properties of hydrazinium nitrate.

Property	SI Units	Other units	References
Molecular mass	95.058 g/mol	10.5197 mol/kg	
Melting point, α -HN	343.6 K	70.5 °C	[9]
Melting point, β -HN	335.6 K	62.5 °C	[9]
Density at 298 K	1.661 g/cm ³		[9]
Enthalpy of formation	-246.2 $\pm$ 0.96 kJ/mol	-58.86 $\pm$ 0.23 kcal/mol	[10]

1.2.1 Melting Point and Phase Diagrams of Hydrazinium(1+) Nitrate

Hydrazinium(1+) nitrate exists in two crystalline forms, the α and the β modification. The β form is unstable, and only a few properties other than its melting point and the refractive index are known. The β modification of HN melts at a lower temperature than the α modification. α -Hydrazinium(1+) nitrate melts at 343.6 K [9, 11], and the β modification melts 8° lower at 335.6 K. Melting points reported 100 years ago differ only by fractional degrees [12]. The solidifying melt kept at a temperature between 335 and 343 K (62 and 70 °C) only slowly converts to the α modification. Table 2 contains a summary of melting points for hydrazinium nitrates.

Table 2: Melting points of hydrazinium nitrates.

Compound	Melting point		Author	References
	K	°C		
N ₂ H ₅ NO ₂	315	42	Miron and Perlee	[13]
β -N ₂ H ₅ NO ₃	335	62	Perlee et al.	[14]
α -N ₂ H ₅ NO ₃	343	70	Patil et al.	[15]
			Rubtsov and Manelis	[16]
α -N ₂ H ₅ NO ₃	343.65	70.5	Robinson and McCrone	[11]
β -N ₂ H ₅ NO ₃	335.65	62.5	Robinson and McCrone	[11]
N ₂ H ₅ NO ₃	343.95	70.8	Zhou et al.	[17]
α -N ₂ H ₅ NO ₃	343.86	70.71	Wang	[18]
N ₂ H ₆ (NO ₃) ₂	374–376	101–103	Breisacher et al.	[19]
N ₂ H ₅ (NO ₃) ₂	376	103	Miron and Perlee	[13]

1.2.1.1 Melting Points of Binary Hydrazinium(1+) Nitrate Systems

On occasions, it may be advantageous to mix HN with other nitrate salts in order to reduce its sensitivity. Various alkali metal nitrates have been mixed with HN to determine low-melting compositions and to find out if they form eutectic melts. The eutectic compositions and melting points of mixtures of five alkali metal nitrates or ammonium nitrate (AN) with hydrazinium nitrate are listed in Table 3.

Table 3: Melting points of hydrazinium nitrate salt binary eutectics.

Additive	$\text{N}_2\text{H}_5\text{NO}_3$	Melting point	
	Mass-%	$^{\circ}\text{C}$	K
Ammonium nitrate	68	43	316
Cesium nitrate	64	43	316
Lithium nitrate	85	25	298
Potassium nitrate	95	54	327
Rubidium nitrate	78	36	309
Sodium nitrate	95	47	320

Data source: [20]

No well-defined compounds or double salts could be identified in these inorganic binary systems. The literature contains melting point diagrams for many binary compositions containing between 100 and 30% hydrazinium nitrate. The data in Table 3 were derived from the melting point minima of these curves.

A study of the phase diagrams of the $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{NO}_3$ and $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{Cl}$ systems revealed formation of the complexes $\text{N}_2\text{H}_4 \cdot \text{N}_2\text{H}_5\text{X}$ ($\text{X} = \text{NO}_3$ or Cl), which dissociate at temperatures close to their melting points (276 and 237 K respectively; +3 and -36°C respectively) [21]. Crystallization of metastable $\beta\text{-N}_2\text{H}_5\text{NO}_3$ depressed the freezing point of the system by $8\text{--}10^{\circ}$. When kept at temperatures lower than the melting points of the eutectics of the system, a phase transition from β - to $\alpha\text{-N}_2\text{H}_5\text{NO}_3$ took place.

Melting points of a eutectic mixture of hydrazinium(1+) nitrate and nitroguanidine (NQ) and fusion enthalpy of the pure components and the eutectic were determined using differential scanning calorimetry (DSC) [22]. The structure of the HN/NQ eutectic was characterized by infrared (IR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). Thermodynamic functions such as excess Gibb's energy, excess enthalpy, and excess entropy of the HN/NQ eutectic were calculated using activity coefficient data. The intermolecular interactions of different molar ratios of the HN/NQ eutectic were determined by density functional theory methods. IR spectroscopic and XRD studies confirmed that there is some interaction between the components during the formation of the eutectic mixture. In particular, the microstructure of the eutectic mixture at a molar ratio of 3:2 was more uniform than others. Similar eutectics were formed with methylnitroguanidine and hydrazinium(1+) nitrate [23].

A study of eutectic and peritectic points in the binary systems HN/nitroguanidine (HN/NQ) and HN/methylnitroguanidine (HN/MeNQ) detected indications of double salt formation with a well-defined stoichiometric ratio. The HN/NQ binary system showed the presence of a new substance, which is probably a HN/NQ co-crystal. No new substance was detected in the MeNQ/HN binary system [24]. The HN/NQ system had two eutectics, one at an NQ mol fraction of 0.226 melting at 322 K (49°C) and another at a mol fraction of 0.95 melting at 416 K (143°C). In between was a peritectic

melting at 500 K (227 °C) with a composition of three mols of NQ per mol of HN. The HN/MeNQ had only one eutectic at a MeNQ mol fraction of 0.307 melting at 341.7 (68.6 °C).

1.2.1.2 Freezing Points of Hydrazinium Nitrate Solutions

The binary system hydrazine/hydrazinium nitrate has been thoroughly investigated. Within a few years of each other, two different organizations, JPL and NOTS, produced two sets of data that agreed quite well with each other. Deviations do not exceed a few degrees at worst, and most of the time the two curves were within 1 °C of each other. The data of Elverum and Cole [25] were used in drawing the phase diagram in Figure 1. The phase diagram indicates the formation of a hydrazinium nitrate hydrazinate $\text{N}_2\text{H}_5\text{NO}_3 \bullet \text{N}_2\text{H}_4$ with a melting point of 274.8 K. There are two eutectics, one located on either side of the 1:1 compound, the lower-melting eutectic containing 45% HN and melting at 223.3 K (−57.6 °F). See also [21].

The melting points in the binary system HN/H₂O have to be known for successful crystallization of HN during the careful preparation of this salt in aqueous solutions, and also to prevent the inadvertent precipitation of the shock-sensitive HN from aqueous HN solutions during storage. The melting point of the hydrazinium nitrate/

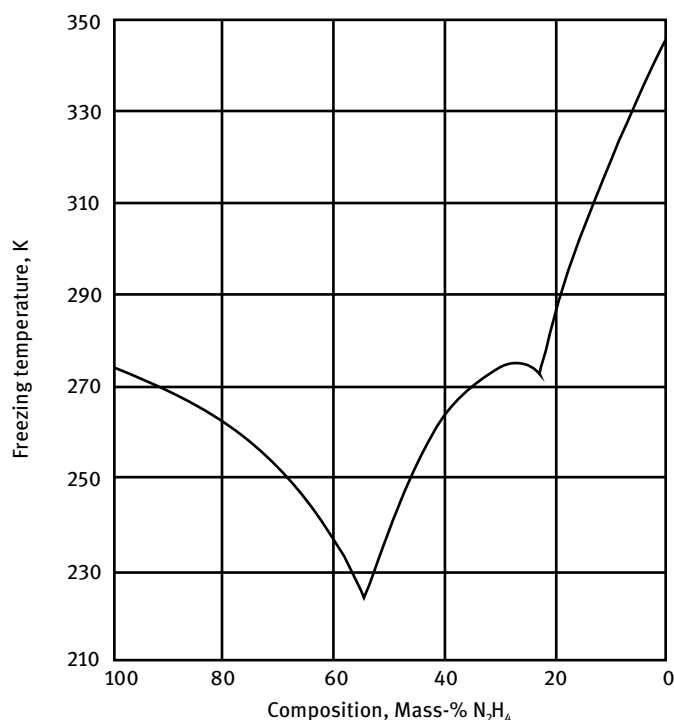


Figure 1: Freezing point of hydrazinium nitrate/hydrazine solutions. (From [2].)

water system was investigated repeatedly during the 1950s, with generally good agreement [25, 26]. The graph in Figure 2 is a combination of data from different sources. The system has a simple eutectic containing 37.5 mass-% HN and melting at 263.9 K (-9.2°C). Melting point data reported by other investigators [27, 28] were less accurate.

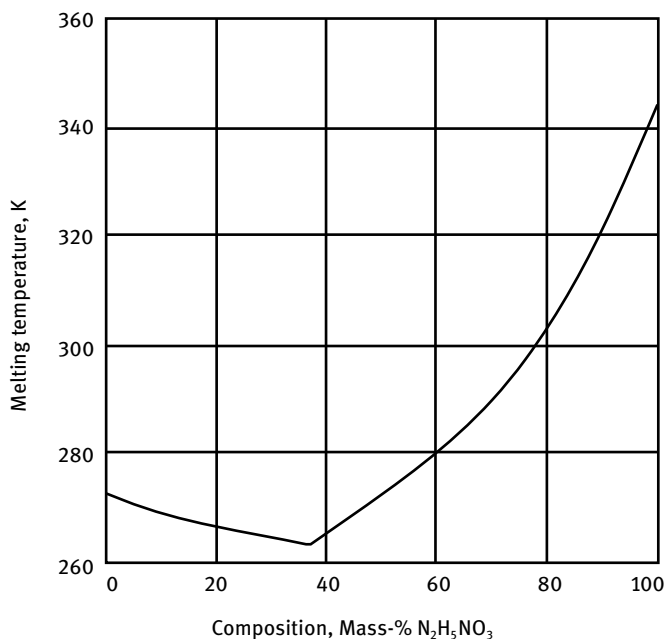


Figure 2: Melting point as a function of composition for the hydrazinium nitrate/water system. (Reproduced and modified from [3].)

1.2.1.3 Melting Points of Ternary Hydrazinium(1+) Nitrate Systems

Phase diagrams of ternary systems involving ammonium nitrate, hydrazinium(1+) nitrate, and any one of the following five nitrates could be calculated and triangular charts drawn using the Krupkowski equation or Kleppa-Hersh equation: lithium nitrate, sodium nitrate, potassium nitrate, hydroxylammonium nitrate (HAN), and hydrazinium(2+) dinitrate [29]. The data are summarized in Table 4.

The lowest-melting eutectic in the latter system was predicted to melt at only 300 K (27°C), which would qualify it as an ionic liquid. Even lower-melting systems are formed with small amounts of water contamination. Many of these low-melting eutectics are of practical interest in emulsion explosives or emulsion propellants. This is an interesting mathematical analytical technique to obtain phase diagrams when experimental measurements are not yet available.

Ternary hydrazinium nitrate systems have been developed both as solid and liquid oxidizers and as monopropellants. One of the most thoroughly investigated

Table 4: Composition, melting points, and densities of calculated lowest melting eutectics of hydrazinium(1+) nitrate/ammonium nitrate/other nitrate ternary systems.

Ingredient XN	Composition, mass-% AN/HN/XN	Melting point		Density g/cm ³
		°C	K	
Lithium nitrate	40/42/18	28	301	1.776
Sodium nitrate	36/53/11	39	312	1.728
Potassium nitrate	27/72/1	53	326	1.667
Hydroxylammonium nitrate	22/36/42	<27	<300	—
Hydrazinium(2+) dinitrate	30/34/36	27	300	1.664

AN = ammonium nitrate, HN = hydrazinium nitrate, XN = other nitrate

Data source: [29]

ternary systems involving free hydrazine (or hydrazine hydrate), one other liquid component, and one salt is the hydrazine/water/hydrazinium nitrate system. The $\text{N}_2\text{H}_4/\text{H}_2\text{O}/\text{N}_2\text{H}_5\text{NO}_3$ system is separated into two regions by the boundary of detonability, as described in Section 1.6.3. Accordingly, it offers an opportunity to formulate a wide range of propellants and explosives, depending on the choice of composition and the intended application. Next to performance as a propellant or explosive, melting point is the most important selection criterion to meet environmental constraints in different climates. A detailed knowledge of the melting points, eutectic points, and eutectic valleys in the ternary system $\text{N}_2\text{H}_4/\text{H}_2\text{O}/\text{N}_2\text{H}_5\text{NO}_3$ enables one to select propellants for maximum I_{sp} or lowest exhaust gas temperature within certain freezing point boundaries. Military and deep space applications frequently require freezing points below that of pure hydrazine and the addition of hydrazinium nitrate is one way to not only lower the freezing point but also to increase performance.

Melting point data of 32 different $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ mixtures were not quite sufficient for construction of a complete ternary diagram with melting point isotherms and did not yet identify the regions of practical interest, such as the boundary of the 219 K (−65 °F) regime considered essential for low-temperature applications of such mixtures [30]. Initial interest in these mixtures arose because of their possible application as liquid gun propellants, but they have never found actual applications as such. Another partial ternary diagram of the $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ system between 50 and 100% N_2H_4 (remainder varying percentages HN and H_2O) covered only the hydrazine-rich side of the triangle (in addition to the two sides of the triangle that represent binary mixtures reported earlier) [25]. Finally, a more complete thermal analysis of the entire ternary system $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ was carried out [26]. These more complete freezing point data are presented in the ternary freezing point diagram (Figure 3).

Mixtures of hydrazine/methylhydrazine (MMH)/HN and also hydrazine/unsymmetrical dimethylhydrazine (UDMH)/HN have been thoroughly investigated. A mixture with a nominal composition of 23.3% hydrazine, 45.3% MMH, and 31.4% HN freezes at 219.2 K (−65 °F) and has subsequently been named Mixed Hydrazine

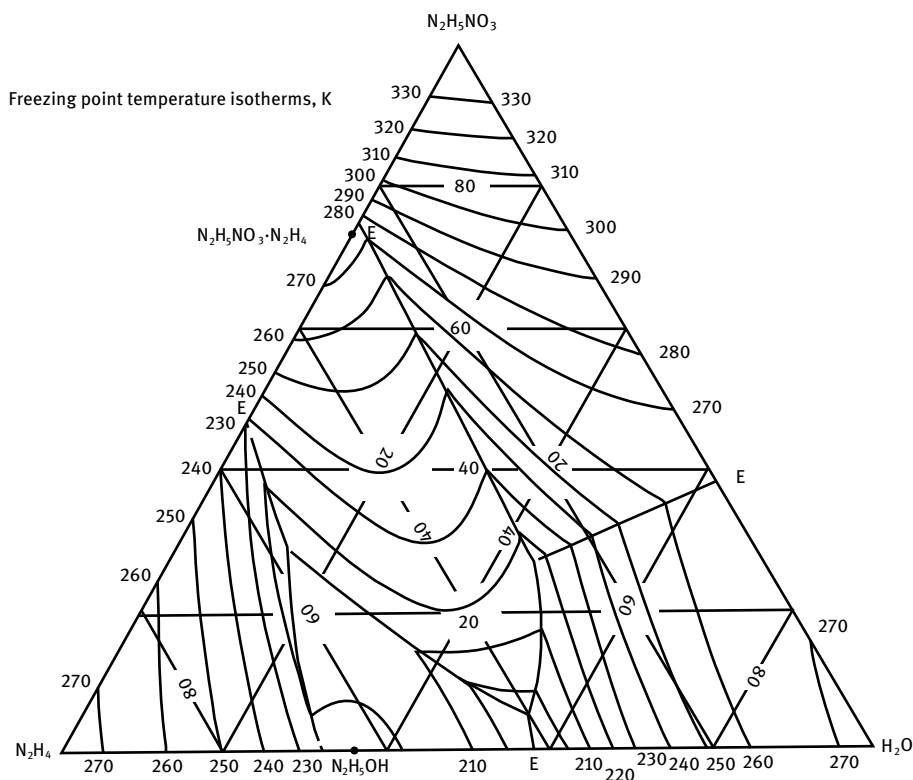


Figure 3: Freezing point isotherms of the hydrazine/hydrazinium nitrate/water system. (Based on data from [26], as modified by [2]).

Fuel-1 (MHF-1). These ternary hydrazine blends will be discussed in *Encyclopedia of Monopropellants*, which describes their use as monopropellants.

Another series of monopropellant blends was made from hydrazinium nitrate, hydroxylamine, and water and the code name was MHF-9 [31] (see *Encyclopedia of Monopropellants*).

Liquid HN-based oxidizers contain a solvent and one additional dissolved oxidizer to achieve low freezing points and high densities. Ternary systems AN/HN/H₂O are already described in *Encyclopedia of Oxidizers*, in the chapter “Nitrate Oxidizers,” and the ternary system hydroxylammonium nitrate (HAN)/HN/H₂O is described in *Encyclopedia of Oxidizers*, in the chapter “Hydroxylammonium Salts.” Another variation on this family of dissolved nitrate oxidizers is a solution of HN in H₂O₂/H₂O mixtures, called “PERSOL-2” [32]. The freezing point diagram of the HN/H₂O₂/H₂O system is illustrated in Figure 4. It is known that hydrogen peroxide and free hydrazine or hydrazine hydrate react instantly in a hypergolic manner. The hydrazine molecule appears to be stabilized against such an attack by protonizing and forming the

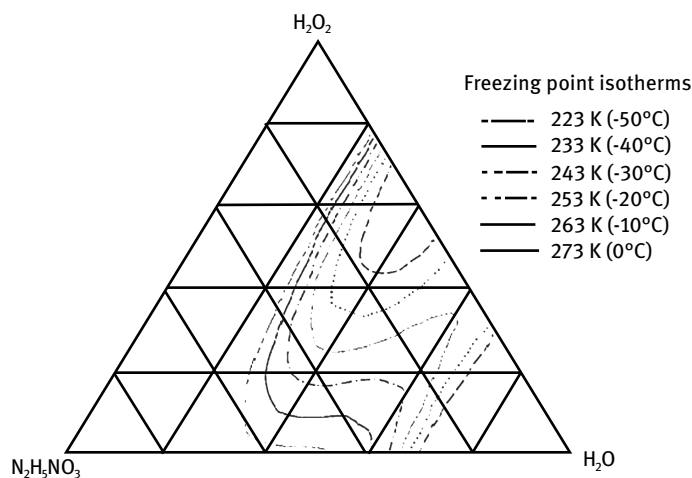


Figure 4: Freezing point diagram of hydrazinium nitrate/H₂O₂/H₂O system. (Reproduced and modified from [32].)

hydrazinium(1+) ion. When looking at PERSOL-2 type oxidizers, there is some concern that the strong oxidizer H₂O₂ might attack the fuel cation N₂H₅⁺, leading to hydrogen azide as an unwanted byproduct of the reaction. The solution must be examined for the presence of azide soon after it has been made.

Ternary and quaternary mixtures of HN with other inorganic nitrates, predominantly ammonium nitrate and sodium nitrate, also have very low melting points [33–35].

1.2.2 Solubility of Hydrazinium(1+) Nitrate in Water

The solubility of hydrazinium(1+) nitrate in water is summarized in Table 5.

Table 5: Solubility of hydrazinium(1+) nitrate in water.

Temperature, K	Solubility, g/100 g Solution	Temperature, K	Solubility, g/100 g Solution
283	63.63	288	68.47
293	72.70	298	76.61
303	80 ^a		
303	80.09	308	83.06
313	85.86	318	88.06
323	91.18	328	93.58
333	95.51		

Data source: [12]; except ^a which is from [36]

1.2.3 Density of Hydrazinium(1+) Nitrate

Density data for crystalline HN are summarized in Table 6.

Table 6: Density of hydrazinium(1+) nitrate.

Temperature, K	Density, g/cm ³	Method	Source	References
—	1.661	—	James, Miron, and Perlee	[9]
	1.688	XRD	Xia, Y.-X., et al.	[37]
298	1.665	Flotation in non-solvents	Robinson and McCrone	[11]
298	1.661	XRD	Robinson and McCrone	[11]
298	1.726	XRD	Grigoriev et al.	[38]

1.2.3.1 Density of Binary Hydrazinium Nitrate Solutions

The temperature dependence of the density of aqueous solutions of hydrazinium nitrate with 0–65% HN is illustrated in Figure 5.

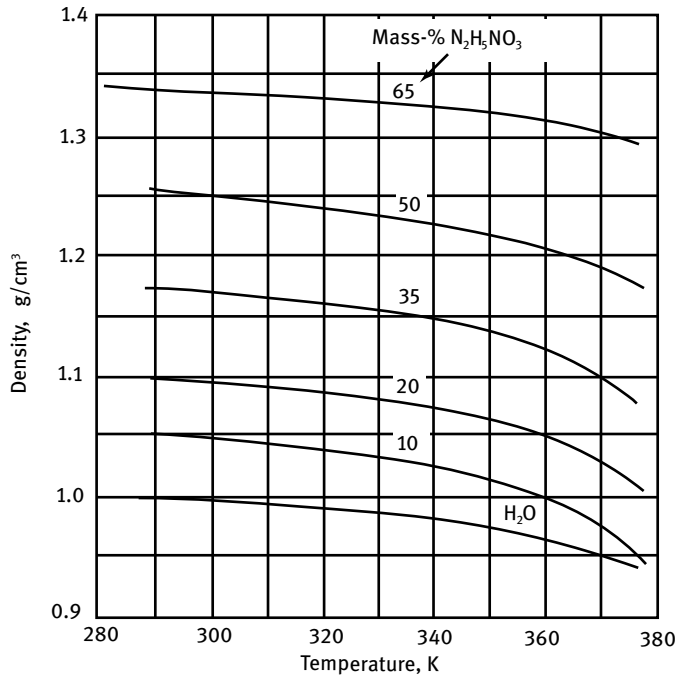


Figure 5: Density of hydrazinium nitrate/water solutions at various hydrazinium nitrate concentrations as a function of temperature. (Reproduced and modified from [3].)

The temperature dependence of the density of solutions of hydrazinium nitrate in hydrazine with 0–75% HN is illustrated in Figure 6.

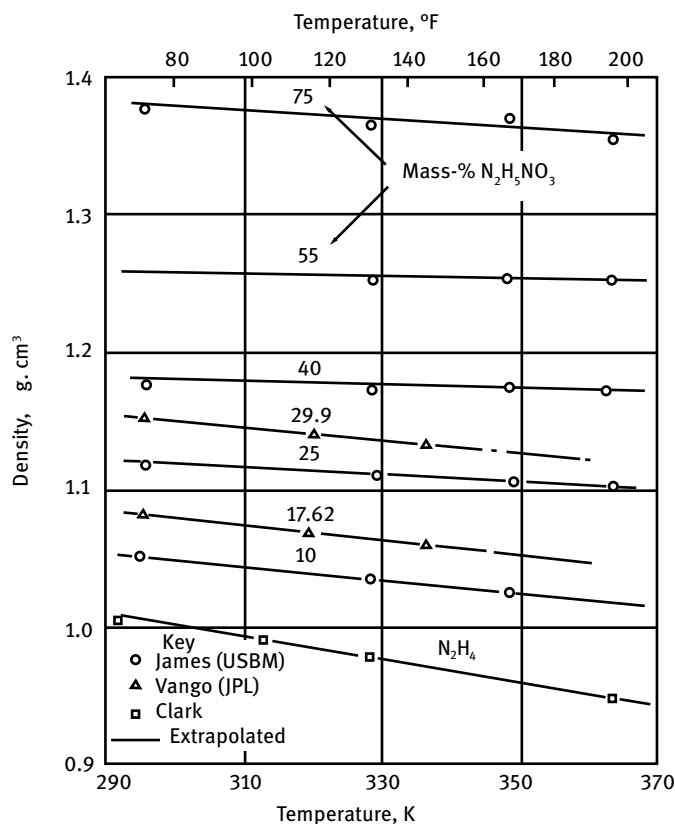


Figure 6: Density of hydrazinium nitrate/hydrazine solutions at various hydrazinium nitrate concentrations as a function of temperature. (Reproduced and modified from [9].)

Other investigations at only one constant temperature (297 K) had shown that the density of HN/water solutions between 0 and 75 mass-% (saturated solution) increased linearly from 1.0 to 1.37 g/cm³ [39] (Figure 7).

1.2.3.2 Density of Ternary Hydrazinium Nitrate Solutions

In the ternary system hydrazine/water/hydrazinium nitrate, the density changes monotonously between the three ingredients (Figure 8).

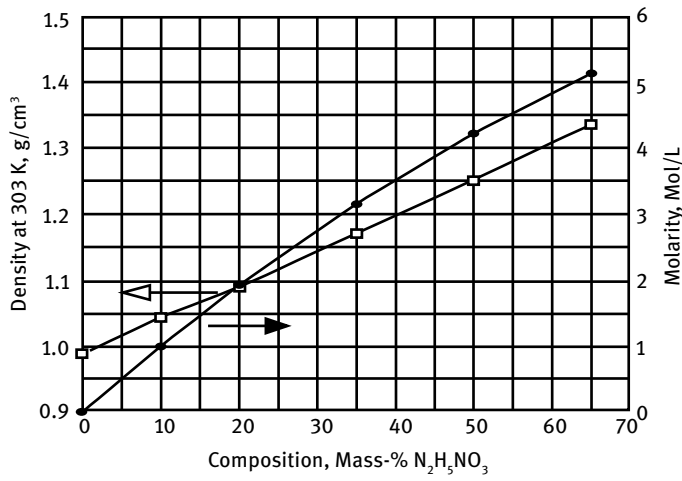


Figure 7: Density and molarity of aqueous hydrazinium nitrate solutions. (Based on data from [39])

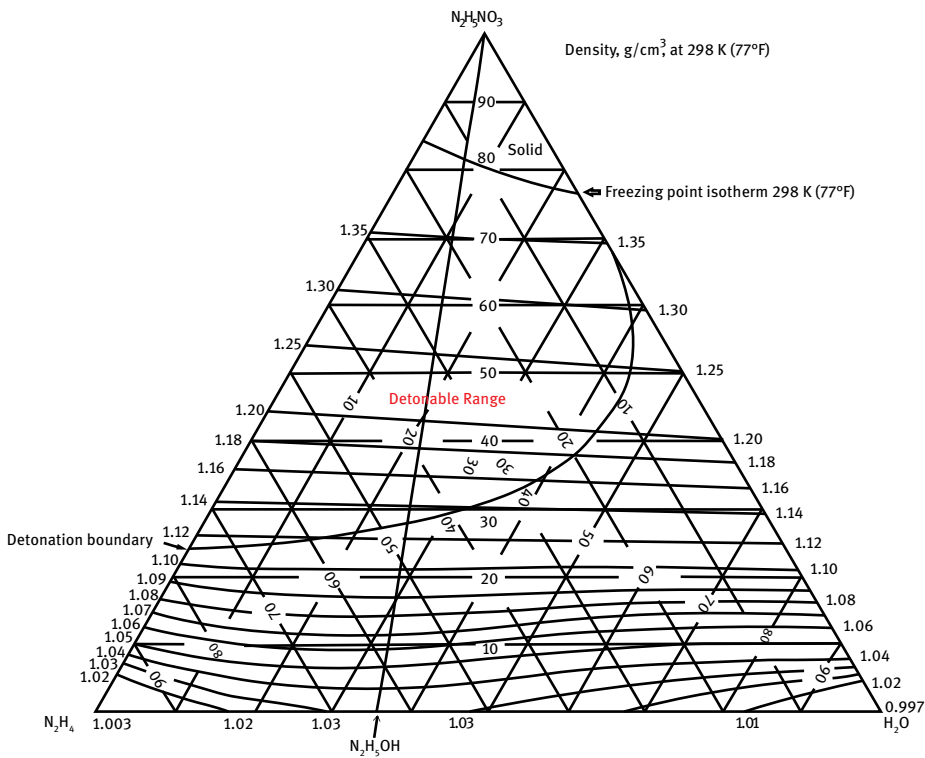


Figure 8: Density of hydrazine/hydrazinium nitrate/water ternary mixtures. (Reproduced and modified from [3].)

1.2.4 Velocity of Sound in Ternary Hydrazinium Nitrate Mixtures

Solutions of hydrazinium nitrate in hydrazine and hydrazine-water mixtures have been tested as rocket propellants and consequently the velocity of sound in several of such solutions has been measured. The velocity of sound is closely related to detonation velocities of liquid explosives. Therefore, the velocity of sound in hydrazine/hydrazinium nitrate/water ternary mixtures was measured and compared with detonation velocity data (*Encyclopedia of Liquid Fuels*, chapter “Hydrazine”) [40]. The velocity of sound can also be used to calculate the compressibility of HN solutions.

1.2.5 Viscosity of Hydrazinium Nitrate Solutions

1.2.5.1 Viscosity of Solutions of Hydrazinium Nitrate in Hydrazine

Comparison of kinematic viscosities of hydrazinium nitrate/hydrazine solutions measured by different investigators in Figure 9 shows that the viscosity of hydrazine increases by one order of magnitude by the addition of 70% HN. Viscosity decreases with temperature as expected.

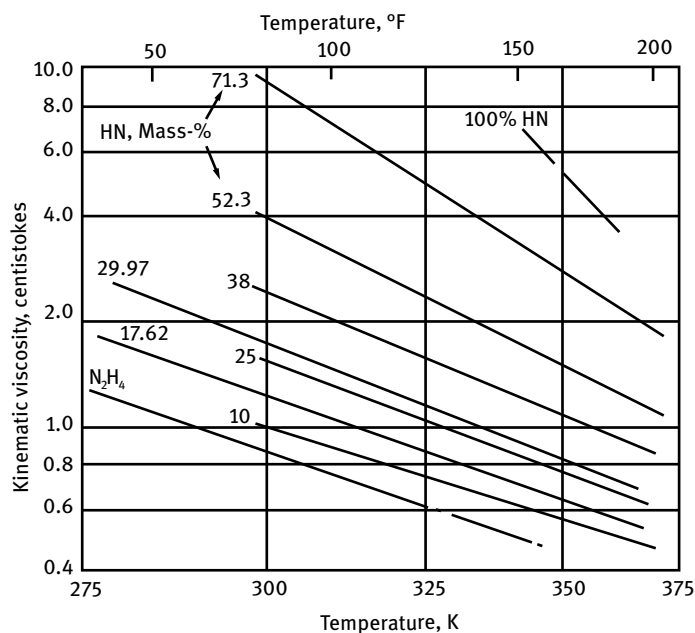


Figure 9: Kinematic viscosity of hydrazinium nitrate solutions in hydrazine at various hydrazinium nitrate concentrations as a function of temperature. (Reproduced and modified from [3].)

Additional data on viscosity and surface tension of HN solutions in hydrazine are available in the literature [2, 3, 41, 42].

1.2.5.2 Viscosity of Solutions of Hydrazinium Nitrate in Water

Viscosity of most solutions decreases with temperature as expected. A similar trend can be observed for solutions of HN in water, but the relative increase from pure water is not as distinct as with hydrazine as a solvent (Figure 10).

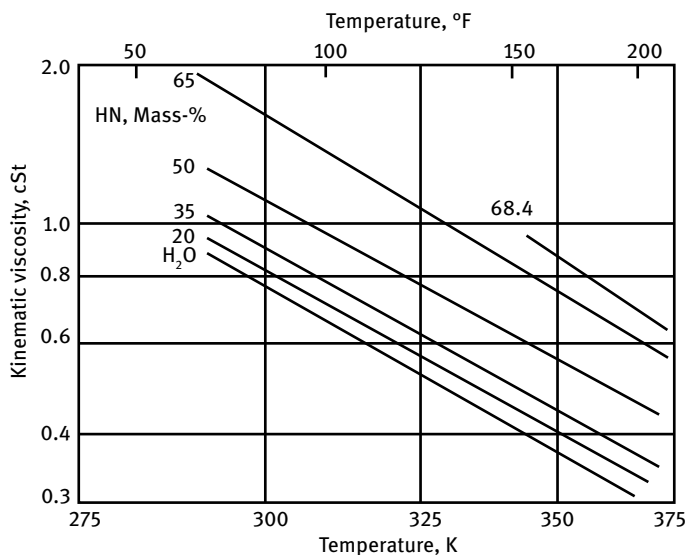


Figure 10: Kinematic viscosity of hydrazinium nitrate/water system at various hydrazinium nitrate concentrations as a function of temperature. (Reproduced and modified from [3].)

Solutions of hydrazinium nitrate in water are of practical interest because they are used in combination with HAN in the reprocessing of nuclear reactor fuel rods.

Somewhat different data for 50, 65, and 76.9% HN solutions in H₂O can be found in Christos et al. [39]. The kinematic viscosity of the most concentrated solution tested (76.9% HN) dropped from 3.2 cSt at 298 K to 1.5 cSt at 327 K. Other authors reported that the kinematic viscosity of HN solutions with 10–72% HN at 293 K increased from 1.0 to 10.5 cSt with increasing HN content [28].

In studying the effect of ion association on viscosity and electrical conductivity, only a few salts are sufficiently soluble in water to study the entire range from 0 to 100 mol-% salt. Hydrazinium salts are sufficiently soluble in water to perform such studies. The dynamic viscosity of HN solutions in water at 298 K increased from 8.95 to 44.37 mPs if the concentration was increased from 0.23 to 38.7 mol-% HN [43]. At 348 K, which is above the melting point of HN, the viscosities could be measured over

the entire range from 2.1 to 100 mol-% HN. In this case, viscosities ranged from 4 to 115 mPs. In combination with simultaneous measurements of electrical conductivity, the conductance-viscosity product, which passes through a minimum at 15 to 20 mol-% salt, was taken as an indication of the dissociation of the salt and beginning association of the ions at higher concentrations.

1.2.5.3 Viscosity of Solutions of Hydrazinium Nitrate in Hydrazine-Water Mixtures

Ternary systems of HN dissolved in hydrazine-water mixtures have been tested as low-freezing monopropellants (see *Encyclopedia of Monopropellants*). Limited viscosity data are listed in Table 7.

Table 7: Viscosity of solutions of hydrazinium nitrate in hydrazine/water mixtures.

HN, mass-%	Water, mass-%	Hydrazine, mass-%	Viscosity, cPs	Viscosity, cSt	at Temp. K
10	27	63	1.984	1.864	298
10	27	63	8.21	7.5	253
10	27	63	112	99.8	219

Data source: [44]

1.2.6 Surface Tension of Solutions of Hydrazinium Nitrate in Hydrazine

The surface tension of hydrazine/HN solutions was measured using a bubble method [45]. The surface tension increased almost linearly with the hydrazinium nitrate mol fraction, except for a narrow range at low concentrations and low temperatures, where the surface tension passed through a shallow minimum. Attempts to calculate the viscosity of 24% HN solution from the parachor were not very accurate. Apparently, the assumptions for incremental addition of parachors are not valid for concentrated, strongly ionized solutions. The surface tension of solutions of HN in hydrazine (Figure 11) or water is a linear function of the temperature and the HN concentration [13].

Mathematical analysis of these data by James et al. [9] showed that the surface tension can be adequately described by the expression

$$\gamma = \gamma_0 + (K_1 C - K_2)(T - T_0)$$

where γ_0 is the surface tension of the solvent in dyn/cm ($T_0 = K$), γ is the surface tension of the solution in dyn/cm ($T = K$), C is the HN concentration (mol-%), and K_1 and K_2 are regression coefficients. For HN-hydrazine solutions, the following data apply: $\gamma_0 = 93.82$, $T_0 = 213.58$, $K_1 = 0.302$, and $K_2 = 0.243$. For aqueous solutions of HN, the following coefficients should be used: $\gamma_0 = 92.69$, $T_0 = 229.45$, $K_1 = 0.220$, and $K_2 = 0.248$. For additional data at constant temperature, compare also Bachmaier and Jimenez-Barbera [28] and Christos et al. [39].

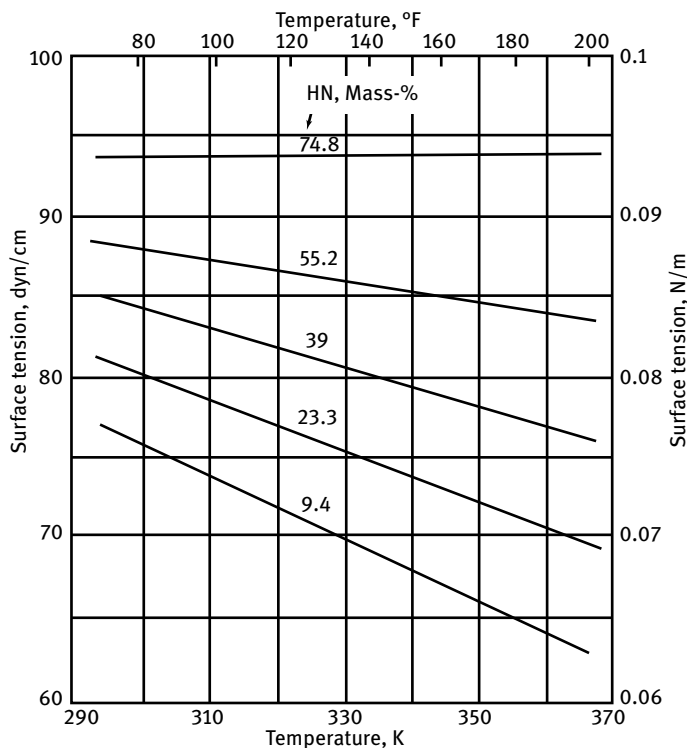


Figure 11: Surface tension of hydrazinium nitrate/hydrazine solutions at various hydrazinium nitrate concentrations as a function of temperature. (Reproduced and modified from [3].)

1.2.7 Optical Properties of Hydrazinium(1+) Nitrate

1.2.7.1 IR Spectra of Hydrazinium Nitrates

The IR spectrum of HN crystals shows absorption bands at 3.1(s), 6.6(w), 7.2(vs), 9(s), 10.3(s), and 12.1(s) μm (Figure 12) [9].

Hydrazinium nitrate in hydrazine solution shows peaks at 3.3, 3.6, 3.9, 4.0, 4.6, 4.8, 7.7, and 12 μm . These absorption bands are very similar to those of dry HN. HN has been found in the reaction product of hydrazine and red fuming nitric acid under simulated rocket conditions and identified by its IR spectrum [46]. These spectra were unfortunately taken in Nujol or hexachloro-1,3-butadiene mulls, which clutter the spectra with extraneous absorption peaks.

Additional information on IR spectra of HN, typically for the range 2–15 μm , is available for $\text{N}_2\text{H}_5\text{NO}_3$, $\text{N}_2\text{H}_5\text{NO}_2$, and $\text{N}_2\text{H}_6(\text{NO}_3)_2$ from Miron and Perlee [13], and additional data for HN are available from Perlee et al. [47] and Saad et al. [48].

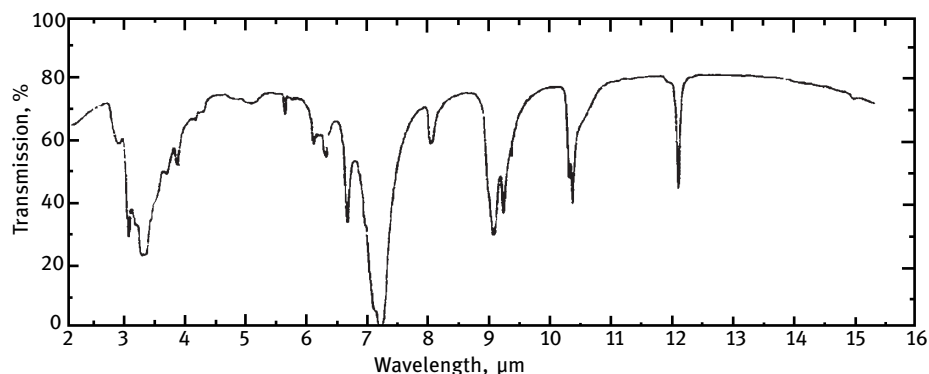


Figure 12: Infrared spectrum of hydrazinium nitrate. (Reproduced and modified from [9].)

1.2.7.2 Refractive Index of Hydrazinium Nitrate

The refractive indices of crystalline α -hydrazinium nitrate in the directions of the three optic axial angles with light at a wavelength of $5893 \text{ \AA}$ at 298 K are: $\alpha = 1.458 \pm 0.003$; $\beta = 1.605 \pm 0.004$; $\gamma = 1.620 \pm 0.003$ [11].

Refractive indices of 36 mixtures in the ternary system $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ were determined [30]. For 5% HN mixtures, the refractive index $n_D^{273\text{ K}}$ decreased from 1.4678 at 5% water to 1.4375 at 30% H_2O . Likewise, starting with 29% HN and 5% H_2O , the refractive index decreased from 1.4766 to 1.4418 when going to 29% HN and 30% H_2O . When represented graphically, in-between values of mixtures with 10–25% HN did not always fall on nice straight parallel lines, but this may have been caused by the scatter of the data and/or uncertainty about the composition of the mixtures. The refractive index alone is insufficient to serve as an analytical tool for ternary mixtures but can be used for binary mixtures.

Hydrazinium nitrate is transported and stored as an aqueous solution. The refractive index determination of HN/water solutions is an easy method of determining the HN content (in the absence of other contaminants); see Figure 13.

1.2.8 Proton Magnetic Resonance Spectra of Hydrazinium Nitrate

Hydrazinium(2+) dinitrate is very hygroscopic and deteriorates rapidly when exposed to room air. The first nuclear magnetic resonance (NMR) investigation of this salt showed that it contains the $\text{N}_2\text{H}_6^{++}$ ion similar to the one in hydrazinium(2+) sulfate [49]. It was estimated that the $\text{H}\cdots\text{H}$ distance in the $\text{N}_2\text{H}_6^{++}$ ion is $1.71 \text{ \AA}$, assuming a symmetrical staggered configuration. If tetrahedral angles are assumed, this leads to a $\text{N}-\text{H}$ distance of $1.048 \text{ \AA}$. In continuation of this study, NMR line widths

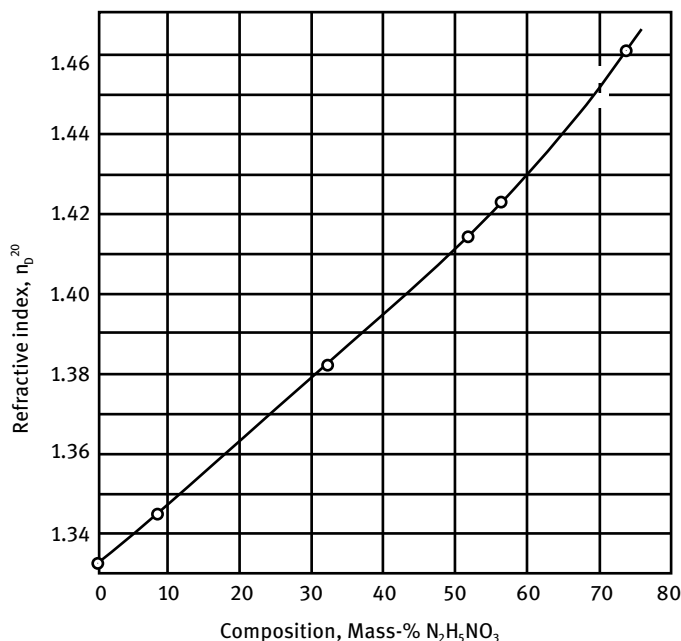


Figure 13: Refractive index of aqueous hydrazinium nitrate solutions. (Reproduced and modified from [3].)

of $N_2H_6(NO_3)_2$ have been measured at 90 K and at room temperature [50]. A line width transition occurs near 150 K and this has been interpreted as a reorientation of the $N_2H_6^{++}$ ion about the N – N axis.

Harrell and co-workers were able to obtain proton NMR spectra on cooled samples at temperatures from 106 to 360 K [51], which indicated the existence of at least two, possibly even four different phases in analogy to hydrazinium(1+) nitrate for which two phases are known. These two known phases were again confirmed in proton NMR measurements at temperatures from 140 to 362 K. The relaxation due to H_2N —motion results from dipole-dipole interactions with the nitrogen nucleus of the H_2N —groups and with protons of the H_3N^+ — group. Similar observations were made with $N_2H_5NO_3$ [52].

1.2.9 Electron Spin Resonance Spectra of Hydrazinium Salts

The spin-lattice relaxation times of protons in polycrystalline hydrazinium(2+) chloride, $N_2H_6Cl_2$, hydrazinium(2+) nitrate, $N_2H_6(NO_3)_2$, hydrazine hydrate,

$\text{N}_2\text{H}_5\text{OH}$, and hydrazinium(2+) sulfate, $\text{N}_2\text{H}_6\text{SO}_4$, have been measured at 60 MHz as a function of temperature between 140 and 450 K [53, 54]. Relaxation time T_1 passed through a minimum of 21.6 ms for each of the first three compounds. The temperature dependence of T_1 was found to be characteristic of a dominant relaxation mechanism, reorientational motion of NH_3^+ groups about the N–N bond direction. The experimental value $(T_1)_{\min} = 21.6$ ms agreed with the estimated value for the first three compounds.

1.2.10 Thermodynamic Properties of Hydrazinium(1+) Nitrate

Because crystalline HN exists in at least two different phases, which differ in their physical and thermodynamic properties, it is important that the phase condition be included in all reported data. At room temperature (298 K), the only stable phase of HN is the α phase. So in most cases one must assume that the reported data are for the α phase of HN.

1.2.10.1 Heat Capacity of Hydrazinium(1+) Nitrate

The heat capacity of solid hydrazinium(1+) nitrate was measured from 220 to 370 K using two different methods with good agreement [17]. The smoothed data are summarized in Table 8. The authors fail to state whether these heat capacity data are for the alpha or beta modification of HN. Because the beta modification is unstable and voluntarily converts to the alpha modification, it is assumed that all the data are for the alpha modification.

Table 8: Smoothed heat capacity of solid hydrazinium(1+) nitrate.

Temperature, K	Heat capacity, $\text{J mol}^{-1} \text{K}^{-1}$	Temperature, K	Heat capacity, $\text{J mol}^{-1} \text{K}^{-1}$
220	110.5	290	138.7
230	114.4	300	143.6
240	116.1	310	149.1
250	121.6	320	155.3
260	125.4	330	164.3
270	129.6	350	195.7
273.15	131.0	360	195.9
280	134.1	370	196.0

Data source: [17]

1.2.10.2 Heat of Combustion of Hydrazinium Nitrates

The heats of combustion of HN and methylhydrazinium nitrates measured in a constant volume combustion bomb are summarized in Table 9.

Table 9: Heat of combustion of hydrazinium nitrates.

Compound	<i>M</i>	Heat of combustion, constant volume				Data source	References
		kJ/mol	kcal/mol	kJ/kg	cal/g		
N ₂ H ₅ NO ₃	95.06	473.4	113.14	4980	1190.2 ± 1.3	Konkova et al.	[10]
N ₂ H ₅ NO ₃	95.06	411.6	98.39	4330	1035	Klapötke, Rien- aecker, and Zewen	[55]
For comparison:							
[H ₂ NNH ₂ (CH ₃)] [NO ₃]	109.09	1136	271.6	10418	2490	Klapötke, Rien- aecker, and Zewen	[55]
[H ₂ NNH(CH ₃) ₂] [NO ₃]	123.11	1824	436	14820	3542	Klapötke, Rien- aecker, and Zewen	[55]

1.2.10.3 Enthalpy of Formation of Hydrazinium(1+) Nitrate

Data for the enthalpy of formation of hydrazinium nitrate are summarized in Table 10.

Table 10: Enthalpy of formation of hydrazinium nitrates.

Compound	$(\Delta H)_{298}^f$				Author	References
	kJ/mol	kcal/mol	kJ/kg	cal/g		
α -N ₂ H ₅ NO ₃	-250	-59.8	-2632	-629	Medard and Thomas 1953 and 1956	[56, 57]
α -N ₂ H ₅ NO ₃	-255	-60.9	-2680	-641	Elverum and Cole 1952	[25]
α -N ₂ H ₅ NO ₃	-246.9	-59.01	-2597	-620.8	Eloirdi 2001	[58]
N ₂ H ₅ NO ₃	-246.2 ± 0.96	-58.86 ± 0.23	-2591	-619.2	Konkova et al. 2009	[10]
N ₂ H ₅ NO ₃	-211.2	-50.47	-2221	-531	Cruise 1979	[59]
N ₂ H ₆ (NO ₃) ₂	-486	-116.1			Korablina et al. 1966a; Korablina et al. 1966b	[60, 61]

M N₂H₅NO₃ = 95.058 g/mol; 10.5197 mol/kg

M N₂H₆(NO₃)₂ = 158.071 g/mol; 6.326 mol/kg

1.2.10.4 Heat of Fusion of Hydrazinium(1+) Nitrate

Data for the heat of fusion of HN are summarized in Table 11.

Table 11: Heat of fusion and entropy of fusion of hydrazinium(1+) nitrate.

Formula	Heat of fusion				Entropy of fusion		Author	References
	kJ/mol	kJ/kg	kcal/mol	cal/g	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹		
N ₂ H ₅ NO ₃	8.74	91.99	2.09	21.99	—	—	Zhevnikov, Strunin and Manelis 1976	[62]
N ₂ H ₅ NO ₃	20.06	210.8	4.79	50.39	—	—	Zhou et al. 1986	[17]
α-N ₂ H ₅ NO ₃	13.16	138	3.146	33.1	41.84	9.28	Wang 1981	[18]

1.2.10.5 Enthalpy of Solution of Hydrazinium(1+) Nitrate

The enthalpy of solution of HN in water is endothermic (Tables 12 and 13), similar to that of AN, but not as strongly endothermic that one would want to use this salt in ice packs to treat athlete's injuries on the football field (where AN is indeed used).

Table 12: Standard enthalpy of dissolution of hydrazinium nitrate in comparison with that of other oxidizers.

Compound	Standard enthalpy of formation, kJ/mol		Enthalpy of dissolution, kJ/mol
	Solid	In solution at infinite dilution	
NH ₃ OHNO ₃	−366.5	−344.8	+22.5
NH ₄ NO ₃	−365.4	−339.9	+25.3
N ₂ H ₅ NO ₃	−246.9	−215.1	+31.8

Data source: [58]

Table 13: Heats of solution of hydrazinium salts in water or hydrazine.

Solvent	Compound	Heat of solution per mol of salt dissolved		Authors	References
		kJ/mol	kcal/mol		
Hydrazine	N ₂ H ₅ NO ₃	+15.5	+3.7	Elverum and Cole 1952	[25]
Water	N ₂ H ₅ NO ₃	−36.5	−8.72	James, Miron, and Perlee 1970	[9]
Water	N ₂ H ₅ NO ₃	−37.95 ± 0.08	−9.07 ± 0.02	Konkova et al. 2009	[10]
Water	N ₂ H ₅ NO ₃	−38.9	−9.3	Elverum and Cole 1952	
Water	N ₂ H ₅ ClO ₄	−38.95	−9.311	Rosolovskii, Kriktsov, and Titova 1968	[63]
Water	N ₂ H ₅ ClO ₄	−26.3	−6.3	Gilbert and Cobb 1935	[64]

1.2.11 Molecular Structure of Hydrazinium Nitrate

Hydrazinium(1+) nitrate exists in two crystalline forms, the α and the β modification. The β form is unstable, and few properties other than its melting point and the refractive index are known. α -Hydrazinium(1+) nitrate melts at 343.6 K [9, 11], and the β modification melts 8° lower at 335.6 K. Even antiquated melting points reported 100 years ago differ only by fractional degrees [12]. A melt of HN supercools readily and results in the unstable β form. The conversion from the β form to the α form is exothermic and monotropic. The heat of conversion is 8.36 kJ/mol (2.0 kcal/mol), as measured by differential scanning calorimetry. No additional thermal phase transformations could be found between the $\alpha \rightarrow \beta$ transition temperature and the melting point, in contrast to AN, which undergoes several phase changes.

The monoprotinated hydrazinium cation forms several types of hydrogen bonds with surrounding nitrate ions. Stronger ones, in which the hydrogen atoms attached to the protonated nitrogen atom take part, link cations and anions into layers. Less strong hydrogen bonds, with participation of H atoms attached to the non-protonated N atom, link the layers into a three-dimensional structure. In addition to hydrogen bonds, short contacts of 2.8607 Å were found between O and N atoms of neighboring nitrate anions. Such contacts can correspond to a weak intermolecular interaction similar to that in organic nitro compounds. Crystal structures of HN and several other hydrazinium salts are listed in Table 14.

1.2.12 Computational Analysis of the Structures of Hydrazinium Nitrates

Hydrazinium nitrate is of interest as an ionic liquid. It was shown that it is quite difficult to achieve an accurate and consistent description of the modified HN ionic crystals [71]. In further work, a systematic force field method was developed that can describe crystal structures for these modified HN ionic materials [72, 73]. In addition, the developed polarizable force field methods were extended to other anions such as azide N_3^- , dicyanamide $\text{N}(\text{CN})_2^-$, and 5-azidotetrazolate CN_7^- in addition to NO_3^- , using seven high-nitrogen-content ionic crystals. After force field validation, Molecular Dynamics simulations were used employing the developed force field method to perform initial investigations of the mechanical properties in the crystalline system and investigate the structural interactions of cations and anions in the crystalline (and in some cases liquid) state. For the seven crystals that were simulated, the largest deviations were seen in those that have the smallest anions. For the $[\text{N}_2\text{H}_5][\text{NO}_3]$ crystal the volumetric deviation between the two sets of data was only ~6% (Table 15). Similar data were obtained for MMH nitrate and UDMH nitrate.

Table 14: Crystal structure of hydrazinium nitrate and other hydrazinium salts.

Compound	Space Group	Symmetry	Unit cell dimensions, 10 ⁻¹⁰ m ^a			β degrees °	Density g/cm ³	Authors	References
			<i>a</i>	<i>b</i>	<i>c</i>				
Hydrazinium(1+) nitrate		Monoclinic	11.23	11.73	5.17	8	1.661	Robinson and McCrone 1958	[11]
Hydrazinium(1+) nitrate	<i>P</i> ₂ ₁ / <i>n</i>	Monoclinic	8.015	5.725	8.156	4	1.688	Xia et al. 2008	[37]
Hydrazinium(1+) nitrate	<i>P</i> ₂ ₁ / <i>n</i>	Monoclinic	7.9649	5.6569	8.1221	4	1.726	Grigoriev et al. 2005	[38]
Hydrazinium(1+) dinitramide	<i>P</i> ₂ ₁ / <i>n</i>		10.56	8.29	5.75	4	1.84	Gidaspov et al. 1995	[65]
Hydrazinium(1+) dinitramide	<i>P</i> ₂ ₁ / <i>c</i>	Monoclinic	8.312 (3)	5.654 (1)	10.659 (3)	4	1.848	Gilardi and Butcher 2000	[66]
Hydrazinium(1+) perchlorate	<i>C</i> 2/ <i>c</i>	Monoclinic	14.412	5.389	12.797	8	1.910	Conant and Roof 1970	[67]
Hydrazinium(1+) perchlorate hemihydrate	<i>C</i> 2/ <i>c</i>		8.657	7.484	15.285	—	—	Liminga 1967	[68]
Hydrazinium(1+) azide	<i>P</i> ₂ ₁ / <i>b</i>	Monoclinic	5.663	12.436	5.506	4	1.407	Chiglien et al. 1974	[69]
Hydrazinium(1+) azide	<i>P</i> ₂ ₁ / <i>n</i>		5.665	5.522	11.401	4	1.400	Pannetier et al. 1972	[70]

^a 10⁻¹⁰ m is equivalent to 1 Å

Table 15: Comparison of measured and calculated crystal properties of hydrazinium(1+) nitrate.

	Crystal lattice parameters			Angles			Unit cell volume
	<i>a</i> Å	<i>b</i> Å	<i>c</i> Å	α °	β °	γ °	Å ³
Experiment	7.965	5.657	8.122	90.00	91.34	90.00	365.854
Simulation	7.44	5.97	7.75	91.33	92.55	89.88	343.370
$\Delta(\%)$	-6.6	5.4	-4.6	1.5	1.3	-0.1	-6.1

Data source: [72]

1.3 Chemical Properties of Hydrazinium Nitrate

1.3.1 Reactions of Hydrazinium Nitrate

In many applications, such as in the reprocessing of spent nuclear reactor fuel rods, HN is used in strongly acidic solutions with nitric acid, often together with HAN, to remove HNO₂ and nitrite ion, which interfere with isotope separation. This opens up the possibility that the hydrazinium cation will become oxidized by nitrate anions and destroyed in an exothermic reaction sometimes catalyzed by metal ions that are also in the solution. HNO₂ and HN₃ are intermediates in this reaction.

In order to determine the temperature threshold for this reaction, initiation temperatures and heats of this reaction, the effects of impurities on initiation temperature and self-accelerating reaction were measured in a pressure vessel type reaction calorimeter [74]. This reaction may also be accelerated by external ultrasound used to accelerate the dissolving of the spent reactor fuel rods.

The effect of ultrasound ($f = 20$ kHz) on the decomposition of HN was investigated in a nitric acid medium [75]. The kinetics of N₂H₅⁺ decomposition and initial HN₃ formation increase in a linear manner with the HNO₃ concentration (from 1 to 6 M) and with the ultrasonic intensity (from 0.5 to 3.1 W/cm²). HN₃ is volatile and diffuses into the cavitation bubbles where it decomposes. The variation of the steady-state HN₃ concentration with the HNO₃ concentration and the ultrasonic intensity suggests the existence of a non-explosive HN₃ thermal decomposition mechanism in the cavitation bubble under the effect of ultrasound. It was also observed at ultrasonic intensities exceeding 3.5 W/cm² that the decomposition of HN₃ led to the accumulation of NH₄⁺ in solution. See also [76].

1.3.2 Analysis of Hydrazinium Nitrate

Hydrazinium nitrate is rarely used in the solid state. Most analytical methods for HN are for HN solutions. Nitrate in aqueous solutions can be determined gravimetrically with nitron, which also precipitates perchlorate if any is present in addition to nitrate.

Hydrazinium nitrate in liquid explosives can be analyzed by titration in acetic acid as the solvent [77–79]. Hydrazinium(1+) nitrate has been determined as a base by non-aqueous titration in glacial acetic acid. The titrant was 0.05-N perchloric acid in glacial acetic acid, which must be prepared without acetic anhydride. Small amounts of water increased the solubility of hydrazine nitrate, but reduced the sensitivity of the method.

The mass spectrum of HN shows peaks at a mass-to-charge-ratio (m/e) of 63 (HNO_3^+), 46 (NO_2^+), 28–32 (N_2^+ , N_2H^+ , N_2H_2^+ , N_2H_4^+ plus possibly NO^+ and O_2^+), and 16 (O^+ or possibly NH_2^+) [46].

1.3.3 Thermal Stability of Hydrazinium Nitrate

1.3.3.1 Decomposition of Hydrazinium Nitrate

Hydrazinium nitrate is thermally unstable and begins to decompose shortly after it melts. In all states, solid or liquid, HN is detonable and constitutes a substantial risk for accidents [80, 81].

1.3.3.2 Slow Controlled Decomposition of Hydrazinium Nitrate

The weight loss of 1-g samples of HN after 6-min. exposure to temperatures from 453 to 523 K increased from barely noticeable at 453 K to 80% conversion at 523 K [82]. The weight loss remained below 5% per 6-min exposure until the temperature reached 493 K. Ammonium nitrate subjected to the same test for comparison decomposed much more slowly, at approximately only half the rate of HN. The addition of potassium dichromate to molten HN at 373 K caused immediate decomposition with an explosion.

When studying the thermal decomposition of hydrazinium(1+) nitrate in a microcalorimeter, it was noted that the reaction rates and the ultimate products are very dependent on the mass loading density m/V and the temperature profile in the reaction vessel [16]. When the reaction was carried out in evacuated and sealed 1.8- to 2.5-mL vials at uniform temperature, the final pressure in the vials was of the order of 1.01–2.02 MPa. The thermal decomposition of HN is self-accelerating. The rate of self-acceleration increases with m/V . The rate equation is

$$\frac{d\eta}{dt} = k_1(1-\eta)^2 + k_2\eta(1-\eta)^2$$

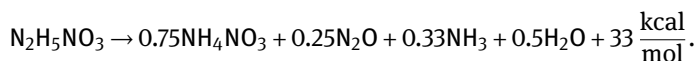
where η is the fractional conversion and k_1 and k_2 are constants; k_1 is a real constant, whereas k_2 increases with m/V . The temperature variation of k_1 when plotted as $\log k_1$ versus $1/T$ is expressed by

$$k_1 = 10^{12.2} e^{\frac{-38000}{RT}} \quad \text{s}^{-1}.$$

For a mass loading of $m/V = 10^{-3} \text{ g/cm}^3$, k_2 is expressed by

$$k_2 = 10^{7.8} e^{\frac{-26500}{RT}} \quad \text{s}^{-1}.$$

The activation energy obtained by numerical integration of the rate curves is 141.4 ± 5.86 kJ/mol (33.8 ± 1.4 kcal/mol). The solid residue left behind in sealed vials weighed approximately 65% of the HN. It melted at 443 K and has been analyzed as AN, formed at the rate of 0.75 mol of AN per mol of initial HN. The decomposition reaction can be written as follows:

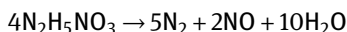


When the thermal decomposition is carried out in a large vessel that is not at uniform temperature, the reaction obeys different kinetics. Some of the HN sublimes and condenses on the colder walls of the vessel, and the reaction continues until the sample in the hot part of the vessel disappears altogether (no AN residue). In agreement with other investigators [82], Rubtsov and Manelis [16] explain the kinetics by assuming that HN first dissociates into hydrazine and nitric acid. The hydrazine then decomposes into ammonia and nitrogen. Nitric acid on the other hand decomposes into nitrogen dioxide, oxygen, and water. The nitric acid decomposition products quickly react with hydrazine under the formation of H_2O , N_2O , NH_3 , and N_2 . This mechanism is supported by the autocatalytic effect of hydrazine or hydrogen chloride. Toward the end of the reaction in sealed vessels, the excess ammonia pressure retards the further decomposition of AN.

By comparison, pure hydrazine decomposes in the temperature range investigated only very slowly. At 475 K the rate of heat evolution of 100 mg of pure hydrazine was so slow that it was at the limit of sensitivity of the calorimeter. When HN was added to liquid hydrazine, however, the rate of decomposition of hydrazine increased sharply. The decomposition rate is proportional to the amount of HN

$$\frac{dc}{dt} = k [\text{N}_2\text{H}_4] [\text{N}_2\text{H}_5\text{NO}_3].$$

Various hydrazine nitrates may form as the result of an incomplete reaction of hydrazine with dinitrogen tetroxide in a rocket engine. Accumulation of such residues and sudden ignition may cause destructive pressure spikes in rocket engines. Vacuum thermal decomposition of hydrazinium(1+) nitrate (= HN) and hydrazinium(2+) nitrate (= "HN-2") with simultaneous mass spectrometry resulted in the evolution of nine identifiable species [19, 83]. When these salts are decomposed in a differential thermal analysis (DTA) apparatus in a vacuum instead of at ambient pressure, the terminal exotherm is replaced by a large endotherm. Apparently, the heat of vaporization of the substantial amounts of water formed per



overshadows all other events. The major products were water, NO, and N_2 . Minor products were N_2O , NO_2 , NH_3 , HN_3 , H_2 , and O_2 . Some N_2H_4 and HNO_3 were also found. This is evidence of dissociation without decomposition. Water and N_2O were the first

decomposition products detected while raising the temperature at around 400 K. NO and NO₂ did not appear before the temperature had reached 470 K. Decomposition was complete at 528 K. The vacuum decomposition DTA/mass spectrometry (MS) of HN-2 showed water formation at a lower temperature (approximately 423 K) accompanied by the first endotherm in the thermogram. In addition, a considerable quantity of NO₂ was evolved at these temperatures. In fact, NO₂, which was only a minor product of HN decomposition, became a major product in the HN-2 decomposition, together with H₂O, NO, and N₂. A larger amount of HN₃ was also produced.

The weight loss rate of molten hydrazinium(1+) nitrate was measured with 20-mg samples having surface areas of approximately 0.2 cm² [9]. At 473 K, the rate was 0.4 wt.%/min, and at 423 K it was 0.06%/min. The weight loss can be attributed entirely to a dissociation process. In other experiments, when HN was heated intermittently to 383 K for a total of 315 h, the average weight loss was 8×10^{-5} %/min [84]. The weight loss rate of a 1-g sample of HN at 500 K was linear with time [13]. Hydrazinium(2+) dinitrate (HN-2) is less stable than HN. It begins to lose mass below its melting point of 353 K. If heated slowly, it melts at 353 K; if heated rapidly, it melts at 376 K; if heated in a water bath at 373 K, HN-2 decomposed, leaving a residue of AN. The reaction of HN-2 with hydrazine at 298 K is exothermic with 63 kJ/mol HN-2 (15 kcal/mol).

The DTA of N₂H₅NO₃ showed a melting endotherm at 343 K and additional endotherms at 451 and 513 K [15]. Other investigators observed a melting endotherm at 345.4 K and an exotherm at 363 K [85] and for α-N₂H₅NO₃ they observed melting at 343.86 K [18].

The thermal decomposition of hydrazinium(1+) nitrate starts soon after melting [86]. See also [17, 87].

Addition of hydrazinium(1+) nitrate to HAN suppressed the decomposition of HAN for several hours [88]. In one instance a sharp explosion occurred at 413 K. Mass spectrometric analysis showed hydrazoic acid as the pyrolysis product, in particular if hydrazinium(2+) dinitrate instead of the (1+) salt was added to the HAN. The (2+) salt shortened the induction period and accelerated the decomposition reaction of HAN.

1.3.3.3 Decomposition of Hydrazinium Nitrate Solutions

Concentrated aqueous HN solutions are not very stable. The thermal stability of concentrated (1 to 5.8 molar) aqueous HN solutions was studied at 303 K as a function of pH and container size [89]. Decomposition as indicated by gas evolution in glass vessels with three different diameters was measured for 30 days at four different concentrations and initial pH values ranging from 3.3 to 5.4. The pH dropped with progressive HN decomposition. In the early phase of the reactions, oxygen in the air space above the samples was consumed and some of the subsequent tests were performed under argon instead of air. Surprisingly, typically 2 to 6% of the HN decomposed during only 1 month of storage at 303 K. One must also anticipate the formation of HA

as a decomposition product. Specifications for commercial sources for 30% or 50% HN solutions limit the allowable azide concentration to 0.01% max. An Arrhenius plot based on gas evolution rates of 1-molar HN solutions at 303 to 348 K and fitted to a first-order rate equation of

$$k = 6.03 \exp(-5300/RT) d^{-1}$$

gave an activation energy of approximately 22 kJ/mol.

Both hydrazinium(1+) nitrate and HAN are shipped commercially in large quantities in aqueous solutions, but the allowable concentration is limited. HN along with HAN nitrate in nitric acid solutions is used in the plutonium uranium reduction extraction (PUREX) process for the reprocessing of spent nuclear reactor fuel elements and the separation of uranium and plutonium and other fission products. There is concern about accidental runaway reactions during the mixing of the reactants in the PUREX process and a series of investigations was made about the exothermicity of reactions involving HN and increasing amounts of nitric acid [90, 91].

The thermal properties of hydrazinium ion in nitric acid solution, which is used for preventing the oxidation of extracted plutonium, were studied by thermal analysis of mixtures under various conditions. From the results of DSC it was revealed that the vessel material has an influence on the thermal decomposition of hydrazine. It was also found that hydrazine reacted with nitric acid in an autocatalytic manner, and the concentration of nitric acid has a strong influence on the thermal hazard of HN and nitric acid mixtures [92, 93]. The onset of thermal decomposition of HN solutions was shifted to lower temperatures by the presence of excess nitric acid.

The thermal stability and ignition behavior of aqueous solutions of HN were measured at pressures up to 4 kbar and temperatures up to 830 K [94]. The technique produced different kinetic data for the two methods of analysis used. The extrapolated rates bracketed the one estimated from detonation experiments.

The effect of ultrasound ($f = 20$ kHz) on the decomposition of aqueous HN solutions was investigated in a nitric acid medium [75]. The kinetics of $N_2H_5^+$ decomposition and initial HN_3 formation increased in a linear manner with the HNO_3 concentration (from 1 to 6 M) and with the ultrasonic intensity (from 0.5 to 3.1 W/cm²). Both rates were equal to that of HNO_2 formation in the absence of $N_2H_5^+$, indicating that the $N_2H_5^+$ decomposition mechanism is the same as that observed during the reaction between HNO_2 and $N_2H_5^+$ without ultrasound. The variation of the steady-state HN_3 concentration with the HNO_3 concentration and the ultrasonic intensity suggested the existence of a non-explosive HN_3 thermal decomposition mechanism in the cavitation bubble under the effect of ultrasound. It was also observed at ultrasonic intensities exceeding 3.5 W/cm² that the decomposition of HN_3 led to the accumulation of NH_4^+ in the solution.

1.3.3.4 Flash Pyrolysis of Hydrazinium Nitrate

The US Bureau of Mines (USBM) “Bruceton up and down” method has been applied to determine the ignition temperature of hydrazinium(1+) nitrate on a hot plate [95]. The 50% probability of ignition was reached at 580 K.

When HN was heated rapidly at atmospheric pressure in air, it decomposed explosively at 680 K [9].

Rapid thermolysis of HN under argon pressure of up to 500 psia (3.4 MPa) and heating rates of 75 and 105 °C/min and analysis of the gas products by Fourier transform infrared spectroscopy (FTIR) showed that the first gas product is N₂O, followed by NH₃ and even subliming NH₄NO₃ [96]. Hydrazoic acid was a major intermediate product. NO and H₂O were among the last products to appear.

1.4 Strand Burning of Hydrazinium Nitrate

1.4.1 Strand Burning of Hydrazinium Nitrate

Dry HN packed into glass tubes of 10, 15, and 20 mm in diameter could not be ignited by an incandescent nichrome wire [82]. While the wire was hot, HN only melted, and the melt burned for 3–5 mm, but combustion soon ceased. Even HN melted and heated to 353 K did not burn. Only after the melt temperature was increased to 373 K did HN burn in a 20-mm tube at 0.073 cm/s. When 10% K₂Cr₂O₇ was added to HN, the powder would even burn at ambient temperature and pressure with a rate of 0.105 cm/s. With less K₂Cr₂O₇ catalyst added, combustion was accordingly slower, 0.05 cm/s at 0.5% K₂Cr₂O₇.

The burning rate of 7-mm strands of HN pressed into plexiglass tubes is dependent on the chamber pressure according to

$$u = 0.33p^{0.82}$$

where u is the burning rate in mm/s and p is the pressure in atm. The addition of potassium, sodium, or lithium nitrate, and surprisingly also potassium chloride, strongly increased the combustion rate but had a weak effect on the lower limit of stable combustion [62]. In the range of 3.84 mass-% additive, lithium nitrate enhanced burning most actively, quintupling the strand burning rate at 101 MPa from 14 to 44 mm/s. If more than 10–15% additive was added, the relative increase passed through a maximum and dropped to the initial value beyond 20%. Molten HN at 373 K at pressures above 404 kPa burned with high velocity (30–100 mm/s), with a strong dependence on pressure, and burning was accompanied by much spattering of unburned material. The additives accumulated on the surface of the burning material, retarding evaporation and allowing a more compact flame front.

Cast instead of tamped or pressed HN and HN-AN was used in a study of surface temperatures of burning solid propellants. The HN and HN-AN eutectics were used as model substances because the melt surface gives a well-defined surface tempera-

ture [97]. Both HN and 32 mol% AN/68 mol% HN (melting point 316 K) castings had to be catalyzed with 1.5 mass-% Cr_2O_3 catalyst, which was mixed in at temperatures a few degrees above the melting point before the cylinders were allowed to solidify in glass tubes as molds. An array of thermocouples was embedded in the cast grain, which recorded the passing of the combustion front. The temperature would level off while the melted zone was passing through. Burn rates of 0.25–0.78 cm/s at 0.68–5.35 MPa were typical for catalyzed AN-HN, whereas catalyzed HN would burn much faster, 1.2 cm/s at 41 bars. The average surface temperature of burning AN-HN was 580 and 468 K for HN by itself.

The surface temperature in the combustion wave of HN, as well as in ammonium dinitramide (ADN), AN, and ammonium perchlorate (AP), is controlled by a dissociation process, similar to that postulated for other onium salts [98].

1.4.2 Strand Burning of Hydrazinium Nitrate Solutions

Hydrazinium nitrate solutions in water and/or hydrazine have been thoroughly evaluated as monopropellants and liquid gun propellants (See *Encyclopedia of Monopropellants*, chapter “Hydrazine Monopropellants”). Strand burning rates have been measured for a wide range of compositions and up to very high chamber pressures.

At Naval Ordn. Lab., White Oak, MD, two burning rate setups were used to characterize the HN blends by burning rate and impetus, one was an 840-cm³ bomb operating at 34.4 to 206 MPa (5000 to 30000 psi) and another operating at 206 to 688 MPa (30000 to 100000 psi). The progress of the flame front through the liquid strand contained in a meltable plastic tube was monitored by break wires that melted when the flame consumed them [30, 99, 100]. In addition to burning rate studies of HN by itself, burning rates of HN with binders and nanometal powders have been measured [101, 102].

1.5 Safety Properties of Hydrazinium Nitrate

1.5.1 Drop Weight Impact Sensitivity of Hydrazinium Nitrate

Most of the more energetic hydrazinium salts are drop-weight sensitive (Table 16). HN, although never handled as a dry solid in bulk quantities, is an important constituent of liquid propellants and liquid explosives. It may crystallize from such solutions on inadvertent evaporation of the solvent. HN was found in the residues of incomplete combustion of hypergolic storable propellants. Its drop-weight sensitivity has been determined by numerous investigators using different experimental methods. Drop-weight sensitivity data reported in the literature for HN differ widely, not only because of the different experimental techniques used, but also because the very hygroscopic samples may not have been totally dry.

Table 16: Drop-weight impact sensitivity of hydrazinium salts.

Compound	Apparatus model	Drop weight mass (kg)	Sensitivity (kg · cm)	Authors	References
β-Hydrazinium(1+) nitrate	USBM	No. 12 tool with sandpaper	55	Perlee et al. 1968	[14]
Hydrazinium(1+) nitrate	USBM	Cup and plunger	175	James, Miron, and Perlee 1970	[9]
Hydrazinium(1+) nitrate	USBM	ERL Type 12	50	James, Miron, and Perlee 1970	[9]
Hydrazinium(1+) nitrate	USBM	5	50	USBM Staff 1968	[105]
Hydrazinium(1+) nitrate		ERL Type 12	32	Smith and Walton 1949	[106]
Hydrazinium(1+) nitrate	Picatinny	2	20	Seamans and Waser 1968 and 1969	[103, 104]
Hydrazinium(1+) nitrate			200–250	Medard 1952	[84]
Hydrazinium nitrate	BAM	5	75	Swart 1965	[107]
Hydrazinium(1+) perchlorate	BAM	1	20	Swart 1965	[107]
Hydrazinium styphnate	—	5	100	Fauth 1960	[108]
Hydrazinium picrate	—	5	300	Fauth 1960	[108]
<i>For comparison</i>					
Ammonium perchlorate, dry	Picatinny	2	91	Seamans and Waser 1968 and 1969	[103, 104]
Nitroglycerin	—	5	50	Fauth 1960	[108]
Nitroglycerin	Picatinny	2	5	Seamans and Waser 1968 and 1969	[103, 104]
RDX	Picatinny	2	35.6	Seamans and Waser 1968 and 1969	[103, 104]
Tetryl	—	5	125	Fauth 1960	[108]
Methylhydrazinium nitrate	Picatinny	2	76	Seamans and Waser 1968 and 1969	[103, 104]
Methylhydrazinium nitrate	USBM	No. 12 tool	83	Perlee et al. 1968	[14]
1,1-Dimethylhydrazinium nitrate	USBM	No. 12 tool	166	Perlee et al. 1968	[14]

BAM = Bundesanstalt für Materialprüfung, Berlin, Germany, Picatinny = Picatinny Arsenal, Dover, NJ, RDX = 1,3,5-trinitro-1,3,5-triazacyclohexane, USBM = U.S. Bureau of Mines, Pittsburgh, PA

Medard [84] measured values of 200–250 kg cm in an unspecified apparatus, which seems to be unrealistically insensitive.

A drop height of 10 cm with a 2-kg weight in a Picatinny apparatus gave a 50% probability of ignition of HN crystals [103, 104]. In the same apparatus, for comparison, the 50% point for nitroglycerin was 2.5 cm, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) 17.8 cm, methylhydrazinium nitrate 38 cm, and ammonium perchlorate (AP) 46 cm.

The impact sensitivity of HN (20 to 25 cm, 50% fires, 2-kg weight) was independent of the water content over a range from 0.01 to 1.71 mass-% H_2O , or the type of anvil surface used (bare anvil or grit paper). HN was only slightly hygroscopic at relative humidities up to 52%.

Using the “Bruceton up-and-down” method, the 50% probability for ignition was reported as 175 kg cm in a cup and plunger and 50 kg cm in an Explosives Research Laboratory (ERL)-type 12 tool [9]. A lower value of 32 kg cm in the same tool was obtained on a different sample.

1.5.2 Shock Sensitivity of Hydrazinium Nitrate

Hydrazinium nitrate could not be detonated or even caused to burn at atmospheric pressure by electrically heated wires [9, 82, 109]. When initiated by a blasting cap or boosted with a high explosive, molten, granular or cast/pressed solid HN detonates. Depending on the mode of initiation, high-velocity detonation (HVD) or low-velocity detonation (LVD) could be observed. In a wedge-shaped container, the detonation may start as HVD (7600–8500 m/s) and may transition to LVD (1400–2400 m/s) after the sample thickness drops below the critical thickness for HVD. Some of the results (also for HN-water and HN-hydrazine mixes) are summarized in Table 17. The critical film thickness is of practical importance if an explosive is sought that is able to propagate detonation into narrow crevasses in rock for explosive fracturing. For monopropellant applications, a thin critical diameter is undesirable because combustion may burn back from the combustion chamber into the manifold or even the propellant tank, which would be disastrous.

Hydrazinium nitrate has been identified as one of the constituents of residues found in dinitrogen tetroxide (NTO)/Aerozine-50 rocket engines after very short vacuum pulse mode operations. These residues are the suspected cause of pressure spikes when they light off and detonate during subsequent pulses. This was a major concern during the development of the Apollo moon landing project in the 1960s. Leaking valves may allow chunks of frozen, unreacted propellant to accumulate in the chamber during idle periods in the vacuum and cold of outer space. Physical properties and detonability of HN mixtures were investigated in an effort to explain hard start and spiking phenomena. The US Bureau of Mines conducted a very thorough evaluation of the hard start phenomena in NTO hypergolic bipropellant engines with hydrazine-type fuels [110]. Next, fuel samples were tested in a ballistic mortar suspended from

a pendulum, with and without NTO, air, or oxygen added as oxidizers [111]. All tests were conducted in triplicate.

When liquid fuels and liquid NTO were encapsulated separately in glass vials, loaded into the mortar, and crushed by firing a cap, the trinitrotoluene (TNT) equivalencies rose to 170%. Improved mixing and highest TNT equivalencies were achieved when the glass vials were coaxial instead of adjacent to each other. In an effort to study the hazard of frozen accumulations of leaked propellants, the fuels and NTO were frozen in liquid nitrogen, pulverized, and carefully mixed at LN_2 temperature, and small 20- to 40-mg samples were loaded into a DSC apparatus. The instrument began taking measurements only after the samples had warmed to 173 K. Beginning exotherms were observed at 205 K and the reaction became very rapid at 218 ± 3 K for $\text{NTO}/\text{N}_2\text{H}_4$. The frozen propellant thawing tests were then repeated on a large scale with 1- to 60-g samples. Typically on thawing there was a violent reaction. Only two out of dozens of samples detonated and pulverized the glass beaker. Small samples thawing slowly were shown to contain hydrazinium(1+) nitrate, identified by its IR spectra. Another segment of the USBM study prepared pure samples of various hydrazinium salts and their solutions in hydrazine or water to determine their physical properties and explosive hazards [13]. Samples of granular (0.7 g/cm^3) and cast (1.6 g/cm^3) HN were subjected to impingement of a shock wave generated by detonation of a gaseous $\text{O}_2/\text{C}_2\text{H}_4$ mixture at varying initial pressures. The initiation pressure spike was between 48 and 434 MPa (475 and 4300 atm) and the elicited response of the HN was detonation at 1.9 to 2.7 mm/ μs and detonation pressures from 68 to 1236 MPa (680 to 12240 atm).

One of the questions was whether the material accumulating in rocket engines was capable of supporting detonation in a thin film, as found in these engines [39]. A trough filled with liquid explosive and slanted gave a wedge-shaped partially confined geometry of the explosive specimen. The thin-film test, summarized in Table 17, showed that molten HN and HN solutions in water or hydrazine with more than 80% HN are capable of supporting a stable LVD in films as thin as 0.25 mm (0.01 in). The detonation, initiated by two 25-g tetryl pellets, would typically start HVD, but convert to LVD when the wedge thickness dropped below the critical film thickness for HVD. In view of the suspicious engine deposits that prompted this investigation, it was concluded that at least 1 g of HN would have to accumulate in the engine to do any structural damage, a much larger amount than what has been removed from pulsed engines in any instance.

The low melting point of HN (343 K) is advantageous for using it and studying it as a liquid explosive. The molten material is easily mixed with other materials (e.g., AN), cast in shaped charges, or used as a liquid explosive [112].

A study of the effect of water on the critical diameter of molten HN showed that the critical diameter at 348 K increases from 4 to 28 mm with 0–24% water in the mixture [113]. Beyond 24% H_2O , the critical diameter increases very rapidly. It was noted that molten HN and its aqueous solutions are capable of detonating at different velocities:

Table 17: Detonation velocity and critical film thickness of hydrazinium nitrate and its mixtures (at 348 K).

Composition	HN Mass-%	HVD		LVD	
		Velocity m/s	Thickness cm	Velocity m/s	Thickness cm
HN	100	8500	0.127	1400	≤0.025 ^a
HN/H ₂ O	85	7600	0.305	2400	≤0.025
HN/H ₂ O	75	Not observed		2100	0.33
HN/H ₂ O	65	No propagation		No propagation	
HN/N ₂ H ₄	80	8600	0.076	1800	≤0.025
HN/N ₂ H ₄	60	8200	0.076	Not observed	
HN/N ₂ H ₄	40	7800	0.254	2200	0.076
HN/N ₂ H ₄	20	No propagation		No propagation	

^a0.025 cm represents the limit of resolution of the apparatus

Data source: [9, 39]

at a high (normal) velocity near 8 km/s and at a low velocity of the order of 2 km/s. Above a critical diameter, the detonation always propagates at a high velocity. Below the critical diameter, or with higher water content, the mixture may detonate with a low-order velocity as long as it is still close to the borderline, or it will not detonate at all. The effect of the water diluent in the critical diameter of HN can be expressed by

$$d^{*'} = \alpha d^* \exp \left[\left(\frac{1 - \alpha}{\alpha} \right) \frac{A}{RT} \right]$$

where $d^{*'}$ is the critical diameter of the mixture, d^* is the critical diameter of pure HN, and α is the mass fraction of liquid explosive in the mixture. The ratio A/RT is equal to 7.1–7.5 for the HN–H₂O system. The detonation velocity of molten HN at the critical diameter is 8150 m/s and slightly higher in larger (four- to fivefold d^*) charges, 8380 m/s. The density of liquid HN at 348 K is 1.544 g/cm³. The detonation velocity of solid HN compressed to the same density is 8220 m/s. At high densities the detonation velocity of HN is equal to or even higher than that of RDX, although the heat of explosion of HN is less than that of RDX.

1.5.3 Shock Sensitivity of Hydrazinium Nitrate Solutions

Hydrazinium nitrate that is intended for use in nuclear reactor fuel element reprocessing and uranium/plutonium separation is usually shipped as a 30% aqueous solution. It has received a shipping permit as Toxic Liquid, Inorganic, N.O.S. (Hydrazine Nitrate Solution) under UN Number: 3287, Class: 6.1, P.G.: III; Label Code: 6.1. See also [114, 115]. There was concern that in large bulk containers this solution might still be detonable. One must remember that the data in the graph in Figure 14 were only obtained in

1-in diameter charges and any geometry above this dimension might still be detonable in a wider range of compositions. This ternary graph with the detonability boundary drawn in has been used extensively in the selection of low-freezing hydrazine monopropellants (see *Encyclopedia of Monopropellants*).

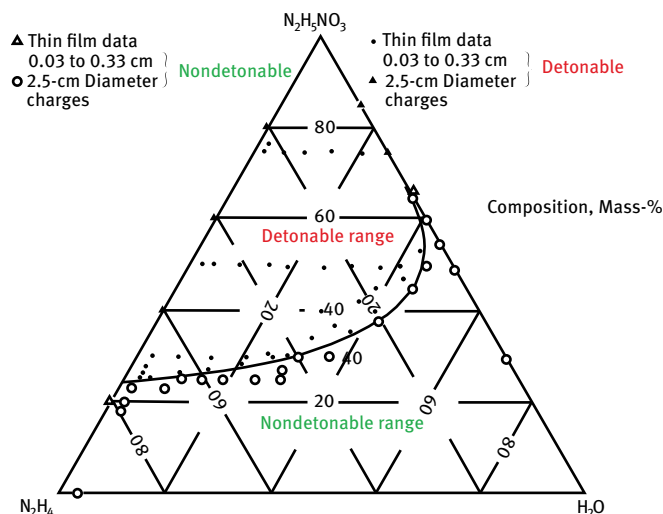


Figure 14: Detonable range in hydrazine/hydrazinium nitrate/water ternary mixtures. (Reproduced and modified from [9].)

1.5.4 Friction Sensitivity of Hydrazinium Nitrate

In the friction sensitivity test apparatus of the West German Institute for Materials Testing (BAM), HN was negative at up to 36 kg_f, but hydrazinium(1+) perchlorate (HP1) was positive at 1 kg_f [107].

1.5.5 Electrostatic Sensitivity of Hydrazinium Nitrate

Hydrazinium nitrate in the dry state is readily initiated by a small discharge of static electricity as the powder is poured from one container to another. HN explosions can be initiated by a hot wire even in HN solutions. Autoignition may occur on heating at 830 K, also under elevated pressure in a pressure bomb [94]. This method can study the ignition in exothermic systems under high pressure and temperature. Experimental details were given for pressures up to 4 kbar and temperatures up to 2000 K. The technique applied to aqueous hydrazine mononitrate had a temperature limit of 830 K and produced different kinetic data for the two methods of analysis used. The extrapolated rates did, however, bracket that estimated from detonation experiments.

The maximum energy for zero probability of ignition using a potential of 5000 V is 12.5 J [107].

1.6 Explosive Performance of Hydrazinium Nitrate

1.6.1 Detonation Velocity of Hydrazinium Nitrate

Explosives can be subdivided into two groups, depending on the nature of critical diameter and its dependence on loading density. Group I explosives (such as pentaerythritol tetranitrate [PETN], tetryl, TNT) exhibit a decrease in critical diameter with an increase in loading density. Group II explosives (such as HN or AP) exhibit an increase in critical diameter with an increase in loading density. In one study, 20-mm-diameter pellets of HN pressed to densities of 1.650–1.676 g/cm³ and initiated with a variety of methods (booster explosives plus flyer plates) detonated with shock velocities of 5.42–6.69 mm/μs and particle velocities of 0.8–2.44 mm/μs [116]. Other pressed pellets were machined to the shape of a wedge. The critical diameter below which detonation no longer propagated could be determined from high-speed photographs taken with a streak camera. Particle velocities and shock pressures were calculated by the impedance matching method. When plotting the shock velocity U versus the particle velocity u of HN, it was noted that the Hugoniot curve has two different slopes, with a distinct change of slope at $u = 0.86$ mm/μs. None of the two curves intersected the detonation pressure point. Below $u = 0.86$, the shock velocity obeyed Equation (1). Above $u = 0.86$, Equation (2) applied instead:

$$U = 1.2 + 4.9u \quad \text{Equation (1)}$$

$$U = 5.0 + 0.53u \quad \text{Equation (2)}$$

The shock pressure at the intersection was about 8 GPa as opposed to a Chapman-Jouguet (C-J) pressure of 30 GPa calculated from theoretical data. Calculated shock and particle velocities were 9.11 and 1.99 mm/μs respectively.

At equal granular density, HN powder detonates more slowly than hydrazinium(1+) azide (HA), 2115 m/s compared with 2460 m/s [117].

Unlike TNT, the critical diameter of granular-pressed HN increases with increasing loading density. Detonation velocity as a function of loading density exhibits a maximum at densities of 0.5–1.5 g/cm³ [36]. The infinite diameter curve giving the detonation velocity as a function of loading density is

$$D = 5.388(\rho_0) - 0.100$$

where D is the detonation velocity in mm/μs and ρ_0 is the density in g/cm³. At finite diameters of 1.27 to 4.14 cm, the D vs ρ_0 curves exhibit maxima. This behavior is to be expected of explosives whose critical diameter increases with increasing loading density, the reverse of the trend exhibited by common explosives such as TNT. The location of the maximum is dependent on the charge diameter ($D_{\max} = 4900$ m/s at $d = 1.27$ cm, 7300 m/s at $d = 2.54$ cm, and 7400 m/s at $d = 4.1$ cm). A charge measuring 1.27 cm in diameter pressed to 1.63 g/cm³ failed to detonate. With extrapolation to infinite charge diameter, an ideal detonation velocity for HN has been calculated from

these data to be 8500 m/s. This was in close agreement with predictions by the RUBY code (8660 m/s at 1.68 g/cm^3 to 5880 m/s at 1 g/cm^3). See also [118].

The detonation velocity and pressure of water-free HN pellets pressed to maximum density (1.68 g/cm^3) is dependent on pellet diameter (Table 18). The failure diameter of pressed HN pellets is between 20 and 30 mm.

Table 18: Detonation velocity of hydrazinium(1+) nitrate pellets.

Pellet diameter d , mm	Detonation velocity D , km/s	Particle velocity u_{CJ} , km/s	Detonation pressure P_{CJ} , GPa
60	8.92 ± 0.05	1.63 ± 0.03	24.4 ± 0.4
40	8.92 ± 0.05	1.63 ± 0.03	24.4 ± 0.4
30	7.61 ± 0.05	1.47 ± 0.03	18.7 ± 0.4
20	5.29 ± 0.05	—	—

Data source: [119]

For comparison, neat methylhydrazinium nitrate (“MMHN”) molten at 318 K contained in a 25-mm schedule 40 steel pipe underwent LVD ($2 \text{ mm}/\mu\text{s}$) when boosted with 50 g of tetryl and zero gap [120]. In a gap test, molten MMHN exhibited minimum film thicknesses of 1.5 and 1.8 mm for propagation at 2.2 to $2.3 \text{ mm}/\mu\text{s}$.

1.6.2 Theoretical Prediction of Detonation Velocity of Hydrazinium Nitrate

There are numerous hydrodynamic thermodynamic codes [121] that are capable of predicting the C-J detonation velocity and detonation pressure of condensed explosives. The main difference between the various codes is the type of the equation of state (EOS) used. Agreement between calculated and measured data for conventional, commercial explosives is sometimes poor owing to varying amounts of carbon formed in the experiment, but the computer programs now available are already a significant improvement over the “back-of-the-envelope” calculations based on the Kamlet and Jacobs technique. It was therefore of interest to compare the accuracy of computer predictions to measured data of explosives that do not contain any carbon, such as most hydrazine-based explosives. The detonation of HN was used to check the accuracy of computer predictions for carbon-free explosives because there were sufficient experimental data available to compare the two methods. The agreement of calculated data with experimental detonation velocities of HN was good [122, 123].

1.6.3 Detonation Velocity of Hydrazinium Nitrate Solutions

Ternary Mixtures. Hydrazine hydrate/HN mixtures containing 65, 68, 70, and 75 mass-% HN were tested in brass tubes measuring 10 or 20 mm in diameter and 150 mm long [124]. It is not quite clear from the translation whether the hydrazine

hydrate used contained 91.24% hydrazine hydrate = 58.4% N_2H_4 or not. For tests at elevated temperatures, the tube was surrounded by a temperature conditioning jacket of water with an outer diameter of 75 mm in a PVC tube. The density ρ of these mixtures at 293 K ranged from 1.322 to 1.388 g/cm³. The detonation velocity at 293 K in the 10-mm tube could be expressed as

$$D = 5.47\rho + 0.47$$

where D is the detonation velocity in km/s and the density ρ (a function of the HN concentration) at 293 K is entered in g/cm³ units. For a given mixture (e.g., the 68% HN mixture) in a 20-mm tube, the dependence of detonation velocity on temperature was

$$D = -0.0032t + 8.13$$

where D is the detonation velocity in km/s and t is the temperature in °C. The ideal detonation velocity in a tube of infinite diameter was extrapolated by plotting D versus reciprocal diameter and extrapolating to $1/d = 0$. The ideal detonation velocity of the mixes containing 65, 68, 70, and 75% HN was 7930, 8100, 8128, and 8318 m/s respectively.

Binary HN/Hydrazine Mixtures. The detonation velocity of hydrazine/HN mixtures in 20-mm plastic tubes increased from 8200 m/s at 55% HN to 8630 m/s at 90% HN (density 1.5 g/cm³) [125]. The curve representing the detonation velocity as a function of composition had not quite leveled off at 90% HN, and would most likely increase further if such mixtures could be kept in the liquid state. In analogous tests with HP instead of HN, the maximum detonation velocity under identical conditions was only 8400 m/s, but lead block indentations were higher than with HN.

Measured and calculated C-J detonation velocities (from two different authors), detonation pressures, and detonation temperatures of HN/hydrazine solutions containing 55 to 80% HN are summarized in Table 19. The agreement between the two sets of calculated data and the measurements is quite good.

Table 19: Measured and calculated Chapman-Jouguet detonation parameters of hydrazinium nitrate/ N_2H_4 solutions.

Property	Composition, mass-%					Source	References
	55/45	60/40	65/35	75/25	80/20		
ρ , g cm ⁻³	1.267	1.293	1.325	1.387	1.421	Kusakabe et al. 1980	[40]
D_{CJ} , m/s	7829	8050	8151	8361	8426	Abdulazeem 1996	[123]
D_{CJ} , m/s	7810	7940	8089	8363	8505	Tanaka 1982	[126]
D_{CJ} , m/s	7793	7952	8058	8339	8492	Kusakabe et al.	[40]
p_{CJ} , kbar	199	209	214	243	262	Abdulazeem 1996	[123]
p_{CJ} , kbar	195	204	216	244	261	Tanaka 1982	[126]
T_{CJ} , K	2162	2351	2459	2897	3149	Abdulazeem 1996	[123]
T_{CJ} , K	2152	2292	2436	2766	2950	Tanaka 1982	[126]

The detonation wave in liquid 21% hydrazine/79% HN detonations is not very luminous. The radiation emitted from the detonation front is insufficient to determine the temperature by black-body radiation as this can be done for the more carbonaceous detonation products of nitromethane [127]. The detonation wave is also not very strongly ionized, so that it is difficult to determine detonation velocities of hydrazine-based explosives by the make-circuit method with ionization probes. In spite of these difficulties, the detonation temperatures of nine different HN/hydrazine and HN/water solutions containing 55 to 95% HN was measured in comparison with conventional high explosives (TNT, RDX, tetryl) [128]. Measured and calculated detonation temperatures (using the Kihara-Hikita [KHT] EOS) for the HN/hydrazine mixtures containing 55 to 75% HN agreed moderately well, but measured detonation temperatures for the HN/water blends containing 80 to 95% HN were more than 1000 K hotter than the theoretical predictions. Obviously, the theory cannot quite handle the cooler-burning explosives yet. A comparison of different computational methods was based on calculating the dependence of the C-J temperature of TNT using five different EOSs (Becker-Kistiakowsky-Wilson [BKW], Jacobs-Cowperthwaite-Zwisler [JCZ3], Lennard-Jones Devonshire [LJD], Weeks-Chandler-Andersen [WCA4], and KHT) [126, 129].

Binary HN/Water Solutions. The detonation velocity of HN slurries and solutions contained in 50-mm diameter cylinders with varying amounts of water decreases with increasing water content (Table 20). The detonation becomes unstable if the sample contains more than 36 mass-% water.

Table 20: Detonation velocity of aqueous hydrazinium(1+) nitrate solutions.

H ₂ O content Mass-%	Density g/cm ³	Detonation velocity <i>D</i> km/s	Particle velocity <i>u_{CJ}</i> km/s	Detonation pressure <i>P_{CJ}</i> GPa
25	1.44	7.49 ± 0.05	1.48 ± 0.04	16.0 ± 0.5
28	1.41	7.20 ± 0.05	1.44 ± 0.04	14.6 ± 0.5
32	1.38	6.98 ± 0.05	1.00 ± 0.04	9.7 ± 0.5
36	1.35	6.33 ± 0.05	0.85 ± 0.04	7.3 ± 0.5
40	1.32	4.51 ± 0.05	—	—

Data source: [119]

1.6.4 Explosive Yield of Hydrazinium Nitrate

In the lead block test, the cavity volume increase by detonation of solid HN is 408 cm³/10 g. For hydrazine/HN solutions, the explosive yield as measured by the increase of cavity volumes in lead blocks depends on the mixture ratio of hydrazinium(1+) nitrate (HN) oxidizer and hydrazine fuel. Maximum Trauzl block indentations were obtained with N₂H₄—N₂H₅NO₃ mixtures away from the stoichiometric composition [125]. The cavity volume increased from 370 to a maximum of 430 cm³ by increasing the HN content from 40 to 60%. Beyond 60% HN, the lead block cavity

volume dropped back to 340 cm³ at 100% HN. Similar mixtures with hydrazinium(1+) perchlorate achieved higher maximum indentations, 470 cm³ instead of 430 cm³.

The explosive force can be measured not only by lead block indentation, but also in a ballistic mortar and expressed as TNT equivalency. In this test 1,1-dimethylhydrazinium nitrate, methylhydrazinium nitrate, and HN measured 106, 136, and 142% equivalent to TNT in a ballistic mortar [13, 14]. These nitrates are thus more powerful explosives than TNT. Accidental accumulation of these nitrates in combustion residues in small rocket engines, in particular following short pulse widths, and subsequent explosion can cause substantial damage to the hardware.

1.6.5 Explosive Applications of Hydrazinium Nitrate

There are hundreds of patents describing the use of HN in explosives, along with a long litany of other ingredients. Most of these patents are for water-based, slurry, and gelled explosives and most of them also include AN or methylammonium nitrate as an ingredient. The reason for adding HN to AN slurries is to increase their cap sensitivity and detonation velocity. Only a few examples of explosives with HN are included here because some of them have compositions similar to those of HN-based monopropellants. HN-based monopropellants are described in *Encyclopedia of Monopropellants*.

In a few instances it was a misbehaving HN-based rocket propellant that was then claimed as a new powerful explosive and developed into a commercial product.

1.6.5.1 Explosives Based on Hydrazinium Nitrate

Owing to its high shock and friction sensitivity, HN cannot be safely used as an explosive for military applications or commercial excavations in the solid state. All detonation experiments with pure HN were done strictly to satisfy academic interest. That has not prevented investigators from looking at HN mixtures and HN solutions for commercial and military applications.

Slabs of cast and solidified HN (180 × 120 × 12 mm) did not detonate stably and required the addition of more than 20% PETN or 30% 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) to achieve a stable detonation at this thin diameter [130]. Melt-processed mixtures of HN with PETN, HMX, or RDX had higher explosive performance as measured by C-J pressure, detonation velocity, and Gurney energy than the pure materials by themselves. Based on tests with twelve different blends, a 30 HN/70 HMX mix had the highest Gurney energy and a 45 HN/55 HMX mix had the highest detonation velocity (9.030 km/s) [131]. X-ray flash photography was used to observe the progression of the detonation front into the sample. HN should not be mixed with nitroguanidine, as it begins an exothermic reaction with ammonia evolution.

Fused mixtures of AN with 5–50% HN have improved detonation properties over those of AN by itself [112]. The explosives may contain 0.5% Al, 3% carbon, and 7.5% TNT as fuels. Detonation velocity and card gap sensitivity increase with increasing HN content of the mixtures.

Some transition metal nitrate/HN double salts or complex salts containing hydrazinium ion or free hydrazine in the ligand sphere can be used as primary explosives [132]. Metal hydrazine nitrate complexes tested for that purpose included $[\text{Ni}(\text{N}_2\text{H}_4)_3](\text{NO}_3)_2$ [133], $[\text{Zn}(\text{N}_2\text{H}_4)_2(\text{NO}_3)_2]_n$, $[\text{Cd}(\text{N}_2\text{H}_4)_2(\text{NO}_3)_2]_n$, and $[\text{Co}(\text{N}_2\text{H}_4)_3(\text{NO}_3)_2]$ [134]. The thermal behavior, kinetics, thermal safety, and storage life of these salts were investigated by DSC, thermogravimetric analysis (TGA), and dynamic pressure measuring thermal analysis methods.

1.6.5.2 Liquid Explosives Based on Hydrazinium Nitrate

A product line of hydrazine-based two-component explosives has been developed by the former Explosives Corporation of America (Excoa) and was at one time marketed under the name “Astrolite®.” The advantage was that the two components could be shipped (or even air-freighted) separately under a less restrictive shipping designation and mixed only at the point of end-use. The mixtures contained 70–92% oxidizer (HN or HN/HP mixture 4:1) including up to 25% of alkali metal nitrates, calcium, or aluminum nitrates or perchlorates, 6–15% hydrazine, and 2–15% ammonia [135]. The mixtures could be made starting with hydrazinium salts and adding ammonia gas, but it was more practical to start with hydrazine and ammonium salts. The ammonia liberated by the reaction of hydrazine with ammonium salts remained in the solution. A sample containing 79% HN, 7% hydrazine, and 14% ammonia had a detonation velocity of 8100 m/s and a freezing point of 251 K (–8 °F). Other cap-sensitive two-component explosives can be prepared *in situ* from AN instead of HN and hydrazine-water mixtures [136]. One such mixture consisted of 60% AN, 30% AP, 15% hydrazine, and 5% water, and had a detonation velocity of 3300 m/s. Later modifications of this explosive composition included aluminum powder and a gelling agent [137]. Example compositions of these heavily aluminized hydrazine explosives consisted of 2–45% Al, 0–18% NH_3 or NH_4^+ , 6–75% N_2H_4 or N_2H_5^+ , and 15–70% NO_3^- ion. Guartec or fumed silica was used as a gelling agent to keep the metal particles in suspension. Typical examples were 19% hydrazine, 48% AN, and 33% aluminum, or 10% hydrazine, 57% HN, and 33% aluminum.

The two-component field mix capability of Astrolite explosives makes these explosives practical for applications where large quantities of live explosive cannot be stored near the application site or where transportation restrictions do not allow the shipping of live explosives (e.g., as air freight). For convenience, the AN can be prepackaged in plastic bottles accompanied by a separate, leak-proof container for hydrazine. Immediately prior to use, the metal can with hydrazine inside a flexible plastic bottle is opened by squeezing a lever and allowed to mix with the AN (Safe-T-Pack). A typical composition was 53.0% AN and 13.2% AP in the solid and 26.4% hydrazine, 4.1% AN, and 3.3% H_2O in the liquid phase [138]. Another mixture consisted of a solid component containing 89.9% AN, 10% AP, and 0.1% inerts and the liquid component consisted of 43.48% hydrazine, 25.22% water, 18.26% methanol, and 13.04% AN [139].

Astrolite-type two-component explosives were tested for oil and gas well stimulation under a series of US Bureau of Mines and US Department of Energy contracts to Petroleum Technology Corporation [140]. The process was called Astro-Frac®.

In testing Astrolite-G (the exact composition is proprietary), it was concluded that the liquid explosive can be initiated with an M6 blasting cap, has the same relative sensitivity to friction or impact as solid secondary high explosives, and is stable at 278–538 K [141]. The drop-weight sensitivity on the Olin drop-weight tester with a 2-kg weight was 27.5 cm, similar to that of unsensitized nitromethane (28.6 cm) but much less sensitive than *n*-propyl nitrate (15.5 cm). In the rifle bullet (0.30 caliber from 90 ft) impact test, the material would detonate when contained in metal containers but would not detonate in polyethylene or rubber bags. Some tests were conducted with the dry crystals (most likely HN) for sensitivity to electrostatic discharge and friction. The crystals withstood 11 J, an electric discharge well above the level of discharge likely to be carried by a person. The dry crystals did not detonate when tested on the Picatinny Arsenal Abrasive Tab Friction Pendulum Apparatus. In the card gap test, liquid Astrolite-G was positive at 20 cards. The addition of 20% water lowered the sensitivity to positive at 12 cards and 32% water lowered it to positive at zero cards. The frozen undiluted explosive had a sensitivity of five cards; it was less sensitive than the liquid. All positive tests went high order, as evidenced by the hole sheared from the witness plate. The detonation velocity of the unboosted (cap initiation only) explosive in stainless steel pipes measuring 25 mm (1 in) in internal diameter (I.D.) with a wall thickness of 1.65 mm (0.065-in) was 8400 m/s. Tests in polyethylene plastic tubes gave similar results. The addition of 22% water lowered the detonation velocity to 7600 m/s.

Solutions of HN in hydrazine hydrate (HH) become detonable once the HN concentration exceeds 40 to 45% [40]. Detonability in this case was determined with the sample contained in a brass tube measuring 20 mm in I.D., 120 mm long with 1-mm walls, and initiated by a 10-g tetryl booster. In a wedge test, the critical thickness was measured for HN concentrations of 45, 55, and 65% and decreased from 5 to 1.3 to 0.6 mm. The low critical thickness of a fraction of a millimeter for the highest HN concentration mix is particularly remarkable, considering that many commercial explosives have critical diameters in the order of several centimeters. The detonation velocity of a blend consisting of 68 HN/29.1 HH/2.9 H₂O ($\rho = 1.3416 \text{ g cm}^{-3}$) as a function of temperature was measured over the range 283–333 K and can be expressed by the equation

$$D = 8.13 - 0.0032(T - 273)$$

where D is the detonation velocity in km/s and T is the temperature in kelvin. It is interesting to observe that the decrease in density due to thermal expansion has a dominating effect on detonation velocity, in spite of the higher energy content of a warmed explosive. The detonation velocity (extrapolated to an infinite diameter) at a constant temperature (293 K) varied linearly with the HN concentration from

7.793 km/s for 55% HN to 8.492 km/s for 80% HN. At concentrations above 70% HN in a sample 20 mm in diameter, the explosive exhibited LVD as well as HVD, but the critical diameter for LVD was much higher than that for HVD.

It was found that HN-based liquid mixtures explode upon coming in contact with alkali metals and their alloys [142]. This method of initiation is suitable for explosive drilling in deep bore holes.

An HN/HH explosive with a density of 1.31 g cm^{-3} had a measured detonation velocity of 7.246 km/s and its lead cylinder compression value was larger than 35.3 mm [143].

Molten HN in a steel tube is very shock sensitive. A sample tube filled with 300 g of molten HN dropped on a steel plate from a height of only 50 cm exploded on impact [130]. HN is more sensitive in the molten state than in the solid state. With TNT, the relationship is the other way around.

Another explosive containing HN is Hydan-II, a mixture of HH and AN developed at Dynamit Nobel Wien in 1994 [144]. It has a detonation velocity of 7150 m/s.

Instead of mixing HN with hydrazine (hydrate), liquid or slurry explosives can also be obtained by mixing HN with organic aliphatic amines [145, 146]. One example is a composition containing 80 mass-% HN, 15% monoethanolamine, and 5% water, which had a density of 1.42 g/cm^3 and a detonation velocity of 7.81 km/s. Explosion did not occur even after dropping a 5-kg weight on the explosive from a height of 60 cm.

1.7 Applications of Hydrazinium Nitrate in Liquid Rocket Propellants

There are many liquid monopropellant blends containing HN and their physical and safety properties should have been reported at this location. However, in a few instances we have discussed these propellants where they were formulated and tested as monopropellants such as in *Encyclopedia of Monopropellants*. The same applies to solid propellants containing HN, which are to be discussed in later volumes planned in this series.

2 Hydrazinium Perchlorates

Hydrazine forms two types of perchlorates when reacted with perchloric acid or other perchlorates, depending on the ratio of reactants, hydrazinium(1+) perchlorate (HP1) or hydrazinium(2+) perchlorate (HP2). A very good summary of properties of hydrazinium perchlorates and other perchlorates is provided in publications by Pearson [147, 148]. Hydrazinium(1+) perchlorate and hydrazinium(2+) (di)perchlorate are both very explosive substances that explode readily when overheated rapidly or subjected to mechanic or electrostatic stimuli [149].

A detailed summary of the properties of hydrazinium(1+) perchlorate and hydrazinium(2+) perchlorate was already published in the author's earlier books on hydrazine [2], pages 120 through 272, and [3], pages 220 through 375. Additional information on hydrazinium perchlorates is contained in the book by Patil and Rattan [4], pages 70 through 74. The main emphasis in the current chapter is on publications that have appeared in the interim or that were not already included in the two earlier books.

2.1 Hydrazinium(1+) Perchlorate

Hydrazinium(1+) perchlorate, also known as hydrazinium monoperchlorate, hydrazine monoperchlorate, HP, HP1, HP-1, CAS RN [27978-54-7], or CAS RN [13762-80-6], is a very sensitive oxidizer and cannot be safely used in the pure state. Hydrazinium(1+) perchlorate is also called hydrazine **monoperchlorate** or hydrazinium **monoperchlorate** in order to differentiate it from hydrazinium **diperchlorate**.

2.1.1 Production of Hydrazinium(1+) Perchlorate

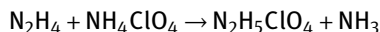
Hydrazinium(1+) perchlorate is easy to prepare by direct neutralization of hydrazine hydrate in dilute solution with diluted perchloric acid under stirring and with adequate cooling. It has been known for a very long time, but has not yet found a practical use [150].

Hydrazinium(1+) perchlorate can be prepared by **slowly** neutralizing 60% HClO_4 with 75% $\text{N}_2\text{H}_5\text{OH}$ at temperatures from 273 to 298 K (0 to 25 °C). The salt precipitates as the hemihydrate from water at 273 K (0 °C) and is filtered cold in sintered glass funnels (avoid the use of filter paper!). The fine white crystals are gently removed from the filter with a Teflon spatula and placed in a drying tube at 343 K (70 °C) for 2 h at a constant vacuum of 0.05 mm Hg to dehydrate the hemihydrate [151]. Only very few hydrazinium salts crystallize with water of hydration, and hydrazinium(1+) perchlorate is one of them.

When preparing hydrazinium perchlorates, one must be careful to use perchloric acid or perchlorates that do not contain any chlorate ion. Hydrazinium chlorate is the most sensitive contaminant in this category and traces of it may alter the behavior of either HP1 or HP2.

Hydrazinium(1+) perchlorate can be prepared by the reaction of barium perchlorate with hydrazinium hydrogen sulfate in aqueous solution. It is easy to filter off the insoluble barium sulfate and concentrate the filtrate (with precautions from behind a barrier).

Hydrazinium(1+) perchlorate can be made by metathetical reaction of hydrazine and AP in aqueous solution



where the equilibrium is shifted to the right by driving off the ammonia [152]. In one example, 0.17 mol of anhydrous hydrazine (AH) was added to a solution of 0.17 mol of AP in 4.4 mol of water at 300 K (27 °C). The mixture was heated with stirring to 373 K (100 °C) for 5 h to drive off most of the ammonia, followed by heating to a higher temperature to drive off 3.3 mol of water and the rest of the ammonia. On cooling the mixture to 278 K (5 °C), the hemihydrate precipitated in the form of white crystals. The hemihydrate can be dehydrated by heating in anhydrous isopropanol. It is unclear why this cannot be made starting with hydrazine hydrate instead of the more expensive AH.

The direct dehydration of HP hemihydrate to the anhydrous salt at 333 K (60.5 °C) was a generally accepted fact for several decades. However, sporadic reports had indicated the possible existence of other hydrates in the $\text{N}_2\text{H}_5\text{ClO}_4/\text{H}_2\text{O}$ system. Detailed reexamination of the phase diagram of this system did not reveal any additional compounds other than the hemihydrate at 19 mass-% H_2O [153]. The melting point curve showed a discontinuity at 19% H_2O , 337 K, indicating the occurrence of a hydrate that decomposes at this temperature. The continuous uninflected line disproved any other hydrates postulated in the previous literature. A eutectic point occurred at 80 mass-% H_2O and 269 K. The melting point of pure crystalline HP was fixed at 415.5 K (142.4 °C). Vapor pressure curves obtained for different salt-hydrate compositions between 278 and 349 K showed that dehydration occurs at 337 K, and the heat of vaporization of water from the hemihydrate was 73.6 kJ/mol (17.6 kcal/mol) at 293 K.

A continuous production process for prilled anhydrous HP1 starts with a simple neutralization reaction between hydrazine (hydrate?) and perchloric acid and the aqueous solution is dehydrated in a flow-through falling film evaporator at or below atmospheric pressure, where all water is evaporated and the HP emerges as an anhydrous melt at 418–423 K (145–150 °C), then sprayed on a spinning plate where it is spun out by centrifugal forces into a cooling tower in which it consolidates to spherical particles [154].

Hydrazinium(1+) perchlorate can be prepared by reaction of barium perchlorate with hydrazinium(1+) chloride in ethanol or isopropanol [155]. Eutectic mixtures of HP1 with lithium perchlorate can be used as oxidizers in rocket propellants and have reduced sensitivity to impact (see Section 2.1.5.1).

2.1.2 Physical Properties of Hydrazinium(1+) Perchlorate

The physical properties of HP1 and its hemihydrate are summarized in Table 21 and in Table 22.

Table 21: Physical properties of hydrazinium(1+) perchlorate $\text{N}_2\text{H}_5\text{ClO}_4$.

Property	SI Units	Other units	Authors	References
Molecular mass	132.504 g/mol	7.5469 mol/kg		
Melting point	411 K	138 °C	Jacobs and Russel-Jones 1966	[156]
	413.6–414.1 K	140.5–141 °C	Shidlovskii, Semishin, and Schmagin 1962	[157]
	415.5 K	142.4 °C	Carleton and Lewis 1966	[153]
	414 K	141 °C	Levy et al. 1965b	[158]
Density	1.939 g/cm ³ at 288 K	1.939 g/cm ³ at 15 °C	Barlot and Marsaule 1949	[159]
	1.927 g/cm ³		Shidlovskii, Semishin, and Schmagin 1962	[157]
Heat of formation	–175.9 kJ/mol	–42.05 kcal/mol	Shidlovskii, Semishin, and Schmagin 1962	[157]
Heat of fusion	16.07 kJ/mol	3.84 kcal/mol	Pearson 1969	[148]
	7.03 kJ/mol	1.68 kcal/mol		
	16.067 kJ/mol	3.86 kcal/mol	Levy et al. 1965a	[160]
Heat of dissociation	244 kJ/mol	58.4 kcal/mol	Levy et al. 1965a; Levy et al. 1966	[109]
Heat of solution (1 : 1000 dilution)	40.9 kJ/mol	9.77 kcal/mol	Shidlovskii, Semishin, and Schmagin 1962	[157]
Solubility in water	23.6 g/100 g solution at 273 K		Barlot and Marsaule 1949	[159]
	68.9 g/100 g solution at 313 K		Barlot and Marsaule 1949	[159]

Table 22: Physical properties of hydrazinium(1+) perchlorate hemihydrate.

Property $\text{N}_2\text{H}_5\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	SI Units	Other units	Authors	References
Melting point	405 K	132 °C	Patil, Nesamani, and Verneker 1980	[161]
Enthalpy of formation	–326 kJ/mol	–78.02 ± 0.1 kcal/mol	Pearson 1969	[148]
Heat of dehydration	29.2 kJ/mol	6.977 kcal/mol	Christensen and Gilbert 1934	[162]

2.1.2.1 Solubility of HP1 in Water

A study of phase equilibria in the system hydrazine perchlorate/water showed that a solid hydrate was formed, decomposing at 337 K (64 °C) and the phase diagram has

a eutectic point at 269.05 K (-4.1°C) and 80% water [153]. The melting temperature of the anhydrous salt was at 415.5 K (142.4°C). A further determination was made of vapor pressures of water vapor in equilibrium with the condensed phases from 278 to 348.7 K (5.0 to 75.6°C). These experiments identified the hydrate as $\text{NH}_4\text{ClO}_4 \bullet \frac{1}{2}\text{H}_2\text{O}$, and fixed the quadruple point at 337 K (64°C) and 88 mm Hg. The solubility of HP1 in water or ethanol is summarized in Table 23. The solubility data are useful in preparing HP1 and HP1 hemihydrate.

Table 23: Solubility of hydrazinium(1+) perchlorate in water or ethanol.

Solvent	Temperature K	Solubility g/100 g Solution
H ₂ O	273	23.6
H ₂ O	288	40
H ₂ O	313	68.9
H ₂ O	333	87.4
H ₂ O	348	93
H ₂ O	373	95
C ₂ H ₅ OH	288	5
C ₂ H ₅ OH	303	27
C ₂ H ₅ OH	313	40
C ₂ H ₅ OH	333	69

Data source: [159]

2.1.2.2 IR Spectra of Hydrazinium(1+) Perchlorate

When it was attempted to record the IR spectrum of HP1 hemihydrate by the pressed KBr pellet method, the measured spectrum corresponded to that of a mixture of potassium perchlorate and hydrazinium bromide, the result of an unwanted metathetical reaction in the presence of water (hydrate water) [156]. Subsequently, three spectra of HP1 hemihydrate in different organic solvents with different peak-free ranges were spliced together.

IR spectra of hydrazinium(1+) perchlorate hemihydrate and the anhydrous salt (both in Nujol mulls and pressed in KBr pellets) were recorded and compared to understand the forces that hold the hydrates in the crystals [163]. The possibility of the proton being shared between the hydrazinium cation and water present as the oxonium ion, H_3O^+ , has been investigated. Absorption frequencies of N_2H_5^+ are observed at 3400 – 3300 , 1570 , and 960 cm^{-1} and those of perchlorate at 1100 and 620 cm^{-1} . It is interesting to note additional bands at 3280 , 2560 , 2000 , and 1570 cm^{-1} , which could be due to oxonium (H_3O^+) ions or H-bonded water as normal H_2O of hydration does not exhibit such absorptions, and only OH protons could be seen. The IR spectra of $\text{N}_2\text{H}_5\text{ClO}_4 \bullet \frac{1}{2}\text{H}_2\text{O}$ and the anhydrous salt in Nujol mull are shown in Figure 15.

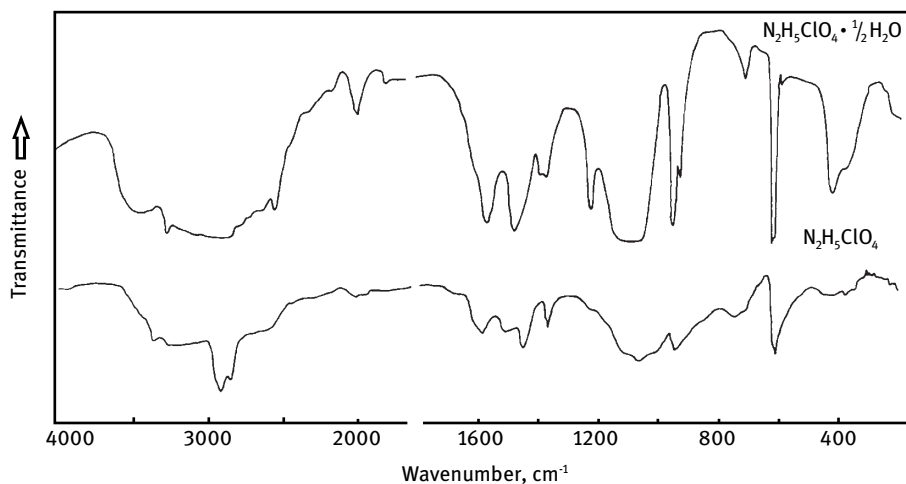


Figure 15: Infrared spectra of (a) $N_2H_5ClO_4 \cdot \frac{1}{2}H_2O$ and (b) the anhydrous salt. (Republished and modified from [163], with permission of © 1983 Royal Society of Chemistry; permission conveyed through Copyright Clearance Center Inc.)

2.1.2.3 Molecular Structure of Hydrazinium(1+) Perchlorate

HP1 crystallizes in monoclinic crystals, space group $C2/c$ with a density of 1.939 g/cm^3 at 288 K. Crystals of hydrazinium(1+) perchlorate and hydrazinium(1+) tetrafluoroborate are isostructural: both are monoclinic, space group $C2/c$, with eight formula units per unit cell [67]. The crystal parameters of HP were already summarized in Table 14.

2.1.2.4 Thermodynamic Properties of Hydrazinium(1+) Perchlorate

Thermodynamic properties of HP were already summarized in Table 21 and additional data are provided in Table 26. The heat of formation of a mixture of AP and HP was determined by calorimetry to be -210.4 kcal/mol .

2.1.3 Chemical Properties of Hydrazinium(1+) Perchlorate

2.1.3.1 Reactions of Hydrazinium(1+) Perchlorate

Hydrazinium perchlorates form ammoniates when the anhydrous salts are saturated with anhydrous gaseous ammonia under pressure [161]. If one attempts this reaction with aqueous ammonia instead of anhydrous ammonia, one only obtains a mixture of salts. Hydrazinium perchlorate ammoniate, $N_2H_5ClO_4 \cdot NH_3$, is non-hygroscopic and can be stored without decomposition. In the IR spectrum one can observe bands at 1400 and 750 cm^{-1} , which are characteristic of coordinated ammonia. In the DTA, hydrazinium(1+) perchlorate ammoniate has a melting endotherm at 410 K (137°C) and

a decomposition exotherm at 513 K (240 °C). A similar diammoniate has been prepared from hydrazinium(2+) perchlorate, which melts at 373 K (100 °C) and decomposes at 491 K (218 °C).

2.1.3.2 Thermal Stability of Hydrazinium(1+) Perchlorate

When dry samples of hydrazinium(1+) perchlorate or hydrazinium(2+) diperchlorate were decomposed slowly in a stream of carbon dioxide, the diperchlorate produced some hydrogen azide, but the monopерchlorate did not [164]. Both liberated nitrogen, oxygen, chlorine, chloride, and ammonium. In the case of hydrazinium(1+) perchlorate, the decomposition reaction and its kinetics can be studied only when the substance is heated slowly.

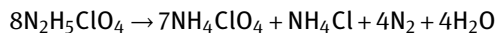
Anhydrous HP1 begins to decompose at temperatures close to its melting point [157]. The weight loss of HP begins between 433 and 523 K. After a 6-min heating period, the following weight losses were observed on 0.2-g samples: not measurable at 433 K, 0.3% at 453 K, 0.7% at 473 K, 3.1% at 493 K, and 5.4% at 513 K. Above 523 K (250 °C) the salt decomposed rapidly and rapid combustion of HP occurred at 523 K. When heated at a rate of 20 °C/min, HP1 in a bath of Woods metal heated at a rate of 20°/min starting at 373 K autoignited at 553 K (280 °C) compared with 633 K (360 °C) for AP. The addition of 5% MnO₂ or Cu₂Cl₂ lowered the autoignition temperature to 527 K (254 °C) and 443 K (170 °C) respectively.

Decomposition products of HP1 are ammonium perchlorate, hydrazinium chloride, water, nitrogen, and a small amount of chlorine [165]. The activation energy is about 83.7 ± 1.2 kJ/mol (20 ± 0.3 kcal/mol).

The thermal decomposition of HP1 was studied between 403 and 473 K (130 and 200 °C) [151, 166, 167]. No decomposition was detected at 403 K (130 °C) for over 100 h. Decomposition between 413 and 473 K (140 and 200 °C) followed a power law relationship during an induction period and a linear law from 10 to 80% completion of reaction. The activation energy of the rate-determining step was 99.6 kJ/mol (23.8 kcal/mol), quite close to that obtained for anhydrous perchloric acid. See also [168].

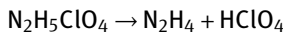
When heated under the necessary precautions, HP1 can be sublimed nearly undecomposed [109, 158, 160]. The heat of sublimation was derived from the slope of the vaporization rate curve and was found to be 124 kJ/mol (29.6 kcal/mol), essentially identical to that of AP. Attempts to sublime HP2 resulted in partial decomposition and the sublimate was essentially pure HP1.

The overall stoichiometry of HP decomposition can be described by

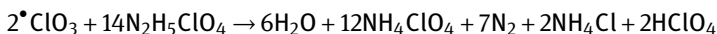
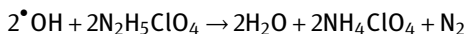
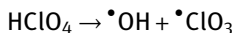


The rate of decomposition accelerated for $0 < \alpha < 0.1$ and remained constant during $0.1 < \alpha < 0.7$. The activation energy during the mid-phase of the reaction sequence was

about 99.6 kJ/mol (23.8 kcal/mol) [169, 170]. One of the several mechanisms proposed starts out with a proton transfer



followed by decomposition of the perchloric acid to form chloryl radicals, which can react with more HP1 (or with N_2H_4):



where it was assumed that the perchloric acid pyrolysis is the rate-controlling step.

Hydrazinium(1+) perchlorate exists in the anhydrous form and in the form of a hemihydrate. The hemihydrate loses water and is dehydrated to the anhydrous salt if heated at 333.6 K (60.5°C) under vacuum. Decomposition studies under vacuum starting with the hemihydrate should be identical to those of the anhydrous salt if the sample is kept near this temperature long enough before increasing the temperature any further.

Table 24 is a summary of the endotherms and exotherms observed during the DTA and DSC thermal analysis of various hydrazinium perchlorates and their hydrates and ammoniates.

Table 24: Differential thermal analysis/differential scanning calorimetry results for hydrazinium perchlorates.

	Endo/exotherms	Authors	Year	References
$\text{N}_2\text{H}_5\text{ClO}_4$	406m, 420–	Verneker, Sharma, and Jain	1976	[171]
$\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$	359+, 497–	Patil, Nesamani, and Verneker	1980	[161]
$\text{N}_2\text{H}_5\text{ClO}_4 \cdot \text{H}_2\text{O}$	405+m, 536–	Patil, Nesamani, and Verneker	1980	[161]
$\text{N}_2\text{H}_6(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	373+, 546–	Patil, Nesamani, and Verneker	1980	[161]
$\text{N}_2\text{H}_5\text{ClO}_4 \cdot \text{NH}_3$	410+m, 513–	Patil, Nesamani, and Verneker	1980	[161]
$\text{N}_2\text{H}_6(\text{ClO}_4)_2 \cdot 2\text{NH}_3$	373+m, 491–	Patil, Nesamani, and Verneker	1980	[161]

Key: + endotherm, – exotherm, m = melting point (melting endotherm)

The thermal decomposition of HP1 in the solid state leads to ammonium perchlorate, hydrogen chloride, nitrogen, and water:



The activation energy for this reaction, as gauged by the rate of HCl evolution measured in a mass spectrometer, is 33.7 kJ/mol (8.05 kcal/mol) between 353 and 393 K

[171]. At 393 K, the weight loss stabilizes at 29% only after 5 days of heating. Doping the HP1 with perchlorates of ammonium, aluminum, or calcium at 1 mol% had no pronounced effect on the rate of decomposition. Higher additive concentrations should have been studied to obtain a noticeable stabilizing or catalyzing effect.

The kinetics of the thermal decomposition of molten HP1 were measured in the temperature range from 418 to 468 K in a constant-volume vacuum line that was initially evacuated to 1.32×10^{-4} Pa (10^{-6} mm Hg) [172]. A liquid nitrogen trap was attached to the system so that all condensables would be immediately removed. The rate of pressure buildup from non-condensable gases was measured with a McLeod gauge. The composition of the gases could also be measured in situ through a side tap connected to the inlet of a mass spectrometer. In addition, TGA and DTA data were taken on other samples. Based on those data, a slightly different equation for the decomposition of HP1 was then proposed:

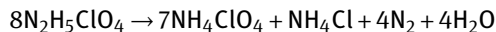


The formation of H_2 and N_2O had not yet been observed by previous investigators.

Analysis of decomposition rate data at different temperatures gave an activation energy of 150 kJ/mol (35.9 kcal/mol). When HP1 was doped with inert diluents (NH_4^+ , Ca^{2+} , Al^{3+} , SO_4^{2-}), a systematic decrease in the reactivity of HP1 was observed. Therefore, it seems possible that the rate-determining step is the formation or dissociation of an associated complex involving $\text{N}_2\text{H}_5\text{ClO}_4$.

The vaporization and sublimation products of HP, as studied by a cold matrix isolation technique and identification of products by IR absorption spectra are hydrazine and perchloric acid [173]. Other IR bands found in the products were assigned to NH_3 , HCl , and H_2O . At higher temperatures (436–483 K = 163–210 °C) the intensity of NH_3 and H_2O IR bands (but not those of HCl) increased more rapidly than those of N_2H_4 or HClO_4 . Comparing the vaporization temperatures of HP, AP, hydroxylammonium perchlorate (HAP), and methylammonium perchlorate, the relative vaporization temperatures could be correlated with the pK values of the bases in aqueous solution.

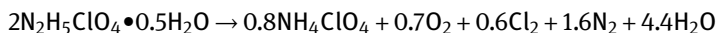
The rate of decomposition of dehydrated HP1 and HP2 between 413 and 473 K in a glass-walled constant-volume reactor was measured by recording the decomposition pressure [170]. Decomposition products were analyzed (gases by MS and condensed products by conventional wet methods). The composition of the products indicated the following reaction:



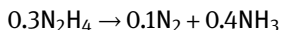
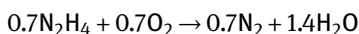
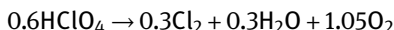
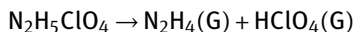
During the initial phase the reaction was self-accelerating, but the rate remained constant between 10 and 70% of complete decomposition. The activation energy in the temperature range of this study was 100 kJ/mol (23.8 kcal/mol). Like other investigators before and after them, Grelecki and Cruice assumed that the initial step in the thermolysis of HP1 is the dissociation into hydrazine and free perchloric acid. Because

the activation energies of HP1 and HClO_4 decomposition are very similar, HClO_4 decomposition is likely to be the rate-controlling step in HP1 decomposition. Addition of acids accelerates HP decomposition. The decomposition of HP is a matter of HClO_4 decomposition, whereas the rate of HN decomposition is determined by the rate of hydrazine decomposing. Some of the HClO_4 decomposition occurs as a heterogeneous reaction on the wall of the vessel [174].

Hydrazinium(1+) perchlorate hemihydrate decomposes in two stages [15]. First, it melts and undergoes dehydration, showing a broad endotherm. The thermal decomposition of hydrazinium(1+) perchlorate hemihydrate slows down with progressive decomposition, and the kinetics did not conform to any of the usual rate equations like those used for AP. The decomposition was studied in a constant volume bomb with condensation of the products in an LN2 trap and also by TGA at atmospheric pressure between 453 and 502 K [175]. The following overall reaction represents approximately the product composition formed:



This may be the result of the following intermediate reaction steps in the temperature range 423–523 K (150–250 °C):



The activation energy of the decomposition reaction between 453 and 553 K was 152.7 kJ/mol (36.5 kcal/mol) based on pressure rise measurements and 179.8 kJ/mol (35.8 kcal/mol) based on weight loss rate measurement. The fact that the volatile products were condensed as soon as formed and thus removed from further reaction may account for the difference between this equation and the one shown earlier. In addition, this experiment was extended to 553 K, where NH_4ClO_4 begins to decompose.

Hydrazinium(1+) perchlorate ammoniate $\text{N}_2\text{H}_5\text{ClO}_4 \bullet \text{NH}_3$ and hydrazinium(2+) perchlorate diammoniate $\text{N}_2\text{H}_6(\text{ClO}_4)_2 \bullet 2\text{NH}_3$ were prepared by reaction of the corresponding hydrates with ammonia gas [161]. The thermal properties of the ammoniates are quite different from those of the corresponding hydrates. In the case of hydrazinium(2+) perchlorate, the ammoniate decomposes at temperatures 50 K below those of the hydrate. If the DTA of hydrates is carried out under vacuum, several steps can be identified that belong to the dehydrated salts as intermediates.

2.1.4 Strand Burning of Hydrazinium(1+) Perchlorate

Strand-burning studies of HP were plagued by the unreproducible burning behavior of some of the samples [157]. Initially, it was not possible to ignite HP packed into glass tubes measuring 1.05 cm in I.D. with an electrically heated wire at atmospheric pressure. The salt melted, ignited briefly, and extinguished after a layer of 1–2 mm was consumed. Rapid combustion occurred only if HP was preheated to 523 K. HP/AP mixtures containing 30–60% HP burned stably at 0.13 to 0.22 cm/s. The rate of HP decomposition was accelerated significantly by adding 5% manganese(IV) oxide, cobalt(II) oxide or copper(I) chloride as combustion catalysts. The linear burning rates of these catalyzed mixtures were much faster than those of the corresponding AP mixtures. The addition of 5% MnO_2 , CoO , or Cu_2Cl_2 as combustion catalysts enabled the strand burning of HP powder at ambient pressure. Observed burning rates were 0.13, 1.0, and 1.6 cm/s, for the three additives respectively. A mixture of AP with 30 to 60% of HP without catalytic additives burned steadily at 0.13 to 0.22 cm/s in a tube 1.05 cm in (inside) diameter at room temperature and at 1 atm.

Smooth deflagration was achieved sporadically for both tamped ($\rho = 1.1\text{--}1.3\text{ g/cm}^3$) and pressed HP pellets ($\rho = 1.8\text{--}1.9\text{ g/cm}^3$) at 24.2 to 434 kPa (0.24 to 4.3 atm), with and without preheating [109]. Later experiments with HP from a different source did not reproduce these results. HP mixed and pressed with a solid fuel (polyacetal) burned in a stable and reproducible manner. Paraformaldehyde and s-trioxane were not suitable for these tests because they reacted prematurely with HP. For stable combustion of pressed HP, a minimum addition of 5% copper chromite or potassium dichromate was required, whereas magnesium oxide was a more effective catalyst and steady burning stabilization was achieved with only 2% of the additive. The upper limit for stable combustion of HP/fuel propellants is 778 kPa (7.7 atm). At times, smooth deflagration was obtained at 202-, 404-, or 606-kPa pressure, but this could not be repeated in later tests. A tamped sample ($d = 1.1\text{ g/mL}$) containing 5% CuCrO_2 burned at a rate of 1.2 cm/s. A similar sample pressed to a density of 1.93 g/mL burned slower, at 0.7 cm/s. Magnesium oxide was less effective than CuCrO_2 as a catalyst. Similar burning rate studies were conducted for HP2 (see Section 2.2.4).

2.1.5 Safety Properties of Hydrazinium(1+) Perchlorate

2.1.5.1 Drop Weight Impact Sensitivity of Hydrazinium(1+) Perchlorate

Hydrazinium(1+) perchlorate has an impact sensitivity of $0.2\text{ kpm} = 2\text{ Nm}$. Other investigators reported that it was giving 88% detonations under a 5-kg weight dropped from a height of 15 cm [157].

The drop weight sensitivity of HP1 is dependent on the amount of water in the sphere of hydration [152]. As shown in Figure 16, the drop height required to achieve a 50% probability of ignition of a 20-mg sample with a 2-kg weight goes through a maximum (least sensitive) at a composition that would correspond to

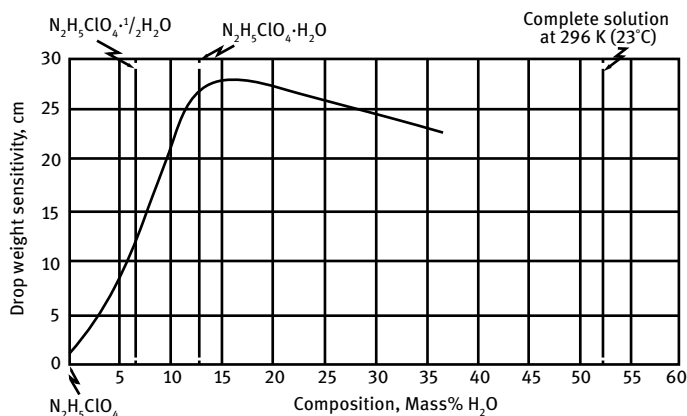


Figure 16: Drop weight impact sensitivity of hydrazinium(1+) perchlorate with varying water content. (Reproduced and modified from [152].)

a monohydrate $\text{N}_2\text{H}_5\text{ClO}_4 \cdot \text{H}_2\text{O}$, but HP1 typically crystallizes as a hemihydrate, not a monohydrate.

Hydrazinium(1+) perchlorate forms two eutectics with lithium perchlorate, one with a 1:1 molar ratio and another one with a 1:2 molar ratio, that have substantially lower impact sensitivity than HP1 itself. The 50% probability of ignition when impacted with a 2-kg weight is 51.2 cm for the 1:2 eutectic and 26.3 cm for the 1:1 eutectic, which is substantially less sensitive than the dry HP1 alone (6 cm) [155, 176, 177].

2.1.5.2 Friction Sensitivity of Hydrazinium(1+) Perchlorate

Although all other tests indicated that HP is very sensitive, the friction sensitivity was reported as only 1 kp = 10 N pistil load with no reaction

2.1.6 Explosive Performance of Hydrazinium(1+) Perchlorate

2.1.6.1 Explosive Yield of Hydrazinium(1+) Perchlorate

In duplicate tests in different sized lead blocks with 10-g samples of dry crystalline HP, lead block indentations of 383 and 388 cm³ were reported [157]. For comparison, triaminoguanidinium nitrate has a Trauzl volume of 350 cm³. The corresponding triaminoguanidinium perchlorate has a Trauzl volume of 465 cm³ and is a more energetic explosive.

The book by Meyer on explosives cites a lead block volume of 362 cm³/10 g. The critical diameter in the steel sleeve test was 20 mm [144].

The explosive force can be measured not only by lead block indentation but also in a ballistic mortar and expressed as TNT equivalency.

Hydrazinium perchlorate contaminated with hydrazinium chlorate is a dangerous product. Hydrazinium(1+) chlorate is less stable than HP or HN and extremely friction

sensitive. In the Trauzl block its indentation was 278% that of mercury fulminate and 100% that of TNT. In the same test, HP gave a lead block indentation of 113% of that of picric acid and 122% of that of TNT [178].

2.2 Hydrazinium(2+) Perchlorate

Hydrazinium(2+) perchlorate, $\text{N}_2\text{H}_6(\text{ClO}_4)_2$, HP-2, HP2, hydrazinium(2+) diperchlorate, hydrazine diperchlorate, CAS RN [13812-39-0] is a very intriguing oxidizer and in spite of many attempts, it was not possible to incorporate it into a stable and storable propellant. Some researchers also refer to the hydrazinium(2+) salts as hydrazonium salts, but that is not correct.

2.2.1 Production of Hydrazinium(2+) Perchlorate

Hydrazinium(2+) perchlorate has been known for a very long time, but it has yet to find a practical application [179]. When reacting hydrazine hydrate with an excess of perchloric acid, the HP2 salt is first obtained in the form of its dihydrate, $\text{N}_2\text{H}_6(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. HP2 can be obtained by reaction of 85% $\text{N}_2\text{H}_5\text{OH}$ and 72% HClO_4 under the necessary precautions (active stirring in an ice bath) to prevent overheating. Although dry HP2 is less sensitive than HP1, the dehydration of the dihydrate can be a dangerous operation and must be conducted at temperatures at or below 353 K (80 °C) under vacuum. The dihydrate salt can also be dehydrated by digestion with excess 70% HClO_4 at room temperature, filtering off the solid, and vacuum drying at a somewhat elevated temperature [180].

Dry anhydrous HP2 is extremely hygroscopic. Powdered HP2 in air at 50% relative humidity (R.H.) absorbs 0.065 mol of water per mol of HP2 within only 40 min [181].

It is very difficult to prepare pure HP2. Common contaminants are HP1 and perchloric acid. Potential contaminants are chlorate and chloride ion. These contaminants may have a strong effect on the thermal stability of HP2.

Anhydrous HP2 can be prepared by reaction of hydrazinium(2+) chloride powder with 72% perchloric acid under heating, which drives off the HCl [182, 183]. After the evolution of HCl has diminished, the mixture is evacuated under stirring to below 1 mm Hg pressure and sparged with nitrogen gas to remove residual HCl. After 4 h the resulting slurry is filtered, giving a filter cake of nearly anhydrous HP2.

Anhydrous hydrazinium(2+) diperchlorate can be made by reacting a hydrazinium(2+) dihalide and a perchlorate of sodium, potassium, ammonium, cesium, or rubidium with hydrogen fluoride under anhydrous conditions [184, 185]. The reaction may take place in an inert atmosphere at a temperature of 283–333 K (10–60 °C). The insoluble product may be separated by decantation or filtration and washed with anhydrous hydrogen fluoride. Residual hydrogen fluoride is removed by subjecting the product to a high vacuum at a temperature above 323 K (50 °C). The

product is free from hydrazinium monoperchlorate and may be used as an oxidizer in propellant compositions.

A process that avoids the use of perchloric acid in the synthesis of HP2 starts out with a suspension of NaClO_4 in aqueous hydrochloric acid and then under stirring, adding hydrazinium(1+) or hydrazinium(2+) chloride with continued stirring [186]. Then, the slurry is heated under stirring to 323–333 K (50–60 °C) until the sodium chloride precipitates. The hot filtrate is cooled to 298 K (25 °C) where the HP2 hydrate crystallizes out. The HP2 hydrate can then be dehydrated by known methods.

Anhydrous hydrazinium(2+) perchlorate, substantially free from hydrazinium(1+) perchlorate, can be made by reacting one molar part of hydrazine with more than two molar parts of perchloric acid, the reaction mixture containing less than 30% by weight of water [187]. Liquid or aqueous hydrazine may be added to a concentrated solution of perchloric acid, and the reaction mixture cooled or evaporated to crystallize out the product. Alternatively, hydrazine vapor in an inert carrier gas can be passed into a concentrated solution of perchloric acid. The reaction product is filtered off and the liquid phase can be recycled after concentration by evaporation.

Hydrazinium(2+) perchlorate forms a double salt $(\text{NH}_4)_2\text{N}_2\text{H}_6(\text{ClO}_4)_4$ with ammonium perchlorate, which is substantially more stable than HP2 itself [188, 189]. The double salt has a higher specific impulse than AP and is less hygroscopic than hydrazinium(2+) perchlorate. It is also compatible with the commonly used organic polymer fuel-binders. The crystal density is 2.08 g/cm³. The impact sensitivity of the double salt H_{50} was 40 cm (16 in), much less sensitive than HP2.

2.2.2 Physical Properties of Hydrazinium(2+) Perchlorate

The physical properties of HP2 are summarized in Table 25.

Table 25: Physical properties of hydrazinium(2+) perchlorate and hydrazinium(2+) dperchlorate dihydrate.

Property	SI Units	Other units	Source, year	References
Hydrazinium(2+) perchlorate				
Molecular mass	232.962 g/mol	4.2925 mol/kg		
Melting point	463–465 K	190–192 °C	Levy and von Elbe 1965	[190]
Density		2.21 g/cm ³	Levy and von Elbe 1965	[190]
Density		2.21 g/cm ³	McHale et al. 1967	[181]
Density		2.11 g/cm ³	Perry, Cohen, and Mann 1994	[151]
Heat of dissociation	154.8 kJ/mol	37.0 kcal/mol	Grelecki and Cruice 1966	[170]
Hydrazinium(2+) perchlorate dihydrate				
Molecular mass	268.993 g/mol	3.7176 mol/kg		
Melting point	368 K	95 °C		

2.2.2.1 Molecular Structure of Hydrazinium(2+) Perchlorate

The hydrazinium(2+) perchlorate dihydrate crystallizes in monoclinic crystals that melt at 368 K (95 °C). The IR spectrum of $\text{NH}_4(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ in a KBr pellet is shown in Figure 17.

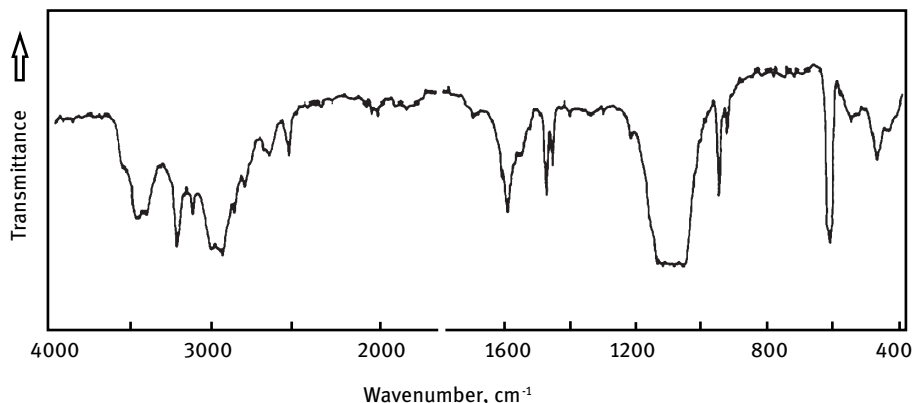
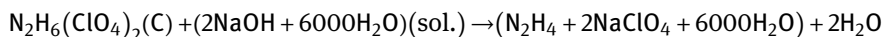


Figure 17: Infrared spectrum of hydrazinium(2+) perchlorate dihydrate. (Republished and modified from [163], with permission of © 1983 Royal Society of Chemistry; permission conveyed through Copyright Clearance Center Inc.)

2.2.2.2 Thermodynamic Properties of Hydrazinium(2+) Perchlorate

The heat of formation of $\text{N}_2\text{H}_6(\text{ClO}_4)_2$ has been determined from the heat released during the reaction [191]:



A summary of thermodynamic data of hydrazinium perchlorates is provided in Table 26.

A double salt of AP and HP2 called DAHTP from Thiokol Chemical Corporation was found to be a 2 : 1 mixture of NH_4ClO_4 and $\text{N}_2\text{H}_6(\text{ClO}_4)_2$. Heat of solution measurements yielded a heat of formation of -880 kJ/mol (-210.4 kcal/mol) [194].

2.2.3 Chemical Properties of Hydrazinium(2+) Perchlorate

2.2.3.1 Reactions of Hydrazinium(2+) Perchlorate

Studies of the stability of HP2 and HAP and their compatibility with binders and curing agents showed that HP2 was more reactive than HAP or AP [195]. Binders investigated included hydroxy- and carboxy-terminated polybutadiene and polyisobutylene prepolymers, and poly-1,2-bis(difluoramino)-2,3-propylene oxide. Binder prepolymers studied were hydroxyl terminated polyisobutylene (UTREZ-diol), carboxyl terminated UTREZ, hydroxyl terminated polybutadiene (R-45-M), carboxyl

Table 26: Enthalpy of formation of hydrazinium perchlorates.

Compound	Mol. mass g/mol	$(\Delta H)_{298}^f$				Authors	References
		kJ/mol	kJ/kg	kcal/mol	cal/g		
$N_2H_5ClO_4(S)$	132.504	-170 ± 1.5	-1284	-40.69 ± 0.36	-307	Rosolovskii, Krivtsov, and Titova	[63]
$N_2H_5ClO_4(S)$	132.504	-179	-1355	-42.9	-324	Shidlovskii, Semishin, and Shmagin	[157]
$N_2H_5ClO_4(S)$	132.504	-177.4	-1339	-42.4	-320	Cruise	[59]
$N_2H_6(ClO_4)_2(S)$	232.962	-293 ± 4	-1259	-70.1 ± 1.0	-301	Caruso, Loprest, and Lum	[191]
$N_2H_6(ClO_4)_2(S)$	232.962	289 ± 2	-1243	-69.2 ± 0.5	-297	Gilliland and Wagman	[192]
$N_2H_6(ClO_4)_2(S)$	232.962	-336	-1441	-80.25	-344	Grelecki and Cruice	[170]
$N_2H_6(ClO_4)_2(S)$	232.962	-292 ± 1.2	-1255	-69.9 ± 0.3	-300	Perry, Cohen, and Mann	[151]
$N_2H_6(ClO_4)_2(S)$	232.962	-322	-1383	-77	-330	Esso Research and Engineering	[193]
$N_2H_6(ClO_4)_2(S)$	232.962	-288	-1238	-68.9	-296	Cruise #493	[59]
$N_2H_6(ClO_4)_2(S)$	232.962	-301	-1293	-71.98	-309	Cruise #485	[59]

terminated polybutadiene (Telagen CT), saturated hydroxyl terminated Telagen, a carboxyl terminated polyisobutylene (EMD-590), and two ethyl acrylate-acrylic acid copolymers. The curing agents studied included four isocyanates, an aziridine curing agent, and an epoxide (ERLA-4221). Studies with AP were included to provide a baseline for comparing the relative merits of the two more energetic oxidizers. Later in the program, and after HP-2 was essentially eliminated as a candidate oxidizer, compatibility of HAP with two NF plasticizers, 1,2,3-tris[1,2-bis(difluoramino)]ethoxy propane and 2,3-bis(difluoramino)-propyl-2,2-dinitropropylcarbonate (P-722) and with aluminum hydride (LMH-I) were studied. At the time this program was initiated, nitronium perchlorate was being eliminated as a candidate advanced oxidizer, HAP and HP-2 were still considered to be attractive oxidizers. During 1967, it became increasingly apparent that HP-2 afforded little prospect of being used in an advanced propellant system, particularly in conjunction with NF binders, plasticizers, and the advanced fuels. HAP, which was slightly more attractive from a compatibility viewpoint than HP-2, was carried along as a candidate advanced oxidizer.

Researchers at the Midwest Research Institute have screened-the reactivity of HP-2 with various structural functionalities found in solid propellant systems [196]. Their approach consisted of measuring the rates as well as determining the nature of oxidizer-substrate reactions and oxidizer decomposition over a range of temperatures, usually 298, 313, 333, and 353 K (25, 40, 60, and 80 °C). They found that HP-2 acted as an oxidizing agent toward organic substrates, although the reaction became apparent and significant only over a relatively long period of time, usually 2 months.

This oxidative behavior of HP-2 becomes important when the long-range aging behavior of propellants formulated with HP-2 is considered. Carbon dioxide evolution from hydrocarbon materials indicated ~1% reaction (on a mole basis) after approximately 2 months. Of special significance, the urethane cure linkage in the binder suffered degradation (through what appears to be decarboxylation) when contacted with HP-2 at room temperatures [197].

2.2.3.2 Thermal Stability of Hydrazinium(2+) Perchlorate

Hydrazinium(2+) perchlorate is an acid-base salt consisting of a stable perchlorate salt (HP) to which a second perchloric acid moiety is loosely bonded. The decomposition of HP-2 is a two-stage reaction in which the first step is the “easy” loss of the loosely held acid moiety to give HP and anhydrous perchloric acid. The rate of the reaction is controlled by perchloric acid decomposition in the second step.

The thermal decomposition of HP2 *in vacuo* is preceded by an extended induction period during which there was only a gradual pressure increase [170]. At the end of the induction period the reaction accelerated sharply and led to complete decomposition within a few hours. However, this phenomenon was not confirmed by later investigators.

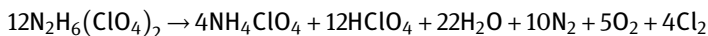
Grelecki and Cruice have reported that after dissociation occurs to the monoperchlorate and free per-chloric acid, the latter decomposes as it is considerably less stable than either HP or HP-2. Grelecki and Cruice, utilizing a manometric technique, have reported a value of 98.3 kJ/mol (23.5 kcal/mol) as the activation energy for HP-2 decomposition between 1273 and 1773 K (1000 and 1500 °C).

Hammond et al. [198] have calculated a similar value of 96.2 kJ/mol (23 kcal/mol) for the HP-2 decomposition process from mass spectral data.

Fast vacuum pyrolysis techniques were combined with a Bendix Time-of-Flight mass spectrometer for the study of the initial reactions occurring during thermal decomposition of HP2 [199]. Primary decomposition mechanisms were postulated, and activation energies calculated. The total ion current trace of the mass spectrometer as a function of sample temperature with a linear heating rate showed two peaks. The initial peak is most likely caused by the loss of one HClO_4 moiety, leaving hydrazinium(1+) perchlorate (HP1). The HP1 then vaporizes at the higher temperature, and yields its characteristic mass spectral cracking pattern. For hydrazinium(2+) perchlorate (HP2), the activation energy values were 96 kJ/mol (23 kcal/mol) for the initiating reaction by the mass spectral thermal analysis method compared with 98 kJ/mol (23.5 kcal/mol) obtained by Grelecki and Cruice, using time-to-acceleration of heated samples contained in scaled, evacuated bulbs.

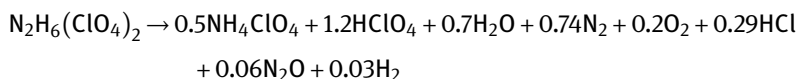
The close similarity of the activation energies for HP-2 decomposition and that for perchloric acid indicate the rate-controlling step to be the decomposition of the free acid.

Analysis of the gaseous decomposition products by MS and analysis of the condensable products by wet chemistry confirmed the following stoichiometry for the decomposition of HP2:



For HP2, there was a very sharp transition at the initiation of the accelerated phase, for example, after 75 h at 413 K. An activation energy of 98.3 kJ/mol (23.5 kcal/mol) was derived from the temperature dependence of the induction period.

Analysis of gaseous and condensed products of HP2 decomposition in the range from 447 to 566 K (174 to 293 °C) indicates a more complicated stoichiometry [109, 158, 160, 181, 200]:



Addition of 1% of perchloric acid dihydrate to fresh HP2 doubled the reaction rate. As perchloric acid is one of the decomposition products of HP2, it is most likely responsible for the autocatalysis observed during HP2 decomposition. Addition of anhydrous perchloric acid instead of the dihydrate accelerated the rate of decomposition at 393 K to a point where it was so fast that it resulted in a runaway situation. The rate under this condition was at least 60 times faster than the normal rate of decomposition. Small amounts of ammonia extended the induction period (a similar effect is observed when adding ammonia to AP).

The effect of dopants, aging, particle size, and pre-irradiation on the thermal decomposition of HP2 has been investigated. All hydrazinium salts are very sensitive to contaminant or non-stoichiometric lattice defects that may lower the threshold temperature of autodecomposition. In the case of hydrazinium(2+) perchlorate, anion vacancies produced a sensitizing effect, whereas cation vacancies had a stabilizing effect [201, 202]. The decomposition of HP2 may involve the migration of ionic species and electron transfer from ClO_4^- to $\text{N}_2\text{H}_6^{2+}$. Data on the uptake of $\text{N}_2\text{H}_6\text{SO}_4$ indicate that these impurities are distributed homogeneously in the HP2 crystal lattice. The rate of decomposition was found to decrease with age. The aging effect was attributed to a decrease in anion vacancy concentration with age. Particle size did not seem to have any effect on the decomposition of HP2. Pre-irradiation was found to affect the decomposition appreciably only when the samples were irradiated for longer durations (1 h), the effect being observed only during the later stages of the decomposition ($\alpha > 0.3$).

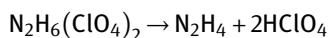
The efficiency of sensitizing additives to HP1 and HP2 decreased in the order $\text{CuCrO}_4 > \text{CuCl}_2 > \text{NiO} > \text{Fe}_2\text{O}_3 > \text{MgO}$ [203]. The activation energy was determined by measuring the delay time to explosion when rapidly heating the sample. The impact sensitivity of some of the sensitized samples was similar to that of mercury fulminate, a primary explosive. The temperatures of explosion (for a 5-s delay) as extrapolated from the plot of explosion delay time versus temperature were 541 and 547 K (268

and 274 °C) respectively for HP and HP2. The optimal amount of additive to achieve the most pronounced lowering of the activation energy (calculated from the change in ignition delay time) was between 2 and 4 mass-%. For example, a maximum of sensitizing of HP2 was observed with 4 mass-% of CuCrO_4 when the temperature of explosion decreased from 551 K (278 °C) (for pure HP2) to 513 K (240 °C) and the activation energy value decreased from 91.2 kJ/mol (21.8 kcal/mol) (for pure HP2) to 49.4 kJ/mol (11.8 kcal/mol).

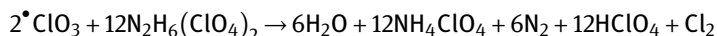
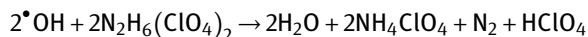
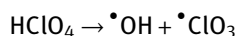
The kinetics of HP2 thermal decomposition were studied by flash mass thermal analysis [198]. In this method, microgram-sized specimens were mounted on a platinum ribbon and inserted into the ionization chamber of a time-of-flight mass spectrometer. Extremely rapid heating rates (up to 3×10^7 K/s) were possible with this arrangement. The decomposition mechanism derived from the mass spectrometer data agreed well with mechanisms proposed by previous investigators [170].

The activation energies for the thermal decomposition of HP1 and HP2 are very similar and both are similar to the activation energy for the decomposition of pure perchloric acid. Therefore, it has been suggested that the rate-determining step in either decomposition reaction is the decomposition of perchloric acid.

The mechanism for the decomposition of HP2 is assumed to be very similar to that of the decomposition of HP1 discussed above:



followed by decomposition of the perchloric acid to form chloryl radicals that can react with more HP (or with N_2H_4):



Hydrazoic acid has been noted among the decomposition products from HP-2.

2.2.4 Strand Burning of Hydrazinium(2+) Perchlorate

Pressed pellets of HP2 burn with a non-luminous flame [109, 158, 160]. During the burn, a melt layer forms on the surface, the thickness of which is pressure dependent and decreases with increasing pressure. There is foaming and bubbling in the liquid layer, best observed at low pressures and less pronounced or invisible at high pressures. If combustion was quenched, the melt layer could be sampled and analyzed. It was shown to contain considerable concentrations of AP. The lowest pressure at which strands could be burned reproducibly was 606 kPa (6 atm). Burning at 101 kPa (1 atm) was not always possible. Extrapolating from data obtained at pressures above 101 kPa, the burning rate at 101 kPa would be 0.002 cm/s.

The deflagration rate of pressed cylinders of HP2 (8 mm diameter by 20 mm length, pressed density 2.11 g/cm^3) after ignition with a glow wire was measured at 0.6–35 MPa nitrogen pressure [181]. The strand burning rate dependence on pressure shows two distinctly different slopes, indicating different mechanisms below and above 10 MPa. Below 10 MPa, the burning rate increases from 0.02 to 1 cm/s, and above 10 MPa, it increases to 1.4 cm/s:

$$\text{Below 10 MPa} \quad r = 1.75 \times 10^{-3} p^{1.44}$$

$$\text{Above 10 MPa} \quad r = 0.28 p^{0.28}$$

where r is the burning rate in cm/s and p is the pressure in atm. At high pressures the flame is stabilized above the oxidizer. Heat from this exothermic reaction zone is radiated back to the condensed phase, causing gasification. At pressures below 2 MPa, the oxidizer is mainly consumed by a rapid, self-sustaining decomposition. At the highest pressures tested, the measured flame temperature approached the theoretical temperature (1604 K). One percent copper chromite increased the burning rate from 0.002 to 0.081 cm/s; 5% increased it to 0.25 cm/s. Sodium nitrosopentacyanoferrate(III) or magnesium oxide were less effective burning rate catalysts.

The flame temperature of hydrazine diperchlorate deflagration was measured using fine wire Chromel Alumel thermocouples [158, 204]. At 28 atm the measured temperature was found to be 200 °C below the calculated product gas temperature. The observed temperature increased with pressure, and at approximately 100 atm the theoretical value was attained. A study of the thermal behavior of hydrazine and perchloric acid was extended to include a review of reactions of chlorine oxides, intermediates in the decomposition of HP1 and HP2 [205].

2.2.5 Safety Properties of Hydrazinium(2+) Perchlorate

2.2.5.1 Drop Weight Impact Sensitivity of Hydrazinium(2+) Perchlorate

The drop-weight impact sensitivity of HP2 was determined in a drop weight sensitivity test apparatus with a 2.26-kg (5-lb) weight by the Bruceton up-and-down method. The drop weight impact sensitivity was compared to that of other energetic materials. The 50% point of HP2, HMX, AP, or dextrinated lead azide was 0.53, 0.58, 1.17, and 0.63 m respectively [180]. The “wet cake,” an interim product consisting of HP2 wet with HClO_4 , was slightly more sensitive (0.43 m) than the dry salt.

2.2.5.2 Shock Sensitivity of Hydrazinium(2+) Perchlorate

Hazard property tests conducted on HP2 before scaling up a process for pilot quantity production indicated that the dry salt is very sensitive in comparison to HMX, AP, or even lead azide [180]. A 60% slurry in water was given an explosive Class B transportation classification, but the dry salt was classified as a Class A Type 4 explosive. Desensitizing additives, such as tricalcium phosphate, were considered to improve the handling and transportation safety of the material. See also [206].

2.2.5.3 Friction Sensitivity of Hydrazinium(2+) Perchlorate

Solid and dry hydrazinium salts may be quite friction sensitive. Friction sensitivity of dry HP2 was surpassed only by that of lead azide, 10.9 kg_f compared with 0.9 kg_f [180]. By comparison, friction sensitivity of HMX and AP in the same apparatus was 15 and 31 kg_f respectively; HP2 wet with HClO₄ tested at 15.9 kg_f.

Hydrazinium(1+) perchlorate is more sensitive to friction than HP2 but both are comparatively less sensitive to friction than mercury fulminate or lead azide [206]. Sensitivity to impact was higher for HP2 than for HP. The friction sensitivities were appreciably increased in the presence of metal oxide additives and the sensitizing efficiency followed the same relative order as impact sensitivity.

2.2.5.4 Electrostatic Sensitivity of Hydrazinium(2+) Perchlorate

Electrostatic discharge sensitivity of dry HP2 powder was intermediate between that of HMX and AP. The dry powder ignited at 0.5 J, whereas HMX ignited at 0.1 J and AP ignited at 1.6 J [180]. Surprisingly, “wet cake,” a mix of HP2 and HClO₄ obtained during the production of HP2, was more sensitive than dry HP2 (0.2 compared with 0.5 J).

2.2.6 Explosive Performance of Hydrazinium(2+) Perchlorate

The detonation velocity of dry HP2 is 4700 m/s [180]. The critical diameter in unconfined samples is 8 mm; in confined samples it is as low as 1.3 mm.

2.2.7 Applications of Hydrazinium Perchlorates

Hydrazinium perchlorates 1 and 2 have been used as the oxidizer in solid propellant formulation studies in combination with various polymeric binder systems.

3 Hydrazinium Nitroformate

Hydrazinium nitroformate, also known as HNF, CH₅N₅O₆, hydrazinium trinitromethide, hydrazinium trinitromethanide, hydrazine trinitromethanide, hydrazine nitroformate, CAS RN [20773-28-8]; also CAS RN [17181-40-7], is a promising oxidizer for solid propellants and liquid monopropellants.

Salts of nitroform (trinitromethane) are sometimes also called trinitromethides or trinitromethanides.

Ammonium dinitramide and hydrazinium nitroformate (HNF) are two new halogen-free oxidizers that compete for applications both in solid propellants and in monopropellants. It depends on which application one has in mind before one can decide which of the two makes a better rocket propellant. Neither contains chlorine, so there would be no hydrogen chloride in the exhaust. Several publications have presented a comparison of the two “green” oxidizers. In looking for environmentally more friendly oxidizers for solid propellants, ADN

and HNF are emerging as likely substitutes for AP. Although both ADN and HNF have lower oxygen balance (+25 and +13% respectively), their enthalpy of formation ΔH_f (−167 and −71 kJ/mol = −40 and −17 kcal/mol respectively) is superior to that of AP. For solid propellants, ADN has the advantage of higher oxygen content, but the disadvantage of hygroscopicity and worse sensitivity [207]. For its intended use as an oxidizer in solid propellants, HNF has several advantages over ADN such as higher melting point, better thermal stability [208, 209], less troublesome hygroscopicity, and ease of synthesis in a single-step reaction. Besides applications in solid propellants, both HNF and ADN have promising properties as green liquid monopropellants when dissolved in water or methanol.

Hydrazinium nitroformate is one of the most powerful solid oxidizers available, but it has poor compatibility with commonly used hydroxy-terminated polybutadiene (HTPB) binders, which is attributed to oxidation of the double bond (C=C) in HTPB by the HNF. In order to characterize HNF, many thermoanalytical techniques, such as DSC and TGA/DTA, have been used to obtain more information about its stability and its compatibility or incompatibility with other materials. When the oxidation of HTPB occurs, it results in deterioration of the binder, which leads to unacceptably low mechanical properties. Isocyanates also show poor compatibility with HNF. Glycidyl azide polymers (GAPs) do not contain carbon-carbon double bonds, may be safely used with HNF, and could offer higher performance than the existing AP/Al/HTPB propellant formulations. The exhaust gases from an HNF/GAP propellant system are halogen free and environmentally more friendly than AP exhaust. The purity of HNF is important as unreacted nitroform or hydrazine gets absorbed in the HNF crystals, posing safety and stability problems during later handling and storage. HNF-based propellants possess high burn rates (30 mm/s at 5.5 MPa) and a high pressure exponent ($n = 0.81 - 0.83$). The pressure exponent can be reduced to 0.59 with suitable burn-rate modifiers. It was estimated that by using HNF-based propellants, an increase in I_{sp} of more than 7% and a payload gain of 10% may be possible.

Additional HNF information is in the author's hydrazine books at pages 90 (preparation), 122 (melting point), 173 (density), 220 (heat of formation), 401 (decomposition), 816 (solid propellant oxidizer) of the first edition [2] and again on pages 118–119 (preparation), 164 (melting point), 231 (density), 291 (heat of formation), 558 (decomposition), 1543–1546 (solid propellant oxidizer) of the second edition [3] of this comprehensive review of hydrazine chemicals.

Several retrospective surveys of the history of the development of HNF as a rocket propellant have been published, including Schöyer et al. [210]. Although HNF was first prepared in 1951 and a major production effort was initiated in the US, research and development was stopped in 1975 because HNF caused unwanted interactions with most solid propellant binders available at that time. HNF was “rediscovered” in 1987 by Nederlandse Organisatie Voor Toegepast-Natuurwetenschappelijk Onderzoek (TNO) Prins Maurits Laboratorium in The Netherlands under a program funded by the

European Space Agency and the Netherlands Agency for Aerospace Programs. The main interest in HNF was centered in Europe, with TNO Prins Maurits Laboratorium (a government entity) and Aerospace Propulsion Products (private industry) cooperatively taking the lead in The Netherlands. Other countries with active HNF research programs included India [211], China [212, 213], and Japan [214].

3.1 Preparation of Hydrazinium Nitroformate

Although the production of HNF is based on a simple acid-base reaction, the quality of the resulting product strongly depends on the preparation and crystallization techniques used. For a propellant oxidizer, control of particle size and size distribution in the production phase of the crystals is important. The effect of different crystallization processes on product quality is very pronounced. Stability depends, among other factors, on purity and/or contamination. Production of HNF is a two-step procedure: The preparation of trinitromethane (nitroform, NF) and the neutralization and salt formation with hydrazine (hydrate). The trinitromethane needed as a starting reactant for HNF production can be obtained by nitration of isopropanol with white fuming nitric acid (see *Encyclopedia of Oxidizers*, chapter “Nitromethanes”). The difficult part is the separation of NF from the excess nitric acid because NF and nitric acid form an azeotrope.

The steps in manufacturing of HNF are as follows: the $\text{H}_2\text{O}/\text{NF}$ mixture is separated by the addition of salt. Nitroform is extracted with dichloroethane (DCE) and separated from the salt solution. Anhydrous hydrazine or hydrazine hydrate is added under controlled conditions to the NF/DCE mixture and HNF precipitates. The remaining steps of the production process are performed to improve the quality and purity of the HNF.

The production of HNF used high-purity grade AH as a starting ingredient. High-purity grade AH has a purity of better than 99.25% and does not contain aniline, but is rather expensive. Experiments showed that using commercial hydrazine hydrate also led to a good-quality HNF product. The costs of hydrazine hydrate are much lower than those of AH. Substantial cost savings are possible and an additional advantage is the reduced hazard level when working with hydrazine hydrate instead of AH. Results of gas evolution during Vacuum Thermal Stability (VTS) tests for hydrazine hydrate-based HNF were superior to AH-based HNF (especially at $353\text{ K} = 80^\circ\text{C}$). The melting temperatures also improved whereas the pH remained within the correct range.

Hydrazinium nitroformate is not compatible with an excess of hydrazine. Excess hydrazine must be avoided when making HNF. Some patents suggest the use of excess nitroform in order to avoid excess hydrazine. The melting temperature T_m of HNF was highest ($387.8\text{ K} = 114.7^\circ\text{C}$) when HNF was produced with minimal excess hydrazine and worst ($385\text{ K} = 111.9^\circ\text{C}$) when HNF was produced with large excess hydrazine. At the same time the VTS values ($333\text{ K} = 60^\circ\text{C}$, 48 h) were 0.67 and 3.59 mL/g respectively.

Constantly measuring the pH during the addition of hydrazine (hydrate) to the NF/DCE mixture and halting the addition of hydrazine at a more acidic point increased the yield from 83 to 87%, and VTS data also improved.

By using hydrazine hydrate instead of AH and recovering methylene chloride and methanol solvents, the cost of HNF production can be substantially reduced and no negative effects on HNF quality were detected after making these process changes. The quality and production yield of HNF were improved by reducing excess amounts of hydrazine hydrate and filtering and washing of raw HNF on the same day it was produced [213].

Hydrazinium nitroformate can be prepared by adding hydrazine dropwise to a solution of trinitromethane in 2-propanol until the precipitation is complete [215, 216]. The heat of neutralization released during this reaction is 84 kJ/mol. The precipitate is washed, recrystallized from 2-propanol, and dried. The salt melts at 394–397 K (121–123 °C) and is stable for 18 months at 373 K. The yield of HNF achieved by this method is only 50%. Another method is described in US Pat. No. 3378594 [217], where equimolar amounts of hydrazine (hydrated or non-hydrated) are mixed with nitroform at 273 to 323 K and atmospheric pressure. Water can be present as a solvent in large amounts or the reaction is carried out in the presence of an organic solvent such as methanol. It appears from US Pat. No. 3378595 that the stability of HNF depends on the ratio of the hydrazine to the nitroform and on the purity of nitroform and solvent.

Most HNF is prepared starting with hydrazine hydrate, which is less costly than AH. It was claimed that it is possible to obtain HNF with a very high purity and yield, starting from high-purity-grade AH. Improved yield and HNF properties are said to be achieved by carrying out the reaction in a liquid/liquid two-phase system [218, 219]. According to these patents, HNF is prepared by dissolving nitroform of a purity of better than 98.5 mass-% in a medium that is a solvent for the nitroform, but is a non-solvent for the HNF to be formed, and then reacting the dissolved nitroform with a stoichiometric amount of hydrazine with a purity of better than 99.0 mass-% while stirring in the presence of a small amount of proton-transferring medium. Both solutions are chilled to 273–278 K prior to mixing and temperature is maintained below 278 K. The proton-transferring medium can be water and/or a lower (C_1 – C_6) alcohol such as methanol or 2-propanol. The solvent for nitroform can be dichloroethane (preferred) or dichloromethane (second-choice alternative). This method enables the production of hydrazine nitroform of such a high purity that it was no longer necessary to use any stabilizer at all, because the lack of stability was found to be caused by the presence of impurities. For reasons of safety, the nitroform is mostly shipped as an aqueous solution containing 32% nitroform. Nitroform can be used by extracting it from the aqueous solution by means of dichloroethane. The nitroform can also be isolated by salting it out from the solution by means of NaCl, KCl, or NaNO₃. NaCl is the most economical choice. In salting out at temperatures just barely above the melting point of nitroform (295 K), a two-phase system is formed, comprising a water layer and

a liquid nitroform layer. The nitroform layer is separated from the brine layer and the residual water/brine is also removed from the nitroform layer to ensure that neither salts nor other impurities present in the water will be carried over into the end product. The presence of chloride ions (inclusions of brine in the HNF layer) can give rise to a reduction of the stability. After all hydrazine has been added, stirring is continued for 60 min at a temperature of approximately 273 K in an ice bath. After stirring, the crude HNF is removed from the reactor, the supernatant liquid is decanted, and the wet product is dried. Optionally, the crude product thus obtained can be purified by means of recrystallization in 2-propanol.

For several years Aerospace Propulsion Products B.V. (APP) in The Netherlands produced HNF in its pilot plant facility. The development of HNF and HNF-based propellants was performed in cooperation with European Space Agency (ESA), TNO (NL), Nobel Energetics (UK), and Avio (Italy), amongst others. APP was the sole commercial producer of HNF world-wide. It was hoped that some of the properties of HNF could be improved by co-crystallization with other oxidizers. The APP production facility, built in 1993, allowed for the simple acid-base reaction that constituted the fundamental step in HNF manufacturing. Reactions took place in a large stirred and temperature-controlled reactor vessel. As of 2002, it allowed for the production of 3–5 kg HNF per batch and had a maximum capacity of ~300 kg HNF per year. All commercially available European HNF during 1993–2008 was produced in this facility. New methods to improve the thermal stability and to control the crystal size were identified and have been implemented in the production process at APP. Work was done on (co)crystallizing HNF with other ingredients such as stabilizers, and the compatibility and thermal decomposition of HNF were investigated. See also [220].

A new method [221] for the preparation of trinitromethane by nitration-hydrolysis of 4,6-dihydroxypyrimidine (DHP) promises to lead to better yields and improved purity of HNF, although the starting materials are more expensive than isopropanol or acetylene [222]. DHP can be prepared via cyclocondensation of dimethylmalonate with formamide as raw materials. NF is then obtained via a nitration-hydrolysis reaction of DHP. The results showed that for up to 80.1% NF yield, the optimal reaction conditions were: the molar ratio of nitric acid to DHP of 5:1, the mol ratio of sulfuric acid to nitric acid of 3.5:1.0, reaction temperature of 318 K (45 °C), and reaction time of 2 h. There is a safe method of isolating NF and converting it to HNF. HNF with a purity of 98.9% was obtained using NF that was prepared under the optimized conditions as a starting material. See also [223].

Nitroform can be prepared by nitration of isopropanol. The mechanism of the nitration reaction was discussed and the optimal reaction conditions of preparing NF were determined as a function of the ratio of (fuming HNO_3):(*i* – PrOH) = 12:1, reaction temperature of 333 K = 60 °C, and reaction time of 3 h [224]. The yield of NF was 46.6%, 21.6% higher than reported in the literature. HNF with a purity of 99.7% was synthesized by the reaction of hydrazine hydrate and nitroform and its structure was characterized by single crystal XRD structure analysis, IR, ^1H NMR, ^{13}C NMR, and MS.

The results showed that the crystal is monoclinic, space group $P2_1/n$. In the crystal lattice, the nitroformate anions and hydrazinium cations connect via hydrogen bonds, and each unit cell contains two independent HNF molecules.

Nitroform can be made by adding a solution of isopropanol in ethylene dichloride (EDC) drop-wise to a nitrating mixture of fuming nitric acid and concentrated sulfuric acid in EDC at 313–333 K (40–60 °C), neutralizing with solid sodium bicarbonate in EDC, followed by extraction with water. HNF is then made by reacting nitroform with a solution of hydrazine hydrate, drying at 323–343 K (50–70 °C), purifying HNF by dissolving in a solvent, filtering and drying the precipitated HNF followed by coating HNF crystals with a surfactant by dissolving HNF in an alcohol/ketone solution containing a surfactant [225].

The influence of various factors such as reaction temperature, time, and amount of anhydrous HNO_3 on yield of nitroform, as well as the effect of temperature on the extraction efficiency, was examined and NF was obtained with an optimal yield of 53.6%, which was far beyond that reported up to that time in the literature (25%) [226]. The synthesis of HNF was achieved by the neutralization reaction of NF with equal molar hydrazine hydrate (80%) instead of AH. The crystal morphology of HNF was adjusted through varied crystallization methods such as anti-solvent crystallization, sono-crystallization, and sequential cooling crystallization in order to decrease the sensitivity. HNF crystals obtained from sequential cooling crystallization displayed excellent morphology with a length/diameter ratio (L/D) close to 1:1. Sensitivity performance toward external stimuli, especially friction and electrostatic discharge, was improved greatly in comparison with that of crude HNF without the crystallization process.

3.1.1 Recrystallization Methods

There were three different recrystallization processes in use during the development of HNF: cooling crystallization (**C**), the solvent/non-solvent process (**S**), and evaporative crystallization (**E**). These lead to crystals with somewhat different characteristics, including size and aspect ratio (L/D), but also different stability characteristics in VTS tests. The HNF that is produced after the addition of hydrazine to the nitroform/dichloroethane mixture must meet certain requirements. In the past, a recrystallization step was necessary to improve purity, thermal stability, and morphology. Now the goal is to produce HNF crystals with the desired shape and purity in one process without recrystallization [227].

During the **C** process, a solution of HNF in methanol is cooled below the saturation point. Seed crystals can be used to induce the nucleation process. The L/D can thus be controlled by adjusting the rate of cooling.

During the **S** process, an HNF solution in methanol is added to a non-solvent, methylene chloride. The methanol dissolves in methylene chloride, causing the HNF

to precipitate. This results in fairly small HNF crystals. Size and L/D of the crystals can be controlled during this process.

During the **E** process, HNF is dissolved in isopropyl alcohol. This solution is subsequently heated, and IPA is vaporized under vacuum while HNF crystallizes. This leads to a better HNF purity, but to a non-controlled morphology and mean crystal size.

Crystallization during ultrasonic agitation (20 kHz) can change the crystal properties. Ultrasonic agitation in combination with the **C** process gave excellent improvements in crystal morphology, a reduction in the particle size, and improvement in the bulk (tap) density. The L/D improved from 4–8 by going to 2.6–3.3. Even the thermal stability of HNF crystals improved (lower gas evolution in VTS). In itself, there is no major objection to a somewhat wider particle size distribution because a high solids load in a solid propellant requires multimodal particle size distribution.

Another method of crystal shape modification is cocrystallization. Cocrystallizing may be done for a number of reasons, including:

- 1) to include a ballistic modifier (e.g., a burning rate modifier) in the oxidizer,
- 2) to include a stabilizer in the oxidizer,
- 3) to coat the crystals with a protective layer, or
- 4) to make a premix of HNF and the binder.

The shape and particle size of HNF crystals can be controlled by recrystallization from a solution of 16–20 mass-% HNF in acetonitrile as a solvent, introducing a predetermined volume of a non-solvent and then cooling the mixed solution of HNF in acetonitrile and the non-solvent [228].

3.1.2 Crystal Shape Modification Methods

A substantial amount of effort has been devoted to the morphology of HNF crystals and new methods for obtaining HNF with different, more processable crystal shapes to start with or to re-crystallize the needle-shaped intermediate product to obtain more spherical particles with a smaller L/D ratio, such as those shown in Figure 19. Ultrasound can be used to induce nucleation at lower supersaturation levels [229]. The application of ultrasound during cooling recrystallization of HNF was already shown to have a positive influence on morphology (aspect ratio and particle size) on a small scale. Scaling up of this production technique to pilot-scale showed that the trend toward morphology and stability improvement can be preserved. The preferred frequency for sonocrystallization is 20 kHz and the amplitude is up to 20 μm . The ultrasound treatment was tested for drowning-out crystallization or cooling crystallization (with and without the addition of seed crystals) and showed improvement in crystal shape for cooling crystallization, but adverse changes for drowning-out crystallization. The stability of HNF was characterized by vacuum stability tests and by headspace gas chromatography-mass spectrometry (GC-MS).

The patents [230, 231] claim a wider range of conditions, e.g., ultrasound with frequency 10–100 kHz and amplitudes of 0.4–10 μ . The same method can be applied to recrystallization of other energetic materials such as CL-20, ADN, AP, RDX, HMX, and PETN.

Another crystallization process applied to recrystallization of HNF is the proprietary ICI process, which results in powders that have more desirable shapes of crystal morphology. HNF from the ICI process had aspect ratios near 1 and only the larger particles (10–90 μ m) had a tendency to form needles. Unfortunately, smaller particles gave a lower onset of exotherm in the DSC and had a higher rate of gas evolution in the VTS. The head space above HNF samples during vacuum stability tests at 313 to 353 K was analyzed by GC-MS and provided additional information beyond that obtained from a traditional VTS. For instance, N_2O could be detected in the headspace after 400 h at 313 K = 40 °C, 200 h at 333 K = 60 °C, and 70 h at 343 K = 70 °C. At 353 K = 80 °C the rate of gas evolution (all gases, with N_2O as the major product) was very rapid and the test had to be terminated after 95 h.

It is common practice to redissolve HNF and recrystallize it, but most recrystallized HNF crystals are still needle-shaped with an L/D of 4 to 5, which makes it difficult to process them into solid propellants. Instead of dissolving and recrystallizing the elongated crystals, it has also been proposed to compress them under a pressure of at most 7 MPa (preferably between 4 and 5.75 MPa) to a semi-solid cake and then reclassify the broken material to form a material having the desired L/D ratio ($L/D < 2.5$) [232]. This patent has been filed in many foreign countries in addition to the Dutch [233], US, European [234], and World [235] filings, including Canada [236], Norway [237], Germany [238], Austria [239], and Australia [240].

Various methods were tried out during HNF crystallization to obtain improved crystal shapes, which include mechanical stirring, ultrasound agitation, and using crystal shape modifiers (CSMs). Experimental results showed that a multi-pronged approach to controlling the shape and size of the crystals by a careful choice of CSMs and crystallization method worked best to counter the preferential axial crystals growth, thus shifting the shape of long needles to near cubical shape [241].

Crystal shapes of many solid propellant oxidizers need to be changed to decrease sensitivity, improve mechanical properties and to get optimal performance from oxidizers such as ADN or HNF [242].

3.1.3 Morphology of HNF Crystals and Methods for Recrystallization

In the as-produced state, HNF often forms long needles (Figure 18) with L/D ratios of up to 8 which do not have a suitable optimal shape for incorporation into solid propellants [210].

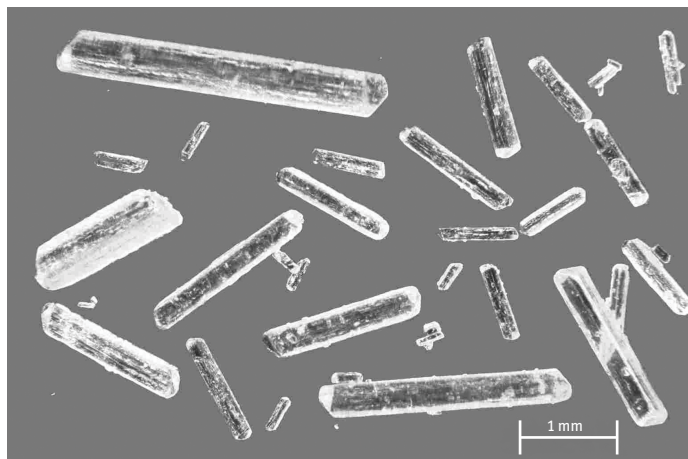


Figure 18: Hydrazinium nitroformate crystallized by slow cooling of a solution, high length/diameter ratio, 1994 technology. (From [210])

If the hot HNF solution is allowed to cool with ultrasonic agitation, the crystals assume a more rounded shape with smaller L/D ratios (Figure 19).

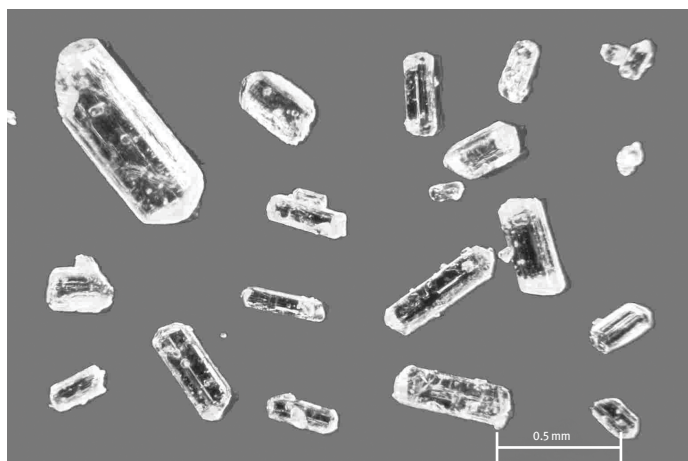


Figure 19: Hydrazinium nitroformate crystallized with ultrasonic agitation, low length/diameter ratio, 1999 technology. (From [210])

A very useful chapter on the crystallization of chemicals with special reference to HNF is contained in [243]. It includes nicely illustrated information on the best crystallization methods for HNF using different solvents and cooling rates.

3.1.4 Coating of HNF Crystals

It has been attempted to reduce the reactivity of HNF with solid propellant binders and to reduce its friction sensitivity by coating with inert polymers that could at the same time aid as bonding agents. Among various coating agents, an HTPB-based clay nanocomposite was found to be most effective for reducing the friction and impact sensitivity of HNF [241]. Using a technique similar to one previously used on wax-coated RDX, the extent of coating on HNF was analyzed by SEM-EDAX so as to achieve a correlation between coating thickness and improved insensitivity. The coating material was thermally stable and compatible with the HNF crystals as revealed by thermal analysis.

It was attempted to prevent incompatibility reactions between HNF and solid propellant polymeric binders by encapsulating the oxidizer particles in a compatible polymer coating.

3.2 Physical Properties of Hydrazinium Nitroformate

The physical properties of HNF are summarized in Section 3.2.1 to 3.2.9. See also [244]. The molecular mass of HNF is 183.081 g/mol.

3.2.1 Melting Point of Hydrazinium(1+) Nitroformate

The melting point of early samples of HNF was reported to be 396.9–397.5 K = 123.8–124.4 °C, but samples of higher purity analyzed in 2000 showed an onset of melting in the DSC at 403.9 to 404.1 K (130.8 to 131.0 °C) [245]. These samples started to decompose at 407.4 K (134.3 °C). Other samples of recrystallized HNF in MeOH/carbon tetrachloride yielded yellow needle-shaped crystals with a melting point of 393 K (120 °C). Inferior grades of HNF may melt at 388 K (115 °C).

3.2.2 Density of Hydrazinium(1+) Nitroformate

The density of two batches of solid HNF was determined using two different methods [245]. The results are the average of duplicate tests and are compared in Table 27. The difference between the density of the two batches is relatively large. It was suggested that batch E8 might be more porous than batch C9.

Because the natural crystal shape of HNF is in the form of long needles that do not pack very well and which are difficult to process into solid propellants, the bulk density (“tap density”) of HNF is sometimes taken as an evaluation criterion for its suitability for solid propellants. If the bulk density of the as-produced HNF is too low, the material may have to be recrystallized.

Table 27: Density of hydrazinium(1+) nitroformate.

Sample	g/cm ³	Method	Authors	References
N ₂ H ₅ C(NO ₂) ₃	1.87	XRD	McHale and von Elbe	[246]
N ₂ H ₅ C(NO ₂) ₃	1.86	pycnometric	Lovett	[217]
N ₂ H ₅ C(NO ₂) ₃	1.87–1.93		Schöyer et al.	[247]
N ₂ H ₅ C(NO ₂) ₃	1.872	XRD		
N ₂ H ₅ C(NO ₂) ₃	1.93 at 113 K	XRD	Dickens	[248]
HNF-C9	1.87	Helium pycnometry	van Zelst and van der Heijden	[245]
HNF-E8	1.83	Helium pycnometry	van Zelst and van der Heijden	[245]
HNF-C9	1.869	Liquid (dodecane) pycnometry	van Zelst and van der Heijden	[245]
HNF-E8	1.846	Liquid (dodecane) pycnometry	van Zelst and van der Heijden	[245]

Note: Density at 298 K unless otherwise noted

3.2.3 Vapor Pressure of Hydrazinium(1+) Nitroformate

The temperature dependence of molten HNF vapor pressure above the burning surface of HNF in the temperature interval from 550 to 750 K can be calculated from [249]

$$\ln P = 17.03 - \frac{9909}{T}$$

where P is the pressure in atm and T is the temperature in kelvin. The slope of this curve corresponds to a heat of evaporation (or sublimation) of 164.8 kJ/mol.

3.2.4 Solubility and Hygroscopicity of HNF

To measure the hygroscopic point, a saturated solution of HNF was placed in a desiccator equipped with a hygrometer [245]. The relative humidity above the saturated solution was 94%. HNF is less hygroscopic than AN, which becomes deliquescent at 62% R.H. No moisture uptake could be measured with samples kept at 20% or 65% R.H. HNF starts taking up moisture only if the surrounding relative humidity is $\geq 94\%$.

The solubility of N₂H₅C(NO₂)₃ (HNF) in water at 293 K (20 °C) is 52.88 mass-% HNF [58]. The solubility of HNF in water is approximately 50% at 293 K (20 °C) and 80% at 328 K (55 °C).

3.2.5 Optical Properties of Hydrazinium(1+) Nitroformate

3.2.5.1 UV-Visible Absorption Spectra

The UV spectra of HNF solutions in water have maxima of absorption at 210 and 352 nm [250] (Figure 20). Because hydrazine by itself has an absorption peak at 210 nm and

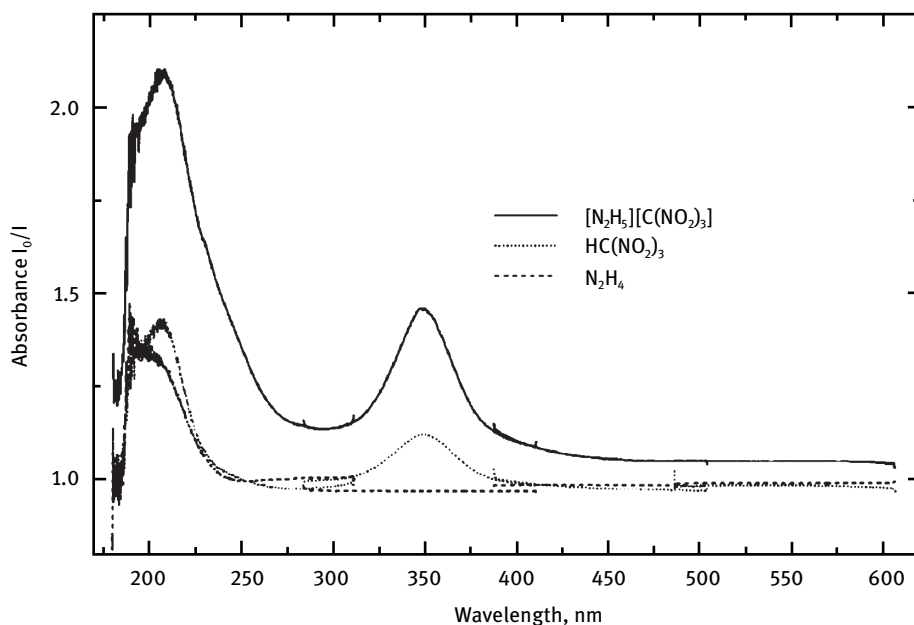


Figure 20: Ultraviolet-visible absorption spectra for hydrazine (bottom), nitroform (middle) and HNF (top) dissolved in water. (Reproduced from [250]; with permission granted by Dr. Jeroen Louwers, 27 May 2020)

nitroform by itself has absorption peaks in that area, it appears that the peaks of HNF are a composite (additive behavior) of its two parent molecules.

The relative peak heights ($\lambda_{\max}$ 210 nm vs 352 nm) of a UV spectrum shown by Dendage, Asthana, and Singh [251] were very similar, whereas the 352-nm peak in Figure 20 above is much smaller. Other sources [252] report a $\lambda_{\max}$ at 348 nm and $\epsilon = 1.5 \times 10^{-4} \text{ L mol}^{-1} \text{ cm}^{-1}$.

The absorption peak at 350 nm can be used for the quantitative determination of HNF in aqueous solutions [253]. The concentration of HNF correlates very well with its optical density at 350 nm within the range 0–8 mg/L with a linear correlation coefficient of 0.9999. This method has the advantages of speed, accuracy, and less expensive equipment, and can be used in the process of synthesis, production, and purification of HNF for quality control and certification.

3.2.5.2 Infrared Absorption Spectra of HNF

The mid-IR spectrum of HNF is shown in Figure 21. Given the structural complexity of solid HNF, the splitting of group vibrational modes was to be expected. The breadth and complexity of the N–H stretching modes results from extensive hydrogen bonding, which causes coupling and Fermi resonances. When solid HNF is squeezed be-

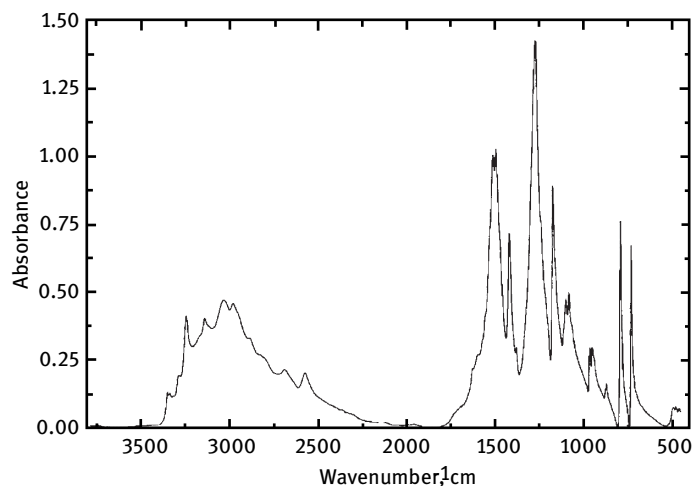


Figure 21: Infrared spectrum of dry, solid hydrazinium nitroformate. (Reproduced from [250]; with permission granted by Dr. Jeroen Louwers, 27 May 2020.)

tween two NaCl plates and heated to the temperature of incipient decomposition, all IR bands were observed to decrease at the same rate. According to the IR spectrum, the only solid product is NH_4NO_3 . There was no evidence for the formation of ammonium nitroformate (ANF) during the rapid thermolysis of HNF.

The best resolution IR spectra of HNF with wave numbers entered at the main peaks were reported by Loebbecke, Schuppler, and Schweikert [254] (Figure 22).

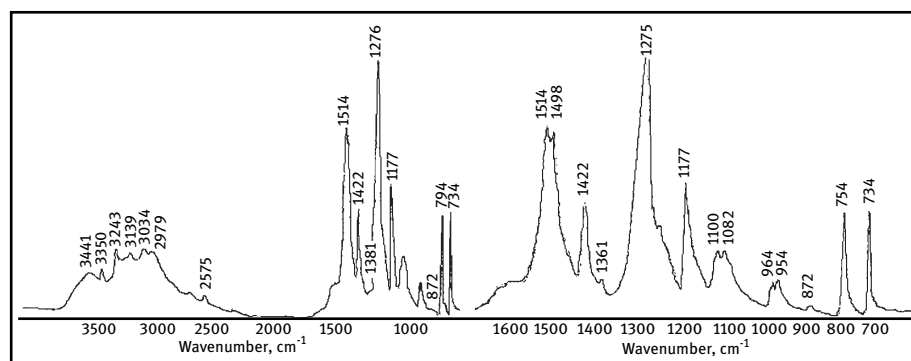


Figure 22: Infrared spectrum of dry, solid hydrazinium nitroformate. (Reproduced and modified from [254].)

The IR spectra of HNF in a KBr matrix pellet have the following absorption bands (with bond assignments and intensities) [255]:

N—H stretch :	3244 cm ⁻¹ (m),
NH ₃ ⁺ deformation :	1615 cm ⁻¹ (w),
NO ₂ asymmetrical stretch :	1512 cm ⁻¹ (s),
NH ₃ ⁺ bend :	1420 cm ⁻¹ (m),
NO ₂ symmetrical stretch :	1271 cm ⁻¹ (s),
NH ₃ ⁺ wagging :	1180 cm ⁻¹ (s),
N—C —N asymmetrical stretch :	1100 cm ⁻¹ (m),
NO ₂ bend :	790 cm ⁻¹ (s),
N—N stretch :	971 cm ⁻¹ (m).

The Dragomir thesis ([256], page 52ff.) contains several IR spectra of the surfaces of burnt and unburnt HNF and a comparison with the spectra obtained by other investigators. A very coarse IR spectrum of HNF was given in Dendage et al. [251], but it is not very useful. The Williams thesis [257] contains an IR spectrum very similar to the one shown in Figure 21.

3.2.5.3 Raman Spectra of HNF

Because HNF rapidly deteriorates under intense white light within the visible range, the Raman spectrum of HNF crystals held in an NMR tube was excited with an IR laser at 1.06 μm (Figure 23).

The band assignments of IR and Raman bands are tabulated in Table 28.

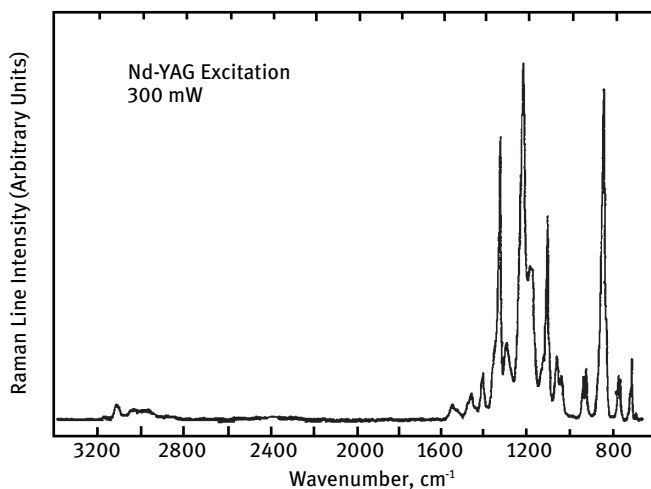


Figure 23: Raman spectrum of dry, solid hydrazinium nitroformate. (Reproduced and modified from [257]; with permission granted by Dr. Graylon K. Williams 22-Mar-2021.)

Table 28: Infrared and Raman band assignments of solid hydrazinium nitroformate.

Infrared	Raman	Assignment
2578–3350 m ^{a, b}	2950–3350 w ^c	N–H stretch
1615 w, sh	1618 w	–NH ₃ ⁺ deformation
1595 w	1595 w	–NH ₃ ⁺ deformation
1512 s		–NO ₂ asymmetrical stretch
1496 s	1522 w	–NO ₂ asymmetrical stretch
1474 m, sh	1463 m	–NO ₂ asymmetrical stretch
1421 m		–NH ₃ ⁺ bending
1396 w	1385 s	–NH ₃ ⁺ bending
1380 w	1345 m	–NH ₃ ⁺ bending
1271 s	1276 s	–NO ₂ symmetrical stretch and –NH ₂ rocking
1241 m	1237 s	–NO ₂ symmetrical stretch and –NH ₂ rocking
1177 s	1166 w, sh	–NH ₃ ⁺ wagging
1153 w, sh	1151 s	–NH ₃ ⁺ wagging
1098 m	1099 m	N–C–N asymmetrical stretching
1084 m, sh	1075 m	N–C–N asymmetrical stretching
1069 m	1075 m	N–C–N asymmetrical stretching
971 m	968 m	N–N stretching
955 m	954 m	N–N stretching
879 w		C–NO ₂ in-phase stretching
872 w	879 s	C–NO ₂ in-phase stretching
794 s	793 m	–NO ₂ bending
788 w, sh	785 m	–NO ₂ bending
734 s	731 m	–NO ₂ bending

^aIntensity: s = strong, m = medium, w = weak, sh = shoulder

^bA broad envelope containing 13 resolvable absorbances

^cA broad envelope containing 6 resolvable bands

Data source: [257]

3.2.6 Magnetic Properties of Hydrazinium(1+) Nitroformate

The ¹H NMR spectra (300 MHz, DMSO-d₆ calibrated) of HNF showed a chemical shift of: $\delta = 7.028$ (s, 5H), and the ¹³C NMR spectra (300 MHz, DMSO-d₆) showed a chemical shift of $\delta = 150.759$ (w, 1C) [255]. In ¹H NMR spectra the expected multiplets were not observed because of peak broadening due to intermolecular exchange of hydrogen on nitrogen atoms. The intensity of the ¹³C peak was very weak, though the spectra was recorded for a large number of pulses (2500) with long intervals (1.0 ms). This may be due to the presence of a quaternary carbon atom in the compound.

3.2.7 Thermal Conductivity of Hydrazinium(1+) Nitroformate

The heat capacity, thermal conductivity, and thermal diffusivity of a range of other oxidizers, binders, and rocket propellants was determined and compared with data in the literature [258]. These measurements are difficult because the porosity of

pressed pellets may vary. The thermal diffusivity α of HNF at room temperature is $2.1 \times 10^{-3} \text{ cm}^2/\text{s}$ to $2.2 \times 10^{-3} \text{ cm}^2/\text{s}$ or $1.88 \times 10^{-3} \text{ cm}^2/\text{s}$ at 273 K (0°C). The thermal diffusivity α of HNF can be calculated from the equation

$$\alpha = 1.62 \times 10^{-3} + 1.2 \times 10^{-6} t$$

where α is the thermal diffusivity in cm^2/s and t is the temperature in °C. For comparison, the thermal conductivity λ of HNF measured with the same apparatus at room temperature is $0.686 \times 10^{-3} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ }^\circ\text{C}^{-1}$. The thermal conductivity λ of HNF as a function of temperature can be calculated from the equation

$$\lambda = 2.50 \times 10^{-3} + 6.8 \times 10^{-6} t$$

where λ is the thermal conductivity in $\text{W cm}^{-1} \text{ }^\circ\text{C}^{-1}$ and t is the temperature in °C.

3.2.8 Molecular Structure of Hydrazinium Nitroformate

The molecular structure of HNF, two ions in suspension (not a crystal lattice) is illustrated in Figure 24.

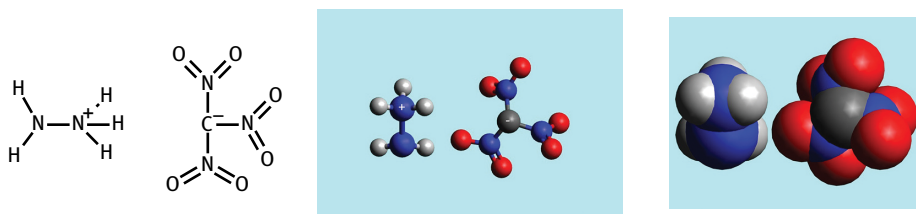


Figure 24: Molecular structure of hydrazinium nitroformate

3.2.8.1 Experimental Study of the Crystal Structure of Hydrazinium Nitroformate

Hydrazinium nitroformate crystallizes in monoclinic crystals that belong into space group $P2_1/n$. The crystal structure of HNF at 113 K (−160 °C) revealed that N_2H_5^+ ions are hydrogen-bonded to neighboring $[\text{C}(\text{NO}_2)_3]^-$ ions [248, 255, 259]. Two crystallographically independent and structurally different formula units are contained in the unit cell. One of the N_2H_5^+ ions is staggered, whereas the other is eclipsed. The $\text{N}-\text{C}-\text{N}$ framework of both $[\text{C}(\text{NO}_2)_3]^-$ ions is planar, but these propeller-shaped ions include dihedral angles between 4 and 74°. The crystal structure parameters are $a = 7.91 \pm 0.02 \text{ \AA}$, $b = 11.77 \pm 0.02 \text{ \AA}$, $c = 13.98 \pm 0.02 \text{ \AA}$, $Z = 8$, $\beta = 104.9^\circ$. The calculated density was 1.93 g/cm^3 . It was concluded that there was extensive hydrogen bonding present within the HNF crystal lattice with 8 units in the unit cell. It was also concluded that the nitroformate anion is non-planar within the HNF crystal and that the precise (crystal) geometry is dependent on the environment. The CN_3 framework of the nitroformate ion may be planar, but the $\text{N}_2\text{C}-\text{NO}$ dihedral angles are between 4 and 74°. This wide

dihedral angle is attributable to the low energy barrier to $-\text{NO}_2$ rotation (typically in the range of 0.3–0.8 kJ/mol). One of the nitro groups is significantly twisted out of the plane of the CN_3 structure. This may allow some degree of freedom of position of the oxygens of the NO_2 group relative to the CN_3 framework, possibly helping to explain the improved stability of the nitroformate structure. The hydrazinium ions present within the cell are hydrogen bonded to neighboring nitroformate ions with two main hydrazinium orientations being suggested. One form has the hydrogen atoms of the N_2H_5^+ ion staggered and the other has the hydrogen atoms of the ion eclipsed.

In addition to XRD, the crystallographic nature and surface chemistry of HNF crystals were examined by SEM, transmission electron microscopy, and X-ray photoelectron spectroscopy (XPS). SEM images showed layered needle-shaped crystals of HNF. The XPS study offered additional information regarding the surface chemistry of HNF and the state of bonding of its C, N, and O atoms. There is evidence of intermolecular hydrogen bonding.

A new (second) HNF modification with a calculated density of 1.938 g/cm^3 was obtained by recrystallizing HNF from ethyl acetate at room temperature [260]. HNF crystallizes in the space group $P2_1/n$ (no. 14) with four formula units per unit cell. The structure reported by Dickens [259] showed two crystallographically independent nitroformate anions with dihedral angles for the nitro groups of 41° , 7° , and 8° for the first anion, and of 74° , 4° , and 5° for the second anion. The two corresponding hydrazinium cations are different and showed staggered as well as eclipsed symmetry of the hydrogen atoms. The newly discovered second modification, however, consists of only one ion pair whereby the nitro groups of the anion have dihedral angles relative to the central C–N3 moiety of 10° , 8° , and 77° , and the hydrogen atoms of the hydrazinium counteranion show a staggered arrangement. The N–N distance in the hydrazinium ion is $1.446(3)\text{ \AA}$, which is in good agreement with the values of the N–N distances of hydrazine cations in the previously described polymorph ($1.44 \pm 0.02\text{ \AA}$ and $1.42 \pm 0.02\text{ \AA}$).

3.2.8.2 Computational Theoretical Studies of the Molecular Structure of Hydrazinium Nitroformate

A variety of computational chemistry methods have been used to predict bond strengths, ion pairing, and dissociation energies of HNF. These methods can also predict reaction paths and eventually ultimate decomposition products.

Discrete Fourier transform methods were used to study the intermolecular interaction of HNF ion pairs [261]. Two fully optimized geometries of HNF ion pairs were examined at the B3LYP/6-31+G** level. The binding energies of ion pairs were corrected for basis set superposition errors and for zero-point energies. The corrected binding energy of the most stable ion pair was predicted to be of the order of -420 kJ/mol . The intermolecular bonds between ion pairs are primarily due to Coulomb interaction but, judged by the electron densities at the bond critical points, covalent interactions also make a remarkable contribution to the bonding. The thermodynamic properties

were calculated based on statistical thermodynamics. The changes of the enthalpy and Gibbs free energy when going from the ions to the most stable ion pair were predicted to be -419.7 and -376.6 kJ/mol at 298 K respectively.

Ammonium nitroformate, ANF, CAS RN [17181-40-7], is an intermediate product of HNF decomposition and may accumulate on the surface of burning HNF pellets. The primary reactions of the thermal decomposition of HNF as well as ANF were investigated theoretically using the G3 multi-level procedure [262]. Calculations were done for the reactions in the gas phase and in the melt and showed that the influence of the melt on the reaction barriers involves the solvation free energies. The most energetically favorable structures of HNF and ANF free molecules in the gas phase are H-bonded complexes. In the melt, the ionic structure is lowest in free energy because of solvation effects. In both the gas phase and the melt, the HNF decomposes preferably to nitroform and free hydrazine. There is no undissociated HNF among the gas-phase decomposition products. Thermolysis of HNF occurs mainly through the intermediacy of nitroform. Contrary to other publications, these computations did not support the suggestion that the *aci*-nitroform is an important intermediate of HNF thermolysis. The primary dissociation reactions of ANF resemble those of HNF. Kiselev and Gritsan is a very good survey article with 77 quite relevant literature references.

Computations of the geometric configuration, weak interaction, and energy characteristics of HNF, ANF, aminotriazolium nitroformate, guanidinium nitroformate (GNF), and aminotetrazolium nitroformate showed that there exist hydrogen bonds in all salts except GNF [263]. The binding energies of the salts were between 390 and 430 kJ/mol and correlated with the densities and thermodynamic stabilities of these compounds, but showed a reverse trend on impact sensitivities. Binding energy calculations indicated that the main interaction between anions and cations is electrostatic interaction. The detonation velocity and specific impulse of five nitroformate salts were predicted to be in the range 8.6–9.1 km/s and 2200–2600 Ns/kg respectively.

3.2.9 Thermodynamic Properties of Hydrazinium Nitroformate

3.2.9.1 Heat Capacity of Hydrazinium Nitroformate

The heat capacity of solid HNF is $0.97 \text{ J g}^{-1} \text{ K}^{-1}$. The heat capacity as a function of temperature in the range 293–383 K (20–110 °C) can be expressed by [258]

$$c_p = 0.198 + 3.41 \times 10^{-4} t$$

where c_p is the heat capacity in $\text{cal g}^{-1} \text{ °C}^{-1}$ and t is the temperature in °C. Heat capacity measurements of HNF pellets by DSC gave the heat capacity curve shown in Figure 25, which can be approximated by a straight line [250]. The specific heat capacity and thermal conductivity were found to have a slight temperature dependence. However, thermal conductivity was found to decrease near the burning surface, owing to cracks during combustion.

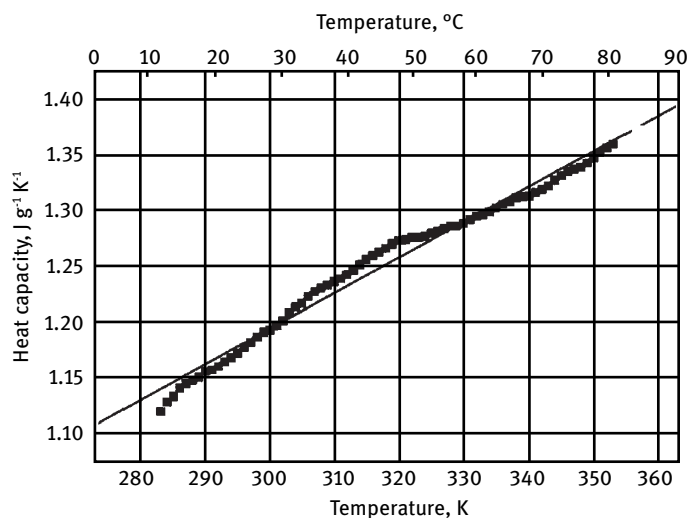


Figure 25: Heat capacity of hydrazinium nitroformate. (Reproduced and modified from [250]; with permission granted by Dr. Jeroen Louwers, 27 May 2020.)

3.2.9.2 Heat of Fusion of Hydrazinium Nitroformate

The heat of fusion of HNF at 397 K (124 °C) was estimated to be 29.5 kJ/mol. The entropy of fusion was estimated to be 74.3 J K⁻¹ mol⁻¹ [264].

3.2.9.3 Heat of Sublimation of Hydrazinium Nitroformate

The only reported value for the enthalpy of sublimation of HNF was measured in the temperature interval 307.5–340.8 K (34.4–67.7 °C) and found to be 193.7 kJ/mol (46.3 kcal/mol) [265].

The enthalpy of sublimation may be identical to the enthalpy of dissociation of solid HNF into its gaseous ions, as suggested by the fact that this value is in good agreement with the enthalpy of HNF dissociation ΔH_{diss} (196.19 kJ/mol = 46.89 kcal/mol) calculated from enthalpies of formation of the solid salt (–76.86 kJ/mol = –18.37 kcal/mol from Konkova and Matyushin [266]), gaseous hydrazine (95.19 kJ/mol = 22.75 kcal/mol), and trinitromethane vapor (24.27 kJ/mol = 5.8 kcal/mol). The value for trinitromethane vapor can be taken from Matyushin et al. [267].

The enthalpy of evaporation of liquid HNF (184.9 kJ/mol = 44.2 kcal/mol) can be calculated as the enthalpy of sublimation minus the enthalpy of melting (with an estimated value of 11.3 kJ/mol = 2.7 kcal/mol).

Experimental data of the sublimation temperature, if plotted in the coordinates of log pressure vs reciprocal absolute temperature, yield another value for the enthalpy of dissociation $\Delta H_{\text{diss}} = 155.2$ kJ/mol (37.1 kcal/mol). The sublimation temperature is of-

ten observed on the surface of burning HNF pellets [268]. This value is less than the one calculated. The enthalpy of sublimation of HNF is 156 kJ/mol = 37.4 kcal/mol [269].

3.2.9.4 Heat of Solution of Hydrazinium Nitroformate

The enthalpy of formation of solid salts can be determined more accurately by measuring the heat of solution than the heat of combustion, but only if the enthalpies of formation of the ions forming in aqueous solution are known. This method was used to determine the enthalpies of formation of the potassium, ammonium, hydrazinium, and guanidinium salts of nitroform [266]. The heats of solution of these salts are tabulated in Table 30 along with their enthalpies of formation of the dry salts.

3.2.9.5 Heat of Combustion of Hydrazinium Nitroformate

The heat of combustion of HNF is 5824 kJ/kg = 1392 kcal/kg.

3.2.9.6 Enthalpy of Formation of Hydrazinium Nitroformate

Up until 1998, data reported in the literature for the enthalpy of formation of HNF were quite contradictory. Some of this uncertainty was a fallout of the inaccurate data provided up to that time for nitroform (trinitromethane) [270, 271]. Table 29 gives a summary of values for the enthalpy of formation of HNF obtained from different sources.

The enthalpy of formation of trinitromethyl anion in infinitely diluted aqueous solutions is -24.94 ± 0.79 kJ/mol. It was calculated on the basis of the data obtained for enthalpies of formation and dissolution of the ammonium and hydrazinium salts of nitroform. These data can in turn be used to calculate the enthalpies of formation of the solid salts (Table 30).

Table 29: Enthalpy of formation of hydrazinium nitroformate.

Upper heat of combustion		Enthalpy of formation				Source	References
kJ/mol	kcal/mol	kJ/mol	kJ/kg	kcal/mol	cal/g		
-1031.23 ± 1.13^a	-246.4	-71.96	-393	-17.2 ± 1.4	-93.9	Anonymous	[272]
		-76.86 ± 1.13	-420	-18.37	-100	Konkova and Matyushin	[266]
		-71	-388	-16.97	-92.7	Dendage, Asthana, and Singh	[251]
		-72.8	-397	-17.39	-95	Cruise	[59]

Molecular mass: 183.081 g/mol; 5.462 mol/kg

^aAverage of five determinations

Table 30: Thermochemical properties of trinitromethane and its salts.

Compound	Enthalpy of solution, kJ/mol	Enthalpy of formation, kJ/mol
$\text{HC}(\text{NO}_2)_3$	19.71 ± 0.08	-44.65 ± 1.13
$\text{NH}_4\text{C}(\text{NO}_2)_3$	39.87 ± 0.08	-197.90 ± 0.88
$\text{N}_2\text{H}_5\text{C}(\text{NO}_2)_3$	50.04 ± 0.08	-76.86 ± 1.13
$\text{CN}_3\text{H}_6\text{C}(\text{NO}_2)_3$	49.12 ± 0.04	-213.14 ± 1.18
$\text{KC}(\text{NO}_2)_3$	64.10 ± 0.08	-341.18 ± 0.80

Data source: [266]

A renewed determination of the heat of combustion of HNF gave -1031.23 ± 1.13 kJ/mol and the enthalpy of formation of solid HNF derived therefrom is now -76.86 ± 1.13 kJ/mol, which seems to be a reliable value. One of the intermediates in the decomposition of HNF is the ammonium salt of nitroform (ANF). Its enthalpy of formation is -197.90 ± 0.88 kJ/mol [266].

A calculated enthalpy of formation had been reported for a compound that was said to have the formula $[\text{N}_2\text{H}_6][\text{C}(\text{NO}_2)_3]_2$, but it is not known if this salt is stable. Nitroform is a weak acid and may not be able to form doubly ionized hydrazinium(2+) salts.

3.3 Chemical Properties of Hydrazinium Nitroformate

Most organic acids have carboxyl groups. Trinitromethane is a different type of organic acid, without a carboxyl group, but nevertheless an acid because the electron pull of the three nitro groups has weakened the C—H bond. Its hydrazine salt is an oxidizer and is undergoing evaluation as a potential rocket propellant ingredient. It decomposes at its melting point (396 K) and autoignites at 673 K.

Replacing hydrogen in methane or other alkanes with electron-absorbing groups ($-\text{NO}_2$, $-\text{NO}$, $-\text{CN}$) draws electrons away from the remaining C—H bonds and makes them easier to split and more acidic. This progression can be seen when comparing the pK of nitromethane, dinitromethane, and trinitromethane. Among the three, trinitromethane (“nitroform”) is the most acidic and forms salts with a wide range of metals and bases.

3.3.1 Reactions of Hydrazinium Nitroformate

One of the reasons why it was so difficult to find a suitable polymeric binder for HNF-based solid propellants is that HNF readily reacts with isocyanates (hexamethylene isocyanate or *p*-toluene isocyanate) used as curing agents for HTPB. It may also react with residual $>\text{C}=\text{C}<$ double bonds in the skeleton of the binder.

The thermally unstable hydrazinium dinitromethanide was synthesized by denitration of HNF with hydrazine hydrate and fully characterized using IR, Raman, and multi-nuclear (^1H , ^{13}C , ^{15}N) MR spectroscopy, and single crystal XRD as well as thermal, impact, and friction stability measurements [273]. It is not suitable as a propellant ingredient, but may be a contaminant in HNF.

In comparison, other dinitromethanide salts, such as guanidinium, triazolium, and tetrazolium dinitromethanide salts are thermally stable and can be relatively insensitive to impact [274].

3.3.2 Analysis of Hydrazinium Nitroformate

Various analytical methods have been investigated that might be used for HNF quality control during the production process. Acidimetric titration does not give an accurate assay of HNF content. Impurities due to processing liquids, for example, MeOH, dichloroethane, and IPA present in HNF, can easily be detected with NMR or GC-MS.

Impurities that are similar to hydrazine, for example, $\text{N}_2\text{H}_6^{2+}$, or similar to nitroform, for example, dinitromethane, cannot be detected by these techniques.

Other techniques such as high-performance liquid chromatography, FTIR, solid-state NMR, XRD, and capillary electrophoresis are even more limited in their possibilities. A simple technique may be available through UV-visible spectroscopy (see Section 3.3.2.1).

3.3.2.1 Spectrophotometric Analysis of HNF

Hydrazinium nitroformate has two absorption peaks in UV: one around 210 nm and another one at 350 nm (Figure 26). The peak height at 210 nm is roughly the sum of the

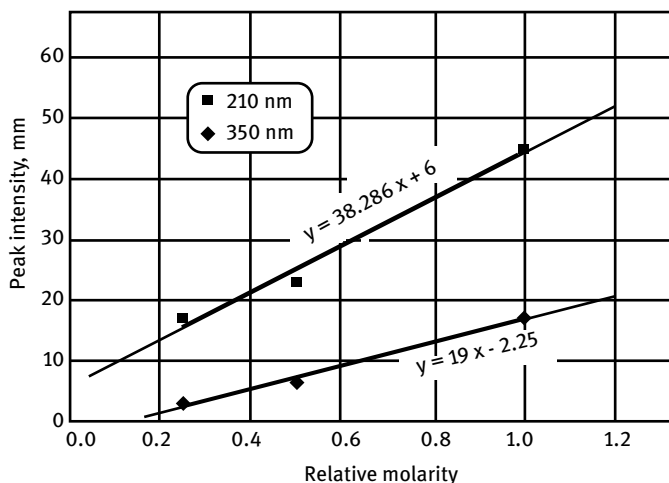


Figure 26: Slope of the intensity of hydrazinium nitroformate peaks in ultraviolet. (Reproduced and modified from [210])

hydrazine peak height and nitroform peak height. For three different concentrations of HNF in water, the heights of the 210- and 350-nm peaks may be compared, and when plotting the absorbance versus molarity, the slope of the 210-nm peak height curve is twice the slope of the 350-nm peak height curve (Figure 26). In this way, it may become possible to determine the hydrazine/nitroform ratio in HNF directly, and the measurement is not affected by the presence of other acidic materials as would be the case in acidimetric titrations.

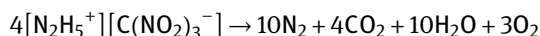
3.3.2.2 Mass-Spectrometric Analysis of HNF

In HNF mass spectra the parent $\text{N}_2\text{H}_5\text{C}(\text{NO}_2)_3$ molecule (mass-to-charge ratio $m/e = 168$) does not appear because of its decomposition prior to vaporization [275]. Fragments were observed in the mass spectrometer at the following m/e values for $\text{NH}_4\text{C}(\text{NO}_2)_3$: 168 (30%); $\text{C}(\text{NO}_2)_3$: 149 (100%); $\text{NH}_4\text{C}(\text{NO}_2)_2$: 122 (18.6%); $\text{HC}(\text{NO}_2)_2$: 105 (16.5%); $\text{NH}_4\text{NO}_3 \cdot \text{H}_2\text{O}$: 97 (9.5%); NH_4NO_3 : 81 (11.4%).

3.3.3 Thermal Stability of Hydrazinium Nitroformate

The thermal stability of HNF is very dependent on the purity of the sample. Excess hydrazine can drastically reduce the stability of HNF.

The decomposition of HNF leads to nitrogen, carbon dioxide, water and oxygen.



HNF is thus an oxidizer because it has extra oxygen beyond that which is required to burn all hydrogen and carbon in the molecule. The decomposition reaction is exothermic, such that HNF solutions could be used as monopropellants if sufficient oxidizer could be dissolved in water.

One of the earliest publications on the thermal decomposition of HNF is the Koroban paper [275]. They studied HNF decomposition under isothermal conditions within the temperature interval from 333 to 373 K (70–100 °C), i.e., below the melting point ($E_a = 169.6 \text{ kJ/mol}$ or 40.5 kcal/mol and $A = 10^{17.6} \text{ s}^{-1}$ for the initial decomposition; $E_a = 144.8 \text{ kJ/mol}$ or 34.6 kcal/mol , $A = 10^{16.1} \text{ s}^{-1}$ for autocatalysis during the end). The activation energy for the overall thermal decomposition of HNF was estimated to be 180 kJ/mol (43 kcal/mol). The reaction products consisted of N_2 , N_2O , CO_2 , and H_2O , and the decomposition is accelerated by autocatalysis. A mechanism was proposed that involved two parallel processes: **(1)** cleavage of $\text{C}(\text{NO}_2)_3^-$ to $[\text{C}(\text{NO}_2)_2]^-$ and NO_2 , followed by reaction of N_2H_5^+ with the two products, and **(2)** interaction of HNF with N_2H_4 . The enthalpy of dissociation of HNF to N_2H_4 and $\text{CH}(\text{NO}_2)_3$ was 171 kJ/mol (41 kcal/mol), very similar to the activation energy for the decomposition.

A study of HNF decomposition under non-isothermal, “combustion-like” conditions in the range from 403 to 673 K (130–400 °C) gave an activation energy of $E_a = 104.6 \text{ kJ/mol} = 25 \text{ kcal/mol}$ and a frequency factor of $A = 10^{11.03} \text{ s}^{-1}$ [276].

In TGA, the first-stage decomposition (temperature range: 378–415 K [105–142 °C]) showed 72.5% weight loss, whereas in the second stage of decomposition (temperature range: 415–483 K [142–210 °C]) the weight loss was 24.5%. FTIR analysis of the off-gassing during thermal decomposition indicated the formation of some cyanamide-like species.

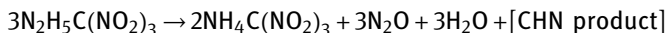
Hydrazinium nitroformate decomposition was examined between 403 and 673 K (130 and 400 °C) by T-jump/FTIR spectroscopy, which included melt/foam decomposition and self-ignition regimes [257]. Reaction regimes included evaporation, conversion to $\text{NH}_4\text{C}(\text{NO}_2)_3$ and progressive decomposition to CO_2 , CO, N_2O , NO, and H_2O . Induction-time decomposition kinetics gave an activation energy of $E_a = 104.6 \text{ kJ/mol}$ (25 kcal/mol) and a natural logarithm of the frequency factor of $\ln(B, \text{s}^{-1}) = 25.3$ of the melt/foam layer. These values agreed reasonably well with previously reported temperature-profile data. HNF samples on a platinum ribbon were heated rapidly (600 °C/s) to a pre-selected temperature (413–673 K = 140–400 °C) and flash-pyrolyzed and the evolution of gaseous decomposition products was measured by shining an IR beam through the cloud of products and recording the absorption with an FTIR instrument. The composition of products changes quickly with time and pre-set target temperature and allows some conclusions about the decomposition mechanism and intermediate products of combustion. Because the platinum ribbon voltage fluctuates while an endo- or exotherm is in progress, the onset temperature of an endo-/exotherm can be measured, but the quantity of heat released is more difficult to estimate (this is not DSC because the sample holder is wide open). No flame is created in this experiment because it is the objective to study the decomposition at the preset target temperature of the heating filament. Free trinitromethane and hydrazine vapors were identified in the vapor space above decomposing HNF. No $\text{NH}_3(\text{G})$ was detected.

Samples of ANF were subjected to the same conditions to see if they could survive (they did not). In a separate TGA experiment, ANF decomposed in a two-step process, where the first step at 385 K (112 °C) corresponded to the decomposition/sublimation of ANF and the second (centered at 443 K = 170 °C) corresponded to the decomposition of NH_4NO_3 .

Several analysis methods were applied to the study of HNF thermal decomposition at 313–353 K (40–80 °C) [277]. These methods included TGA combined with mass spectrometry (TGA-MS), headspace GC-MS, NMR, FTIR, and DSC. Samples were kept under isothermal conditions and the evolution of decomposition products was followed as a function of time.

The decomposition of solid crystalline HNF was investigated by heating small samples (0.5 g) of the material in closed septum-sealed glass vials (10 cm³ capacity) at temperatures between 60 and 80 °C [278]. Gases evolved from the decomposition were captured and analyzed by headspace GC-MS over a range of ageing times at each temperature. Condensed-phase residues were investigated by FTIR spectroscopy and by NMR spectroscopy. Under all conditions, the major gas detected was nitrous oxide

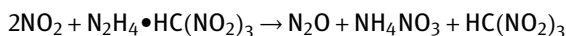
(N₂O). Only in the latter stages of ageing at the higher temperatures could other gases, notably nitrogen and carbon dioxide, be observed. ¹H and ¹⁴N NMR analysis indicated that the hydrazinium ion is lost very rapidly from the HNF at the higher temperatures and that ANF is the principal initial solid product. The formation of ANF was also supported by the observed changes in the 1400- to 1500-cm⁻¹ region of the FTIR spectrum of HNF during ageing. On the basis of these results, an overall decomposition reaction of HNF has been proposed as follows:



See also [279].

Differential scanning calorimetry in open Al crucibles and TGA/DTA of two HNF samples (different grades and batch numbers) showed the onset of melting at 404 K (131 °C) and the onset of exotherm and decomposition at 407–408 K (134–135 °C). The mass loss at the end of complete decomposition was 97.4 to 98.3% [207, 245].

A thermoanalytical study of HNF to determine the exotherm(s) of HNF decomposition and the time-resolved detection of thermal decomposition products by IR spectroscopy evolved gas analysis (IR-EGA) revealed the formation of a product with an IR spectrum not much different than the spectrum of HNF [254]. This product was identified as ANF, because the characteristic IR functionality of ammonium ion NH₄⁺ was found as a sharp peak centered at 3237 cm⁻¹. The presence of ANF has also been confirmed by the disappearance of N–N stretch absorption around 950 cm⁻¹ of the hydrazinium group, thus explaining its transformation to an ammonium. Besides ANF, small amounts of CO₂ and N₂O as well as ammonia and nitroform have been detected as decomposition products of HNF. At temperatures above 493 K (220 °C), only CO₂ and N₂O and some traces of water were detected as the final IR-active decomposition products. The absence of NO₂ formation during the entire decomposition process should be noted and this contradicts observations by others. The absence of NO₂ could be explained by its instant reaction with HNF:



Based on TGA measurements, the decomposition of HNF at high heating rates is a two-step process (Figure 27). This figure shows the mass loss and the rate of mass loss at a heating rate of 10 K/min.

The effect of different heating rates on the onset of exotherm and the shape of the thermograms of HNF decomposition in a DSC is shown in Figure 28. The onset of exotherm was 391 K (118 °C) at 0.5 K/min., 395 K (122 °C) at 1 K/min., and 398 K (125 °C) at 2 K/min.

The thermal stability of HNF was measured by DSC with a heating rate of 5 °C/min in closed vessels that could withstand a pressure of about 80 bars [280, 281]. Two grades of HNF were tested: an S and an E type, referring to their production techniques (solvent/non-solvent and evaporative crystallization respectively). By applying different heating rates, an analysis of the decomposition kinetics could be performed to give

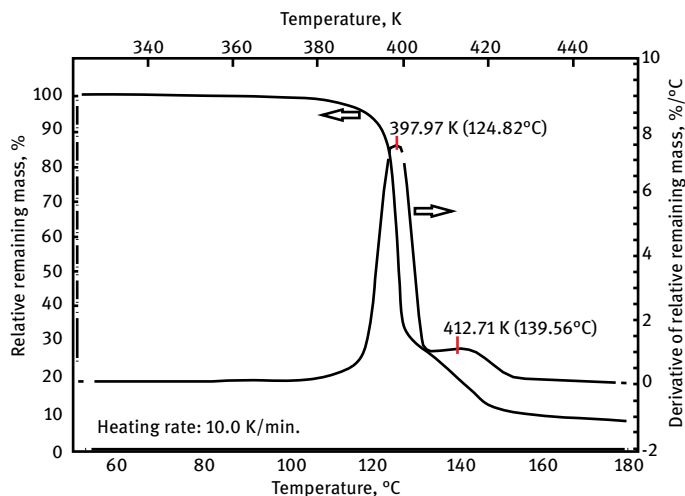


Figure 27: Thermogravimetric analysis of hydrazinium nitroformate decomposition; mass loss (solid line) and mass loss rate (dashed line). (Reproduced and modified from [254].)

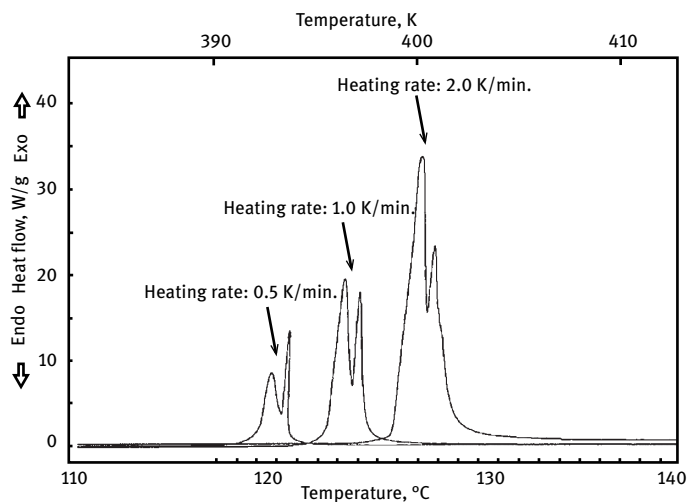


Figure 28: Effect of different heating rates on the onset of exotherm and shape of the differential scanning calorimetry thermogram of hydrazinium nitroformate decomposition. (Reproduced and modified from [254].)

additional information on the activation energy of the decomposition process and the predicted shelf-life of the material, when it is stored at above normal temperatures. The DSC showed that immediately after an endothermic effect, a strong exothermic effect occurs, starting at 398.5–399.2 K (125.4–126.1 °C). It was concluded that there is

a single reaction occurring for this decomposition process. The averaged kinetic parameters for the process are:

$$E_a = 226.2 \frac{\text{kJ}}{\text{mol}} \quad A = 5.44 \times 10^{27} \text{ s}^{-1} \quad n = 1$$

In addition to DSC and DTA/TGA, samples of HNF were analyzed in a microcalorimeter for signs of premature decomposition [282].

Hydrazinium nitroformate has a much higher heat of explosion than AP, 5579 J/g compared with 1972 J/g for AP. All advantages together could allow us to make HNF-based propellants with better performance than AP-based propellants. However, a disadvantage is the poor thermal stability of HNF, which is much worse than that of AP. Therefore, an extensive investigation was performed on the thermochemical stability of HNF. Three sample lots of HNF of different purity were investigated at Fraunhofer Institute of Chemical Technology (ICT), and its thermal stability was determined by five methods [283, 284]: **(1)** autoignition temperature with 0.2 g at 5 °C/min heating rate of the Wood's metal bath, **(2)** vacuum stability test, **(3)** mass loss as function of time and temperature, **(4)** heat generation rate as function of time and temperature, and **(5)** adiabatic self-heating rate. All curves from both methods indicated self-accelerating behavior described with autocatalytic reaction kinetic models. The Arrhenius parameters were determined for one production lot from mass loss data and for two other lots from heat generation data. The activation energies for the intrinsic decomposition reaction were 166, 139, and 132 kJ/mol and for the autocatalytic reaction they were 159, 128, and 117 kJ/mol. The frequency factor was $A = 10^{13} \text{ s}^{-1}$. There was a significant difference between the three lots investigated. These data can be used for calculating the lifetime at different storage temperatures.

The thermal decomposition of HNF was analyzed using TGA, TGA-FTIR, DTA, and DSC [285]. The purity of the synthesized HNF was determined by high-performance liquid chromatography, and the synthesis product was further characterized by elemental analysis, UV, IR, ^1H NMR, ^{13}C NMR, and electron impact mass spectroscopy. DTA, TGA, and DSC results indicated a two-stage decomposition of HNF. The DSC thermogram (Figure 29) exhibited two exotherms with a maximum temperature of decomposition (T_{max}) at 409 and 411 K (136 and 138 °C) respectively. Decomposition temperatures of these exotherms were in close agreement with the data reported earlier by Schöyer et al. [247].

The energy of activation for the first and second exotherms for both stages of decomposition obtained from the data generated at different heating rates was 150 kJ/mol, with pre-exponential factors of 1.3×10^{19} and 1.5×10^{19} respectively. This activation energy was close to that reported by Williams and Brill [276]. In TGA the first-stage decomposition (temperature range: 378–415 K [105–142 °C]) showed a weight loss of 72.5%, whereas in the second stage of decomposition (temperature range: 415–483 K = 142–210 °C) the weight loss was 24.5%.

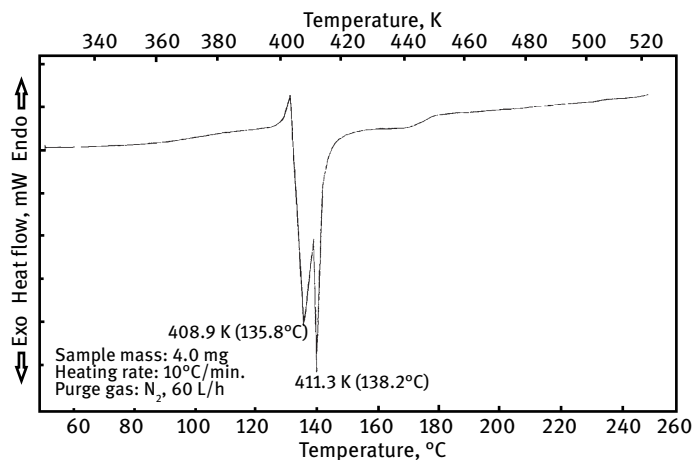


Figure 29: Thermogram of thermal decomposition of hydrazinium nitroformate. (Reprinted and modified from [251] with permission from © 2003 Taylor Francis Ltd., <http://www.tandfonline.com>)

Results of earlier decomposition studies using T-jump/FTIR by Williams and Brill [276] for the fast decomposition of HNF in the range 123–260 °C with identification of the intermediate products agreed with later results by Schöyer et al. [210] for H_2O , CO , NO , and N_2O , and the absence of NO_2 ; but whereas Williams and Brill also detected ANF aerosol, $\text{HC}(\text{NO}_2)_3$, and N_2H_4 , these were not observed by Dendage et al. [251] during the TG-MS measurements at 393 K = 120 °C. On the other hand, Williams and Brill did not report the presence of NH_3 , OH , N_2 , HCHO , O_2 , and CO_2 . In fact, Williams and Brill stated that CO_2 was only detected above 533 K = 260 °C. The differences may be due to different experimental conditions (393 K = 120 °C isothermal vs 396–533 K = 123–260 °C ramp-up, different heating rates, and different analysis techniques), but it may also be that the improvements in the purity of HNF itself affected the products of decomposition. The most likely first step in the decomposition mechanism of HNF is a proton transfer, after which N_2H_4 and HONO are released.

Samples of HNF (~0.5 g) were sealed in air in glass vials and maintained at the appropriate ageing temperature of 333, 343, and 353 K (60, 70, and 80 °C) [286]. After set periods of time the individual vials were removed from ageing and cooled in a refrigerator until completion of the rest of the samples. Analysis of all the vials from a given temperature trial was carried out at the same time after ageing of the whole series was completed. Analysis of the decomposition gases was performed by headspace GC-MS. As is seen from the GC-MS data, nitrous oxide is the main decomposition gaseous product (Figure 30). However, at that time the identity of possible carbon-containing product(s) from HNF decomposition was still unresolved.

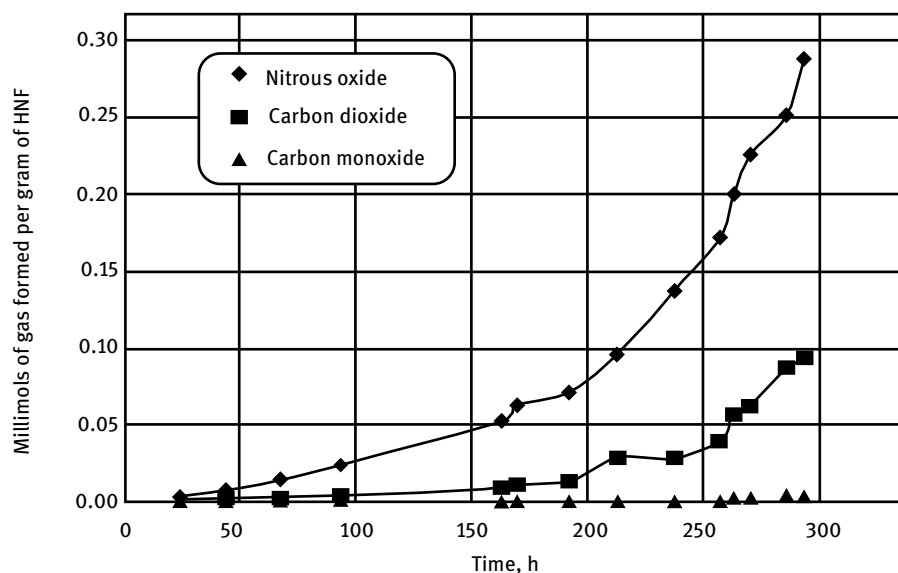


Figure 30: Product gases from hydrazinium nitroformate aged at 343 K (70 °C). (Reprinted and modified from [286], with permission from Dr. Alessandro Ciucci 19 July 2020.)

Single and double (asymmetrical) methyl substitution on hydrazine, using MMH or UDMH instead of hydrazine or hydrazine hydrate for neutralization of trinitromethane, yields the MMH and UDMH salts of trinitromethane, abbreviated as monomethyl hydrazinium nitroformate MMHNF and dimethyl hydrazinium nitroformate (DMHNF), analogs to HNF that are thermally more stable and less impact sensitive than HNF [287]. The new compounds were characterized by elemental analysis, IR, NMR, TGA, and DTA, and their theoretical performance as explosives was calculated. The properties of the three salts are compared in Table 31. The activation

Table 31: Properties of hydrazinium nitroformate (HNF) and its methyl-substituted derivatives.

Properties	HNF	MMHNF	DMHNF
Melting point °C	120–122	128–130	137–140
Activation energy of decomposition (kJ/mol)			
First step	223	245	265
Second step	110	134	149
Impact sensitivity (50%, height, cm)	20	30	35

For comparison:

Sensitivity to impact: RDX 28–30 cm; HMX 23–25 cm; Tetryl 74–78 cm

MMHNF = monomethyl hydrazinium nitroformate, DMHNF = dimethyl hydrazinium nitroformate

Data source: [287]

energies of thermal decomposition increase with increasing methyl substitution, indicating that the methyl-substituted compounds are thermally more stable than HNF.

A study of the degradation of crystalline HNF and HNF/polyNiMMO propellants showed that the contribution of gas/solid autocatalysis in the degradation of the crystalline phase was very low [288]. GC-MS analysis results suggested that the presence (and eventual release) of a solvent impurity, isopropyl alcohol, is a significant contributor to the eventual autocatalytic breakdown of the crystal matrix. It appeared that a significantly different reaction scheme dominates the events at 353 K (80 °C) compared with either 333 or 313 K (60 or 40 °C). Hydrazine scavengers would be expected to improve the thermal stability of HNF.

Three sample lots of HNF provided by Aerospace Propulsion Products BV, The Netherlands, were investigated at ICT in Germany [289]. The thermal stability was determined by autoignition temperature with 0.2-g samples at 5°/min heating rate in a Wood's metal bath, vacuum stability test (VST), heat generation rate as a function of time and temperature, mass loss as a function of time and temperature, and adiabatic self-heating rate. Two lots were characterized by heat generation rate and by mass loss at 333, 338, 343, and 348 K (60, 65, 70, and 75 °C). Samples from another lot were extensively used for mass loss determinations in the temperature range from 323 to 353 K (50 to 80 °C). All samples showed high heat generation rates and self-accelerating autocatalytic decomposition behavior. There was a substantial lot-to-lot variation. The Arrhenius parameters were determined from mass loss data and from heat generation data.

Rate constants of the dominant HNF combustion reaction in the pressure range of 0.04–1 MPa were obtained from the Zeldovich expression, taking the surface temperature as the ANF dissociation temperature [249]. The average specific heat was taken as 1.67 kJ kg⁻¹ K⁻¹ (0.4 cal g⁻¹ °C⁻¹), the thermal diffusivity of the condensed phase as 1.35 × 10⁻⁷ m² s⁻¹, the density of the sample as 1.74 g/cm³, and the heat of melting as 11.3 kJ/mol (2.7 kcal/mol). As illustrated in Figure 31, the results derived from this combustion model for the temperature range 550–675 K,

$$k = 10^{14.43} \cdot \exp(-18400/T), \text{ s}^{-1},$$

marked by gray dot symbols, are in satisfactory agreement with the rate constants of HNF decomposition reported by others.

Data points (solid black dots) obtained from the Sinditskii combustion model fall on the dashed line drawn through data extrapolated to the high-temperature area. Decomposition data obtained by Williams and Brill [276] and de Klerk, van der Heijden, and Veltmans [280] differ considerably from data of other investigators (Wingborg and van Zelst [207], Bohn 2005 [283, 284] and Sinditskii et al. [268] and [269]). This may be due to some methodical mistakes of measurement of the decomposition rate or different quality of the chemicals used.

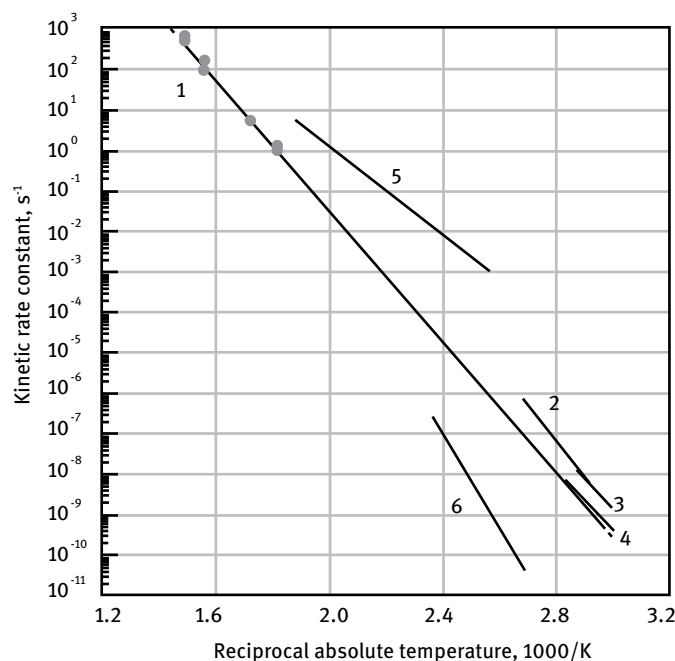


Figure 31: Comparison of rate constants of the leading reaction of hydrazinium nitroformate combustion and rate constants of hydrazinium nitroformate decomposition reported by several authors. (Republished and modified from [249], with permission of © 2009 Elsevier Science Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

Source identification: (1) black dots and dashed line Sinditskii et al. [249], (2) = Koroban et al. [275], (3) = Bohn 2005 [283], (4) = Wingborg and van Zelst [207], (5) = Williams 1995 [276], and (6) = de Klerk, van der Heijden, and Veltmans [280].

The thermal decomposition of HNF was studied by DSC, TGA, and a VST [290]. Based on the peak temperatures of DSC curves and conversion degrees (α) of TGA curves at 5, 10, 15, and 20 °C/min, the apparent activation energy (E_k and E_a) and pre-exponential factor (A_k) for the thermal decomposition reaction of HNF were calculated by two different methods, the Kissinger method and the Ozawa method. Thermodynamic parameters (free energy of activation ΔG , enthalpy of activation ΔH , and entropy of activation ΔS) for thermal decomposition reaction of HNF and thermal safety parameters (critical temperature of runaway thermal explosion T_{bpo} and self-accelerating decomposition temperature T_{SADT} for HNF) were calculated. The volume of gas evolved from HNF decomposition in the VST was 0.41 mL/g, which does not exceed the standard of 2 mL/g, indicating that HNF has good thermal stability. The exothermic decomposition process of HNF after melting can be divided into two stages: $E_k = 257.10$ kJ/mol, $A_k = 1.74 \times 10^{33}$ s⁻¹, $\Delta G = 103.37$ kJ/mol, $\Delta H = 253.82$ kJ/mol, $\Delta S = 380.78$ J · K⁻¹ · mol⁻¹, $T_{bpo} = 400$ K, and $T_{SADT} = 395$ K. The kinetic equation of

exothermic decomposition reaction may be described as follows: for the first stage in the α range of 0.20~0.65:

$$\frac{d\alpha}{dt} = kf(\alpha) = A \exp\left(\frac{E}{RT}\right) f(\alpha) = 5.14 \times 10^{21} \times (1 - \alpha) [-\ln(1 - \alpha)]^{\frac{1}{2}} \exp(-1.81 \times 10^4/T),$$

and for the second stage in the α range of 0.65~0.80:

$$\frac{d\alpha}{dt} = Kf(\alpha) = A \exp\left(\frac{E}{RT}\right) f(\alpha) = 3.30 \times 10^{14} \times (1 - \alpha) [-\ln(1 - \alpha)]^{-1} \exp(-1.33 \times 10^4/T).$$

3.3.3.1 Vacuum Stability of Hydrazinium Nitroformate

For the vacuum stability test, a sealed and evacuated tube containing the sample and connected to a mercury manometer was immersed in a thermostatted bath at 343 K (70 °C) for 48 h [245]. The gas evolution from two different samples differed by more than a factor of 1.6, indicating potential contamination of one of the samples. The more stable sample developed 0.58 mL of gas, whereas the impure sample evolved 0.93 mL of gas. These data indicate that HNF is much less stable than other oxidizers (AP or RDX). Similar vacuum stability tests were also performed on HNF in combination with various solid propellant binders.

3.3.3.2 Kinetics of Hydrazinium Nitroformate Decomposition

Various kinetic paths for the decomposition of HNF have been proposed, based on analysis of intermediate and ultimate products.

Quantum chemical calculations confirmed that the proton transfer has the lowest energy barrier (activation energy 84 kJ/mol) [250]. According to these calculations, this is followed by a reaction between the *aci* nitroform and N_2H_4 .

Koroban et al. [275] and Williams and Brill [276] discovered ANF as a product of HNF decomposition. The enthalpy of ANF dissociation, 164.77 kJ/mol (39.38 kcal/mol), is less than that of HNF and agrees closely with the experimental value. Based on this fact, the surface temperature of burning HNF was proposed to be determined by dissociation of ANF as a product of the condensed-phase reaction [291].

For the mechanism of HNF transformation in the condensed phase it has been suggested that the HNF decomposition process might comprise the nitroform decomposition reaction with high activation energy and concurrent reactions of lower activation energy between radicals formed in nitroform destruction and hydrazine moieties of neighboring HNF molecules. The heat produced by the total reaction was estimated as $Q = 1674$ kJ/kg (400 cal/g). The result of a considerable amount of heat generated in the HNF condensed phase is also attested by the ability of HNF to sustain burning at low pressures in the absence of the gas flame [268, 269].

Reacting species including N_2H_4 , NH_3 , and N_2O were known to be present near the surface of burning HNF since the early investigation of HNF combustion. In addition, planar laser-induced fluorescence from the near surface region of burning HNF pellets

indicated the presence of NO_2 as a reaction intermediate [292]. These four species are formed in the upper (foamy) layer of the solid phase.

3.3.3.3 Thermal Stability of Hydrazinium Nitroformate Mixtures with Other Energetic Materials

In an effort to improve the thermal stability of HNF, it was mixed in a 1:1 mass ratio with HMX, hexanitrohexaazaisowurtzitane (HNIW), triaminotrinitrobenzene (TATB), and tetranitrodibenzo tetraazapentalene (TACOT), all thermally stable high-energy explosives, and the thermal stability of the mixtures was measured by DSC [251]. HNIW and HMX decomposing in the temperature range 523–553 K (250–280 °C) did not influence the decomposition of HNF and *vice versa*. The more stable TATB and TACOT decomposing at 633–683 K (360–410 °C) also did not show any interaction with HNF. The DSC thermograms at 10 °C under GN_2 showed three nicely resolved exotherms, two for HNF in the range 403–423 K (130–150 °C) and one for the other compound well above 523 K (250 °C).

3.3.4 Storage Stability of Hydrazinium Nitroformate

Storage stability of HNF depends, among other factors, on purity and/or contamination. Several analytical methods were used to determine the hydrazine and nitroform content of HNF. Because it was demonstrated that excess hydrazine in HNF strongly affects HNF stability, such analytical methods are important for quality control.

A sample of HNF prepared by Rocketdyne and stored at AFRL at Edwards AFB for more than 20 years under CCl_4 had a melting point of 390–391 K (117–118 °C), close to that of the original material.

Examination of HNF in sealed and unsealed environments indicated that samples in sealed containers degraded at a higher rate than those in open containers. This suggests some degree of autocatalysis in the degradation of the HNF molecule where preliminary degradation species re-attack other HNF molecules within the bulk material. Vacuum thermal stability testing of HNF confirmed this acceleration of degradation rate during storage with the total gas volume measured showing exponential growth during storage. VTS data for HNF gas evolution during ageing generally show an initial rapid evolution of gaseous products followed by a near plateau region. Following this plateau, autocatalysis eventually starts to occur. This profile is more accelerated at increased storage temperature. The first rapid increase is often attributed to solvent or impurity loss. The slow natural decomposition of HNF during storage was demonstrated to be a first-order reaction. The storage stability is measured by VTS tests at 333 K (60 °C) [210]. In most of the VTS tests it was observed that the major gas evolution took place during the first 1.5 h (or less); usually the amount of gas increased by not more than twice the initial gas evolution during the remainder of the 48 h. This is an indication that much of the gas evolution is due to the evaporation of processing and washing liquids that adhere to the surface of the HNF crystals or to adhering free

hydrazine. By the introduction of more washing and drying cycles, the VTS gas evolution decreased dramatically. For example, one wash/drying cycle led to an initial VTS (333 K = 60 °C, 1.5 h) of 0.54 mL/g, which, after 48 h, had increased to 0.94 mL/g; three washing and drying steps improved these values to ~0.18 and 0.36 mL/g respectively.

The time to produce 3 mL of gas per gram of HNF was measured at 333, 353, and 363 K (60, 80, and 90 °C), as well as the point where the reaction started to run away. Two different types of HNF gave the same activation energy (slow decomposition 157 kJ/mol, run-away 147 kJ/mol), confirming that the slow (low-temperature) decomposition of HNF is essentially a first-order reaction. One may use these data to estimate the time to generate 3 mL/g gas during normal storage conditions at room temperature, that is, at 293 K (20 °C). The predicted storage life was 712 to 610 years respectively, for two samples of different pedigree.

3.3.5 Stabilizing Additives for Hydrazinium Nitroformate

Already soon after the discovery of HNF as a propellant ingredient the lack of thermal stability was recognized as a potential problem. It also became apparent that the instability was caused by excess hydrazine. From the large number of publications about possibly suitable stabilizers for HNF, it appears that finding a stabilizer that really works and outlives the patent claims would be a worthwhile effort, but it has been an elusive target for a long time. A drawback of the use of stabilizers in a rocket propellant is that they add inert mass to the fuel and decrease the performance because they do not contribute to the supply of energy.

Numerous publications from the 1960s and 1970s indicate that HNF produced in this way did not exhibit the desired stability. As described in US Pat. No. 3418183 [293], the hydrazine nitroform tends to form bubbles, or, as it is called, the hydrazine nitroform “gasses” during storage. This tendency to “gas” is attributed to the impurities of the hydrazine nitroform produced. As the years progressed, numerous patents followed that suggested various stabilizers. Besides US Pat. 3418183, where anhydrides of dicarboxylic acids (preferably a dodecenyl succinic acid anhydride) were proposed, the proposed stabilizing additives included nitroguanidine [294]. Another patent disclosed the addition of non-volatile aldehyde compounds such as benzaldehyde as hydrazine getters for increasing the stability of hydrazine nitroform [295]. Non-volatile aldehydes would form azines that bind the hydrazine liberated by HNF decomposition in a harmless form. Other patents disclose the stabilization of HNF with oxalates [296], salts of oxalic, phosphoric, or phosphorous acid, or an excess of nitroform [297].

3.3.6 Thermal Decomposition of Hydrazinium Nitroformate Solutions

Solubility of HNF in water is only 50 mass-%. It is unlikely that the catalytic decomposition of HNF solutions by themselves in the absence of fuels will ever find rocket propulsion applications, but it is a very important initial step in the application of HNF-based monopropellants in catalytic reactors, regardless of the type of fuel

present. In addition, the thermal stability of HNF solutions has to be known because concentrated HNF solutions are heated during recrystallization and purification of the material.

The thermal stability of 65/35 HNF/H₂O solutions was investigated and tests showed that boiling started at 373 K (100 °C). At 383 K (110 °C), a pH indicator paper strip turned red, indicating evolution of acidic vapors with a pH around 1–2 owing to decomposition of HNF in hot water [210]. Recrystallization of HNF from water must be done at low temperatures.

Aqueous solutions of 40% HNF were thermally and catalytically decomposed on Pt/SiO₂ catalysts and the results were compared with similar tests performed with 40 and 79 mass-% HAN solutions [298]. The reactions were tracked by TGA and DTA and the reaction products withdrawn from a batch reactor were analyzed by mass spectrometry. In the presence of a catalyst, HAN displayed a single exothermic peak whereas HNF showed two separate exotherms. Figure 32 shows the thermogram of decomposing 40% HNF solutions. The main exotherm starts at about 393 K (120 °C).

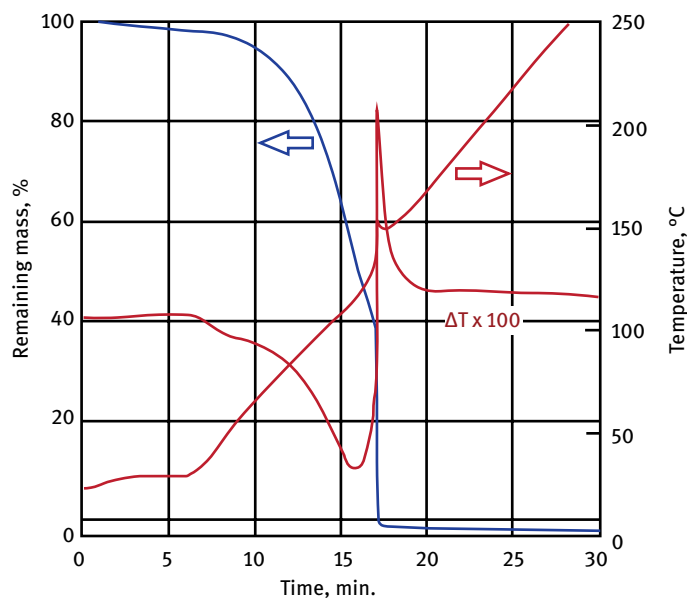


Figure 32: Thermal decomposition of 40 mass-% hydrazinium nitroformate solution. (Reprinted and modified from [298], with permission from Dr. Charles Kappenstein.)

3.3.7 Catalytic Decomposition of Hydrazinium Nitroformate Solutions

The catalytic decomposition of HAN (20, 40, 79 mass-%) and HNF (about 40 mass-%) solutions was compared in a constant volume reactor with differential thermal monitoring [299]. Comparing the reactivity of the two oxidizers with the same catalyst, HNF

solutions gave lower performances than HAN solutions, suggesting that other catalysts need to be invented for this oxidizer.

3.4 Strand Burning of Hydrazinium Nitroformate

The surface temperature of burning HNF is strongly dependent on the pressure at which the combustion takes place. HNF can burn as a compressed pellet or as a melt in a quartz tube at atmospheric pressure. The combustion of HNF is different from the very slow natural decomposition that is a first-order reaction, whereas the combustion reaction is roughly between one and one-half and second order. The strand burning is sometimes called “deflagration.” Neat HNF shows self-sustained combustion at pressures above 0.025 MPa.

The dependence of the burning rate as a function of pressure and temperature is a valuable design parameter, either using HNF by itself or using HNF with a binder. The burning rates of solid propellants formulated with HNF and a binder will be discussed in future volumes.

The combustion products of HNF have a low molecular weight and a high flame temperature because of the low C:H ratio and high enthalpy of formation. HNF has 13% excess oxygen and its combinations with binders as fuels have even higher flame temperatures and better performance as a rocket propellant. It has the advantage over other solid propellant oxidizers that it does not create hydrogen chloride in the exhaust gases, making it environmentally more friendly.

3.4.1 Experimental Determination of Strand Burning Rates of Hydrazinium Nitroformate

One of the first burning rate measurements with pressed pellets of HNF was reported in 1964 [300]. Granular HNF was tamped into glass tubes and the deflagration rates were measured at pressures of 0.02 to 6.88 MPa (3 to 1000 psia). Rates were independent of tube diameter, increased linearly with pressures 138 kPa (20 psia), and were independent of pressure at low pressures. Quenching occurred below critical tube diameters ranging from 0.3 cm at 13.8 kPa (2 psia) to 0.01 cm at 6.88 MPa (1000 psia).

The deflagration of solid HNF has been studied at pressures of 21–6900 kPa (3–1000 psia) and compared with that of AP and HAP [246]. HNF sustains deflagration in a tube down to a pressure of at least 25.2 kPa (0.25 atm) and also exhibits an upper pressure limit at 7.07 MPa (70 atm). No burning rate dependence on tube size was observed as long as the diameter was above the quenching diameter by a factor of at least 1.5. Material compacted to 1.1–1.5 g/cm³ (considerably below crystal density of 1.87 g/cm³) burned at 0.1 cm/s at atmospheric pressure. The pressure exponent is $n = 1.0$ above 202 kPa and less than 1 below 101 kPa.

In a later investigation, the density of pressed HNF pellets used for burning rate studies was 1.740 g/cm^3 . Experimental observation showed that the burning surface temperature was $T_s = 523 \text{ K}$ and the linear burning rate was $r_b = 0.77 \text{ mm/s}$ at 0.1 MPa [301].

There are many experimental methods for studying the burning rate of energetic materials and their response to chamber pressure oscillations. One method uses ultrasound to sense the location of the regressing solid surface [302]. This is similar to an echo sounding for the bottom of the ocean. Another method is to illuminate the burning surface with a laser, steady-state or modulated to see how the burning material responds to the additional non-chemical energy input.

As part of the study of the transient combustion of HNF, laser-assisted regression rates of HNF were determined for a narrow range of chamber pressures from 1 to 6 atm [303]. HNF crystals were pressed into pellets with densities of 1.774 g/cm^3 , which is 94.9% of the theoretical maximum density of 1.87 g/cm^3 . The pellets were burned by themselves (no fuel added) in an IR $10.6\text{-}\mu\text{m}$ CO_2 laser recoil device at pressures from 101 to 606 kPa (1 to 6 atm) and the recoil force was measured with a sensitive load cell. During combustion the laser energy is absorbed in the condensed phase near the burning surface and locally increases the regression rate. The laser-assisted regression rate data allowed further validation of combustion models, in particular, those attempting to explain combustion instabilities. The laser flux was set at two different mean power levels with sinusoidal oscillations of $21 \pm 11.5 \text{ W/cm}^2$ or $52 \pm 5.9 \text{ W/cm}^2$. Oscillations were logarithmically swept over the range from 4 to 80 Hz. Burn rate vs laser flux was measured up to 60 W/cm^2 at 101 to 606 kPa (1 to 6 atm) pressure. The slope of the burn rate vs laser flux was nearly the same at each pressure. Ignition delay times decreased from 760 to 78 ms as the laser flux increased from 21 to 67 W/cm^2 . Ignition times also decreased with increasing pressure. HNF burned nicely with a steep burn rate slope of 0.892 down to 34 kPa (5 psia). The burn rate data fit the equation $r = B \cdot P^n$, where r is the burning rate in cm/s, $B = 0.00666$, n is the pressure exponent = 0.892, and P is the pressure in psia.

Louwers and others have also done steady and transient combustion modeling for HNF burning [304–306]. HNF burned with a high regression rate (40 mm/s at 10 MPa) and a high burn rate exponent. A slope break was observed around 2 MPa . (From $n = 0.95$ to $n = 0.85$). The surface temperature T_s increased with increasing pressure: at 0.1 MPa $T_s = 530 \text{ K}$, and at 1 MPa $T_s = 680 \text{ K}$. Thermocouple measurements showed a bend in the condensed phase temperature profile. This bend was attributed to cracks that form during combustion. At low pressures, a small amount of residue was found after combustion of these samples. However, at 2 MPa the pellets combusted without residue. Samples containing 5% graphite had a constant pressure exponent of $n = 0.81$. At around 10 MPa , the burn rate became equal to that of neat HNF. Also, paraffin-based combinations burned with a low pressure exponent $n = 0.81$ at low pressure. Samples containing 20% aluminum powder had a burn rate at 1 MPa that was about 30% higher than that of neat HNF.

The strand burning rates of HNF were compared with those of ADN, RDX, HMX, CL20, and AP [307]. Cylindrical pellets (6.6 mm in diameter) of HNF were pressed under dry air conditions at 6.21 MPa for 5 min. The density of the resulting pellets was 93–95% of theoretical maximum density. Like ADN, HNF has a low melting point (398 K), restricting the evaluation of burning rate temperature sensitivity over a wider range of temperatures. The ambient temperature burning rates obtained at the Naval Air Warfare Center Weapons Division (NAWCWD) are compared with data from the Atlantic Research Corporation (ARC) in Figure 33.

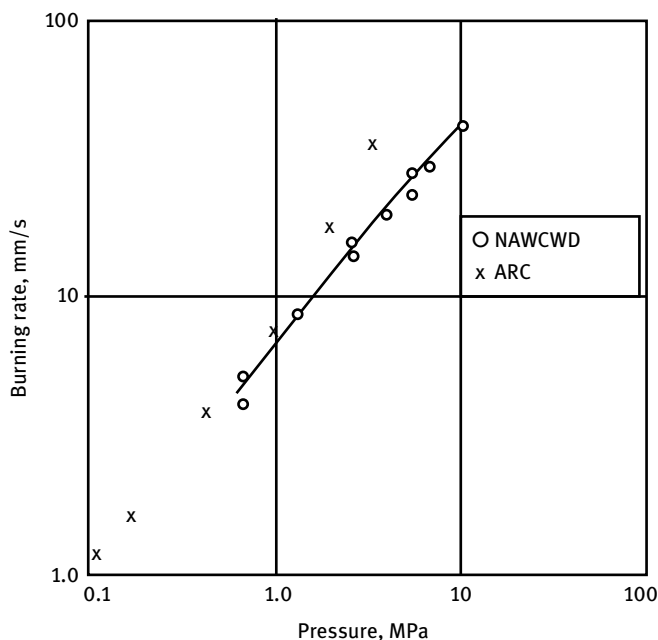


Figure 33: Strand burning rates of hydrazinium nitroformate at room temperature; Comparison of Naval Air Warfare Center Weapons Division and Atlantic Research Corporation data. (Republished and modified from [307] with permission of American Institute of Aeronautics Astronautics; permission conveyed through Copyright Clearance Center, Inc.)

The ARC burning rate data were generated using straws filled with HNF powder instead of pressed pellets; thus, the combustion at pressures of 2 MPa and higher may be more representative of convective burning rather than a laminar burn. Elsewhere, the burning rates are comparable. The HNF burning rate data at three initial temperatures (223, 298, and 348 K) are presented in Figure 34 for pressures from 0.69 to 10.3 MPa. The three curves are very close to each other.

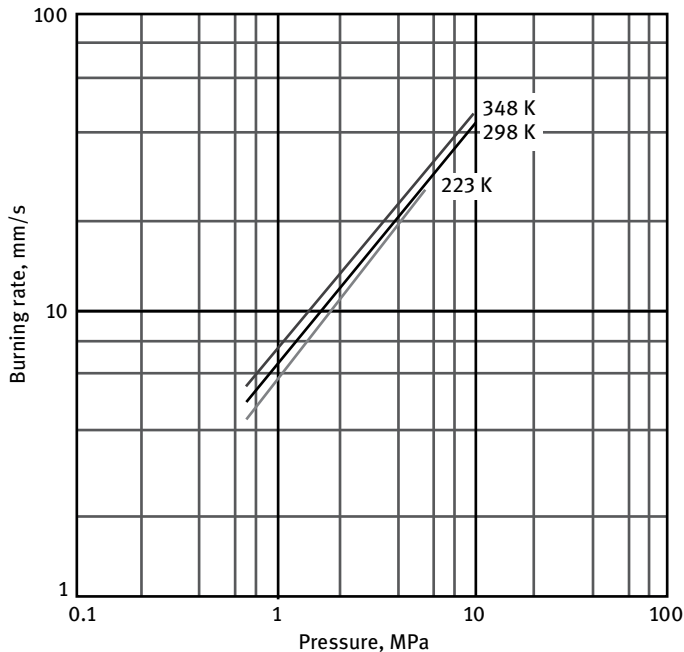


Figure 34: Strand-burning rates of hydrazinium nitroformate at three different temperatures. (Republished and modified from [307] with permission of American Institute of Aeronautics Astronautics; permission conveyed through Copyright Clearance Center, Inc.)

In extending these burning rate and pressure exponent measurements, additional data were used to determine the temperature sensitivity coefficient σ_p of the burning rate of HNF and four other oxidizers [308].

The simplest means of determining a value of σ_p is to measure the burning rate of a particular material as a function of initial temperature, take the natural logarithm of the burning rate values, and determine the burning rate temperature sensitivity as the slope of the line through a plot of the natural logarithm of the burning rate vs the initial temperature. The main requirement is to obtain a consistent and reliable set of burning rate data at various initial temperatures and pressures. In the case of HNF, the temperature sensitivity remains essentially flat over a wide pressure range (Figure 35).

The burning rate of HNF pellets measuring 6 and 9 mm in diameter was determined in two different strand burner bombs and the data were plotted together on the same graph (Figure 36) and compared with literature data from the Naval Air Warfare Center [250]. This is part of a PhD thesis that contains a very thorough investigation of many aspects of HNF decomposition and combustion.

The burn rate curve shows a slight slope break around 2 MPa from $n = 0.95$ going to $n = 0.85$ at higher pressures. Below 2 MPa, no inhibitor was used on the outside of

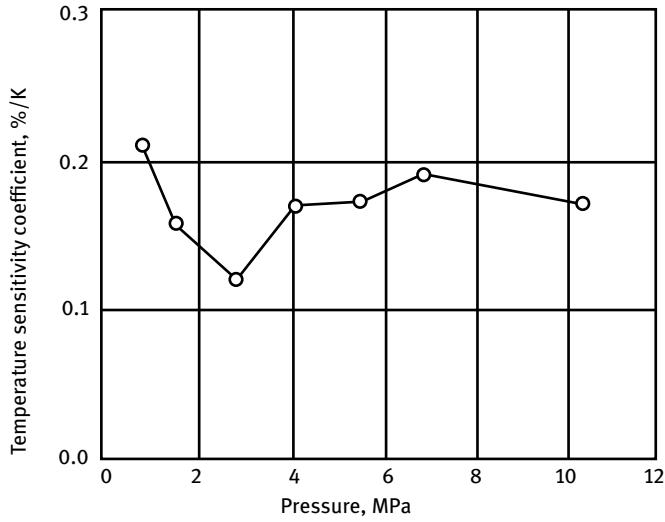


Figure 35: Temperature sensitivity coefficient of strand-burning rate of hydrazinium nitroformate. (Republished and modified from [308], with permission of © 1999 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

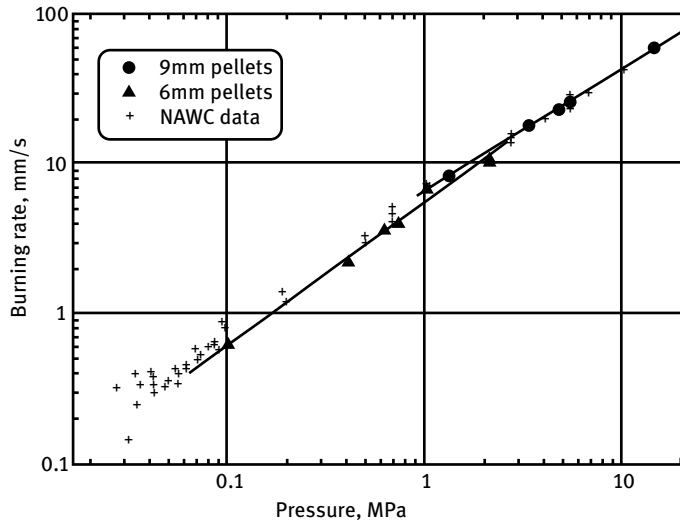


Figure 36: Burning rate of hydrazinium nitroformate pellets. (Reproduced and modified with permission from [250]; with permission from Dr. Jeroen Louwers, 27 May 2020.)

the pellets. Above 2 MPa, a thin layer of silicon grease was applied to the cylindrical part of the pellets. Similar curves were obtained for HNF mixed with 20% aluminum, 10% paraffin or 5% graphite. In addition to traditional regression rate measurements based on high-speed imagery with windowed bombs, an ultrasound regression rate analyzer has been evaluated, which is particularly useful for studying unsteady combustion that cannot be recognized in a constant volume bomb. An ultrasonic pulse is emitted into the burning pellet, reflected at the burning surface and the echo is recorded. A major restriction to the use of ultrasound in thick media is the attenuation. The attenuation and the speed of propagation of ultrasound in HNF pellets was therefore measured.

The HNF flame structure and decomposition gases were studied by UV and visible light absorption [250]. In addition to linear burn rate determinations in combustion bombs, planar laser-induced fluorescence was used to image the flame structures. The planar laser-induced fluorescence was used to establish concentration profiles of $\bullet\text{OH}$ and $\bullet\text{CN}$ radicals in the axial direction of the flame. This work showed that the decomposition and combustion of HNF is initiated by a proton transfer step. HNF combustion takes place in a narrow zone. Even at ambient pressure, most heat release occurs within the first millimeter of the flame. Although the chemical composition of HNF is very similar to that of nitramines and double-base propellants, the flame structure of HNF does not have a clear two-stage combustion zone. Most energy is released by reaction of NO_2 with other decomposition products. In a second stage the NO decomposes to O_2 and N_2 via slow, energetically neutral, reactions.

For combustion experiments, samples of HNF measuring 6 and 9 mm in diameter were pressed at pressures up to 236 MPa [210]. The density of these samples ranged from 93 to 96% of theoretical mean density. The samples had a smooth shiny surface. The value for friction sensitivity of pressed HNF is in the same range as what had been observed with crystalline HNF, but the drop height value for impact sensitivity has increased substantially (i.e., decreased sensitivity). Inserting microthermocouples into pressed HNF allowed the HNF temperature profile and surface temperature to be measured during burning. The surface temperature varied with pressure in the low-pressure range from 530 K at 0.1 MPa to 683 K at 1 MPa. These data agreed well with published data by Sinditskii et al. [268, 269, 309]. Sinditskii et al. [268] took thermocouple measurements at 0.04, 0.1, 0.5, 1, and 2 MPa. In the condensed phase, the temperature rose monotonically from the initial temperature to the melting point temperature (396 K). This region is followed by a melt/foam layer. At low pressures, this layer may be divided into two zones. In the first zone, the temperature increases slowly. For instance, at 0.1 MPa the temperature increases from 400 to ~ 425 K over the distance of 0.1 to 0.15 mm. In the zone of exothermic reaction the temperature increases more quickly. For example, at 0.1 MPa the temperature increases from 400 to 425 K at the solid boundary to 615 K over a distance of 0.15 mm. They measured a surface temperature 615 ± 11 K at 0.1 MPa and 698 ± 9 K at 1 MPa. At 2 MPa, they measured a surface temperature of 750 ± 10 K. Within 2 mm above the surface (at ambient pressures), the HNF

flame temperature was close to adiabatic. The temperature profiles in the gas phase showed two distinct flame zones. In the first flame, the temperature jumps from the surface temperature to 1320–1540 K, depending on pressure. This is followed by a dark zone, which is most often observed at 0.4 MPa but practically disappears at 2 MPa. After the dark zone, the temperature again begins to rise sharply to 2300–2720 K, which is just shy of the adiabatic flame temperature for HNF. It is assumed that 1.46 mol of NO per mol of HNF remain undecomposed in the equilibrium exhaust composition. It was theorized that decomposition of nitroform and oxidation of ammonia and carbon-containing intermediates (e.g., nitrile *N*-oxide CNO, or its isomer isocyanate free radical NCO) take place in the first flame zone. The second flame zone exothermicity may be due to decomposition of N_2O and NO. Emission spectroscopic measurements identified NO, O_2 , OH, NH, CN, and CH as major species in the flame, whereas absorption measurements indicated that the mol fraction of NO decreased away from the surface. Pressed neat HNF has a high burning rate with a burning rate exponent $n = 0.95$ for pressures below 2 MPa and $n = 0.85$ at pressures above 2 MPa up to 10 MPa [210]. Under similar conditions, Sinditskii et al. [291] reported $n = 0.92$ and 0.76, respectively. Differences between the Sinditskii data and those of other authors may be due to different methods of preparation of the strands. From the slope of the pressure vs reciprocal absolute temperature graph one can derive an enthalpy of sublimation of $156.5 \text{ kJ/mol} = 37.4 \text{ kcal/mol}$ for HNF.

A different burning rate measuring technique uses a sandwich of alternating layers of oxidizer and fuel. In one case, a layer of HNF can be sandwiched between two layers of combustible fuel (a solid propellant binder, e.g., GAP) and the diffusion flame structure can be observed [310]. The combustion of HNF takes place with a very short flame standoff, high rate of regression, high pressure exponent, and high monopropellant flame temperature compared with AP. Planar laser-induced fluorescence was used to study the structure of the flame in a sandwich arrangement with HNF and GAP. The flame structure is a combination of the HNF flame (a premixed flame) and a HNF/GAP flame (a diffusion flame). Small samples of neat HNF or sandwiches were ignited by zapping it with a pulse from a CO_2 laser in a high-pressure bomb with sapphire windows. OH or CN fragments were excited by shining a sheet of light across the flame in a direction perpendicular to the burning surface. Induced fluorescence was detected by a synchronized charge-coupled device camera and a filter perpendicular to the laser-illuminated sheet. Operating pressure was from 0.14 to 0.35 MPa. It was noticed that at higher pressures the area where no OH is seen is smaller and that the boundaries are sharper owing to the decreasing diffusion. It was concluded that the influence of the diffusion flame was extremely small. This matches with the observation that the burning rate of HNF-based propellants is essentially independent of the particle size. Figure 37 shows the burning rate of HNF/GAP propellants with coarse and fine HNF. For comparison, the burning rates of neat HNF and GAP are also shown.

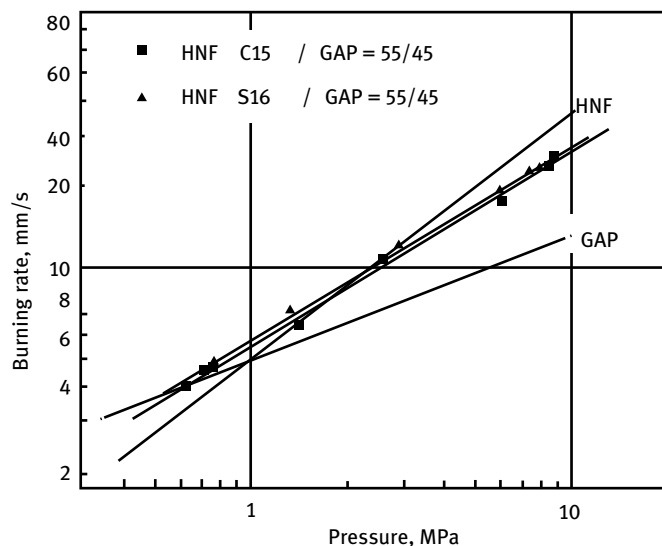


Figure 37: Regression rate of hydrazinium nitroformate (HNF)/glycidyl azide polymer (GAP) propellants compared with that of neat HNF and GAP. (Reproduced and modified from [310]; Public domain.)

The methods of the study of solid propellant combustion include SEM analysis of quenched samples of partially burned propellant. Examining quenched samples of singed HNF at high magnification showed evidence for the formation of a foam layer [256, 311]. Measuring the bubble size and size distribution is an indication of the amount of gas evolving and bubbling to the surface before the sample was quenched. The thickness of the foam layer was dependent on the operating pressure (Figure 38).

Fourier transform infrared spectrometry and mass spectrometry of pyrolysis products can also provide details on intermediate species formation during decomposition and combustion. Attenuated total reflectance (ATR) spectra obtained by pressing the IR window against the quenched surface identified the residues on the surface. The difference between the spectra before and after burning and quenching is mainly due to the appearance of a small, new peak at 3450 cm^{-1} . Based on the analysis of the results, investigators identified probable overall reactions in the low pressure regime HNF decomposition around 0.1 MPa. It was found that decomposition of HNF takes place through the formation of ANF, and through dissociative vaporization. The gas phase near the surface of burning HNF may contain a large amount of hydrazine, ammonia and nitrogen dioxide (as decomposition products of nitroform). Nitrogen dioxide is subsequently reduced to molecular nitrogen in the secondary flame reactions. The primary reaction zone of the HNF flame is exchanging energy by radiative heat transfer with exothermic gas phase reactions of these fragments and fed by diffusional mass exchange from the subliming surface.

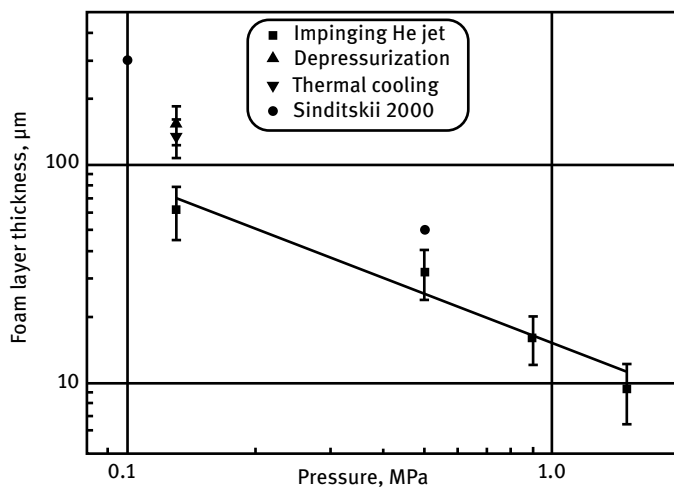


Figure 38: Thickness of the hydrazinium nitroformate foam layer as a function of pressure. (Republished and modified from [311], with permission from © 2009 Elsevier, permission conveyed through Copyright Clearance Center, Inc.)

The effects of the additives, urea and ammonium metavanadate, on the HNF burning rate was studied in a chimney burner equipped with four polycarbonate windows. For high-pressure combustion, the chimney burner was pressurized with N_2 gas up to 10 MPa. The combustion process was recorded with a video camera through one of the windows. The video recordings were used to determine the burning rate of the pellets. Addition of 5% urea did not change the burning rate or burning rate curve slope of HNF significantly, whereas the NH_4VO_3 catalyst increased the burning rate of HNF pellets. The pressure exponent of a HNF/5% NH_4VO_3 pellet is 0.54 ± 0.02 , which is lower than 0.87 ± 0.01 found for a neat HNF pellet. However, ammonium metavanadate is not compatible with HNF and is not a practical choice.

The strand-burning rates of two different samples of HNF obtained from two different sources were very similar [312]. The strand-burning rates of HNF were compared with those of 3,6-bis(1H-1,2,3,4-tetrazol-5-amino)-2-tetrazine and di-amino-azo-tetrazine.

One of the concerns when formulating propellants with HNF is the high pressure exponent, which may lead to instability and runaway pressure spikes. Various burning rate modifying additives have been sought that would lower the pressure exponent to a safe level.

Instead of searching for burning rate modifiers to reduce the reaction order of the leading gas phase reactions in HNF deflagration, burning rate modifiers were sought enabling exothermic reactions in the upper layer of the solid phase. Recent data on decomposition and combustion suggest N_2H_4 , NH_3 , N_2O , and NO_2 to be present in the

solid phase. Planar laser-induced fluorescence experiments in the near surface region of burning HNF indicated that NO_2 is indeed present and reacting in the solid phase. Because of its high catalytic activity, finely powdered V_2O_5 was added to HNF, leading to an increase in burning rate by a factor of 11 with respect to neat HNF, at 0.1 MPa [292]. The pressure exponent was reduced to only 0.28, far below the target value of 0.5 required for practical application of HNF in propellant formulations. A handicap is that none of the catalysts tested so far is compatible with HNF.

3.4.2 Modeling of Strand-Burning Behavior of Hydrazinium Nitroformate

One rarely trusts a totally theoretical model to provide reliable data on the strand-burning rate of solid propellant ingredients. At best, models are used to extrapolate from experimental data to other temperature, density, and pressure regimes that were not yet experimentally covered. There are many models for the combustion of solid propellants and solid propellant ingredients, but not many models show good correlation with experimental data. One of the more recent models is the Ward-Son-Brewster (WSB) model developed at Los Alamos National Laboratory [313, 314]. This model can handle steady, unsteady, linear, and non-linear dynamic burning.

Because HNF burns so cleanly, it was chosen as a model substance for comparison of experimental and model prediction data. Although HNF has not yet been studied as exhaustively as AP, HMX, or AN, it was chosen for this comparison because there were several sets of recent experimental data available. First, the steady-state combustion of HNF was modeled using the WSB model [315, 316]. Burning rate, surface temperature and flame standoff all showed good agreement between theory and experiment for steady-state operation.

Other studies of HNF combustion used the $\alpha\beta\gamma$ model [317] for modeling unsteady combustion. The gas phase was treated in two ways: the classical high-activation-energy limit (Denison-Baum-Williams [DBW] model) and the low-activation-energy limit WSB model. Both limits allowed for an analytical solution of the gas-phase energy equation. The WSB approach was found to match the experimental observations much better than the DBW models for HMX and double-base propellants and it also gave good correlation for HNF. Assuming a condensed-phase activation energy of $E_c = 75 \text{ kJ/mol}$ was found to give good results in the whole pressure range of interest. This value is close to the 84 kJ/mol required to dissociate HNF into liquid hydrazine and nitroform.

Figure 39 shows the results of the calculated regression rate for both models, compared with experimental data taken from [301]. Like most energetic materials, the regression rate of HNF can be described by

$$r_b = ap^n.$$

The high-activation-energy limit yields the familiar $n = \delta/2 = 1$, whereas $n = 0.89$ was found experimentally for HNF combustion (least-squares fit to all data points). This pressure exponent is uncomfortably high.

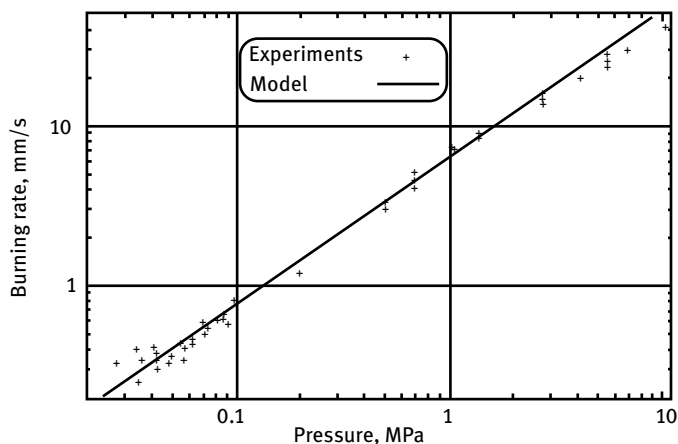
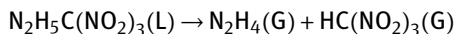


Figure 39: Comparison of calculated and measured regression rate of neat hydrazinium nitroformate samples. (Reproduced and modified from [250], with permission from Dr. Jeroen Louwers, 27 May 2020.)

Later, the modeling was extended to include an advanced version of the WSB model that can handle unsteady and transient situations [318–320]. Combustion of HNF was modeled and the results were compared with experimental observations including steady regression rate (pressure, initial temperature, and radiant flux sensitivities), surface temperature, and linear frequency response to radiation. The results indicated that HNF combustion is overall slightly exothermic (increasing with pressure) with activation energies similar to that of proton transfer between hydrazinium and nitroformate ions. The gas-phase flame is highly exothermic with low activation energy, suggesting that the gas-phase reaction is more like a low-energy barrier (low E_g) chain-reaction process than a high-energy thermal process. This is similar to what has been suggested for nitrocellulose-nitroglycerin double-base propellants and for RDX. For both of these materials, and now for HNF, the low- E_g model has been shown to be in good agreement with experimental data for both steady and unsteady burning rate. The model also demonstrated the ability to capture the undesirable onset of non-linear combustion. In general, the calculated results exhibit motor behavior in agreement with that observed experimentally for different L^* -values at low pressures. As L^* increases from low, subcritical ($< L_o^*$) to high, supercritical ($> L_o^*$) values, burning rate and motor pressure go from erratic and/or oscillatory to steady and stable. Several non-linear combustion phenomena such as rapid initial (over-) pressurization, propellant extinction, chuffing, and dual-frequency and limit-cycle oscillations

that have been observed experimentally but which are beyond the capability of linearized models are also predicted. A rapid rate of initial pressurization can cause an ignition spike commonly attributed to erosive burning and/or igniter mass flux, but it may also be due to non-linear dynamic burning at low L^* . This pressure spike has been simulated for both high pressure-exponent homogeneous propellants and low pressure-exponent AP-composite propellants. A chuffing phenomenon (probably resulting from non-linear dynamic combustion) for HNF was predicted at low L^* . This is in contrast to the dynamic extinction phenomenon observed computationally for double-base propellants. The low gas-activation-energy WSB model was then used to model the non-linear unsteady combustion of energetic solids and additional validation of the model was obtained by modeling HNF combustion. Comparison of predictions for HNF combustion with a wide range of experimental observations including steady regression rate (pressure, temperature, and radiant flux sensitivities), surface temperature, and linear frequency response to radiation showed good agreement. Results indicated that HNF condensed-phase decomposition is overall slightly exothermic (increasing with pressure) with activation energies similar to those for proton transfer between hydrazinium and nitroformate ions. The gas-phase flame is highly exothermic with low activation energy, suggesting that the gas-phase process might be more like a low-energy barrier, chain-carrier process than a high-energy thermal process, similar to what has been suggested for nitrocellulose/nitroglycerin (NC/NG) and HMX.

A computer model was developed for the calculation of HNF flame temperatures and reactant concentration profiles [265, 321]. The dissociative evaporation of HNF according to



was analyzed on the basis of literature data on the thermal decomposition and combustion of HNF. The structure of HNF flames at 0.4, 1, and 5 atm was modeled by using data on the composition of products on the combustion surface that correspond to the reaction within the condensed phase and in agreement with chemical composition and enthalpy of formation of HNF. The gas-phase reaction of nitroform with hydrazine (and partially with ammonia) occurs in the flame zone at a higher temperature near 1300 K. Further increase of the temperature in the flame is due to the reactions in $\text{H}_2\text{O}/\text{N}_2/\text{N}_2\text{O}/\text{NH}_3/\text{NO}/\text{NO}_2/\text{HNO}_2/\text{CO}/\text{CO}_2/\text{HCNO}/\text{HCN}$ mixtures. The calculated results, illustrated in a series of graphs where the abscissa is the distance from the burning surface in millimeter, were then compared with published experimental data on the temperature and reactant concentration profiles of HNF flames. Figure 40 shows that the model predictions for flame temperature approximate experimental data points quite nicely. The two predicted temperature profiles 1 and 2 are for different kinetic factors, but both agree quite well.

In this work, the flame structure was modeled using a detailed kinetic mechanism containing 47 species: O, O_2 , H, H_2 , OH, H_2O , HO_2 , N, N_2 , N_2O , HNO, NH_3 , NH_2 , NO,

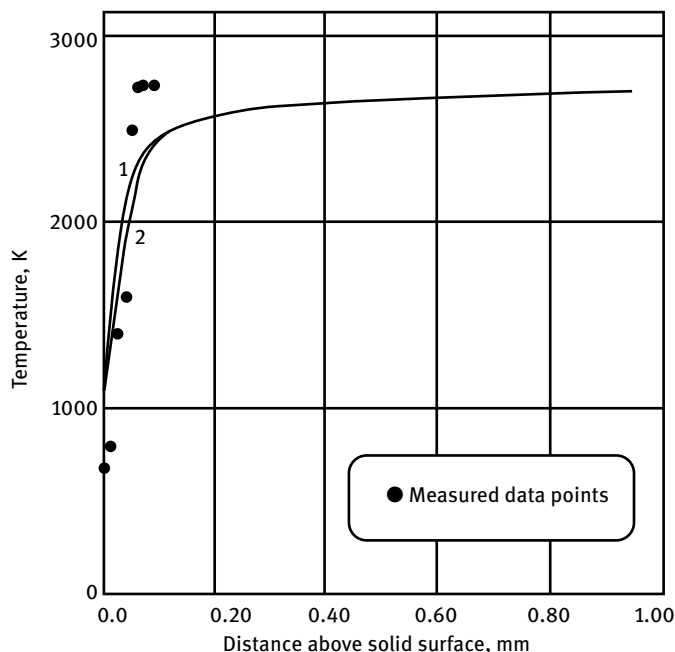


Figure 40: Measured (black dots) and predicted (1 and 2 lines) flame temperature profile above burning hydrazinium nitroformate at 5 atm. (Reprinted and modified from [265], with permission granted by Dr. Ermolin.)

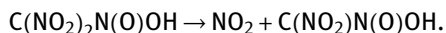
NO_2 , N_2H , NH , N_2H_2 , H_2O_2 , HNO_2 , HNO_3 , NO_3 , H_2NO , N_2H_3 , N_2H_4 , CO , CO_2 , HCO , H_2CO , CN , HCN , HNC , CNO , NCO , NCN , C_2N_2 , HNCO , HOCN , HCNO , $\text{HC}(\text{NO}_2)_3$, $\text{HC}(\text{NO}_2)_2$, HCNO_2 , $\text{HC}(\text{O})\text{NO}_2$, $\text{C}(\text{NO}_2)_2\text{N}(\text{O})\text{OH}$, $\text{C}(\text{NO}_2)\text{N}(\text{O})\text{OH}$, $\text{C}(\text{NO}_2)\text{NO}$, and $\text{HC}(\text{O})\text{NO}$. It also contained 283 reversible reactions. Only monomolecular routes for the decomposition of nitroform and its fragments were considered. Except for the reaction



the rate constants of the reactions involving $\text{HC}(\text{NO}_2)_3$ and its fragments are unknown. The calculations were performed under the assumption that the rate-determining reaction of nitroform decomposition is the dissociation of nitroform



or its isomer



Increased computing power (even of desktop computers) has enabled significant advances in the modeling and numerical simulation of solid propellant combustion using simplified kinetics. For premixed, homogeneous energetic materials (called

“monopropellants”), a mathematical rigorous high activation energy condensed-phase decomposition model (high E_c) and low activation energy gas-phase reaction model (low E_g) gives significant improvement in predicting both steady and unsteady combustion [322]. The usefulness of that model was demonstrated for sample cases like the steady and unsteady combustion response of HNF, NC/NG, and HMX. For non-premixed, composite propellants, the laminate propellant configuration was used to refine modeling assumptions. See also [323].

3.4.3 Flame Structure and Temperature Profile of Burning Hydrazinium Nitroformate

The successful modification of combustion characteristics of HNF requires a better understanding of the combustion phenomenon, which can be achieved by a detailed study of the HNF combustion wave structure and its physicochemical processes. Specifically at low pressures (0.2 MPa), the combustion wave structure of HNF consists of different reaction zones, which interact by heat and mass transfer and not always in a steady-state manner.

Absorption experiments to resolve neat HNF flame structure at sub-atmospheric and elevated pressures (0.03–1 MPa) were carried out in a windowed bomb with sapphire windows [324, 325]. The obtained absorption spectra were used to determine NO concentration and NO temperature profiles above the surface. The NO reduction to N_2 and O_2 is slow. At ambient pressure the NO mol fraction decreased from 18% close above the burning surface to 10% at 9 mm above the surface. The HNF flame reached temperatures close to adiabatic near the burning surface. These high temperatures were reached with still considerable amounts of NO present (mol fraction 0.1). Following the combustion of HNF at low pressures, a yellow condensate was found in the windowed bomb. The absorption spectrum of a solution of this material was found to be similar to that of HNF so it must be sublimed HNF. This indicates that transition to the gas phase occurs by evaporation or by ejection of small particulates (or a combination of both).

Temperature profiles in the combustion wave of HNF were measured using fine tungsten/rhenium thermocouples, which were embedded in the HNF oxidizer pressed into quartz tubes with an internal diameter of 7 mm [326]. It was found that in the first zone the temperature rose from the surface temperature to the first flame temperature, which varies with pressure from 1320 to 1540 K. This zone was followed by a dark zone, which was most often observed on profiles at a pressure of 0.4 MPa and practically disappeared at 2 MPa. After the dark zone the temperature began to rise sharply to as high as 2300–2700 K.

Additional investigations of HNF monopropellant flames at low pressures were performed to estimate the global kinetic rates for the reactive gas-phase regions above the burning surface [256, 327, 328]. Laser Doppler anemometry (LDA) in conjunction with simultaneously recorded video images of the burning pellets have provided useful information on the flame structure of HNF oxidizer, such as the velocity profile

and the thickness of the two near-surface regions (the fizz zone and the dark zone). The global reaction rates and the overall reaction orders were determined from measurements of burning rate and flame zone thickness and their pressure dependence. The averaged gas velocity estimated from LDA velocity measurements, was used to determine the density of reacting gases in the fizz zone and dark zone.

An experimental investigation of the flame structure of HNF extended the range of experiments to pressures of 0.06 and 0.13 MPa [329]. Laser diagnostics, including LDA and coherent anti-Stokes Raman spectroscopy (CARS) techniques were used to obtain the gas velocity and temperature profiles above the burning surface of HNF pellets. Gas velocity and temperature in the flame regions close to the burning surface (primary reaction zone and non-luminous zone) was measured as a function of the distance to the condensed phase surface. The laser beams of the CARS system are much more intense than the laser beams of the LDA. Their intensity is so high that it can break the sapphire windows of the combustion chamber. Therefore, two of the sapphire windows were replaced with antireflection-coated BK7 laser windows. As a by-product of the LDA and CARS measurements, it was found that these flames contain dispersed two-phase regions with aerosols and gaseous reactants being irregularly released from bubbles formed at the foam layer. Aerosols larger than approximately 0.1–0.2 μm have been detected in the region between the foam layer and the primary reaction zone. At greater distances from the surface, the aerosols shrink to a size below 0.1 μm until they are fully consumed in the beginning of the brightly luminous flame. It appears that at a fixed location above the surface, one intermittently finds final products or gaseous reactants with the balance between the two shifting toward the hot products with increasing distance from the surface.

3.4.4 Surface Temperature of Burning Hydrazinium Nitroformate

For combustion experiments, samples of HNF pellets measuring 6 and 9 mm in diameter were pressed at pressures up to 236 MPa; the density of these samples ranged from 93 to 96% theoretical mean density. Figure 41 from Louwers [250] indicates a strong variation of surface temperature with combustion pressure in the low-pressure range from 530 K at 0.1 MPa to 683 K at 1 MPa. Under similar conditions, Sinditskii et al. [291] measured a surface temperatures 615 ± 11 K at 0.1 MPa and 698 ± 9 K at 1 MPa. At 2 MPa, they measured a surface temperature of 750 ± 10 K.

Spontaneous Raman spectroscopy was used to determine the temperature above the burning surface of HNF at 0.1 MPa [330]. These measurements showed a temperature of about 1800 K at 0.35 mm above the surface. At 1.2 mm above the surface, the N_2 contour was consistent with the adiabatic flame temperature (2766 K).

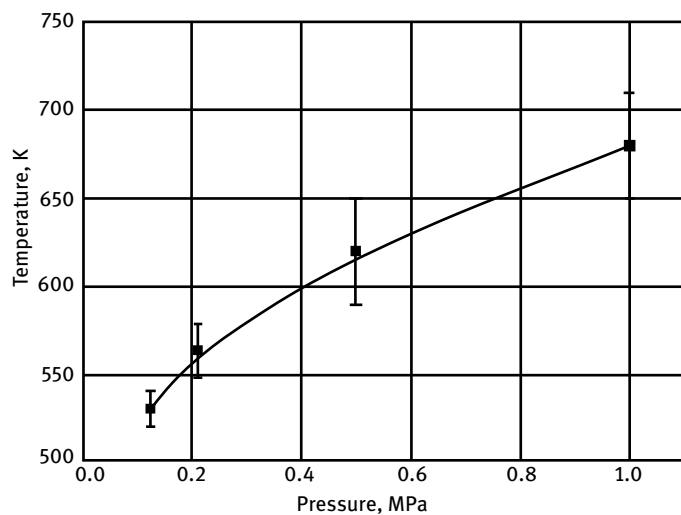


Figure 41: Surface temperature of burning hydrazinium nitroformate pellets. (Reproduced and modified with permission from [250]; with permission from Dr. Jeroen Louwers, 27 May 2020.)

3.5 Safety Properties of Hydrazinium Nitroformate

The sensitivity data for crystalline HNF are summarized in Table 32.

Table 32: Sensitivity data for crystalline hydrazinium nitroformate.

Parameter	Units	Value
BAM Fallhammer	J	2–5
BAM Friction tester	N	12–36
Rotter impact tester	Figure of impact	33
R rotary friction tester	Figure of friction	1.3–1.5
Critical diameter	mm	10
Detonation velocity	km/s	8.2–8.5
UN 3(d) response to flame		passed
UN 4(b) 12-m drop test		passed
Electrostatic discharge	mJ	726–4500

BAM = Bundesanstalt für Materialforschung und Prüfung

Data source: [210]

Hydrazinium nitroformate as an unpackaged material is too friction sensitive at this point to meet the criteria from the United Nations (UN) Recommendations on the

Transport of Dangerous Goods. However, packaged in standard UN boxes, 4.5 kg of HNF passed the UN 4(b) 12-m drop test and, thus, can be transported as 1.1 D material.

During the development phase, samples of up to 333 g of HNF could be transported as a 1.4S class material in special *Explosafe* containers.

3.5.1 Drop Weight Impact Sensitivity of Hydrazinium Nitroformate

The drop weight impact sensitivity of HNF is 2.5 Nm [210].

3.5.2 Shock Sensitivity of Hydrazinium Nitroformate

Hydrazinium nitroformate detonates if initiated with a blasting cap. Dry HNF is more sensitive than AP and can be detonated by a detonator cap [214, 331].

3.5.3 Friction Sensitivity of Hydrazinium Nitroformate

When comparing HNF with ADN, the high friction sensitivity of dry HNF is often cited as a disadvantage and a matter of considerable concern. The friction sensitivity of HNF can be improved by co-crystallizing it with a stabilizer or by applying a coating. For instance, friction sensitivity of uncoated HNF in the BAM friction tester was 20 N, and for stabilized and coated HNF the number went up to 35 and 29 N respectively [210]. Other sources [245] reported a friction sensitivity of uncoated HNF of 12–16 N in the BAM friction tester.

Different grades of HNF were used by different laboratories in determining the sensitivity of HNF as summarized in Table 33. When comparing data, one must make sure that the information about the grade and pedigree of the material is carried along in the test report.

Table 33: Impact and friction sensitivity of hydrazinium nitroformate.

Sensitivity test	Apparatus	Result	Source
Impact sensitivity	BAM	3 J	van Zelst and van der Heijden [245]
Friction sensitivity load	BAM	16 N	
Impact sensitivity	BAM	2–5 J	Schöyer [210]
Friction sensitivity load	BAM	12–36 N	

BAM = Bundesanstalt für Materialprüfung

The friction sensitivity could be reduced significantly by phlegmatizing HNF with 9.8 to 20% paraffin wax. The load applied to the spinning disk to achieve ignition increased from 36 to 60 N before a reaction was observed.

3.5.4 Electrostatic Sensitivity of Hydrazinium Nitroformate

The electrostatic discharge sensitivity of HNF is 726 to 4500 mJ (50/50 no fire) (Louwers [250]; Schöyer [210]).

3.6 Toxicity of Hydrazinium Nitroformate

The lethal dose of HNF in rats is LD₅₀ 128 mg/kg body weight.

3.7 Applications of Hydrazinium Nitroformate

In a search for new storable and environmentally friendly high-performance solid propellants for the European Space Agency, HNF was identified as a very promising ingredient for a new generation of composite propellants. Two distinct advantages of HNF-based propellants over the current AP-based propellants are: **(1)** a very high specific impulse, which significantly increases the performance of the solid propellant and **(2)** chlorine-free exhaust products that prevent the formation of hydrochloric acid in the environment. In particular in the high atmosphere, chloride would promote ozone depletion.

3.7.1 Propellants with Hydrazinium Nitroformate.

Solid propellants with HNF, burning rates of propellants with HNF, and sandwich combustion experiments with HNF will be discussed in detail in future volumes in this series. There is some unavoidable overlap between these future three sections and the following section.

One of the earliest references to the use of HNF in solid propellants is in an evaluation of barrel-wear-reducing additives to gun propellants [332].

The promised increase in I_{sp} when using HNF-based propellants in comparison with state-of-the-art AP-based solid propellants is 2 to 7%. The main incentive in switching from AP to HNF as the oxidizer in solid propellants is the chlorine-free exhaust resulting in less air pollution at the start sites and a reduction of the ozone depletion potential in the stratosphere. The other advantage is that HNF is not as persistent as perchlorate ion and does not accumulate in the ground water if it is spilled accidentally. Similar improvements could be achieved with ANF, but it is not as energetic and not as stable as HNF.

Several survey papers were published that primarily deal with the formulation of HNF-based solid propellants, but also provide additional information about the production of HNF and its competitive position in comparison with other oxidizers. Among the new oxidizers vying to replace AP and create a more environmentally friendly propellant, ADN and HNF compete for the favorite spot. Several studies

have compared the advantages and disadvantages of ADN and HNF and some have prepared propellants under identical conditions for side-by-side evaluation. See also [333]. Coating HNF granules with a binder that is a Lewis acid, e.g., a boron-organic polymer, can stabilize and desensitize the solid propellant [334].

3.7.2 Monopropellants with Hydrazinium Nitroformate

An early patent described mixtures of dinitromethane (which is not very stable) or trinitromethane with hydrazine or UDMH as monopropellants [335]. Later studies on the use of HNF in monopropellants were conducted mostly in Europe under ESA sponsorship. The results will be discussed in *Encyclopedia of Monopropellants*. If applications for HNF can be found both in solid propellants and in monopropellants, the increased demand might encourage industry to establish a broader supply base for this energetic chemical.

3.8 Other Nitroformate Salts

After the success with HNF, it was logical to look for properties of salts formed from other high-nitrogen bases with nitroform as the acid. These salts can be prepared either directly from the base and trinitromethane or by substitution of the cation in ANF or HNF. These salts are discussed in other chapters of this book. Ammonium nitroformate is discussed in *Encyclopedia of Oxidizers*, chapter “Dinitramide Oxidizers,” immediately following the chapters on ADN, and contains the nitro groups in the anion attached to nitrogen instead of carbon, so that the two salts have some structural similarity and are discussed next to each other. Several specific nitroformate salts of organic amines are listed in *Encyclopedia of Liquid Fuels*, chapter “Aliphatic Amines,” following the description of their parent amines. Other applications will be contained in future more general chapters on high nitrogen compounds as additives to solid propellants, gun propellants, and gas generants.

Here are two good papers by Göbel and Klapötke describing a wide range of nitrogen-rich nitroformate salts, including ANF and HNF [260, 336].

Two derivatives of HNF, namely monomethylhydrazinium nitroformate and dimethylhydrazinium nitroformate, were synthesized and suggested to be promising new, less sensitive high-performance energetic materials [287]. Nitroformate salts of 4-amino-1,2,4-triazole and 3,6-diguanidino-1,2,4,5-tetrazole would make good high-nitrogen additives [337].

Methylhydrazinium nitroformate was prepared and its crystal structure was examined by XRD, NMR, Raman and IR spectroscopy and the enthalpies of formation predicted by computational chemistry [338].

The thermal stability and decomposition kinetics of potassium nitroformate (KNF) was investigated by DSC and TGA/DTA to obtain information on safety for handling,

storage, and use [339]. The main thermal degradation for KNF occurs during two temperature ranges of 543–603 K (270–330) and 633–703 K (360–430 °C). Crystallized KNF dehydrated (at about 381 K = 108 °C) before its decomposition.

Potassium nitroformate is not likely to find its way as a rocket propellant, but it is a useful intermediate in the synthesis of more complex molecules that carry the trinitromethyl group. The reaction mechanism of the thermal decomposition of KNF has been investigated by density functional theory [340]. The geometric structures of reactants, intermediates, transition states, and products were fully optimized. There are four feasible reaction pathways. The energy barrier of the rate-limiting step is 216.30 kJ/mol. The dominant products predicted theoretically were KNO_2 , NO_2 , NO , and CO , which is in agreement with experiments.

4 Hydrazinium Dinitramide

Hydrazinium(1+) dinitramide, $[\text{N}_2\text{H}_5][\text{N}(\text{NO}_2)_2]$, $\text{N}_5\text{H}_5\text{O}_4$, HDN, CAS RN [165603-97-4], is an energetic salt that has not yet been as thoroughly investigated as ADN.

4.1 Physical Properties of Hydrazinium Dinitramide

4.1.1 Melting Point and Phase Diagrams of Hydrazinium Dinitramide

The melting point of HDN is 353–355 K (80–82 °C) [10], lower than that of ADN, which melts at 365.6 K (92.44 °C). Other sources reported that HDN exists in the crystalline state under normal pressure conditions with a melting point of 356 K (83 °C).

4.1.2 Density and Partial Molar Volumina of Hydrazinium Dinitramide

A summary of literature data on the density of HDN is given in Table 34.

Table 34: Density of hydrazinium dinitramide.

Density, g/cm ³	Method	References
1.83	X-ray	Schmitt, Bottaro, and Penwell [341]
1.848	X-ray	Gilardi and Butcher [66]

4.1.3 Thermodynamic Properties of Hydrazinium Dinitramide

4.1.3.1 Enthalpy of Formation and Heat of Combustion of Hydrazinium Dinitramide

The heat of combustion of HDN in a calorimetric constant volume bomb is $\Delta U_{\text{B}} = -5109 \pm 7.1 \text{ J/g}$ ($-1221 \pm 1.7 \text{ cal/g}$) in comparison with that of ADN, which is $\Delta U_{\text{B}} =$

$-3592 \pm 6.3 \text{ J/g}$ ($-858.48 \pm 1.5 \text{ cal/g}$) [10]. From this number, the enthalpy of formation of the two salts can be calculated, which turns out to be $-13.64 \pm 1.2 \text{ kJ/mol}$ ($-3.26 \pm 0.28 \text{ kcal/mol}$) for HDN and $-134.6 \pm 0.5 \text{ J/g}$ ($-32.16 \pm 0.11 \text{ kcal/mol}$) for ADN. The enthalpy of formation of HN determined under the same conditions was $-246.2 \pm 0.96 \text{ kJ/mol}$ ($-58.86 \pm 0.23 \text{ kcal/mol}$). The enthalpy of formation of HDN ($-13.6 \text{ kJ/mol} = -3.26 \text{ kcal/mol}$) is much less negative than that of ADN ($-134.6 \text{ kJ/mol} = -32.16 \text{ kcal/mol}$), which may lead to better rocket propellant performance. Table 35 gives a summary of the enthalpy of formation data for HDN.

Table 35: Enthalpy of formation data for hydrazinium dinitramide.

Enthalpy of formation		Method	Authors	Year	References
kJ/mol	kcal/mol				
-33.5	-8	Calculated	Schmitt, Bottaro and Penwell	1993	[341]
-13.64 ± 1.17	-3.26 ± 0.28	Measured, calorimetric	Konkova et al.	2009	[10]

See also [342].

4.1.3.2 Heat of Solution and Dissociation of Hydrazinium Dinitramide

The enthalpy of solution of HDN in water at infinite dilution is $47.32 \pm 0.08 \text{ kJ/mol}$ ($11.31 \pm 0.02 \text{ kcal/mol}$), in comparison with that of HN, which is 37.95 kJ/mol (9.07 kcal/mol) and that of ADN, which is 36.44 kJ/mol (8.71 kcal/mol) [10].

4.1.4 Optical Properties of Hydrazinium Dinitramide

4.1.4.1 Infrared Spectra of Hydrazinium Dinitramide

Predicted IR spectra in the gas phase and in solution were obtained from quantum mechanical calculations [343]. There were four characteristic regions in the simulated spectra: The frequencies near 3426 cm^{-1} in the gas phase and 3353 cm^{-1} in solution are caused by N—H stretching vibrations. The strongest peak, which appeared at 2462 cm^{-1} in the gas phase (2786 cm^{-1} in solution), was attributed to the vibration of protons between the two fragments of HDN. The frequencies at about 1625 and 1220 cm^{-1} in the gas phase were attributed to symmetrical and asymmetrical N=O stretches. The frequency at about 876 cm^{-1} in the gas phase was assigned to the asymmetrical $\text{O}_2\text{N—N—NO}_2$ stretching vibration and a shoulder owing to the $\text{O}_2\text{N—N—NO}_2$ symmetrical stretching vibration appears in solution. The frequencies below 800 cm^{-1} were mainly associated with in-plane and out-of-plane stretches of $\text{O}_2\text{N—N—NO}_2$ and the shear swing of N—H. The calculated IR spectra in the gas phase and in solution were quite different because of their differences in conformation and environment.

4.1.4.2 Ultraviolet Spectra of Hydrazinium Dinitramide

The UV spectrum that arises from the transition of the valence electron can provide useful information, such as quantitative or qualitative analysis and simple structural analysis. Calculations predicted a strongest peak at 253 nm, which comprised several excitations. The electron transitions happened inside the $\text{N}(\text{NO}_2)_2^-$ anion.

4.1.5 Molecular Structure of Hydrazinium(1+) Dinitramide

Hydrazinium(1+) dinitramide, $[\text{N}_2\text{H}_5]^+ [\text{N}_3\text{O}_4]^-$, is a very energetic, but also very sensitive high-energy density material. Its crystal structure was examined as part of a series of publications on a new class of flexible ion energetic salts [66]. Hydrazinium(1+) dinitramide crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions $a = 8.312(3) \text{ \AA}$, $b = 5.654(1) \text{ \AA}$, $c = 10.659(3) \text{ \AA}$, $\beta = 93.73(3)^\circ$, $Z = 4$, $\rho_c = 1.848 \text{ g/cm}^3$. See also Table 14. The structure of HDN in the solid state contains cations and anions that are linked by hydrogen bonds. The structure contains protonated amine cations and dinitramide anions linked by hydrogen bonding and provides a constrained local environment for the dinitramide anions owing to extensive hydrogen bonding. Atomic coordinates, bond lengths and angles, and equivalent isotropic displacement parameters for the salts were calculated and tabulated. The molecular structure of isolated ions of HDN is illustrated in Figure 42.

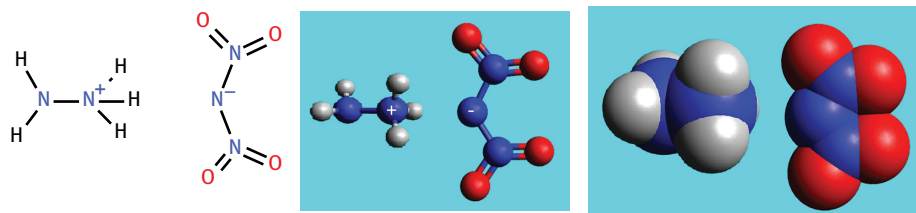


Figure 42: Molecular structure of hydrazinium dinitramide

The structures of HDN in the gas phase and in aqueous solution have been studied by using quantum chemical calculations at different levels of theory [343]. The intramolecular hydrogen bond interactions in HDN were studied in comparison with those in ADN, HNF, and ANF. The calculation showed that HDN possessed the strongest hydrogen bonds, with the largest hydrogen bond energy ($-47.95 \text{ kJ/mol} = -11.46 \text{ kcal/mol}$) and the largest total hydrogen bond energy ($-60.29 \text{ kJ/mol} = -14.41 \text{ kcal/mol}$). The charge transfer between the cation and the anion, the binding energy, the energy difference between the frontier orbitals and the second-order perturbation energy of HDN were all largest among the four investigated compounds. These strongest intramolecular interactions accounted for the highest onset of decomposition temperature of HDN among all four compounds. A calculation of the

binding energies of HDN and ADN with water molecules (-70.16 kJ/mol for HDN and -73.24 kJ/mol for ADN) demonstrated that ADN had a stronger ability to absorb water molecules than HDN, i.e., it is more hygroscopic.

4.2 Thermal Stability of Hydrazinium Dinitramide

Hydrazinium dinitramide has inadequate thermal stability to make it a useful rocket propellant ingredient. The DSC thermogram of HDN is shown in Figure 43, from Schmitt et al. [341]. See also [344].

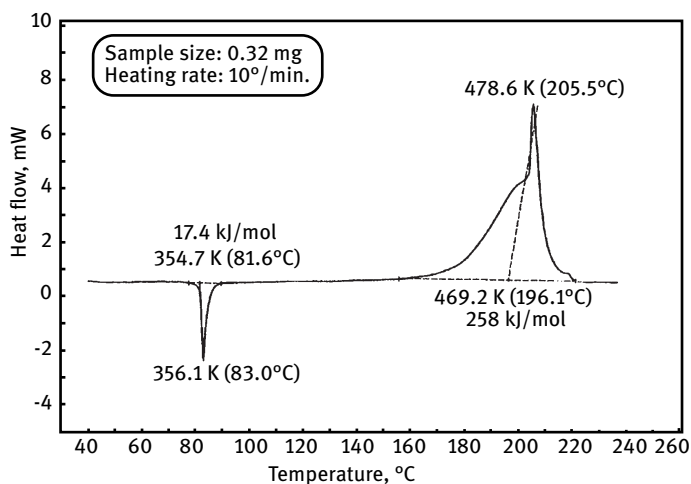


Figure 43: Thermogram of hydrazinium dinitramide decomposition. (Reproduced and modified from [341].)

4.3 Explosive and Fire Hazards of Hydrazinium Dinitramide

Hydrazinium dinitramide is highly shock (impact) sensitive and thus has no practical value [341]. Additionally, as observed in DSC, the melting point is slightly lower than that of the ammonium derivative, further reducing the possibility of this compound having practical value as a solid compound. It is quite soluble in water, so it could be used to formulate monopropellants similar to those derived from ADN.

The predicted detonation velocity ($D = 8.34$ km/s) and detonation pressure ($P = 30.18$ GPa) of HDN were both higher than those of ADN ($D = 7.55$ km/s and $P = 24.83$ GPa) [343].

5 Hydrazinium Azide

Hydrazinium azide, also known as N_5H_5 , $N_2H_5N_3$, $[N_2H_5^+][N_3^-]$, HA, HAZ, hydrazine azide, hydrazine trinitride, CAS RN [14662-04-5], is not an oxidizer, but it is a very energetic compound and we opted to list it here immediately following the other hydrazinium salts that are true oxidizers. It is the compound with the highest nitrogen content (93 mass-%).

There are two different Chemical Abstract Service Registry Numbers listed for HA: [38551-29-0] and [14662-04-5]. It is not known which is the correct (preferred) one. There is a different CAS RN for hydrazinium(1+) azide hydrazinate, which is [14546-45-3].

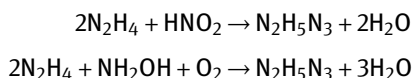
Hydrazinium azide, $N_2H_5N_3$, is closely related to another hydronitrogen, ammonium azide, NH_4N_3 , which is described in *Encyclopedia of Liquid Fuels*, chapter “Azido Compounds,” along with organic azido compounds. That is not a very logic location for an ionic azide compound such as ammonium azide, but it had to be either spliced in with ammonium salt oxidizers such as AN or AP, or listed here, close to the HA section.

5.1 Preparation of Hydrazinium Azide

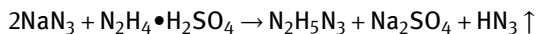
Whereas most other acids used in the preparation of hydrazinium salts are readily available, hydrazoic acid HN_3 is not readily available because it is unstable and explosive; moreover, it must be prepared fresh and handled (in solution) with extreme care if used in the preparation of HA. The preparation of HN_3 by acidifying azide salts and driving the diluted HN_3 vapor with an inert diluent gas into a quantity of hydrazine contained in a receiving flask has been practiced, but this is an extremely hazardous operation [345].

A safer and cleaner method is the preparation of hydrazoic acid by passing a solution of sodium azide through a H^+ -charged cation exchange resin, followed by distillation (again with an inert carrier gas) into a hydrazine sorbent solution. A dilute solution of hydrazoic acid can be prepared by ion exchange and then neutralized with hydrazine hydrate [346–348]. Crystals of HA obtained from a concentrated aqueous solution can then be filtered off and dried over P_2O_5 in a desiccator.

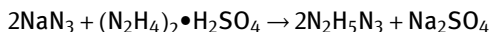
Hydrazinium azide can also be prepared by treatment of ammonium azide with hydrazine or by reacting a solution of AH in ethanol with an ethereal solution of hydrogen azide [349]. The chemistries of hydrazine and hydrogen azide are closely related, and it is quite feasible that HA is formed during partial oxidation of hydrazine or decomposition of hydrazinium(1+) nitrate solutions:



Hydrazinium azide can be prepared by reaction of sodium azide and hydrazinium(2+) sulfate, but half of the azide is lost as hydrogen azide [350]:



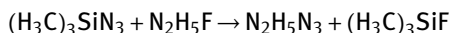
This reaction is carried out by using finely pulverized starting materials in refluxing *n*-butanol as a solvent. The sodium sulfate is insoluble in butanol, but HA is slightly soluble and precipitates after decanting the hot solution from undissolved sodium azide and cooling. Reported yields range from 37 to 70% of theoretical yield. A similar method was developed by Thiokol RMD, using methanol instead of butanol. One can make better use of the azide by reacting sodium azide with hydrazinium(2+) sulfate and additional hydrazine (hydrate) or by using the dihydrazinium(1+) sulfate:



The reaction is carried out in ethanol or isopropanol as the solvent, in which the sodium sulfate is insoluble and can be separated from the alcoholic HA solution [351].

Hydrazinium azide can be synthesized by bubbling nitrogen-diluted gaseous hydrogen azide, made from stearic acid and sodium azide at 403 K (130 °C), into an ice-salt-cooled ethanolic solution of hydrazine hydrate. The crude colorless salt can be recrystallized in absolute methanol to obtain crystals with a melting point of 345 K (72 °C) [352, 353]. The same method can also be used to prepare the azides of methylhydrazine, 1,1-dimethylhydrazine, phenylhydrazine, and acethydrazide [354–357]. As more methyl groups are attached to hydrazine, the melting point of the azide salt decreases. The volatility of the compound increases. With more methyl groups on the nitrogen base, the elimination of HN_3 from the molecule by dissociation gets easier.

Hydrazinium(1+) azide can be prepared by reaction of trimethylsilyl azide with hydrazinium(1+) fluoride in methanol [358]:



The same method can also be used for preparation of ammonium azide or hydroxylammonium azide.

A HA hydrazinate $\text{N}_2\text{H}_5\text{N}_3 \cdot \text{N}_2\text{H}_4$ was obtained by Dresser, Browne, and Mason [349] by treatment of a nearly saturated solution of HA in AH with an equal volume of ethanol. The precipitate of white crystals was dried over sulfuric acid and had to be stored in a desiccator over calcium chloride under nitrogen. The hydrazinate is very deliquescent and melts at 339.5 K.

A double salt of HA and triaminoguanidinium azide is obtained from triaminoguanidine, sodium azide, and hydrazinium sulfate by refluxing in methanol [359]. After filtering off the insoluble sodium sulfate, the product can be crystallized from methanol. It has a formula $\text{CH}_{14}\text{N}_{14}$, a molecular weight of 222.2 g/mol, a standard heat of formation $(\Delta H)_f^{298} = +664.8 \text{ kJ/mol}$ (+158.9 kcal/mol), and de-

composes at 423 K (150 °C). The high nitrogen content (88% by weight) would make this compound a valuable ingredient for low-temperature, nitrogen-producing solid propellants, but the volatility prohibits any such use. The propellant would have to be stored in the refrigerator all the time.

5.2 Physical Properties of Hydrazinium Azide

The melting point of anhydrous, hydrazine-free HA was reported to be 343.6 K (70.5 °C). Discrepancies in the melting point of HA reported a few decades ago, in 1979, melting point = 355 K = 82 °C [15] and 1972, melting point = 343.6 K = 70.5 °C [360] and those reported by earlier investigators (year 1969), melting point = 347.6 K = 74.5 °C; year 1933, melting point = 347.6 K = 74.5 °C [349] are most likely caused by varying amounts of excess hydrazine tenaciously adhering to the crystalline salt samples. HA prepared by reaction of trimethylsilyl azide with hydrazinium(1+) fluoride in methanol had a melting point of 348 K (75 °C) [358].

5.2.1 Melting Points of Systems with Hydrazinium Azide

The question arose if solutions of hydrazinium salts in water or hydrazine should be dealt with here under hydrazinium salts or in the chapter on their parent base, hydrazine. Although these solutions are not solid, they are discussed here along with the properties of these salts before they were dissolved in a solvent. The binary system hydrazine/HA has been investigated repeatedly since the beginning of the twentieth century. Dresser, Browne, and Mason reported a eutectic mixture melting at 255.6 K and containing 77% N_2H_4 [349]. The melting temperature rises very steeply on the HA-rich side of the eutectic points (Figure 44).

Kahrs and Seamans found a minimum melting composition at 258 K that contained 76.2% N_2H_4 [351, 361]. Finally, Pannetier and Margineanu [360] arrived at a melting point of 257 K with a mixture containing 76.3% hydrazine. These variations in melting point were most likely caused by unrecognized traces of water in the mixtures. The ternary system $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{N}_3/\text{H}_2\text{O}$ has been investigated for four hydrazine-water solvents initially containing 85.2, 90.5, 95.9, and 98.8% N_2H_4 . The HA content in the ternary mixture was varied from 0 to 50 mass-% $\text{N}_2\text{H}_5\text{N}_3$. The small number of data points along the $\text{N}_2\text{H}_4 - \text{H}_2\text{O}$ axis of the system did not allow construction of a complete ternary diagram (Figure 45). Compositions with higher water content (higher than 15%) are of less practical interest because the specific impulse of such ternary mixtures when used as monopropellants begins to suffer.

Hydrazinium azide hydrazinate is less hygroscopic and less volatile than HA itself. In DSC with hermetically sealed sample pans, two endothermic phase transitions were observed. Melting without decomposition occurred at 338 K (65 °C), and with de-

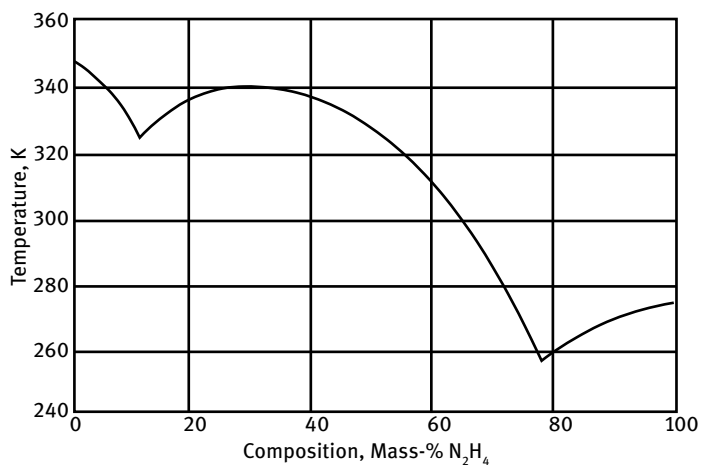


Figure 44: Freezing point diagram for the hydrazine/hydrazinium azide system. (Reprinted and modified from [349], with permission from © 1933 American Chemical Society.)

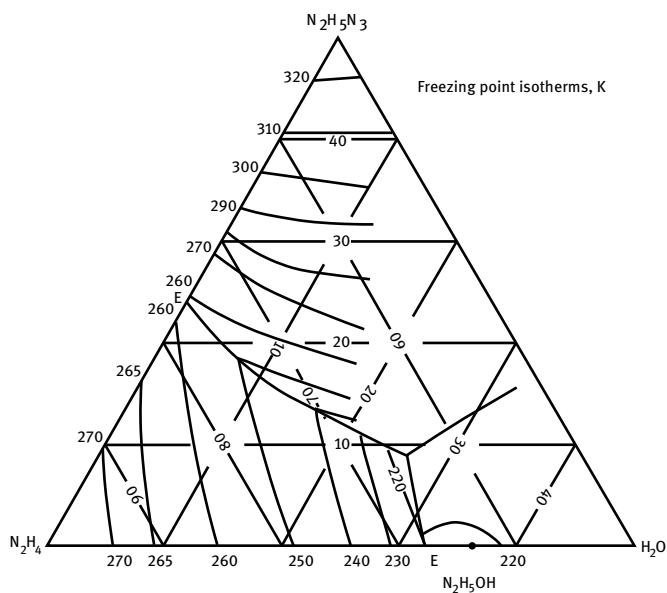


Figure 45: Freezing point diagram of ternary hydrazine/hydrazinium azide/water mixtures. (Reproduced and modified from [347] as shown in [2].)

composition at 424 K (151 °C). Explosion of $[\text{N}_2\text{H}_5]^+[\text{N}_3]^- \bullet \text{N}_2\text{H}_4$ yielded dinitrogen, ammonia, and dihydrogen. Compared with HA, the hydrazine adduct produced larger amounts of ammonia in the explosion. See also [345, 346].

5.2.2 Density of Hydrazinium Azide

Data for the density of crystalline HA are summarized in Table 36.

Table 36: Density of hydrazinium azide.

Density, g/cm ³	Method	Authors	References
1.40	pycnometric	Yakovleva, Kurbangalina, and Stesik 1974	[117]
1.407	XRD	Chiglien et al. 1974	[69]
1.400	XRD	Pannetier et al. 1972	[70]
1.419	XRD	Zhao et al. 2019	[358]

XRD = X-ray diffraction

A mixture of 24% HA, 1% water, and 75% hydrazine had a density of 1.104 g/cm³. A similar mix consisting of 19% HA, 4.5% water, and 76.5% hydrazine had a density of 1.087 g/cm³ [362]. The density of binary $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{N}_3$ and ternary $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{N}_3/\text{H}_2\text{O}$ mixtures can be calculated by using the equations summarized in Table 37.

Table 37: Density of hydrazine/hydrazinium azide/water mixtures.

Density as a function of temperature		
X^a , Mass%	Density, g/cm ³	References
20	$\rho = 1.2710 - 0.006814T^c$	Kahrs and Seamans [351];
21.8	$\rho = 1.2697 - 0.006686T$	Seamans, Kahrs, and Huson [361]
27.6	$\rho = 1.2782 - 0.006428T$	
Density as a function of composition		
W^b , Mass-%	Density at 298 K, g/cm ³	References
1.2	$\rho = 0.002880X + 1.0065$	Pannetier and Margineanu [360]
4.1	$\rho = 0.002865X + 1.0085$	
9.5	$\rho = 0.002828X + 1.01246$	
14.8	$\rho = 0.002796X + 1.01525$	

^a X = mass-% $\text{N}_2\text{H}_5\text{N}_3$ in the final mix.

^b W = mass-% water contained in the hydrazine-water mix prior to addition of hydrazinium azide

^c T = temperature, K

5.2.3 Solubility of Hydrazinium Azide

Hydrazinium azide is very hygroscopic and it is difficult to obtain an absolutely water-free sample for determination of its physical properties. It is best to avoid the use of water as a solvent if one wants to obtain a truly water-free salt. HA can be re-crystallized from methanol or ethanol in which it is quite soluble (Table 38).

Table 38: Solubility of hydrazinium azide in non-aqueous solvents.

Compound	Solvent	Temperature, K	Solubility, g/100 g solution	Authors	References
$\text{N}_2\text{H}_5\text{N}_3$	CH_3OH	296	5.75	Dresser, Browne, and	[349]
$\text{N}_2\text{H}_5\text{N}_3$	$\text{C}_2\text{H}_5\text{OH}$	296	1.186	Mason 1933	

5.2.4 Optical Properties of Hydrazinium Azide

The IR spectrum of HA is shown in Figure 46.

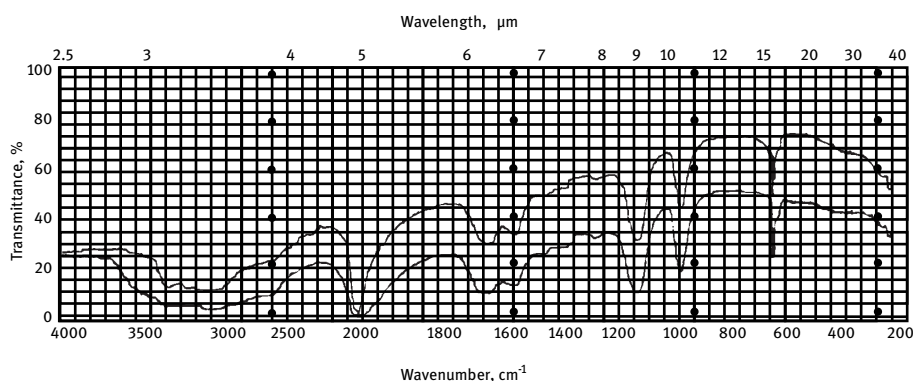


Figure 46: Infrared spectrum of hydrazinium azide. (Reproduced and modified from [13, 111])

Absorption bands of the hydrazinium ion in hydrazinium(1+) azide are very similar to those in hydrazinium halogenides. Absorption at 2036, 645, and 636 cm^{-1} stems from the azide ion [70, 354]. The sharp peak at 2034 cm^{-1} is the dominating feature of the spectrum (Figure 47).

Absorptions in the IR spectrum of hydrazinium(1+) azide prepared from trimethylsilyl azide and hydrazinium fluoride, crystals embedded in a KBr pellet, were at 3356, 3285, 3053, 2033, 1598, 1508, 1338, 1234, 1094, 953, 649, 643, and 460 cm^{-1} [358].

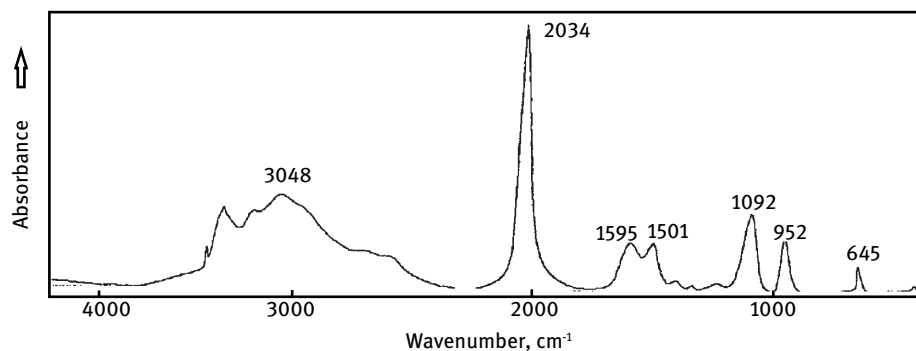


Figure 47: Infrared spectrum of hydrazinium azide. (Reproduced and modified from [354], with permission from Professor T. M. Klapötke.)

5.2.5 Molecular Structure of Hydrazinium Azide

The crystal structure of HA was already listed in Table 14 along with the crystal structure of other hydrazinium salts. $\text{N}_2\text{H}_5\text{N}_3$ is a monoclinic structure with the structural parameters $a = 5.663(2) \text{ \AA}$, $b = 12.436(3) \text{ \AA}$, $c = 5.506(2) \text{ \AA}$, and $\gamma = 114.0(1)^\circ$.

The structural parameters of monoclinic HA crystals with a space group of $P2_1/n$ obtained by crystallographic XRD measurements are $a = 5.641(2) \text{ \AA}$, $b = 5.521(2) \text{ \AA}$, $c = 11.306(4) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 93.261(4)^\circ$, $Z = 4$ [358]. The calculated crystal density was 1.419 g/cm^3 .

The data for the crystal structure of HA were already listed in Table 14 above. HA crystallizes as the monohydrazinate, with an extra molecule of hydrazine as a ligand in the hydration sphere of the ions. HA hydrazinate, $[\text{N}_2\text{H}_5]^+[\text{N}_3]^- \cdot \text{N}_2\text{H}_4$ was synthesized from equimolar amounts of HA and hydrazine and characterized by single crystal XRD: monoclinic, space group $P2_1/c$, $a = 6.3704(2) \text{ \AA}$, $b = 12.1111(4) \text{ \AA}$, $c = 6.9940(2) \text{ \AA}$, $\beta = 91.8666(2)^\circ$, $V = 539.32(3) \text{ \AA}^3$, $Z = 4$, $\rho = 1.320 \text{ g/cm}^3$ [352, 353].

The structural, elastic, mechanical, electronic properties, formation energy, and cohesive energy of orthorhombic NH_4N_3 and monoclinic $\text{N}_2\text{H}_5\text{N}_3$ crystals were calculated by the plane-wave method based on the first-principles density functional theory [363]. The calculated results of the two compounds were in agreement with previously published values. The orthorhombic NH_4N_3 is more energetically stable than $\text{N}_2\text{H}_5\text{N}_3$. The independent elastic constants, bulk modulus, shear modulus, Young's modulus, and Poisson's ratio of the two compounds were investigated. The electronic band structures, density of states and charge density distributions of orthorhombic NH_4N_3 and monoclinic $\text{N}_2\text{H}_5\text{N}_3$ were analyzed so as to better understand electronic properties and chemical bonding in these compounds.

Structural, elastic, mechanical, and electronic properties of monoclinic $\text{N}_2\text{H}_5\text{N}_3$ at ambient and very high pressure were investigated using a plane-wave ultrasoft pseudopotential method within the density functional theory [364]. Calculations of the

pressure dependencies of structural parameters, elastic constants, mechanical properties, band gaps, and density of states of monoclinic $\text{N}_2\text{H}_5\text{N}_3$ showed that monoclinic $\text{N}_2\text{H}_5\text{N}_3$ is unstable at pressures exceeding the value 126.1 GPa. Monoclinic $\text{N}_2\text{H}_5\text{N}_3$ was predicted to behave in a ductile manner in the pressure range from 0 to 200 GPa. $\text{N}_2\text{H}_5\text{N}_3$ is a monoclinic structure with the structural parameters $a = 5.663(2) \text{ \AA}$, $b = 12.436(3) \text{ \AA}$, $c = 5.506(2) \text{ \AA}$, and $\gamma = 114.0(1)^\circ$. The density functional theory calculations predicted the following structural parameters: $a = 5.9846 \text{ \AA}$, $b = 12.1388 \text{ \AA}$, $c = 5.5580 \text{ \AA}$, and $\gamma = 117.921^\circ$. A comparison showed that the parameters a , c , and γ were overestimated, but b was underestimated.

The transformation of HA to molecular N_8 has been investigated at high pressures up to 68 GPa using confocal micro-Raman spectroscopy and synchrotron powder XRD [365]. The results showed that HA undergoes structural phase transitions from solid HA-I to HA-II at 13 GPa, associated with the strengthening of hydrogen bonding, and then to N_8 at 40 GPa. The transformation of HA to the recently predicted N_8 ($\text{N} \equiv \text{N}^+ - \text{N}^- - \text{N} = \text{N} - \text{N}^- - \text{N}^+ \equiv \text{N}$) is evident by the emergence of new peaks at 2384, 1665, and 1165 cm^{-1} , arising from the terminal N—N stretching, the central $\text{N} = \text{N}$ stretching, and the N—N stretching respectively. However, upon decompression, N_8 decomposed to $\epsilon\text{-N}_2$ below 25 GPa, but the remnant can be seen at pressures as low as 3 GPa.

5.2.6 Thermodynamic Properties of Hydrazinium Azide

Thermodynamic properties of HA are summarized in Table 39.

Table 39: Thermodynamic properties of hydrazinium azide.

Compound	$(\Delta H)^f_{298}$		Authors	References
	kJ/mol	kcal/mol		
Enthalpy of formation				
N ₂ H ₅ N ₃ (S)	+246	+58.9	Yakovleva, Kurbangalina, and Stesik 1974	[117]
N ₂ H ₅ N ₃ (S)	+246 ± 1.6	+58.9 ± 0.4	Kirpichev et al. 1973	[366]
N ₂ H ₅ N ₃ •N ₂ H ₄ (S)	+294.1 ± 3.3	+70.3 ± 0.8	Kirpichev et al. 1973	[366]
Heat of fusion				
N ₂ H ₅ N ₃ (S)	15.81 ± 0.25	3.78 ± 0.0	Abello and Margineanu 1972	[367]
Entropy of fusion				
N ₂ H ₅ N ₃ (S)	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹	Abello and Margineanu 1972	[367]

5.3 Chemical Properties of Hydrazinium Azide

5.3.1 Reactions of Hydrazinium Azide

The reaction of HA with sulfuric acid released hydrogen azide and formed hydrazinium(2+) sulfate, which was identified by its crystal structure [368].

Hydrazinium azide forms a 1 : 1 solvate with hydrazine.

5.3.2 Thermal Stability of Hydrazinium Azide

In DTA, HA melts at 355 K and begins to decompose at 446 K [15, 369]. HA may undergo a phase transition above room temperature [354]. Figure 48 shows a thermogram of HA in a pierced aluminum tube measured by DSC. The peaks before the melting point (339.0 K = 65.9 °C) could not be identified and may be due to adsorbed moisture or free hydrazine as a solvate. The DSC thermogram in Figure 48 shows that HA that was stored in an desiccator behaves differently from what one would expect from the TGA experiment.

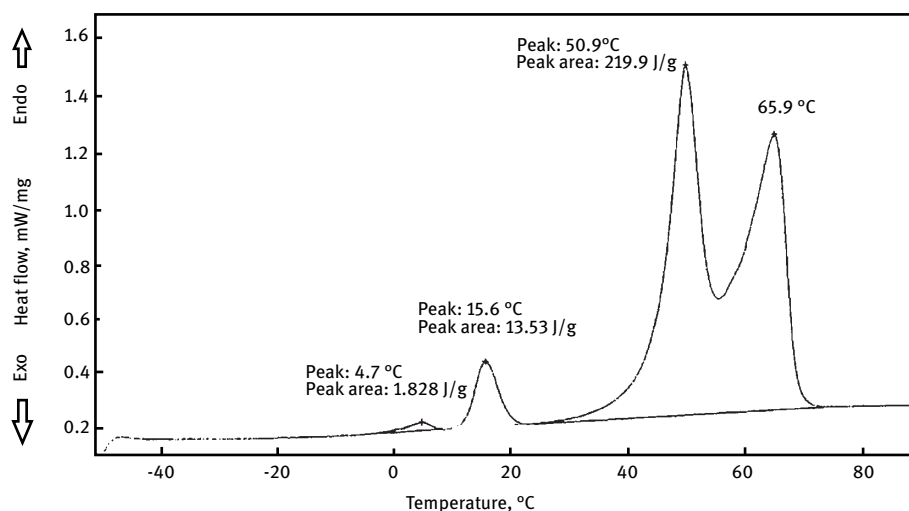


Figure 48: Differential scanning calorimetry thermogram of hydrazinium azide at a heating rate of 5 °C/min. (Reproduced and modified from [354], with permission from Professor T. M. Klapötke.)

The DSC thermogram of a sample of HA prepared from trimethylsilyl azide and hydrazinium fluoride showed only a melting endotherm at 348.8 K (75.66 °C) and a subliming endotherm at 448.7 K (175.57 °C) (Figure 49).

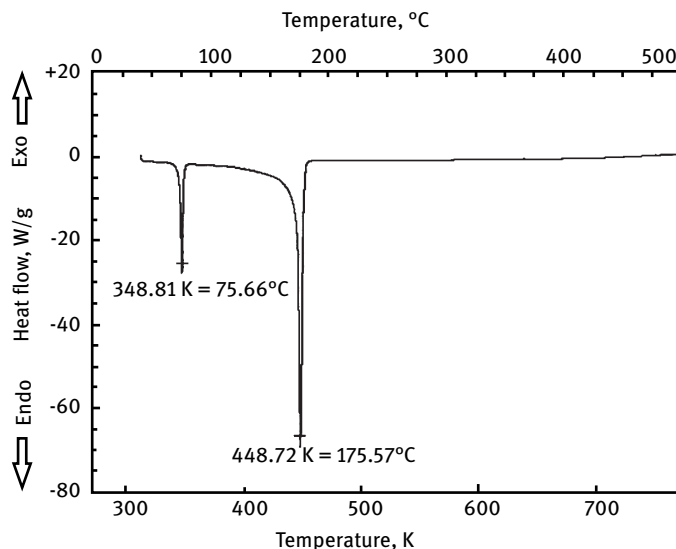


Figure 49: Differential scanning calorimetry thermogram of hydrazinium azide at a heating rate of 5 °C/min. (Reprinted and modified from [358], with permission from © 2019 American Chemical Society; permission conveyed through RightsLink.)

5.4 Strand Burning of Hydrazinium Azide

The steady-state unoxidized combustion of ammonium azide and hydrazinium(1+) azide at pressures from 0.1 to 36 MPa was studied in a windowed bomb [370]. Hydrazinium(1+) azide burned 3–4 times faster than ammonium azide over the entire pressure range. The combustion temperature of both compounds was 240–430 K higher than the temperature calculated for the thermodynamic equilibrium composition of the combustion products due to the presence of large amounts of undissociated NH_3 (0.97 and 0.87 mol-% per mol of NH_4N_3 and $\text{N}_2\text{H}_5\text{N}_3$ respectively). The reaction at the combustion surface was the dissociation of the salts into HN_3 and the parent base. The azide salts are very volatile and dissociate into free hydrazoic acid and the parent base prior to burning.

Hydrazinium azide can be used in solid propellants with boron compounds [371] or in gas dynamic laser gas generants [372]. Monopropellants containing HA will be described in *Encyclopedia of Monopropellants*.

5.5 Explosive and Fire Hazards of Hydrazinium Azide

In the BAM drop hammer apparatus, the lower threshold of initiation was 40 Nm, which is not very sensitive [354]. In the BAM friction test apparatus, the onset of reaction was at a piston load of 80 N. In the electrostatic-sensitivity test apparatus, a discharge of 32 J did not initiate an explosion.

Hydrazinium azide is one of the more energetic hydrazine salts that may not only decompose but also detonate when heated. The drop-weight sensitivity number of HA was lower (i.e., it was more sensitive, easier to initiate) than that of tetryl, in the range 10 kg × 25 cm. The first experiments showed that the dry salt can detonate under both low- and high-velocity conditions [373]. To obtain more reproducible results, investigators used charge diameters that were at least five to six times greater than the critical diameter for stable detonation [117]. The single crystal density of HA is 1.4 g/cm³. The critical diameter depends on the bulk density of the sample and increases with bulk density from 4 mm at 0.6 g/cm³ to 20 mm at 1.2 g/cm³. Dependence on this form is typical for explosives with a low heat of reaction, such as ammonium nitrate. It is thought to be caused by slowing down the dissociation of the salt into an acid and a base, which precedes decomposition. The detonation velocity of low-density (0.68-g/cm³) charges increased with charge diameter and leveled off at 4950 m/s at 20 mm, which is five critical diameters. Using steel and glass casings for confinement and charges 20 mm in diameter, the dependence of detonation velocity on charge density was also determined. The detonation velocity increased from 2500 m/s at very low densities to 7000 m/s at 1.2 g/cm³. Under most conditions of confinement and sample diameter, the detonation velocity decreased when the density was increased beyond 1.2 g/cm³. This type of maximum had also been observed with ammonium azide. In the linear slope of the curve, the dependence of detonation velocity on density can be described by the equation

$$D = 1.80 + 4.60\rho$$

where ρ is entered in g/cm³ and D is the detonation velocity in km/s. The detonation velocity of HA exceeds even that of powerful explosives, such as hexogen or PETN, in spite of the fact that its heat of explosion is less than that of hexogen or PETN. Its detonation velocity is even higher than that of solid HN [113]. In spite of this higher detonation velocity, HA will not become an industrial explosive because it is very difficult to prepare and because it is so hygroscopic.

6 Other Hydrazinium and Nitrohydrazinate Salts

The discovery of the dinitramidic acid and its salts has given great impetus to the search for similar energetic nitrogen compounds containing N—NO₂ groups suitable as oxidizers in solid propellants. Replacing one hydrogen on ammonia with a nitro group has led to nitramine; replacing two nitro groups on ammonia has led to dinitramidic acid. Can the same substitution be made with hydrazine? These compounds may not be stable, but at least on paper (or on the screen of the computer) they can be looked at. The remaining hydrogen on a nitrogen or carbon atom adjacent to a nitro group becomes quite acidic owing to the drain of electrons toward the electrophilic nitro group. So nitrohydrazine and 1,2-dinitrohydrazine should be acids similar to dinitramidic acid, forming nitrohydrazinate salts. Sometimes the salts are more stable than the parent acid.

It is known that the reaction of N₂H₄ with NO₂ or N₂O₄ is one of the most vigorous hypergolic reactions. Obviously that is not a good way to replace hydrogen atoms on the N₂H₄ molecule with —NO₂ groups in an effort to synthesize high-energy compounds. Two chlorine-free but oxygen-rich hydrazine derivatives (hydrazine modified with —NO₂ and NO₃[−] groups) were envisioned with lots of phantasy and then computationally optimized to obtain molecular geometries and electronic structures [374]. Some basic properties such as bond dissociation enthalpy, density, natural bond orbitals, thermodynamic parameters, molecular orbital energy, and strand-burning rates were then calculated. Predicted performance was excellent, with significant superiority over traditional oxidants found in current propellants. The performance of the as yet unknown 1,2-dinitrohydrazine: O₂NNHNNHNO₂ and nitrohydrazinium nitrate O₂NNHNNH₃NO₃ was compared with that of the well-known hydrazinium(1+) nitrate. The predicted strand-burning rates were compared in Figure 50.

Hydrazinium salts of alkylhydrazines will be described in *Encyclopedia of Liquid Fuels*, chapters “Alkylhydrazines,” “Dimethylhydrazines,” and “Methylhydrazine.” This includes hydroxyethylhydrazinium nitrate, which is used as a fuel in HAN-based monopropellants. The alkylammonium nitrates and perchlorates were dealt with immediately following the free amines in *Encyclopedia of Liquid Fuels*, chapter “Aliphatic Amines,” and they can be compared with alkylhydrazinium salts.

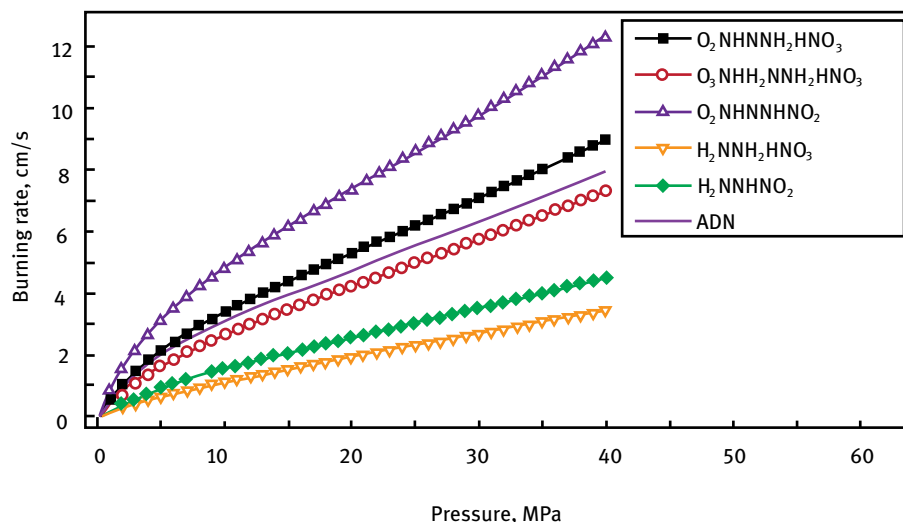


Figure 50: Predicted strand-burning rates of 1,2-dinitrohydrazine and nitrohydrazinium nitrate in comparison with other oxidizers. (Republished and modified from [224], with permission of © 2013 Springer; permission conveyed through Copyright Clearance Center, Inc.)

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Hydrogen Peroxide

1 General Information on Hydrogen Peroxide

Hydrogen peroxide, H_2O_2 , also known as hydroperoxide, hydrogen dioxide, CAS RN [7722-84-1], is a colorless liquid with a chemical composition and appearance similar to that of water, but with distinctly different physical and chemical properties. The compound is sometimes erroneously called “hydrogen superoxide”. This is incorrect because hydrogen superoxide refers to unstable hydrogen oxides containing more than two oxygens. A commonly used abbreviation for H_2O_2 in the English-language rocket propulsion literature is HP or HTP, which stands for **high-test peroxide**.

Although this chapter deals with hydrogen peroxide H_2O_2 as a rocket propellant, properties on its isotope analog (isotopologue) D_2O_2 are sometimes listed here for comparison, in particular in Section 3.11 on spectroscopic properties. For one, there is always some D_2O_2 and DHO_2 present in commercial H_2O_2 due to the natural isotope distribution in water and hydrogen the chemical is made from, and this small percentage may affect some of the physical properties. Although D_2O_2 will not be used as a rocket propellant, some of its properties were included here for reference, nevertheless.

This chapter in *Encyclopedia of Oxidizers* gives the physical and chemical properties of hydrogen peroxide as a chemical. *Encyclopedia of Monopropellants*, the chapter “Hydrogen Peroxide” will give a summary on hydrogen peroxide as a monopropellant. A future *Encyclopedia of Hypergolic Bipropellant Combinations*, the chapter “Hydrogen Peroxide” will give a summary on hypergolic bipropellant combinations with hydrogen peroxide as the oxidizer. A future *Encyclopedia of Non-hypergolic Bipropellant Combinations*, the chapter “Hydrogen Peroxide” will give a summary on non-hypergolic bipropellant combinations with hydrogen peroxide as the oxidizer.

1.1 Monographs and Bibliographies

There have not been many new monographs devoted exclusively to hydrogen peroxide in the past 30 years, but many of the older standard most-quoted references are still in use, see [1–6], and additional summary reports and book chapters have become available [7–10]. The best summary on the safety properties of hydrogen peroxide is a NASA report [11]. There are detailed chapters on hydrogen peroxide in many of the popular encyclopedias that serve as standard reference sources for all chemists [12–15]. Other books deal with applications of hydrogen peroxide in the chemical industry but are of less interest to a rocket propellant chemist [16, 17]. There are also several books on hydrogen peroxide in foreign languages [18–20].

1.2 Manufacturers' Literature

Manufacturers' literature continues to be a valuable source of information on hydrogen peroxide, although it may become irrelevant or obsolete quickly. The author has a file of ancient hydrogen peroxide literature that is obsolete and now has only historical value. We hesitate to reference manufacturers' literature that is no longer available or has only historical value, but here is a list of references leading the reader to what once was available and continues to be referenced by other authors: [21–28]. It would be useful to scan these documents and post them on a website for access to all propellant chemists.

One of the best company brochures for hydrogen peroxide properties, uses, storage, and handling was the booklet that was once provided by the Shell Chemical Co., Ind. Chem. Div. [29]. It contained an annotated list of 338 references that are otherwise nearly impossible to obtain.

On the other hand, just because the documents are no longer available to the general public, it is important to summarize the data contained therein and relay them on to future generations of chemists, so the measurements do not have to be repeated. Many of the former manufacturers of concentrated hydrogen peroxide (Becco, Shell) have either gone out of business, discontinued their involvement with HTP, or been acquired by other chemical companies and now operate under different names. Today, there are still many chemical companies that manufacture 70% hydrogen peroxide as a bleaching agent for paper and pulp mills and for wastewater treatment, but only a few of those have the capability of manufacturing more concentrated or stabilizer-free H_2O_2 solutions for rocket applications.

1.3 Literature Surveys

There are many review articles with summaries about the industrial production of hydrogen peroxide [30]. The situation in the industry changes rapidly in the course of one decade, and these reviews need to be updated periodically. There were once dedicated JANNAF meetings on hydrogen peroxide and its application in rocket propellants. Most of the older literature on hydrogen peroxide is difficult to locate and may be obsolete by now [31].

1.4 Internet Resources

URLs of websites change periodically, and the following information may have only limited value. URLs change as often as the weather. It is not always possible to amend a URL with the notation of "Last accessed on ... (date)" and keep it up to date.

As of 2021, a very good website of information on hydrogen peroxide was maintained by USPeroxide for non-rocket applications [32].

Thermodynamic properties of H_2O_2 (and D_2O_2) can be found at the NIST Chemistry WebBook [33] and the NIST Standard Reference Database Number 69 website [34].

As of 2021, a good summary of HTP history was still posted on the surviving archived website [35] of the late General Kinetics LLC, the one-time provider of HTP monopropellant thrusters and gas generators in the US. It included a history of the several phases of HTP development.

1.5 Other (Competing or Non-competing) Applications for Hydrogen Peroxide

Other uses for hydrogen peroxide will consume many orders of magnitude more of this chemical than has ever been used or will ever be used in rockets. The market price for hydrogen peroxide is determined by the other uses and is not affected by the small amount that goes (went) into rocket propulsion. Hydrogen peroxide is an important industrial chemical and is widely used as a disinfectant and bleaching agent and for wastewater treatment and deodorization. Many attractive movie actors owe(d) their blond hair to bleaching with hydrogen peroxide. For industrial applications hydrogen peroxide is usually transported as a 70% solution, although it is rarely used at this concentration. For the large community of H_2O_2 manufacturers and users, it is just more economical not to carry too much water between points of manufacture and end use. A good compromise between transport economics, storage stability and handling safety is 70% H_2O_2 , which is then diluted with water at the point of end use. Food grade H_2O_2 is often shipped as a 35% solution. In the analytical chemical laboratory, 30% H_2O_2 is a common, stabilizer-free analytical reagent that is usually diluted for further use.

In addition to H_2O_2 itself, many peroxy compounds prepared with the use of H_2O_2 have a variety of uses, including as food additives such as calcium peroxide for the artificial aging of flour before baking bread. Other industrial applications for hydrogen peroxide include the production of sodium percarbonate, sodium persulfate, and sodium perborate, used as mild bleaching agents in laundry detergents.

Hydrogen peroxide is used in the production of certain organic peroxides such as dibenzoyl peroxide, which are then used in polymerizations and other chemical processes. Hydrogen peroxide is also used in the production of epoxides from alkenes. The reaction of H_2O_2 with carboxylic acids produces corresponding peroxy acids. Peracetic acid and *m*-chloroperoxybenzoic acid are prepared from acetic acid and *m*-chlorobenzoic acid, respectively, which can be reacted with alkenes to give the corresponding epoxide.

The French PCUK (later Atochem) process for a halogen-free production of hydrazine hydrate [36] is based on hydrogen peroxide, such that some of the new hy-

drazine hydrate production facilities were colocated with existing hydrogen peroxide production sites for logistic reasons [17].

Recently, the development of a process for the production of 1,2-propylene glycol by the oxidation of propylene has evolved as a new application for hydrogen peroxide. Large 1,2-propylene glycol production facilities now under construction have their own hydrogen peroxide production unit nearby for captive use. 1,2-Propylene glycol is used as a deicing fluid on airplanes, as a less toxic anti-freeze for winterizing drinking water systems (for example, in recreational vehicles), as a moisturizer in cosmetics, and many more applications.

There are many well-established and many more potentially new applications for hydrogen peroxide, but they do not all require hydrogen peroxide to be in such high concentrations as the rocket applications do [37].

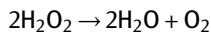
Looking into the crystal ball and trying to predict future applications for hydrogen peroxide takes a lot of imagination. Nevertheless, a promising future has been predicted for other non-propulsive applications for hydrogen peroxide [38].

1.6 Applications as a Rocket Propellant

The application of hydrogen peroxide as a rocket propellant plays (and has played) only a minor role in the market situation for hydrogen peroxide as a bulk chemical as long as one stays with 70% H_2O_2 , which has many other uses. However, for higher concentrations above 90%, the only major use of this type of hydrogen peroxide is as a rocket propellant. In this application, hydrogen peroxide can serve as a monopropellant as well as an oxidizer in liquid bipropellant and hybrid rocket propellant combinations. Looking at the history of hydrogen peroxide development helps to better understand its potential advantages and disadvantages [39]. Monopropellant applications will be discussed in *Encyclopedia of Monopropellants*. Liquid bipropellant combinations with hydrogen peroxide will be discussed in later sequels for hypergolic and non-hypergolic combinations. Hybrid rockets with hydrogen peroxide may be discussed in future volumes.

Since 1934, hydrogen peroxide has played an important and historical role in the pioneering development of rocket engines as an extension of prior work on torpedo and submarine propulsion systems based on this chemical. The pioneering work was conducted by H. Walter at a shipyard in Kiel, Germany, leading to rocket engines with the model designations 109–500, 109–507 and 109–509. The 109–509 engine was used in the piloted interceptor Me-163B, which was the first piloted airplane to exceed the 1000 km/h speed limit in horizontal cruise. Other applications during WWII were in piloted airplanes such as He-52, FW-56, NATTER and in jet-assisted take-off (JATO) units. The monopropellant applications in steam generators, torpedoes, submarines,

rockets, rocket planes, and satellites are based on the exothermic decomposition of hydrogen peroxide into water (steam) and hydrogen peroxide



The monopropellant engines have been called “cold” engines (as opposed to bipropellant engines in which hydrogen peroxide serves as the oxidizer with a combustible fuel). “Cold” can only be understood as a relative statement since the chamber temperature in “cold” rocket engines and steam generators can well exceed 763 K (490 °C).

After WW-II, initially all testing in the UK used 80% German hydrogen peroxide, which had been impounded at various locations. Eventually, local industries evolved in the UK and in the US, which were capable of producing HTP. As the development progressed, hydrogen peroxide/kerosene engines were widely used in England to power rocket airplanes, jet-assisted take-off (JATO) units, missiles, and satellite launch vehicles [40].

1.6.1 The “pros” and “cons” of Hydrogen Peroxide as a Rocket Propellant

Regardless of whether we discuss the advantages and disadvantages of HTP as a rocket propellant if it is used as a monopropellant or as an oxidizer in bipropellant or hybrid engines, there are some advantages and disadvantages that apply to either application when HTP is compared with other storable rocket propellants. There are many polemic publications on this sometimes hotly debated topic, and we can bring up only a few for discussion here. Quite often, the discussion is reiterated and brought back to the surface by marketing personnel and not necessarily by technically trained engineers or scientists.

One of the author’s favorite writers in rocket propulsion history writings, John D. Clark in his 1972 book *Ignition!*, wrote an unfavorable assessment of HTP and listed the following disadvantages (quoted verbatim here) [41]:

- “peroxide and fuel mixtures can detonate
- peroxide could explode if exposed to gross contamination
- peroxide is not stable and is dangerous in storage
- peroxide has ignition problems and is hypergolic only with hydrazine
- peroxide has an undesirably high freezing point.”

Proponents of HTP use took issue with these unfavorable assessments and tried to disarm each of the arguments [42]. As to detonability, Clark should have cited test results using standard test methods accepted in the propulsion community, such as American Society for Testing and Materials (ASTM), United States Bureau of Mines (USBM), Joint Army Navy Air Force (JANAF) or Interagency Chemical Rocket Propulsion Group (ICRPG) test methods, instead of quoting anecdotal information. As to gross contamination causing explosions, peroxide should not be singled out for special attention. Similar explosions could occur with other rocket propellants (N_2H_4 , LOX) if contam-

inants are negligently allowed to enter the system. The third point, lack of storage stability, is generally recognized, continues to be an unresolved issue, and must be included in mission planning. There are many storage tests reported in the literature (Section 7.1.1.3) and differences in results from different laboratories are typically due to the different passivation methods used for the storage vessels, the different amounts of stabilizers added, or errors occurring in sampling and analysis.

At the time when Clark wrote his landmark book, it may have been true that the only fuel found to be hypergolic with HTP was hydrazine (hydrate), but in the 50 years since he wrote that book, several readily available fuels have been doped with catalysts and additives that make them hypergolic with HTP (to be seen in a future *Encyclopedia of Hypergolic Bipropellant Combinations*).

Finally, the high freezing point of HTP is no less of a disadvantage than the high freezing point of anhydrous hydrazine, which has not prevented spacecraft designers from using hydrazine in thousands of satellites and dozens of space probes. There is usually enough electric power on board the satellites to heat the tanks and lines and prevent the propellants from freezing. In any case, the argument that HTP is frequently supercooling and that supercooling will expand the useful liquid range is naive. Nobody would want to rely on supercooling to prevent the propellant from freezing if the spacecraft ends up in the shadow of the Earth or the tank and line heaters fail in orbit.

Altogether, during the past 50 years, Clark's arguments have lost weight, and some have been proven to be unsubstantiated, but some of the other disadvantages of HTP persist.

1.7 Application of Hydrogen Peroxide in Steam Generators

Steam generators generating high-pressure superheated steam to drive aspirators (jet pumps) for "pressure recovery" in chemical lasers is one of the new applications for hydrogen peroxide, both on the ground and in airborne chemical lasers. This application will be discussed in detail in *Encyclopedia of Monopropellants*.

In 2003, the Defense Logistics Agency [43] issued a request for bids for a 3-year supply contract for 518 metric tons (1161000 lbs) of Hydrogen Peroxide, Type 70, Bulk, IAW, Item Description, H_2O_2 dated 20 December, 2002, FOB White Sands Missile Range, NM. It is assumed that much of this hydrogen peroxide was used for chemical laser tests.

Less concentrated hydrogen peroxide is used as a water treatment and water analysis chemical. The National Stock Number for the 30% Hydrogen Peroxide is 1H 6810 01-044-4188 X2.

The need for HTP with higher and higher concentrations was driven by the desire of rocket propulsion engineers to achieve higher specific impulse with lighter dry system masses. A good summary of HTP history was once provided at the website [44] of General Kinetics LLC, the one-time provider of HTP monopropellant thrusters and gas

generators in the US. Another good historical summary was compiled by a veteran of the hydrogen peroxide usage in the UK [45].

2 Production of Hydrogen Peroxide

2.1 Natural Occurrence of Hydrogen Peroxide

Hydrogen peroxide occurs naturally and is an important intermediate in the metabolism of many living things, including humans. Hydrogen peroxide helps living cells breathe and digest hydrocarbons to derive energy and is part of vital hydroxylation and oxidation reactions. Traces of hydrogen peroxide have even been detected in the air exhaled by humans [46]. In this case, and in very small concentrations, it cannot be that dangerous after all.

A most unusual occurrence of hydrogen peroxide in nature was discovered in studying the defense mechanism for the African bombardier beetle (*Stenoporus insignis*), which in its body produces H_2O_2 solutions up to a concentration of 28% H_2O_2 . The spray of the beetle contains *p*-benzoquinones, compounds well known for their irritant properties, which are ejected at a temperature of $\sim 373\text{ K}$ (100°C). The hot fluid is generated explosively at the moment of ejection by mixing two streams of chemicals stored in separate bladder-shaped glands. The larger of two glands contains premixed 10% hydroquinones and 25% hydrogen peroxide while the smaller one contains a mix of enzymes (catalysts, specifically, catalases and peroxidases). To activate the spray, the beetle mixes the contents of the two compartments, causing oxygen to be liberated from the hydrogen peroxide and the hydroquinones to be oxidized by the free oxygen, which is an exothermic reaction. The free oxygen also acts as the pressurant gas to squirt the hot corrosive solution in a defensive posture on the beetle's enemies, which are usually large ants. The discharges are accompanied by audible popping noises. This is like a monopropellant rocket, and this is why a picture of the bombardier beetle in action is shown in Figure 49.

In the non-living world, H_2O_2 occurs naturally in the high atmosphere as a result of water photolysis by UV and ionizing radiation and the decomposition of ozone in the presence of water vapor.

2.1.1 Natural Occurrence of Hydrogen Peroxide on Earth

Concentrations of H_2O_2 found in the atmosphere vary with the intensity of solar radiation, humidity, and temperature. About twice as much H_2O_2 is formed at 100% relative humidity than at 50% humidity (ambient temperature $298\text{ K} = 25^\circ\text{C}$). During daytime H_2O_2 concentrations range from $0.4\text{--}4\text{ }\mu\text{g}/\text{m}^3$, falling to below $0.01\text{ }\mu\text{g}/\text{m}^3$ at night. H_2O_2 in the atmosphere tends to concentrate into cloud droplets (where concentrations in the liquid can reach $8000\text{ }\mu\text{g}/\text{L}$) and is removed by rain-out. During fog

and severe smog, atmospheric concentrations may rise to $4000\mu\text{g}/\text{m}^3$. Seasonal differences between summer and winter can cause concentrations to vary by a factor of 16. Ice cores taken from glaciers in Greenland or Antarctica show measurable quantities of H_2O_2 down to a depth of 22km, giving us a historical account of hydrogen peroxide prevalence in the atmosphere over several hundred years. Hydrogen peroxide formed in the upper atmosphere may be stabilized and its lifetime extended if it condenses on suspended dust or ice particles.

During the Proterozoic Era, Earth experienced two intervals with one or more episodes of low-latitude glaciation, which are called “Snowball Earth” events [47]. Although the severity of the historical glaciations is debated, theoretical “hard snowball” conditions are associated with the nearly complete shutdown of the hydrological cycle. It has been proposed that, during such long and severe glacial intervals, a weak hydrological cycle coupled with photochemical or radiochemical reactions involving water vapor, liquid, or ice would give rise to the sustained production of hydrogen peroxide, which would then be preserved in the glacial ice, away from sunlight. The photochemical production of hydrogen peroxide was proposed previously as the primary mechanism for oxidizing the surface of Mars. During a Snowball Earth glaciation, hydrogen peroxide could be stored in the ice [48]. Hydrogen peroxide is a good storage medium for oxygen. Upon melting during the next warming period, H_2O_2 would then be released directly into the ocean and the atmosphere, decompose to release molecular oxygen, and could mediate global oxidation events in the aftermath of the Snowball glaciation. Similar conditions may still exist on other planetary bodies or their icy moons.

Hydrogen peroxide plays a key role in atmospheric pollution, where it may combine with nitric acid and acetic acid in the atmosphere or react with suspended aerosols. Peroxynitric acid and peroxyacetic acid are the most irritating contaminants in urban smog.

Heterogeneous reactions of H_2O_2 on aerosols suspended in the air may play an important role in tropospheric chemistry. The heterogeneous reactions of H_2O_2 vapor on SiO_2 and $\alpha\text{-Al}_2\text{O}_3$ particles, two major components of mineral dust aerosol, was studied using transmission-Fourier Transform InfraRed (T-FTIR) spectroscopy and high-performance liquid chromatography (HPLC) [49]. In looking for H_2O_2 sinks in the atmosphere, it was found that H_2O_2 molecularly adsorbs on SiO_2 , and a small amount of molecularly adsorbed H_2O_2 decomposes due to its thermal instability. For $\alpha\text{-Al}_2\text{O}_3$, some decomposition of H_2O_2 evidently occurs, but there is also a small amount of H_2O_2 molecularly adsorbed on the particle surface. Heterogeneous reactions of H_2O_2 on suspended mineral oxide dusts play a significant role in atmospheric chemistry. Similar reactions, but at much higher H_2O_2 concentrations, occur with H_2O_2 on the surface of catalysts in rocket engines.

Surface water H_2O_2 concentration in the North Pacific Ocean varied from less than 10 to more than $250\text{nmol}/\text{L}$ [50]. The net rate of photoproduction in the ocean near Hawaii in full sunlight was determined to be $8\text{nmol}\text{L}^{-1}\text{h}^{-1}$, similar to rates reported

for the central Atlantic Ocean and Antarctic. However, this maximum estimate of photoproduction is also similar to probable rates of H_2O_2 input from other mechanisms (biological production and rain). This concentration of H_2O_2 is too low to economically win hydrogen peroxide from seawater, but its presence affects the oxygen cycle of biota in the ocean.

The concentration of hydrogen peroxide in rainwater over the South and Central Atlantic Ocean varied from 3.5 to $71\text{ }\mu\text{M}$ with an average ($n=25$) and a standard deviation of 26 and $22\text{ }\mu\text{M}$, respectively [51]. These values are similar to previously reported average hydrogen peroxide concentrations in marine rainwater of the Gulf of Mexico ($40\text{ }\mu\text{M}$), the western Atlantic Ocean ($13\text{ }\mu\text{M}$), and Florida Keys ($28\text{ }\mu\text{M}$).

2.1.2 Natural Occurrence of Hydrogen Peroxide on Mars

The presence of extraterrestrial hydrogen peroxide has also been reported on the surface and in the atmosphere of Mars and the Jupiter moon Europa [52]. If the concentrations there are high enough to harvest the materials as a rocket propellant, this would open new methods of in-situ resource utilization (ISRU) for future manned spaceflight to those destinations. The presence of perchlorate in ice on Mars also indicates that the surface chemistry is highly oxidizing, making it more difficult for life forms (as we know them) to thrive.

Direct observations of hydrogen peroxide in the atmosphere of Mars were rare until recently. Ever since the Viking mass spectrometer failed to detect organics on the surface of Mars in 1976, H_2O_2 has been suggested as a possible oxidizer of the Martian surface. However, the search for H_2O_2 on Mars was unsuccessful for three decades. In 2003, H_2O_2 was finally detected using two terrestrial ground-based independent techniques, first with submillimeter heterodyne spectroscopy and then again with thermal infrared imaging spectroscopy. A few available observations and most 1-D model simulations suggested an H_2O_2 column in the range from 10^{15} to 10^{16} molecules/ cm^2 or a mixing ratio in the lower atmosphere of nearly 10–30 ppb.

The 362.156 GHz absorption spectrum of H_2O_2 in the Mars atmosphere was observed in 2003 through the James Clerk Maxwell Telescope submillimeter facility on Mauna Kea, Hawaii [53]. Radiative transfer analysis of this line absorption yielded an average volume mixing ratio of 18 ± 0.4 ppbv within the lower (0–30 km) Mars atmosphere, in general accordance with standard photochemical models

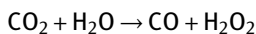
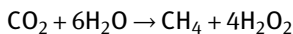
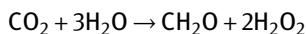
Another estimate of the content of hydrogen peroxide in the atmosphere of Mars used an atmospheric general circulation model with chemistry kinetics [54]. These simulations confirmed the correlation between the amounts of water and hydrogen peroxide and predicted an important role for condensation of H_2O_2 in the polar regions.

Concentrations of H_2O_2 in the Mars atmosphere have been mapped over the seasons using an imaging spectrometer at a large terrestrial astronomical observatory with an infrared telescope. New maps of Martian water vapor and hydrogen perox-

ide distribution were obtained in 2005 using the Texas Echelon Cross Echelle Spectrograph at the NASA Infra-Red Telescope facility at Mauna Kea Observatory [55]. The inferred mean H_2O_2 abundance was 15 ± 10 ppb, which is significantly lower than the 2003 result and lower than expected from photochemical models, taking into account the change in season. Its spatial distribution showed some similarities with the map predicted by models

Submillimeter heterodyne spectroscopy has been used to simultaneously monitor the abundances and spatial distributions of H_2O_2 and H_2O on Mars as a function of the seasonal cycle [56]. A comparison with global climate models showed that the observations favor simulations taking into account heterogeneous chemistry. It has been suggested that large amounts of hydrogen peroxide could be generated by triboelectricity during dust storms or dust devils.

Because many life forms are not resistant to hydrogen peroxide, its presence on extraterrestrial bodies very much limits life forms as we know them. On the other hand, extremophiles have learned to adapt to environmental conditions (acidity, temperature, lack of oxygen) under which other life forms would be quickly eradicated. Extremophiles living in a cold climate (as on Mars) will need an anti-freeze in their water-based blood to thrive. Hydrogen peroxide lowers the freezing point of water. It has been speculated that extremophiles might even adapt to an oxidizing environment and use low-freezing $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ liquids as their biological fluid and source of oxygen [57, 58]. That might even explain some of the Viking Lander 1976 biology experiment results. Possible overall metabolic pathways are:



The source of energy for these reactions to take place might be electric discharges in the dust devils that have been seen swirling across the Mars scape. The presence of H_2O_2 in the polar caps of Mars (along with the prevalence of ozone in the atmosphere) might even have implications for future extraterrestrial in-situ resource utilization by concentrating the H_2O_2 from the polar ice and using it as a rocket propellant or as a source of breathing oxygen for the astronauts. H_2O_2 may also be chemisorbed or included in the sphere of hydration of minerals on the surface of Mars, one explanation for the oxygen evolution observed during the Viking experiments when water was added to Martian soil. However, the Mars Phoenix Lander did not identify H_2O_2 (but it found ClO_4^-) [58].

2.1.3 Natural Occurrence of Hydrogen Peroxide in Icy Moons

Many of the moons revolving around the big planets Jupiter and Saturn are worlds of ice, some even with geysers spouting ice crystals. It has been speculated that it would

be difficult for life as we know it to exist on Europa because the ice is rich in hydrogen peroxide from being bombarded by cosmic radiation and immersed in a cloud of ions from Jupiter's radiation belt.

Ice samples at 16 and 77 K were irradiated with 30 keV singly charged H, C, N, O, and Ar ions. By measuring the absorption of the hydrogen peroxide band by *in-situ* infrared spectroscopy between 3.50 and 3.52 μm (2860 and 2844 cm^{-1}), it was found that H_2O_2 is produced at the two different temperatures by all the different ions tested [59]. This result showed that H_2O_2 may be produced by radiolysis of water ice on the surface of the satellite Europa. The amount of H_2O_2 produced by N and Ar implantation did not vary significantly with temperature but notably for H and especially for O more H_2O_2 was produced at 77 K than at 16 K.

Spatially resolved IR and UV wavelength spectra of Europa's leading, anti-Jovian quadrant observed from the Galileo spacecraft showed absorption features resulting from hydrogen peroxide [60]. Comparisons with laboratory measurements indicated surface hydrogen peroxide concentrations of about 0.13%, by number of mols, relative to water ice, the matrix for frozen H_2O_2 . The inferred abundance was consistent with radiolytic production of hydrogen peroxide by intense energetic particle bombardment and demonstrated that Europa's surface chemistry is dominated by radiolysis.

Radiolysis and photolysis are the chemistry that follows the bond breaking and ionization produced by incident radiation, producing H_2O_2 , $\cdot\text{OH}$, O_2 , and a little H_2 from irradiated H_2O ice [61]. Sputtering is the ejection of molecules by incident radiation. Both processes are particularly effective on ices in the outer solar system, which may be transported from one planetary body to another.

Would it not be nice to land on one of these bodies and find a polar cap of frozen H_2O_2 , ready to be scooped up and used as propellant for the return trip? Further ISRU studies will try to answer that question.

2.1.4 Natural Occurrence of Hydrogen Peroxide in Interstellar Space

Hydrogen peroxide formed in interstellar space may be stabilized if it condenses on interstellar dust or ice particles [62].

Hydrometeorites, rarely found clumps of cometary and primordial ice that survive the plunge through the Earth's atmosphere, probably contain hydrogen peroxide from the long exposure to cosmic radiation, but once they arrive on Earth they are rarely preserved long enough to be analyzed and most often melt before someone has a chance to put them into a freezer compartment and preserve them for later analysis.

2.2 Other Sources of Hydrogen Peroxide

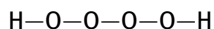
A potential source of H_2O_2 for human consumption is from drinking water that has been sterilized with ozone and UV radiation. The authorized residual concentration of H_2O_2 in potable water is 0.1 mg/L in the USSR and Germany and 0.5 mg/L in France.

In addition to its applications in rockets and the chemical industry, hydrogen peroxide is a major reactive oxygen species in living organisms. Its overproduction in cellular mitochondria is implicated in the development of many severe diseases such as cancers and neurodegenerative Parkinson's and Alzheimer's diseases. It would, therefore, be very useful if one could visualize the H_2O_2 spatial distribution and concentrations in living cells by a yet to be developed imaging technique.

Traces of H_2O_2 form due to recombination of hydroxyl-free radicals in an oxygen/hydrogen torch if the hot flame is impinging on a block of ice, quenching the reaction products (Section 2.5.1.)

2.3 The Postulated Existence of Other Oxides of Hydrogen: Hydrogen Polyoxides

It would be nice to stabilize some hydrogen polyoxides and use them as rocket propellants. These would be energetic, clean oxidizers with a higher oxygen content and even more powerful than hydrogen peroxide. Stabilization may be possible by trapping them in a matrix of solid oxygen or suspending them as a slush in liquid oxygen. In connection with the simplest peroxide, $\text{H}-\text{O}-\text{O}-\text{H}$, we also want to mention efforts to synthesize peroxy compounds with two or three $\text{O}-\text{O}$ bonds in the molecule, such as hydrogen tetraoxide, H_2O_4 , CAS RN [29683-94-1], also called hydrogen tetroxide or hydrogen superoxide, with a postulated structure of



In addition to linear superoxide molecules, branched or ring structures with four or more $\text{O}-\text{O}$ bonds have been theorized. It was attempted to synthesize superoxide compounds by reaction of atomic hydrogen with H_2O_2 vapor or liquid ozone and quenching the reaction products by flash-freezing them. A group of Russian authors started reporting work on H_2O_4 in 1956 and claimed to have isolated H_2O_4 in products of a glow discharge in water and by reaction of atomic hydrogen with ozone [63–68]. The glow discharge in water is said to have produced 15% H_2O_4 , and the ozone/hydrogen reaction is said to have produced a 60% H_2O_4 concentration, but that could not be confirmed. However, the material was stable only at very low temperatures (83 K = -190°C), and for a long time it was not certain if this is a compound or a trapped collection of $\text{HOO}^\bullet$ free radicals in a matrix of other products [69].

The magnetic properties of peroxide-radical condensates synthesized from dissociated water vapor and also obtained from the reaction of atomic hydrogen and liquid 100% ozone in the temperature range 123 to 293 K (-150 to 20°C) showed that before

the start of decomposition (below 163 K = -110 °C), the peroxide-radical condensates were weakly diamagnetic with a susceptibility of -0.1×10^{-6} to -0.2×10^{-6} CGSM [70]. With increased temperature there was increased paramagnetism, associated with the appearance of oxygen released on the decomposition of the peroxide radical condensate. The data indicated that the molecular oxygen released on decomposition of the peroxide-radical condensates does not appear in the condensates in the adsorbed or occluded form, but forms as a result of the decomposition of the unstable compound H_2O_4 , a higher peroxide of hydrogen which has linear structure: $\text{H}-\text{O}-\text{O}-\text{O}-\text{O}-\text{H}$.

It was attempted to prepare higher oxides of hydrogen by electrolysis and UV irradiation of dilute hydrogen peroxide solutions, but this did not produce any higher peroxides [71]. The reactions of hydrogen atoms with ozone at 77 K = -196 °C gave compounds behaving like superoxides, presumably $\text{HOO}^\bullet$ and H_2O_4 . These species decomposed at 153 and 183 K (-120 and -90 °C), respectively, to give molecular O and H_2O_2 . The heat of formation is $+54 \pm 41$ kJ/mol ($+13 \pm 10$ kcal/mol) for HO_2 and -8.3 ± 41 kJ/mol (-2 ± 10 kcal/mol for H_2O_4). The products obtained from H_2O and H_2O_2 in a discharge tube and by the reaction of H atoms with O were compared to the peroxides formed in the hydrogen atom/ozone reaction.

The infrared absorption of products from electrically dissociated H_2O or D_2O vapor and other hydrogen-oxygen systems trapped at liquid nitrogen temperature was measured between 4000 and 300 cm^{-1} in search of higher polyoxides like H_2O_3 or H_2O_4 [72]. Four new absorption bands were found in the deuterated systems at 857, 820, 760, and about 440 cm^{-1} . By isotopic substitution of ^{18}O the frequencies were shifted to 806, 775, 717, and $\sim 420\text{ cm}^{-1}$ as was expected for O—O vibrations. In the hydrogen systems, this region was obscured by the strong libration bands of H_2O and H_2O_2 molecules. Temperature and composition effects showed that more than one new species was involved. Accordingly, the new spectra were assigned to the often postulated polyoxides, H_2O_3 or H_2O_4 , stabilized in the water-peroxide matrix. The more abundant, and also more stable, H_2O_3 has a half-life of some 5 h at 208 K (-65 °C). The observed frequencies were consistent with zigzag chain structures linked by single covalent bonds as already observed in the more stable hydrogen polysulfides. Relative concentrations of the polyoxides were estimated at 5 to 10 mol-%, depending on the composition of the starting material. It remains to be seen whether these compounds can be stabilized and used as rocket propellants.

The kinetics of oxygen evolution on warming the trapped products (at 77 K = -196 °C) from water H_2O or H_2O_2 vapor dissociated in a glow discharge were studied by a manometric method [73]. Under closely controlled conditions it was possible to clearly distinguish the onset of decomposition of the two intermediates, H_2O_3 and H_2O_4 . The latter begins to decompose measurably following crystallization of the glassy solid at about 158 K (-115 °C), and the H_2O_3 decomposes readily between 223 and 238 K (-50 and -35 °C). It has been suspected that the gas evolution at that stage is mainly a physical desorption process and not the decomposition of a chemical compound. Typically, the yields of H_2O_3 from dissociated H_2O vapor were of the

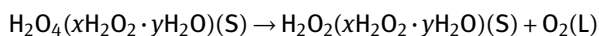
order of 3–5 mol-%, but those of H_2O_4 were only about one-tenth as much. It was attempted to optimize the yield by varying the distance between the microwave discharge and the cold trap. Only a small fraction of the peroxide is formed via the H_2O_4 intermediate in these systems. More of the higher oxides were obtained from dissociated H_2O_2 than from H_2O vapor. The deuterated systems showed some unusual isotope effects. The yields of D_2O_3 were always higher (up to twice and even more) than those of H_2O_3 under similar conditions. The deuterium polyoxides decomposed at slightly higher temperatures (10–15°) than their hydrogen analogs.

Peroxy-radical condensate (PRC) is a yellowish glassy substance that is formed during the condensation of H_2O and H_2O_2 vapors dissociated in an electrical discharge, mixtures of $\text{H}_2 + \text{O}_2$, as well as the products of the reactions $\text{H} + \text{O}_3$ (liq), $\text{H} + \text{O}_3$ (gas) or $\text{H} + \text{O}_2$ (gas) on a cold (77 K) surface [74]. The yield of $\text{HO}_2^\bullet$ and H_2O_4 in a glow discharge of hydrogen-oxygen mixtures depends on many operating variables, including pressure [75], temperature [76], or the type of reactor vessel wall materials [77]. The peroxy-radical condensate has been analyzed by many methods, including IR spectroscopy [78], Raman spectroscopy [79], X-ray diffraction (XRD) [80], electron-proton resonance spectroscopy (EPR) [81], and other methods [82, 83].

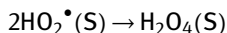
X-ray studies of the products of the reaction of atomic hydrogen and liquid ozone have shown that the hydrogen atom-ozone product as formed does not contain hydrogen peroxide [80]. Upon warming to 195 K (–78 °C) some hydrogen peroxide is produced. The higher polyoxide product is not a well-defined crystalline compound and its presence could only be hinted by a halo at about 3.4 Å.

The kinetics of low-temperature reactions leading to the accumulation of $\text{HO}_2^\bullet$ [84] and formation of H_2O_4 by recombination of $\text{HO}_2^\bullet$ radicals [85] or premature dissociation of H_2O_4 need to be better understood before one can optimize the synthesis methods and before one can decide if this work is strictly to satisfy academic interest or if it ever will find a practical application [86, 87]. Instead of analyzing the PRC in search of H_2O_3 and H_2O_4 immediately after it has condensed, it has been common practice to allow the condensate to sit at an intermediate temperature where the $\text{HO}_2^\bullet$ radicals have enough mobility to recombine. The rate of recombination of $\text{HO}_2^\bullet$ radicals during the annealing period depends on their mobility and ability to diffuse through the matrix to find each other [88].

It was shown that at 138 K (–135 °C) the $\text{HO}_2^\bullet$ radicals disappear rapidly. Samples were annealed at 138 K (–135 °C) for over 0.5 h prior to recooling to 77 K (–196 °C). Peroxy-radical condensate (PRC) samples prepared by two different methods were then allowed to decompose in a calorimeter [89]. The heat of decomposition at 77 K (–196 °C) of the PRC superoxide made from dissociated water in a glow discharge was $-74.5 \pm 9.2 \text{ kJ/mol} = -17.8 \pm 2.2 \text{ kcal/mol}$ and the heat of decomposition of the PRC superoxide made from $\text{O}_3 - \text{H}^\bullet$ atom reactions was $-112.1 \pm 10.9 \text{ kJ/mol} = -26.8 \pm 2.6 \text{ kcal/mol}$. Using the value of $-74.5 \pm 9.2 \text{ kJ/mol} = -17.8 \pm 2.2 \text{ kcal/mol}$ for the reaction



at 77 K (−196 °C), the heat of formation of H_2O_4 (S) is $-116.7 \text{ kJ/mol} = -27.9 \text{ kcal/mol}$. The recombination of $\text{HO}_2^\bullet$ radicals will lead to the formation of H_2O_4 . Using literature data for the heat of formation of gaseous $\text{HO}_2^\bullet$ radicals ($+20.9 \text{ kJ/mol} = +5 \text{ kcal/mol}$) and assuming this radical has the same thermal properties as hydrogen peroxide, the heat of reaction at 77 K (−196 °C) of the equation



is $-16.7 \text{ kJ/mol} = -4 \text{ kcal/mol H}_2\text{O}_4$.

The most remarkable property of PRC is its decomposition during heating above 150 K with the release of dioxygen and the formation of a concentrated hydrogen peroxide solution. It is assumed that this is caused by the presence of considerable amounts of higher peroxides H_2O_3 and H_2O_4 in PRC. One of the methods for the synthesis of peroxy-radical condensates is the condensation at liquid nitrogen temperature of an $\text{H}_2 + \text{O}_2$ mixture dissociated in an electrical discharge at low pressure. Peroxy-radical condensates were shown to contain substantial quantities of higher hydrogen peroxides H_2O_3 and H_2O_4 . A study of the influence of experimental parameters on the synthesis of peroxy-radical condensates from an $\text{H}_2 + \text{O}_2$ mixture resulted in recommendations for the optimal experimental conditions for the synthesis in a U-tube electrical discharge reactor with an inner diameter of ~15 mm, immersed in liquid nitrogen, at rather low pressure ($66\text{--}132 \text{ Pa} = 0.5\text{--}1 \text{ Torr}$) [90]. The maximum conversion of initial O_2 into higher hydrogen peroxides was observed at a composition of initial gas mixture of 66.7% $\text{H}_2 + 33.3\% \text{ O}_2$.

It would be difficult to stabilize $\text{HO}_2^\bullet$, H_2O_3 , or H_2O_4 [91]. The best method to preserve these compounds for further investigation is to keep them very cold [92].

Theory predicts that hydrogen trioxide H_2O_3 can occur in two rotational isomers: *cis*-HOOOH and *trans*-HOOOH. A theoretical study of the electronic spectra and molecular structure was able to predict equilibrium geometries of *cis*-HOOOH and *trans*-HOOOH using a density functional theory (DFT) method, a complete active space self-consistent-field method and a coupled cluster with single and double replacement method [93]. The harmonic vibrational frequencies on the optimized geometries were calculated using the DFT method. The potential energy curve of the isomerization between the *trans*-HOOOH and *cis*-HOOOH was obtained by DFT calculations. Computed results showed that the *trans*-isomer should be more stable than the *cis* isomer. There are two possible pathways for the conversion between the *trans*-HOOOH and *cis*-HOOOH.

The structures of polyoxides HOOH, HOOOH, HOOOOH, and HOOO were investigated by computational chemistry employing the CCSD(T) methodology and the correlation consistent basis sets [94]. H_2O_3 and H_2O_4 would make good rocket propellants, if one could stabilize them. For all molecules, fundamental vibrational frequencies, structural parameters, rotational constants, and rotation-vibration corrections were calculated. For HOOOH, a good agreement between calculated results and microwave and IR spectra measurements was achieved, although for the symmetric O—O

stretch some important differences were found. Heats of formation were computed using atomization energies: $\Delta H^\circ_{f,298}(\text{HOOOH}) = -89.9 \text{ kJ/mol}$ (-21.50 kcal/mol) and $\Delta H^\circ_{f,298}(\text{HOOOOH}) = -44.39 \text{ kJ/mol}$ (-10.61 kcal/mol). The $\Delta H^\circ_{f,298}(\text{HOOO})$ was $+23.0 \text{ kJ/mol}$ (5.5 kcal/mol).

Hydrogen tetroxide H_2O_4 and hydrogen trioxide H_2O_3 have been prepared and characterized as components of peroxy radical condensates. The polyoxides were characterized by the Raman spectra of the oxygen framework [79]. Lines at 500, 756, and 878 cm^{-1} correspond to skeletal oscillations of H_2O_3 in the condensate (OOO bend, asymmetric OO stretch, symmetric OO stretch). Lines at 449, 589, 624, 827, and 865 cm^{-1} match the skeletal vibrations of H_2O_4 (OOO bend 1, OOO bend 2, center OO stretch, asymmetric OO stretch, symmetric OO stretch). The line of the O_4 torsion vibration of hydrogen tetroxide was not observed experimentally. For the first time, convincing evidence was now provided for the existence of hydrogen tetroxide (in low-temperature solids).

Hydrogen trioxide, HOOOH , H_2O_3 , CAS RN [14699-99-1], has been prepared by reduction of ozone, decomposition of hydrotrioxides (ROOOH), and by reaction of hydrogen peroxide with ozone and has been identified by infrared (IR), ^1H , and ^{17}O nuclear magnetic resonance (NMR) spectra, and a substantial amount of information on this molecule has been gathered in the meantime [95]. It may even occur naturally; it is just very hard to find at the very low concentrations.

The composition of low-temperature condensates obtained by the reaction of hydrogen atoms with liquid ozone has been determined from the Raman spectra and data of the molar ratio of O_2 to H_2O_2 in the decomposition products [96]. The main constituents are hydrogen tetraoxide H_2O_4 , hydrogen trioxide H_2O_3 , and hydrogen peroxide H_2O_2 in comparable amounts and also some water H_2O . H_2O_4 , H_2O_3 , and H_2O_2 are formed in the diffusion-controlled reactions between OH and HO_2 in the liquid ozone layer and stabilized by transfer to the solid phase. $\cdot\text{OH}$ and $\cdot\text{O}_2\text{H}$ radicals are generated via a sequence of the reactions initiated by the interaction $\text{H} + \text{O}_3(\text{L})$.

2.4 Industrial Production of Hydrogen Peroxide

Before starting to use hydrogen peroxide as a rocket propellant, it helps to know by which process the chemical was produced. Contaminants that are carried over from the reactants during H_2O_2 production may cause problems during its use as a rocket propellant. The types of contaminants differ depending on the process used for the production of H_2O_2 . Military specifications for propellant-grade hydrogen peroxide had to be modified each time a different H_2O_2 production process was brought online. The adverse effects of contaminants depend on the application of hydrogen peroxide, if it is to be used as an oxidizer in a bipropellant engine or as a monopropellant. If hydrogen peroxide is to be used as a monopropellant, the specifications would be more restrictive than if it was to be used as an oxidizer in a bipropellant or hybrid rocket

propulsion system. Stabilizers act as contaminants and may poison catalysts. There are many possible methods for production of hydrogen peroxide:

- production from peroxy compounds
- production from hydrogen and oxygen
- production from carbon monoxide, oxygen, and water
- electrochemical processes
 - Degussa-Weissenstein Process
 - Münchner process
 - production by cathodic reduction of oxygen
- production by autoxidation of organic compounds
 - 2-propanol autoxidation (Shell Process)
 - anthraquinone derivative autoxidation

Of the three main methods that were historically used (in the chronological sequence listed below) for the industrial production of hydrogen peroxide:

- acidification of earth alkaline metal or alkali metal peroxides
- electrolysis of sulfuric acid or ammonium sulfate at high current densities
- oxidation and reduction of anthraquinone derivatives

only the latter method is still in use. The other two methods have been historically important but have long since been replaced due to different economics and concern about disposal of byproducts. Another method for production of H_2O_2 is the cumyl-hydroperoxide method (Hock-process). This process produces acetone and phenol as the main products.

The electrochemical production avoids the use of organics and has the capability of producing a high purity product free of organics contaminants. It is (was) attractive for locations where electric power is (was) cheap. The electrochemical method can also be used for *in-situ* production of H_2O_2 in dilute aqueous solutions for sterilization or wastewater treatment, also in remote locations. All three methods result in dilute aqueous solutions of H_2O_2 , which must subsequently be dehydrated to more economical concentrations for storage and transport. For safety reasons, the concentration process rarely goes beyond 90% H_2O_2 . All concentration steps require pure starting materials and extremely clean process equipment to prevent accidents during processing and lack of storage stability in the shipped product. For use as a laboratory chemical and chemical reagent, a 30% H_2O_2 solution is the most practical concentration and is readily available from most chemical supply companies. Food-grade H_2O_2 is often sold as a 35% solution.

2.4.1 History of the Industrial Production of Hydrogen Peroxide

The interest in hydrogen peroxide as a rocket propellant has fluctuated through periods of high and low interest. In the 1990s, in the wake of increasing concern about

the handling hazards of hypergolic storable bipropellants and monopropellant hydrazine, as part of the search for “green” (i.e., environmentally friendly) rocket propellants, hydrogen peroxide experienced a “renaissance” and several chemical companies embarked on establishing or expanding existing production facilities for HTP.

It helps to get a better understanding of the current situation with hydrogen peroxide if one spends a little time studying the history of hydrogen peroxide production. If the demand for HTP in the US does not increase as predicted by some green propellant supporters, some of the HTP production sites may shut down again.

As of 1961–1966, there were three producers of HTP in the US, and each was using a different process. FMC Corporation was producing HTP by electrolysis of persulfuric acid; E.I. DuPont de Nemours & Company was producing HTP by a modified anthraquinone process, and Shell Chemical Company was producing HTP by high pressure oxidation of isopropyl alcohol. The DuPont and Shell products were usually referred to as “organic” process peroxides. Producers using the electrolytic process claimed that peroxide manufactured by organic processes is inferior in its performance. The significant analytical difference between the various peroxides pertains to the carbon content. All three processes satisfied the military specification (MIL-P-1600SE) requirement of a maximum of 200 ppm carbon. FMC peroxide has a carbon content of approximately 6 ppm, DuPont peroxide approximately 15 ppm, and Shell peroxide approximately 175 ppm. It should be noted, in regard to this variation of carbon content, that no catalyst degradation has been reported to date that could be blamed on carbon contamination.

2.4.2 Electrochemical Processes

The formation of hydrogen peroxide via the electrolysis of aqueous sulfuric acid was discovered in the middle of the nineteenth century. During this electrolysis, peroxodisulfuric acid that forms first is subsequently hydrolyzed by water to give sulfuric acid and hydrogen peroxide via the peroxomonosulfuric acid (Caro’s acid) intermediate. After the change to ammonium sulfate as the starting material, the production of H_2O_2 increased steadily. Until the mid-1950s, around 80% of the H_2O_2 produced globally was made by this route. All electrochemical processes lost their competitiveness after the introduction of the AO process because of their high energy (electric and thermal) costs. Only in places with low energy costs, such as some states from the former Soviet Bloc, did the electrochemical route continue to be used for a few more years.

2.4.2.1 History of Degussa Hydrogen Peroxide Production

As of 1998, Degussa had 87% H_2O_2 available from its production and concentration plant in Rheinfelden, Germany. The capacity of this plant was sufficient to satisfy European demand and even to export some of the product to the US. Degussa was also evaluating the need to produce a more concentrated 90% HTP [97–100]. This production capability, which began as a small semi-batch process carried out in glass-

lined reactors, eventually reached a fully functional level with the startup in 1987 of a vacuum distillation unit exclusively dedicated to the production of HTP.

In 2006, RAG Foundation acquired Degussa AG, which was later renamed Evonik-Degussa GmbH. As of 2008, Degussa Propulse™ was distributed in the US by a new company called *Evonik Industries*. Evonik Industries is an industrial corporation in Germany owned by the RAG Foundation and one of the world's leading specialty chemicals companies. It was created in 2007 as a result of restructuring of the mining and technology group RAG. Evonik Industries united the business areas of chemicals and energy of RAG. As of 2021, Evonik offered three high-concentration hydrogen peroxide products: Propulse™ 825 HTP, Propulse™ 875 HTP, and Propulse™ 980 HTP high-test hydrogen peroxide [101].

In October 2011, a Russian Soyuz-ST carrier rocket launched its first satellite from the Kourou Space Center in French Guiana. The primary propulsion propellant pump was powered by a steam generator for the first time fed with Propulse™ made in Germany.

2.4.3 Organic Chemical Processes

The autoxidation of hydroquinones was the first continuous industrial process for producing hydrogen peroxide but was ultimately replaced in the late 1930s by the Riedel-Pfleiderer or BASF process, which uses alkylated anthraquinones [97]. In 1953, Du Pont of Memphis, Tennessee, commissioned the first hydrogen peroxide production plant in the US based on the AO process. In 1962, Degussa started the first industrial-scale plant using the AO process [102]. In current practice, the auto-oxidation process uses an alkylated anthraquinone (such as 2-alkyl-9,10-anthraquinone or 2-ethyl-9,10-anthraquinone), which first is reduced with hydrogen in the presence of a catalyst to form the corresponding hydroanthraquinone. This hydroquinone is then air-oxidized to yield hydrogen peroxide and 2-alkyl anthraquinone, which is returned to the loop (leaving a trace of organics behind in the H₂O₂ product, which must be removed if it interferes with the intended application). The autoxidation process is carried out in an inert, organic medium. The working solution is typically a proprietary solvent blend chosen for its ability to solubilize both quinones (which dissolve well in non-polar aromatics) and hydroquinones (which dissolve well in polar solvents). Inert, non-volatile solvents used are diisobutylcarbinol and methyl naphthalene, and traces of these may be found in the products. The working solution must be non-toxic and chemically stable in both strongly hydrogenating and oxidative reaction environments. Crude hydrogen peroxide is then extracted with water, and the anthraquinone is recycled back to the hydrogenator for reuse. The aqueous hydrogen peroxide from the extractor has a concentration of only 15–30% H₂O₂ and is contaminated with dissolved organic matter that is formed by the chemical degradation of the working compound (anthraquinone) and the working solution. These organic impurities must be removed by a variety of purification methods, and the peroxide is then sent to a concentration

unit where it is distilled up to active levels of 50–70% H_2O_2 . At this point in the process, the peroxide is treated with chemical stabilizers (typically sodium pyrophosphate and sodium stannate at levels between 0.01 and 0.25%, depending on the grade and intended application) and then transferred into bulk storage tanks. To bring the product up to concentration levels above 70% involves where it begins to be of interest as a rocket propellant, a second distillation process in which additional water is removed. Since pure hydrogen peroxide has a boiling point of 423 K (150 °C), and the favorable fact that water and H_2O_2 do not form an azeotrope (unlike water and hydrazine), vacuum distillation is a viable process that can be used to produce HTP from a 70% starting material. However, there are three important factors that make this distillation process one that requires a high level of technical sophistication in order to be carried out in a safe and efficient manner:

- The non-volatile impurities (e.g., heavy metals) in the product are concentrated as well.
- The H_2O_2 decomposition rate increases about 2.3 times for each 10 °C rise in temperature.
- H_2O_2 vapors above certain concentration limits will decompose explosively, even at ambient temperatures.

2.4.3.1 History of BASF Hydrogen Peroxide Production in Germany

Between 1935 and 1945 BASF developed the anthraquinone process in a pilot plant with a monthly production of 30 metric tons. Two large plants were then constructed at Heidebreck and Waldenberg, each having an annual capacity of 2000 metric tons to support the war effort. Both plants were partially complete when construction was halted at the end of World War II. In 1953, E. I. DuPont de Nemours commissioned the first hydrogen peroxide plant using the AO process in the US, and subsequently the production capacity of hydrogen peroxide was greatly increased every year. In 1996, world capacity stood at 1.3×10^6 metric tons (reported as 100% hydrogen peroxide).

2.4.3.2 History of Solvay Hydrogen Peroxide Production

As of 1998, the Solvay Interlox group of companies was the world's largest producer of hydrogen peroxide with a 24% capacity share of the world market and 18 manufacturing sites that focused exclusively on hydrogen peroxide and its derivatives [103]. As of 2012, Solvay Interlox, Inc. was 100% owned by Solvay America, Inc. which was, in turn, 100% owned by Solvay S.A., a chemical and pharmaceutical company with operations in 41 countries, employing more than 35000 people and headquartered in Brussels, Belgium. The origins of the current group of companies, however, date back to the initially independent operations of Solvay (Belgium) and of Laporte, a UK-based chemical company. The latter company actually began production of hydrogen peroxide more than 100 years ago. In 1970, Laporte and Solvay formed a worldwide joint venture in peroxygen chemicals by the creation of

the Interlox group of companies. In 1992, Solvay acquired a 100% interest in the H_2O_2 activities of Interlox, leaving Laporte to focus on some of the more highly specialized peroxygen compounds, such as organic peroxides.

As of 1998, HTP was still produced in Germany. Solvay Interlox had one of its two HTP producing facilities located near Munich, and this site has produced up to 86% H_2O_2 for many years, primarily for captive use in the manufacture of organic chemicals. The other facility is located in Warrington, England and is a former Laporte site.

Laporte first began production of hydrogen peroxide in the late 1800s using a barium peroxide process to generate solutions of 3% H_2O_2 . This was later replaced with an electrolytic process that provided 35% H_2O_2 , some of which was concentrated via distillation to produce 85% HTP. As new production capacity was added to the growing business, a switch to the autoxidation or AO process was made. Today, all major producers of H_2O_2 utilize AO process chemistry in their plants. Organics employed industrially include 2-*tert*-amylanthraquinone, 2-*iso-sec*-amylanthraquinone, and 2-ethylanthraquinone. Laporte built its first AO process plant at Warrington in 1958, and it was this plant that supplied all of the 85% HTP for the British rocket development programs, including the Black Knight rocket. Initially, the process used a mixture of benzene and secondary alcohols as process solvent. Later, they used cyclohexyl acetate or a mixture of dimethyl phthalate and xylene or trimethylbenzene as the process solvent. As of 1998, 40 years later, production of HTP at the Warrington site continued, primarily for on-site captive use in the production of chemical intermediates.

During the 1990s, only limited drum quantities of 85% HTP were provided by Solvay Interlox to aerospace and defense-related companies for propulsion applications. During this period, the demand for HTP in the US was, in practice, very small, which explains the hesitation to step up commercial HTP production in the US. Historically, in the long, distant past when the Mercury project was the first manned US space program, US demand was more significant, and both the Shell Chemical Company and the FMC Corporation were producers of 90% H_2O_2 at that time, the latter company also producing some 98% H_2O_2 for a short period of time. Shell's hydrogen peroxide business was ultimately acquired by Interlox, and FMC ceased its production of HTP in the early to mid-1980s.

A new, so-called "high-productivity/high-yield" process, based on a mixture of isomers of 2-amyl anthraquinone, has been developed by Solvay. In 2008, Solvay announced the construction of a "mega-scale" single-train plant in Zandvliet (Belgium). The plant has an annual production capacity more than twice that of the world's next-largest single-train plant. An even larger plant was commissioned in 2011 by a joint venture of Solvay and Dow in Map Ta Phut (Thailand). This plant has a projected production capacity of 330000 tons of hydrogen peroxide per year (number based on 100% H_2O_2 concentration) [104].

2.4.3.3 History of Shell Hydrogen Peroxide Process with 2-Propanol

Another autoxidation process, based on the oxidation of 2-propanol (IPA), was developed by Shell Chemicals. The process was employed by Shell in its 15000 metric tons per annum facility at Norco, Louisiana, between 1957 and 1980. The oxidation of 2-propanol in the liquid phase with oxygen does not require a special catalyst, because it is catalyzed by a small amount of hydrogen peroxide, which is added to the feed stream as a seed in order to shorten the induction phase. The acetone coproduct can either be sold or hydrogenated back to isopropyl alcohol for recycling. Several plants operating on this process were built in the former Soviet Union, which have been operating since 1968 and 1972. Regarding the use of IPA in this process, one must remember that efforts to recycle IPA that was used as an industrial cleaning solvent by redistilling it risk explosions caused by accumulation of organic peroxides in the distillation residue. Solvent grade IPA contains a substantial amount of acetone, one of the autoxidation products. Acetone and hydrogen peroxide also react to form an explosive substance that can crystallize on the walls of cold parts of the equipment.

A similar liquid phase oxidation process of isopropyl alcohol with molecular oxygen has been used in the USSR (Russia) for quite some time, even after the US chemical industry quit using it [105]. Russia is the main user of hydrogen peroxide as a monopropellant in its Soyuz crewed space capsules and as a gas generant to drive the propellant pumps in the Soyuz launch vehicle. The method of hydrogen peroxide production by isopropyl alcohol autoxidation is more environmentally friendly than the anthraquinone method. The only waste products are non-toxic gases and acetone, which can be hydrogenated back to isopropyl alcohol. This method is widely used in Russia for the hydrogen peroxide that is concentrated to become a rocket propellant. Mixtures of air and isopropyl alcohol or hydrogen peroxide and isopropyl alcohol encountered during this process are more explosive than anthraquinone autoxidation intermediates [106]. The product of the isopropyl alcohol autoxidation production method is a 30–40% hydrogen peroxide solution that needs to be further concentrated to make rocket-grade hydrogen peroxide (RGHP). This aqueous solution still contains impurities such as acetic acid, acetone, isopropyl alcohol, acetone peroxide, and heavy metal ions. Organic impurities contents in the product are limited by Russian specifications to 0.55–0.7 mass-%, containing 0.2–0.3 g/dm³ of isopropanol, 6–8 g/dm³ of acetone, and 6–8 g/dm³ acetic acid [107–109].

2.4.3.4 History of Lyondell Hydrogen Peroxide Production

Another version of the oxidation of a secondary alcohol to hydrogen peroxide and a ketone is the process developed by Lyondell (ARCO) Chemical, using methylbenzyl alcohol as a hydrogen carrier. This material is an intermediate in a propylene oxide/styrene process. The oxidation coproduct, acetophenone, is hydrogenated back to methylbenzyl alcohol in a step that is a part of the Lyondell styrene technology.

In December 2007, the Lyondell Chemical Company and Basell completed their merger to create LyondellBasell, one of the world's largest polymers, chemicals, and

fuels companies. They make propylene oxide and mono-, di-, and tripropylene glycol by a peroxide process. Instead of isolating hydrogen peroxide from a direct synthesis from the elements catalytic process, the hydrogen peroxide is used in situ to oxidize propylene to propylene oxide in a reactor with a suspension of a catalyst slurry fed with a mixture of propylene, hydrogen, and oxygen (US Patents 6710194, 6500311, and 7501532).

Different trade names have been registered by H_2O_2 manufacturers and distributors, such as

- Oxypure™ by FMC
- Perhydrol® by Merck
- Hyprox™ by Arkema
- Propulse™ by Evonik (former Degussa)
- Interlox® by Solvay

It may be of interest to look at the historical evolution of installed production capacity for hydrogen peroxide. This rapid growth was caused mostly by the realization that the use of chlorine and (to a lesser extent) chlorine dioxide in the paper and pulp industry would leave undesirable byproducts in chlorine-bleached paper and caused many persistent pollutants (dioxin, PCB) to be discharged with the wastewater. In many of these applications, chlorine has been replaced by hydrogen peroxide. To a lesser extent, hydrogen peroxide also competes with chlorine in the use of chlorine and hypochlorite as a disinfectant in water treatment.

The electrolysis process generates hydrogen gas as a byproduct that would have to be flared off or collected for other uses. It is possible to combine the electrolytic and chemical production of hydrogen peroxide by the anthraquinone reduction/oxidation route at the same locale. The hydrogen would then be used for reduction of anthraquinone.

A more recent process is the direct synthesis of hydrogen peroxide from the elements on a nanocatalyst.

2.4.3.5 History of FMC/Becco Hydrogen Peroxide Production

In 1958, FMC formed joint ventures in Japan and Brazil to manufacture hydrogen peroxide. In 1978, FMC became the world's second largest producer of hydrogen peroxide. In 1990, FMC opened a new hydrogen peroxide plant in Prince George, British Columbia, to serve western Canada. In 1994, FMC built a hydrogen peroxide plant in Delfzijl, The Netherlands.

In 2010, FMC announced realignment of hydrogen peroxide manufacturing operations at Bayport, Texas. The key elements of the improvements at the Bayport site included upgrades to increase production of high-purity grades of hydrogen peroxide in support of growing specialty applications, especially those with ultra-pure quality requirements and mothballing of certain unit operations effectively reducing the overall capacity of standard grade hydrogen peroxide by approximately 90 million pounds

per year, driven by significantly reduced demand from the pulp and paper industry, historically a large volume consumer of hydrogen peroxide. As of 2012, FMC still offers hydrogen peroxide solutions in concentrations ranging from 3 to 90% HTP [110].

2.4.3.6 Summary of Hydrogen Peroxide Production in the US

There are essentially six major producers in the United States that produce H_2O_2 . DuPont has withdrawn from the hydrogen peroxide production. In 1998, the Memphis, TX, plant was sold to Elf Atochem, the Canada (Gibbons, Alberta) and New Zealand plants were sold to Degussa, and the Maitland (Canada, Ontario) plant was sold to Evonik.

2.4.3.7 Summary of Hydrogen Peroxide Production Outside the US

High-purity hydrogen peroxide in concentrations usually not exceeding 70% is produced in many other countries, including mainland China [111]. While actively gearing up to significantly expand domestic hydrogen peroxide production, China is cautiously observing capacity developments in other countries [112, 113].

As of 2011, one of the largest international hydrogen peroxide producers, Evonik, had an annual production capacity of approximately 600000 tons of hydrogen peroxide and was building a new facility for a further 230000 tons per year in Jilin (China) [114]. There, H_2O_2 will be used as an environmentally friendly oxidant for the direct chemical synthesis of propylene oxide. Evonik production facilities already exist in Germany, Belgium, Austria, the United States, Canada, Brazil, Korea, Indonesia, New Zealand, and South Africa. H_2O_2 is employed for a very wide range of applications. The largest quantities are still used in pulp bleaching and in manufacturing laundry detergent powders and liquids.

2.4.4 New Developments for the Production of Hydrogen Peroxide

New processes to produce hydrogen peroxide directly from the elements have been of interest for many years [29, 115]. Water can be produced from the elements without too many problems but making hydrogen peroxide from the elements is a different story. The problem with the direct synthesis process is that, due to the laws of thermodynamics, the reaction of hydrogen with oxygen favors the production of water. Hydrogen peroxide is an intermediate in this reaction that decomposes just as fast as it is formed, unless the reaction is quenched or diverted. It had been recognized for some time that a finely dispersed catalyst is beneficial in promoting selectivity to hydrogen peroxide, but, while selectivity was improved, it was still not sufficiently high to permit commercial development of the process [116]. Nanometer-size phase-controlled noble metal crystal particles (gold-palladium nanoparticles) on a carbon support can improve the yield of hydrogen peroxide in water or liquid carbon dioxide as the solvent. This process results in low concentrations of hydrogen peroxide

(about 5–10 mass-% versus about 40 mass-% H_2O_2 obtainable by the anthraquinone process).

An electrochemical process to produce alkaline hydrogen peroxide has been developed by H-D Tech Inc., formerly a joint venture of Huron Technologies Inc. and Dow Chemical of Canada, but now wholly owned by Dow. The process employs a monopolar cell to achieve an electrolytic reduction of oxygen in a dilute sodium hydroxide solution.

2.5 Other Methods for Formation of Hydrogen Peroxide

There are many other methods how hydrogen peroxide may form from water or from the elements, but these methods may not necessarily be industrially lucrative. These methods are listed here only for comparison or in the remote chance that they may become competitive under a special set of circumstances, for instance on the surface of the moon or another planet. Naturally occurring hydrogen peroxide forms by one of these mechanisms. Natural occurrence of hydrogen peroxide was already described in Section 5.2.1, but the mechanisms leading to the formation of H_2O_2 under those conditions are discussed here. In many cases, the same mechanism also plays a role in the decomposition of H_2O_2 , so that under many conditions, a stationary concentration of H_2O_2 is maintained.

2.5.1 Formation of Hydrogen Peroxide from the Elements

2.5.1.1 Direct Combustion Methods

Some H_2O_2 is formed during the combustion of hydrogen in oxygen-rich flames. If the flame from a lean O_2/H_2 flame is directed at an ice cube, the high-temperature composition in the flame is quenched, and H_2O_2 is preserved from further decomposition while the reaction products cool off. Theoretically, a rocket taking off with LOX/ LH_2 propellants could be spewing H_2O_2 in its exhaust plume, but these engines typically operate on the fuel-rich side of the stoichiometric composition, so the formation of H_2O_2 under those conditions is less likely. Automobiles operating on gaseous hydrogen in air typically operate with lean mixtures, and it is possible that H_2O_2 can be found in the exhaust of those machines.

Hydrogen peroxide is an intermediate in the oxygen/hydrogen reaction, but it decomposes just as fast as it forms [117].

It is generally assumed that combustion of hydrogen-air mixture in a power producing device, such as an internal combustion engine, should lead to clean exhaust (except for the emission of traces of nitric oxide). However, an experimental study with a hydrogen-fueled engine indicated that another pollutant, hydrogen peroxide, may be emitted in the exhaust gases in concentrations as high as 220 ppm [118]. A model

for the combustion of hydrogen-air mixtures was derived, which included reactions leading to H_2O_2 .

2.5.1.2 Isothermal, Non-combustion Reactions

Passing oxygen/hydrogen gas mixtures with compositions between the second and third explosion limit through a heated zone at 773–873 K (500–600 °C) results in the formation of traces of hydrogen peroxide. The production of hydrogen peroxide in hydrogen-oxygen mixtures under conditions between the second and third explosion limits was studied using a flow method in an isothermal reactor at 839 K (566 °C) [119]. Hydrogen and oxygen were dried, and their flow rates measured on flow-meters. The gases were mixed and passed through a narrow-bore tube into a cylindrical silica reaction vessel, which they entered tangentially at the bottom. They flowed out of the reaction vessel from the center of the top via a 2-mm inner diameter (ID) tube into two consecutive U-tube cold traps cooled in liquid oxygen in which water and hydrogen peroxide were frozen out and analyzed. The residence time in the reactor was 2 to 10 s. Unwanted explosions sometimes took place in the vessel, potentially caused by catalytic walls.

2.5.1.3 Direct Synthesis of Hydrogen Peroxide from the Elements by Catalytic Methods

Instead of operating a flame at high temperature, O_2 and H_2 can be combined to H_2O_2 on a catalyst during catalytic non-combustion reactions at moderate temperatures, usually in an inert process solvent to maintain constant temperature and good heat transfer, typically with an excess of O_2 . These methods would have the advantage that they would produce an organics-free hydrogen peroxide that is better suited for rocket applications than hydrogen peroxide produced by the anthraquinone or 2-propanol air oxidation methods. One of the first catalysts tested successfully for this application was a palladium catalyst [120–122].

A porous metal phosphonate compound $\text{Zr}_2(\text{PO}_4)(\text{O}_3\text{PCH}_2\text{CH}_2\text{-bipyridinium-CH}_2\text{CH}_2\text{PO}_3)\text{X}_3 \cdot 3\text{H}_2\text{O}$ (X = halide) allows the direct production of hydrogen peroxide from hydrogen and oxygen [123]. Platinum and palladium colloids can be incorporated into the structure by ion-exchanging the free halide X with a solution of K_2MCl_4 (M = Pd or Pt) followed by hydrogen reduction. These materials selectively reduce oxygen to hydrogen peroxide. Treatment of aqueous suspensions of these porous catalysts with H_2 and O_2 gases at atmospheric pressure leads to H_2O_2 solutions with concentrations as high as 0.21 M. Reactions carried out at higher pressures lead to even higher concentrations of H_2O_2 . The yield of H_2O_2 based on H_2 consumed was estimated at 40%.

For the direct synthesis of H_2O_2 from the elements at low temperature (275 K) the Au-Pd catalysts performed significantly better than the pure Pd/ TiO_2 or Au/ TiO_2 materials [124]. Au-Pd particles had a core-shell structure, with Pd concentrated on the

surface. The highest yields of H_2O_2 were observed with uncalcined catalysts, but these were unstable, losing active metals during use. In contrast, samples calcined at 673 K were stable and could be reused several times without loss of performance. Strangely, these catalysts exhibited low activity for CO oxidation at 298 K but conversely, catalysts effective for low-temperature CO oxidation were inactive for H_2 oxidation to H_2O_2 . This anti-correlation was difficult to explain.

Palladium catalysts supported on Cl^- , F^- or Br^- -doped zirconia were tested for the direct synthesis of hydrogen peroxide under very mild (101 kPa and 293 K) and non-explosive conditions [125]. The catalysts were characterized by thermogravimetric/differential scanning calorimetry analysis, N_2 physisorption, and temperature-programmed reduction before and after catalytic tests to investigate the oxidation state of the metal. The best catalytic results were observed in methanol as a solvent, using H_2/O_2 non-explosive mixtures containing a large excess of oxygen and using a sulfate-doped zirconia catalyst. Surface-oxidized PdO catalysts showed high catalytic activity and the highest selectivity.

Bimetallic Pd-Pt and Pd-Au samples supported on sulfated zirconia were successfully tested for the direct synthesis of H_2O_2 under very mild conditions (101 kPa and 293 K) and outside the explosion range [126]. The effect of the addition of Pt to Pd in enhancing the yield of H_2O_2 was sensitive to the Pt amount; only by using a low Pt content was it possible to improve H_2O_2 selectivity (from 55 to 70%) and productivity with respect to the monometallic sample. The addition of gold in 1:1 amount to palladium improved both the productivity and even more the selectivity of the process, producing a H_2O_2 concentration already useful for industrial applications and maintaining a stable selectivity (62%) after 12 h of time on-stream.

2.5.1.4 Formation of Hydrogen Peroxide from Water

Water, water everywhere (at least on this planet), and under the right conditions with additional energy input in the form of ionizing radiation, ultraviolet light or electric discharges, with or without dioxygen available from ambient air, hydrogen peroxide will form from water in the solid, liquid, or vapor state. The natural occurrence of hydrogen peroxide is ascribed to these reactions, and observations where H_2O_2 can be found naturally are described in Section 2.1. Hydrogen peroxide has been detected in some unexpected, exotic places. This may have implications for extraterrestrial resource utilization, where crewed stations on other planets can harvest H_2O_2 as a source of water, oxygen, and energy.

The same energy input that allows formation of hydrogen peroxide from water will also cause some of the freshly formed H_2O_2 (or D_2O_2) to decompose in reversal of the reactions that led to its formation. The radiolysis and plasma decomposition of H_2O_2 is described in detail in Sections 4.11.2 and 4.11.3. There is some overlap between the experiments investigating the decomposition of H_2O_2 and the studies of the formation of H_2O_2 from water and oxygen.

2.5.1.5 Ultraviolet Radiation

The formation of H_2O_2 by UV illumination of water ice is a mechanism of H_2O_2 formation that may prevail on a large scale on any celestial body that has accumulated an ice crust, such as Jupiter's moon Europa or several of the Saturnian satellites.

H_2O_2 can be photolytically produced (and destroyed) on a water ice surface by illumination with 157 nm UV at 90 K [127]. H_2O_2 thus formed can then be characterized by photodissociation with 300–350 nm UV leading to the production of gaseous OH radicals that can be directly monitored using resonance-enhanced multi-photon ionization. Surface defects produced by HCl deposition on the water ice lead to a higher production rate of H_2O_2 in the 157 nm photoirradiation of water ice.

Even whatever little UV is in sunlight on the surface of Earth (enough to give one a sunburn and cause skin cancer) is sufficient to cause H_2O_2 formation in surface water [128]. A rapid increase in the concentration of hydrogen peroxide was observed when samples of natural surface and groundwater from various locations in the United States were exposed to sunlight [129]. Hydrogen peroxide is photochemically generated from organic constituents present in water. Humic materials (some containing aromatic phenols and hydroquinones) are believed to be the primary agent producing the peroxide. Studies with superoxide dismutase suggest that the superoxide anion may be a precursor of peroxide. The photochemical accumulation rate of H_2O_2 in sunlight was measured for several surface waters and pond waters and was found to be 2.7×10^{-7} to $48 \times 10^{-7} \text{ mol L}^{-1} \text{ h}^{-1}$ in waters containing from 0.53 to 18 mg L^{-1} dissolved organic carbon (DOC), respectively. These rates were determined in midday sunlight, 0.4 W m^{-2} (295–385 nm) at a latitude of 24.3° N . Apparent quantum yields decreased with increasing wavelength, from 10^{-3} in the near ultraviolet to 10^{-4} in the visible spectral range. Freshwater in the southeastern United States has a natural H_2O_2 content of $0.9\text{--}3.2 \times 10^{-7} \text{ mol/L}$, which upon more intense illumination can be bumped up to $6\text{--}70 \times 10^{-7} \text{ mol/L}$. Seawater in the Biscayne Bay in Florida contains $0.14\text{--}2.1 \times 10^{-7} \text{ mol/L}$.

2.5.1.6 Photocatalytic Synthesis Methods

Light photons (even less energetic light in the visible range) impinging on solid state catalysts can enable them to convert water (liquid or vapor) to hydrogen peroxide.

A new method for the photochemical synthesis of hydrogen peroxide was discovered when in the course of investigations on the photochemical production of hydrogen peroxide in the liquid phase, it was noticed that finely ground photocatalyst became loaded with H_2O_2 when it was allowed to stand exposed to room lights for long periods [130]. This led to the development of a gas-phase photochemical synthesis method for hydrogen peroxide photocatalyzed on solids.

Achieving photosynthetic splitting of water to form dihydrogen and dioxygen as a means of solar energy conversion and storage has long been the holy grail of photochemists and has still not achieved industrial maturity. A variation of this push for water splitting is the attempt to split water into hydrogen and hydrogen peroxide actu-

ally would be even better because hydrogen peroxide is easier to store than oxygen gas [131]. A system like this might work on the moon or on Mars (only after more water is found there). The electrolytic synthesis of hydrogen and hydrogen peroxide from water has been demonstrated. One such system consisted of a hydrogen electrode with platinum mesh, a hydrogen peroxide electrode with carbon material, and an electrolyte with Nafion[®].

2.5.1.7 Catalytic Methods

H₂O₂ can be synthesized from O₂ and H₂O in the presence of a complex such as (PPh₃)₂PdO₂ with equimolar proportions of H₂O₂ and CO₂ being formed [132]. The reaction proceeds at room temperature in a stirred, two-phase water-dichloromethane system.

2.5.1.8 Neutron Radiation

Thousands of tons of heavy water circulate in heavy-water moderated nuclear power plants, and radiolysis of D₂O in close proximity to nuclear reactors forms noticeable quantities of D₂O₂. Spent nuclear reactor fuel rods are stored in large pools filled with natural water (H₂O with a natural amount of D₂O) while they cool off and are waiting for reprocessing. Under all these conditions, hydrogen peroxide forms and greatly changes the corrosive behavior of the water.

2.5.1.9 X-Ray Irradiation

X-rays penetrating through water (or living tissue) in the presence of oxygen cause the formation of traces of hydrogen peroxide. Hydrogen peroxide and the free radicals associated with its formation and decay may be a contributing cause to radiation damage suffered in living tissue. Each time we undergo an X-ray for the diagnosis of a medical condition, there may be a “puddle” of hydrogen peroxide forming in our bodies.

Irradiation with X-rays produced no chemical change in air-free water. With oxygen present, hydrogen peroxide was formed due to a primary activation of the water [133]. The initial production of hydrogen peroxide was independent of the oxygen pressure, from 40 to 700 mm Hg but was dependent on the hydrogen ion concentration.

Hydrogen peroxide yields obtained by the action of 150-keV X-radiation on air-saturated solutions of KBr were strongly pH dependent [134]. There are several hypotheses on the various mechanisms for the formation of hydrogen peroxide by these reactions.

2.5.1.10 Gamma Radiation

A better understanding of the effects of gamma radiation on peroxide formation in water is needed to predict the abundance of hydrogen peroxide in extraterrestrial ice on planets, their moons, and on comets. The destructive power of gamma radiation in living tissue may also involve free hydroxyl radicals. Recombination of OH radicals

formed by γ -radiolysis of water forms hydrogen peroxide [135]. When air-saturated KBr solutions were subjected to cobalt γ -radiation, the initial yield of H_2O_2 was dependent upon the concentration of KBr. The yield of H_2O_2 (formed by the combination of OH radicals in regions of high ionization density) was 0.75 molecule per 100 eV in sulfuric acid solution at a pH of 2 and 0.78 molecule per 100 eV in 0.8-N sulfuric acid [136, 137].

Pure, oxygen-saturated water was irradiated with ^{60}Co gamma radiation [138]. At low doses, the G-factor (H_2O_2) was 2.6. At doses greater than 2000 rad, the G-factor (H_2O_2) was 1.33. Over the entire dose interval $G(\text{H}_2)$ was constant at 0.17. The G values of 1.33 and 0.17 agreed with published data. The results were compared with the generally accepted mechanism for the radiolysis of oxygen-saturated water and the conclusion was reached that this mechanism was in error, at least in the low dose range. An alternate mechanism was proposed to account for the experimental results where H_2O^+ and e^- are proposed as the primary species in the radiolysis of water.

The concentration of hydrogen peroxide formed in thawed γ -irradiated air-saturated ice as a function of dose did not fit a linear plot [48]. By extrapolation of an empirical equation to very low dose, $G \text{ H}_2\text{O}_2$ was evaluated to be 0.32.

Spent nuclear reactor fuel rods are stored in large pools filled with water while they cool off and are waiting for reprocessing. Under all these conditions, exposed to neutron-, α -, β -, and γ -radiation, hydrogen peroxide forms and adversely changes the corrosive behavior of the water. The water may also contain suspended solids, aluminum oxide and zirconium oxide particles that have corroded from the cladding of the fuel elements. This information is important for the safety of an operating nuclear power plant or of a repository for spent nuclear fuel.

Hydrogen peroxide is the main stable oxidizing species formed in the radiolysis of water, and its long-term yield was found to be dependent on several variables. The yields of hydrogen peroxide in the radiolysis of aqueous solutions of acrylamide, bromide, nitrate, and air in the pH range of 1–13 were measured [139]. Experiments with γ -irradiation showed that the primary yields of hydrogen peroxide were nearly independent of pH in the range of 2–12. The G-factor (expressed in mol/100 eV) decreased from 0.71 to 0.5 if the pH was increased from 1 to 12. Slightly higher primary yields were suggested at very low pH, in particular when O_2 was present, while the yields decreased at very high pH. In addition to γ -radiation, other irradiations were performed with 5-MeV H ions, 5-MeV He ions, and 10-MeV C ions to evaluate the intratrack and homogeneous kinetic contributions to H_2O_2 formation with different ions. Many of the same trends in hydrogen peroxide yields with pH observed with γ -irradiations are observed with irradiation by the heavy ions.

Suspended alumina or zirconia particles, corrosion products from deteriorating nuclear reactor fuel elements, will alter the rates of formation and decomposition of H_2O_2 in water-filled pools where spent fuel rods are in temporary storage, awaiting reprocessing. Therefore, the yields of H_2O_2 in aqueous alumina slurries in the pH range of 1–13 with various amounts of added Al_2O_3 nanoparticles were determined [140]. The

addition of Al_2O_3 generally decreased H_2O_2 yields at all pH values within this range in the γ radiolysis of both deaerated and aerated slurries, except at pH above 11.

The first-order and second-order rate constants for the decomposition of H_2O_2 in the presence of ZrO_2 slurries at $T = 298\text{ K}$ produced the values

$$k_1 = (6.15 \pm 0.04) \times 10^{-5} \text{ s}^{-1}$$

$$k_2 = (2.39 \pm 0.09) \times 10^{-10} \text{ mol s}^{-1}.$$

The activation energy for the reaction was obtained in the temperature interval 294–353 K from the dependency of the reaction first-order rate constant with temperature and was $E_a = 33 \pm 1.0 \text{ kJ mol}^{-1}$ [141].

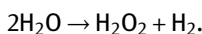
In addition to alumina slurries, the adsorption and decomposition of H_2O_2 on nano- and micrometer-sized particles of other ceramic metal oxides, ZrO_2 , TiO_2 , and Y_2O_3 were characterized by measuring the reaction rate constants, the Arrhenius activation energies, and the activation enthalpies for the processes of adsorption and decomposition of H_2O_2 [142]. The experimentally obtained enthalpies of activation for the decomposition of H_2O_2 catalyzed by these materials are $30 \pm 1 \text{ kJ/mol}$ for ZrO_2 , $34 \pm 1 \text{ kJ/mol}$ for TiO_2 , and $44 \pm 5 \text{ kJ/mol}$ for Y_2O_3 . Other ceramic oxides studied included SiO_2 , Al_2O_3 , TiO_2 , CeO_2 , and ZrO_2 [143].

2.5.1.11 Microwave Plasma Discharge

Water vapor flowing at low pressure through the resonant cavity of a microwave oven will glow and become ionized. This method of exciting a glow discharge is also called “electrodeless discharge”. The formation of hydrogen peroxide by dissociation of water vapor in an electric discharge was studied for the purpose of preparing sizeable quantities of deuterium peroxide D_2O_2 [144]. The apparatus featured a large pumping capacity and a high-frequency electrodeless discharge (20 MHz). The dissociated gas went directly into a large liquid air cooled trap where it formed a glassy deposit. On warming, this deposit first evolved hydrogen, then at about 158 K (-115°C) some oxygen. Solutions of hydrogen peroxide with concentrations of up to 56% were obtained. With $\frac{1}{2} \text{ kW}$ dissipated in the discharge, an optimum yield of 15 g of 50% peroxide per hour was reached.

Similar results can be obtained with glow discharges in a tube filled with water vapor at low pressure and carrying electrodes with electrically conductive feedthroughs at both ends, similar to a neon tube for advertising [145].

At low flow rates ($0.7\text{--}2.8 \text{ mmol h}^{-1}$) and long residence times (2.3–8.5 s), nearly 60% of the input water vapor was decomposed by a 13.56-MHz high-frequency plasma discharge [146]. Downstream of the glow discharge a trap cooled by liquid nitrogen collected nearly constant yields of H_2O_2 . The decomposition was representable by the equation



The overall rate of decomposition was found to depend on the absorbed power density. Heating the rf plasma and its spatial afterglow from 298 to 873 K (25 to 600 °C) did not significantly change the percent decomposition of H_2O and the formation of H_2O_2 .

2.6 Methods for Concentrating Hydrogen Peroxide

In many cases, the concentration of hydrogen peroxide available in the open market may not be sufficient for the intended rocket application. Several organizations have developed methods for concentrating H_2O_2 to higher concentrations needed for rocket applications. Due to the explosion potential, this must be done extremely carefully and only with the proper equipment and adequate safety precautions.

There are now high-purity grades (“electronic grade”) of H_2O_2 solutions available for the etching of semiconductors, which do not contain any stabilizers and are suitable for concentrating when the unwanted accumulation of stabilizer is expected to interfere with the intended application.

2.6.1 Evaporation and Distillation Methods

Because water and hydrogen peroxide do not form an azeotrope and because the boiling points are far apart (H_2O : 373 K = 100 °C; H_2O_2 : 423.3 K = 150.2 °C), separation by evaporation and distillation is relatively simple. Up to a concentration of 65% H_2O_2 , distillation can even be done at atmospheric pressure. Beyond 65% H_2O_2 , the process becomes dangerous and needs to be done at reduced pressure [147, 148].

In the early years of hydrogen peroxide evaluation as a rocket propellant, a distillation column for the fractionation of the hydrogen peroxide/water system was designed, built, and tested [149]. With a feed rate of about 0.03 kg/min. of material containing 35 mass-% hydrogen peroxide, a product containing 82.6 mass-% hydrogen peroxide was obtained. About 76% of the input hydrogen peroxide was contained in the product, and a total of about 91% of the input hydrogen peroxide was recovered in the sum of the product and in the distillate.

At NASA Stennis Space Center a skid-mounted modular concentration facility was once set up by Degussa (as of 2007, this company is now called Evonik), which was capable of producing Propulse® 980. An external view of this facility is shown in Figure 1.

The Propulse™ 980 unit was a transportable, modular processing plant that enriched aerospace grade hydrogen peroxide from 90 to 98% final concentration [150]. The unit was developed by Degussa, in cooperation with Orbital Sciences, NASA Marshall Space Center, and NASA Stennis Space Center. The system was a self-contained unit that housed all of the process equipment, instrumentation and controls to perform the concentrating operation nearly autonomously. It was designed to produce non-bulk quantities of 98% hydrogen peroxide. The unit was first tested, then dis-



Figure 1: Hydrogen peroxide concentrating facility once located at NASA Stennis Space Center. (Photo credit: NASA.)

assembled at the Degussa plant in Theodore, AL, transported to NASA Stennis Space Center, reassembled, and subjected to a series of checkout tests to verify that all design objectives had been met. The production goal for the enrichment unit was to produce a minimum of 1000 pounds of 96% H_2O_2 product per day safely and automatically.

In addition to industrial methods for concentrating hydrogen peroxide to obtain rocket-grade high-test peroxide, there have been several methods described in the literature that were used by academic institutions or amateurs that wanted HTP free from stabilizers or could not afford to obtain commercial quantities of HTP delivered in drums or tank cars.

The primitive and not advisable method described in [151, 152] used open-air evaporation of food-grade 35% H_2O_2 containing both stannate and phosphate stabilizers in 1-L glass beakers on hot plates in a fume hood. Over a period of 18 h, the residue reached a concentration of 85% and about one-fourth of the H_2O_2 was lost with the water vapor. Not only H_2O_2 , but also all contaminants and stabilizers were concentrated in this way in the residue, resulting in an intermediate product with ~80 ppm of impurities. This material was then distilled in a Rotavapor from a warm water bath not exceeding 323 K (50 °C) under vacuum at 1.3 kPa (10 mm Hg). Table 1 gives a comparison of analysis results of the commercial food grade HP and the concentrated and distilled product.

In tests at Purdue University [153], concentrating of HP starting with 50% supplied by Interlox was performed by remote heating in 4000-mL Erlenmeyer flasks until a batch of 4 to 5 gallons of 85% H_2O_2 was gathered. This was done to minimize batch-to-batch variations of fluid physical properties on the fired motor data. Concentrating HP by this method of course also concentrated the stabilizer and all other unwanted contaminants in the original fluid. For concentrating HP from 50 to 85%, the boiling began around 380 K (225 °F) and was terminated at 411 K (280 °F). At such an elevated fluid temperature, only glass containers may be used to avoid spontaneous decomposition. This method may only be used with highly stabilized HP because thermal decomposition takes place in unstabilized HP above 70% concentration at that temperature. In some instances, the energy from a vapor-phase detonation in the space

Table 1: Comparison of analysis results of concentrated and distilled hydrogen peroxide.

Organization Constituent	Unit	Purchased, as received	Sandia Livermore Concentrated and distilled
H ₂ O ₂	% by mass	35	85
Ca	mg/kg	0.01	0.03
K	mg/kg	2.6	<0.1
Na	mg/kg	1.2	<0.1
P	mg/kg	3.9	<0.5
S	mg/kg	0.04	0.05
Sn	mg/kg	3.7	0.08
Ammonium	mg/L	1.13	<0.4
Nitrate	mg/kg	4.7	5.9
Phosphate	mg/kg	7.4	<0.02
Sulfate	mg/kg	0.4	1.6
TOC	mg/kg	<0.1	<0.1

Data source: [151, 152]

above the boiling surface initiated a thermal decomposition wave (boil-off) in the liquid during this research program. While these vapor-phase detonations were not terribly energetic (many of them sounded like a small firecracker exploding), some were strong enough to crack/shatter the flasks used for boiling.

Preparation of electronic grade high-concentration hydrogen peroxide requires operating with an all-fluoropolymer apparatus avoiding contact of the liquid with glass or other contaminating surfaces, maintaining the pressure in the evaporator below 100 mm Hg, maintaining the vapor phase concentration of H₂O₂ in the evaporator below 26 mol-% by connecting to a dynamic vacuum pump (water aspirator), and maintaining an inert purge gas flow [154].

Another vacuum concentrating process operates at a vacuum of at least 10 mm Hg and consists of two cojoined but separable pieces of equipment: a distillation column at the top and a falling film evaporator at the bottom. The bottoms of the distillation column are fed into the falling film evaporator, giving a solution with at least 90% H₂O₂ [155]. This once-through process avoids the accumulation of concentrated product in the still.

While the concentrating methods described by Tillotson or Bloomfield are not economical because their operation requires use of vacuum pumps, the method patented by Carden operates at atmospheric pressure circulating compressed, heated, dry (dew point -40 to -75 °C) air countercurrent in a mass transfer device (bubble cap column, packed column, air stripping column or falling film evaporator) and then through a fluid (air) dryer [156]. This method was later adopted by Beal Aerospace Corp. for a 5-ton-per-day hydrogen peroxide concentrator at McGregor, TX.

Stabilizers and impurities may accumulate in the pot residue of H₂O₂ concentrating distillation units and form a sediment. The problem of sediment formation in the

concentrating process of hydrogen peroxide, the analysis of sedimentary deposits, and preventive measures were described [157].

A microstructured falling film evaporator made from AlMg₃ was used to evaporate 50 mass-% aqueous hydrogen peroxide solutions in a concentrator at elevated temperatures (about 403 K = 130 °C) [158]. After an initial self-passivation procedure under operating conditions, the relative decomposition related to the evaporated amount could be reduced to values of about 10%. From the experimental results, it was concluded that the decomposition occurred mainly in the liquid phase during evaporation and not in the vapor phase by contacting the non-wetted surfaces of the evaporator and pipes. At an operation temperature of 403 K = 130 °C, 10 vol.-% of hydrogen peroxide in the vapor could be reached, which almost corresponded to the vapor/liquid equilibrium at the top of the evaporator. See also [159–161].

The main hazard during concentrating during a four-stage distillation of hydrogen peroxide that was made by the isopropyl alcohol autoxidation process is the potential accumulation of triacetone triperoxide, a highly explosive material [107]. The heat of explosion of triacetone triperoxide is 2803 kJ/kg, which is 88% of TNT equivalent. The velocity of detonation triacetone triperoxide is 5300 m/s at a density of 1.2 g/cm³ and about 1430 m/s at 0.47 g/cm³. The content of acetone and isopropyl alcohol impurities should be kept below 0.02 mass-% in order to provide a good quality product and maintain appropriate safety of the concentrator. Another explosive byproduct is peracetic acid.

2.6.2 Fractional Crystallization and Zone Melting Methods

Concentration of hydrogen peroxide by fractional crystallization is based on a thorough understanding of the solid-liquid phase diagram (see Figure 2 and 3) for the system hydrogen peroxide-water. Figure 2 and 3 show the depression of the freezing point of each component by addition of the other component and two eutectic points. For concentrating and purifying the 70% H₂O₂ liquid feed stock is chilled to 218 K (–55 °C), which forms a two-phase system consisting of solid hydrogen peroxide and a 62% H₂O₂ concentration liquid. Because the solid hydrogen peroxide slush occludes significant amounts of mother liquor, it gets centrifuged and separated before thawing. The majority of impurities remains in the liquid rather than in the solid. For reuse the 62% H₂O₂ liquid needs to be distilled to 70%. Even though this process is safer than a distillation, nobody used it on a commercial scale. The Propulse 980™ unit at NASA Stennis is only a pilot plant scale. The Propulse 980™ portable concentrating unit developed by Degussa for NASA uses a fractional crystallization method. The feedstock (90%) is separated into 80% H₂O₂ byproduct (“mother liquor”) and the 98% finished product. The process yield is about 50%. Stabilizers and contaminants in feedstock are greatly reduced in the finished product. Production of >92% H₂O₂ should always be done by fractional crystallization and not by distillation.

2.6.3 Membrane Separation Methods

Semipermeable membranes can selectively allow passage of water, leaving more concentrated H_2O_2 behind.

Semipermeable membranes capable of separating a H_2O_2 solution from a sweep gas or permeate (water) are selective due to the preferred permeability of water over the permeability of H_2O_2 , thereby concentrating the H_2O_2 solution through the removal of water through the membrane to the permeate. Membranes can be made of PTFE and a perfluorinated polysulfone copolymer having sulfonic acid functional groups [162]. The membrane system was designed so that the hydrogen peroxide solution was on one side of the membrane and dry sweep air was on the other side. The water capacity of the sweep air was increased by increasing the temperature, but the temperature was kept below the spontaneous decomposition temperature of hydrogen peroxide. This method would provide HTP at the point of use where commercial grade 70% hydrogen peroxide can be enriched to 85%. In this process, HTP is not exposed to reactive surfaces. As of 2012, NASA was offering the use of this patent to potential licensees for industrial use.

Instead of simple air stripping (which has problems of liquid entrainment), the mixture of sulfuric acid, H_2O_2 and water obtained after electro-oxidation of sulfuric acid and hydrolysis of persulfuric acid can be separated by passing a hot carrier gas through the mixture and separating the vapor by a hydrophobic membrane [163]. The acid is concentrated in the residue and returned to the electrolyzer.

Pervaporative separation of corrosive liquids is challenging in terms of selecting a suitable polymeric membrane that can withstand the harsh environment especially when attempting to concentrate an aqueous solution of an oxidizing liquid such as hydrogen peroxide. The choice of membrane material is limited to fluoropolymers and perfluoropolymers. Perfluorodimethyldioxole-tetrafluoroethylene (PDD-TFE) copolymer membranes (CMS-3 and CMS-7) were used to concentrate hydrogen peroxide from its aqueous solutions [164]. The feed solution composition was varied between 4 and 40 mass-% H_2O_2 , and the process was operated at 298, 303, and 308 K (25, 30, and 35°C). The best water- H_2O_2 selectivity of ~12 was observed in a CMS-3 membrane at an H_2O_2 concentration of 43 mass-% with a total flux of $6.15 \times 10^{-3} \text{ g h}^{-1} \text{ cm}^{-2}$. For CMS-7, values of 9.2 and $9.6 \times 10^{-3} \text{ g h}^{-1} \text{ cm}^{-2}$ were found for water- H_2O_2 selectivity and total flux, respectively, at the same H_2O_2 concentration. The total permeated flux increased with temperature at the cost of selectivity for both membranes. Extended-term immersion of CMS-3 and CMS-7 membranes in 35 mass-% H_2O_2 indicated that both were quite stable for tests carried out over periods of 162 and 145 days, respectively.

2.7 Methods for Purifying Hydrogen Peroxide

Methods for concentrating hydrogen peroxide may not necessarily improve its purity; quite often the opposite is achieved if non-volatile contaminants accumulate in the concentrated product after the water is driven off. Most concentrating methods require a more than one-step operation to arrive at a product with both the desired purity and the required H_2O_2 concentration.

2.7.1 Purification of Hydrogen Peroxide by Distillation

The Shell Development Co. of Emeryville, CA, used a continuously operating flash distillation unit operating at low pressure and temperatures below 333 K (60 °C) to prepare some 5-gal storage samples of HTP purified by additional distillation [165, 166]. Samples of HTP-98 prepared by distillation at low pressure and temperature were prepared for long-term ground storage tests.

Highly purified hydrogen peroxide can be obtained by vacuum distillation from the products of a peroxysulfate process when the underflow of a fractionation column is condensed [167].

High-purity hydrogen peroxide can be obtained by fractionated sublimation from a frozen mixture of hydrogen peroxide, water and dihydrate in a thin film in ultrahigh vacuum, leaving the less volatile H_2O_2 behind [168]. The use of a microbalance enabled the investigators to quantify the stepwise distillation process. Infrared spectra were taken periodically during the sublimation to monitor progress of the purification process.

2.7.2 Purification of Hydrogen Peroxide by Recrystallization

Concentrating and purifying hydrogen peroxide by freezing and crystallization is a much safer process than heating and distillation.

In one crystallization concentrating process, the 90% H_2O_2 to be purified is charged to a stirred crystallizer with a conical bottom on top of a long cooling-jacketed rectifying column in which liquid enters at the bottom, and the crystals slowly sink in the opposite direction [169]. Because the density of the crystals is higher than that of the mother liquor, they settle to the bottom of the crystallizer, but are kept in suspension by the upward flow of additional liquid to be frozen and concentrated. This process can be carried out as a batch process or a continuous process, but it would be very difficult to scale it up because in a wider column back mixing would occur. In the continuous process, crystals sink to the bottom, melt, and then become the washing fluid for the younger crystals in the upper layers. The H_2O_2 starting material is cooled in a rectifying column to such an extent that there forms a two-phase system consisting of a solid crystal phase and a liquid mother liquor. The temperature along the rectifying column is so controlled that it increases slowly from one end to the other. Owing to the higher density of the crystallized hydrogen

peroxide, the crystals and the mother liquor flow in a countercurrent relative to one another. A disadvantage of that continuous suspension crystallization process is the sophisticated equipment required to carry it out. Such a technical outlay appears justified only if very highly concentrated hydrogen peroxide is required regularly and/or in large amounts. If one wants to scale up this process, as the diameter of the rectifying column increases, unforeseeable back-mixing occurs, as a result of which both the purification function is impaired, and the process efficiency is decreased considerably. The rectifying column according to this patent is in principle operated as a gravity washing column. In the lowermost portion of the column, some of the crystals melt again, and the melt thus acts as the washing medium. In such washing columns, working on the countercurrent principle, solid-liquid separation and further purification of the solid take place in one apparatus, but the scale-up problems remain.

In another version of a crystallization process, a batch process suitable for producing small quantities of the pure product, seed crystals of pure frozen hydrogen peroxide are first coated on a cold panel prior to introducing the charge to be concentrated and purified [170]. The use of seed crystals avoids the notorious tendency of hydrogen peroxide solution to supercool. After the cold panel is covered with frozen H_2O_2 , the mother liquor is drained, and the crystals are melted. The process can be repeated if needed and will yield HTP with >90% H_2O_2 .

A crystallization process for the continuous preparation of highly concentrated hydrogen peroxide starting out with >80 mass-% H_2O_2 operates by suspension crystallization and aftertreatment of the H_2O_2 crystals [171]. The aftertreatment by countercurrent washing in a hydraulic washing column with freshly molten hydrogen peroxide as the washing medium in a packed crystal bed results in crystals with 99.9 to 100 mass-% H_2O_2 and a TOC, nitrate, phosphate, nickel, and tin content of less than 4 mg/L.

2.7.3 Purification of Hydrogen Peroxide by Adsorption

Organic contaminants in hydrogen peroxide can be removed by adsorption on activated carbon (activated charcoal) to make ultrahigh purity hydrogen peroxide [172]. Other methods for reducing the amount of dissolved organic compounds include treatment of the crude product with polyethylene, ion exchange, or extraction with immiscible hydrocarbons.

Hydrogen peroxide (15–80% H_2O_2) can be purified and stabilized by passing it through an absorption column packed with granular activated non-alkaline alumina [173].

2.7.4 Purification of Hydrogen Peroxide by Ion Exchange

There have been several instances where HTP was found to be slowly decomposing in the storage yard behind the rocket test stand, and as a matter of precaution, the

entire batch of HTP had to be destroyed. It would be nice if there was a filter apparatus no bigger than a 55-gallon drum where the contaminated HTP could be poured through, which would remove all contaminants and give the HTP a new lease on life. Ion-exchange resins might be one of the methods for purification. Most ion exchange resins have been applied to hydrogen peroxide purification at the production site. There is no experience with a field unit that would achieve the same objective with aged HTP. Acid-treated β -stannic acid granules have been used as an ion-exchange bed for removal of transition metal cations from HTP [166, 174, 175]. Various combinations of inorganic ion exchange media including tin(IV) phosphate were evaluated but turned out not to be more effective than β -stannic acid alone in reducing the decomposition rate of the treated HTP. Evaluation of HTP-90 that had been treated by a β -stannic acid bed and stored in aluminum for approximately 1 year showed the HTP to have about 1/3 of the decomposition rate of the untreated feedstock.

In one patented purification process, the hydrogen peroxide solution is passed through a membrane with a very small pore size, which contains a hydrogen-loaded ion-exchange resin that is capable of removing alkali and alkaline earth metal ions from the solution [176].

While it is relatively easy to remove cation contaminants by cation-exchange resins, the removal of anion contaminants by ion exchange has been more difficult [177]. Resins of the type Amberlite IRA-400 have worked well. Acid impurities can be removed by passing hydrogen peroxide through an anion exchange resin bed loaded with bicarbonate anion [178]. Ion exchange resins of the type Amberlite IRA-400, Amberlite IRA-401, Dowex-1 or Dowex-2 can be used for that purpose. Passing HTP through a tightly packed column of ion exchange resins as is commonly done with aqueous solutions has resulted in occasional explosions. It is safer to pass the HTP through a fluidized bed of ion-exchange resin particles where concentrated local heat evolution is avoided, and heat is carried away with the exiting liquid [179].

Hydrogen peroxide in the concentration range 5–70% can be purified by ion exchange with a strongly basic anion-exchange resin, followed by treatment with a cation-exchange resin [180].

2.7.5 Purification of Hydrogen Peroxide by Reverse Osmosis

One method to purify hydrogen peroxide regardless of its concentration is by reverse osmosis. Hydrogen peroxide that is commonly used in the wafer cleaning and surface conditioning processes in the semiconductor industry must have exceptional purity. The operation of a multi-stage reverse osmosis purification plant has been modeled mathematically as a non-linear programming problem [181]. The network model integrated reverse osmosis membrane modules, mixers, and split functions, defined by the equations of mass balances, and a transport model for the description of the permeate flux and the metal rejection coefficients at each membrane stage.

A reverse osmosis process for manufacturing highly pure aqueous hydrogen peroxide used aromatic polyamide, polypiperazineamide, polysulfone, or polyacrylonitrile membranes [182].

3 Physical Properties of Hydrogen Peroxide

Hydrogen peroxide is an energetic compound, and its physical properties must be known accurately to safely design rocket engines and other machines that use the energy provided in the hydrogen peroxide molecule and its decomposition. Studies of the molecular structure through spectroscopic methods allow us to calculate the thermodynamic properties, which in turn are needed to calculate the theoretical performance as a rocket propellant. The determination of the physical properties of hydrogen peroxide is difficult. For one, it is difficult to obtain highly pure H_2O_2 where residual water and other contaminants do not give wrong measurements. For another, even if pure H_2O_2 can be obtained, sometimes pure H_2O_2 is decomposing already while its physical properties, in particular those at elevated temperatures, are being measured. The molecular mass of hydrogen peroxide is 34.0147 g/mol.

Many physical properties were determined not only for H_2O_2 with its natural occurrence of deuterium and ^{18}O , but also for hydrogen peroxide where varying amounts of H atoms had been replaced by deuterium atoms (D, ^2H) or varying amounts of ^{16}O were replaced by ^{18}O . Such isotopomer compounds are used for tracer studies in kinetic rate determinations, in environmental studies, or in the determination of physical properties. This isotope substitution brings about measurable changes in physical properties. Most often, isotope substitution is used to identify absorption bands in infrared and Raman spectra, since the isotope shift is quite pronounced. There is no application of deuterated hydrogen peroxide in rocket propulsion, and we do not summarize the literature on HOOD and DOOD. However, tons and tons of heavy water are circulating in heavy-water moderated nuclear power plants, and D_2O in close proximity to nuclear radiation forms noticeable quantities of D_2O_2 . Thus, there is quite a bit of interest in D_2O_2 and its properties in comparison to H_2O_2 .

Hydrogen peroxide was evaluated as an oxidizer for an advanced liquid propellant staged combustion feasibility program, and its physical, chemical, and handling properties were compiled in a handy summary report, although most of the data were taken from the book by Schumb and from HTP manufacturers' product bulletins [183]. It is just that these product bulletins are no longer available because some of HTP manufacturers are no longer in business. However, the Anderson summary is still available on the Internet, although the quality of reproduction is poor, and some of the text is hard to read. The Anderson [183] summary is the most comprehensive collection of hydrogen peroxide data that we have found so far on the Internet.

3.1 Freezing Point of Hydrogen Peroxide

The high freezing point of hydrogen peroxide is one of the disadvantages for its use as a rocket propellant. Consequently, various freezing point depressants have been evaluated to widen the liquid range of hydrogen peroxide.

It is very difficult to determine the freezing point of hydrogen peroxide and its aqueous solutions because it has a notorious tendency to supercool (Table 2).

Table 2: Freezing point of hydrogen peroxide.

Composition Mass-% H ₂ O ₂	Freezing point			Source	Year	References
	K	°C	°F			
100	272.72	−0.43	31.226	Chemical abstracts		
98	270.55	−2.60				
90	261.62	−11.53				
100	272.69	−0.461	31.170	Foley and Giguere	1951	[184]
100	272.26 ^a	−0.89	30.398	Cuthbertson, Matheson, and Maass	1928	[185]
	272.72	−0.43	31.226	Schumb, Satterfield, and Wentworth	1955	[186]

^a This is the value accepted by NIST

The purpose of some investigations was to redetermine the freezing point of pure H₂O₂, to investigate the possibility of solid solutions in the system H₂O₂-water and to use freezing point measurements for evaluating the purity of very concentrated H₂O₂ [187]. The freezing point of pure H₂O₂ was reported as −0.461°C and is believed to lie within a few thousandths of a degree of the true value because it is the highest temperature observed in a direct determination and could be duplicated to the limit of accuracy of the measurements (0.001°) with two different samples. The melting point of the dihydrate was 221.05 K = −52.10°C. Two eutectics occur at concentrations of 45.2 and 61.2% H₂O₂ and at temperatures of 220.7 and 216.6 K (−52.4 and −56.5°C), respectively. Using a radioactive tracer technique it was determined that water and H₂O₂ do not form solid solutions together.

If hydrogen peroxide is used as a solvent, and the freezing point depression used as a measure of the molecular mass of the dissolved species, the cryoscopic constant is 1.72 [184, 187].

The triple point was estimated to be 272.73 K = −0.42°C at 34.5 Pa = 0.26 mm Hg [188].

3.1.1 The Hydrogen Peroxide/Water Liquid/Solid Phase Diagram

Hydrogen peroxide and water form two eutectics and a peritectic, indicating formation of some type of hydrate in the solid state. The eutectic points are at 45.2 mass-% H_2O_2 with a melting point of $220.95\text{ K} = -52.2^\circ\text{C}$ and at 61.2 mass-% H_2O_2 with a melting point of $217.05\text{ K} = -56.1^\circ\text{C}$. Compound formation, a dihydrate, $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ appears to occur at 48.6 mass-% with a melting point of $221\text{ K} = -52^\circ\text{C}$.

The original phase diagram (Figure 2) in Schumb is cluttered with numerous data points of dubious origin. The wide scatter of data points is due to the tendency of these mixtures to supercool.

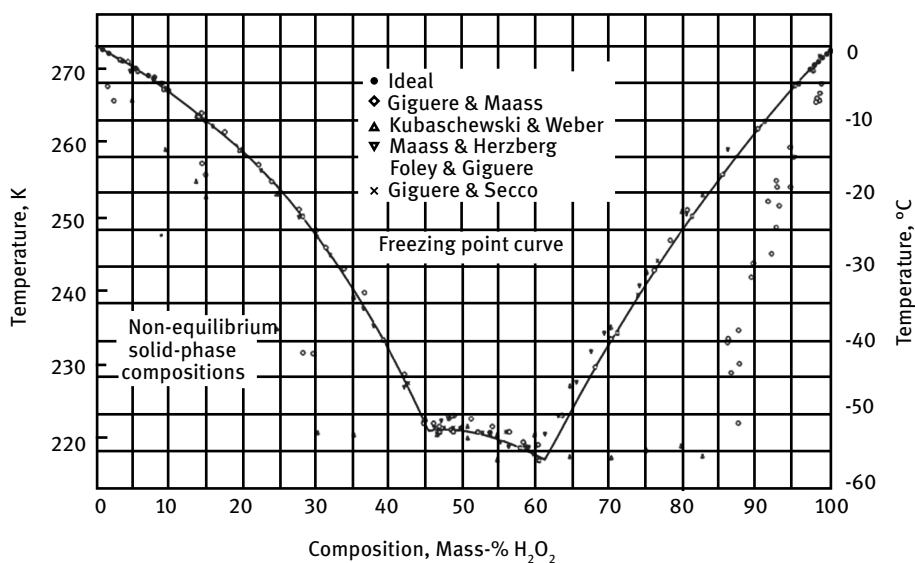


Figure 2: Solid-liquid phase diagram of the hydrogen peroxide-water system. (Reproduced and modified from [4].)

A similar phase diagram was shown in a Laporte Chem brochure and that was the one that was used in a 1968 edition of a book on rocket propellants; it is shown in Figure 3.

A thorough understanding of the phase diagram of the H_2O_2 - H_2O system is required for all efforts to concentrate and purify H_2O_2 by fractionated crystallization or zone melting. Initial attempts to separate H_2O and H_2O_2 by fractionated crystallization did not provide clear results. An attempt was made to determine the exact composition of the first crystals that separate out on freezing solutions of H_2O_2 and H_2O of various concentrations. Special care was taken to ensure complete removal of any liquid wetting the solid phase. In all cases, the crystals were found to contain both components and in proportions usually different from those in the mother liquor [189]. The results from this test were inconclusive.

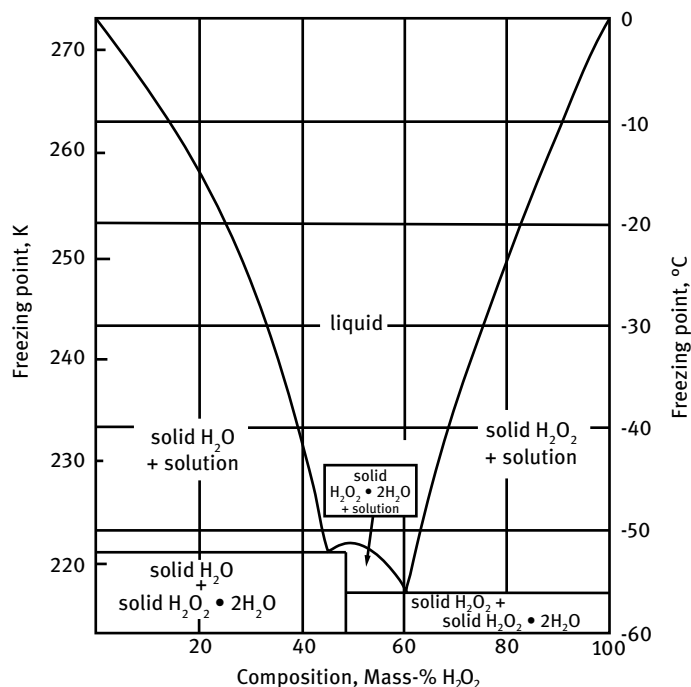


Figure 3: Liquid phase diagram of the $\text{H}_2\text{O}_2\text{-H}_2\text{O}$ system. (Reproduced and modified from Laporte Chem. Ltd.)

Hydrogen peroxide forms hydrates with specific stoichiometric ratios. Crystalline $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ and its deuterated analog were studied at 80 K by IR and Raman spectroscopy [190]. The six O—H stretching modes predicted by group theory were observed and correlated with the three kinds of H-bonds found by X-ray diffraction. The introduction of one peroxide bond per three mols of H_2O in the crystal lattice of ice lowers the symmetry and reduces the stability of the hydrate considerably, although the intermolecular forces should be almost the same in ice and $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$.

The discovery of H_2O_2 in the ice on the surface of the moon Europa [52] in orbit around the planet Jupiter has revived interest in the $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ phase diagram. Early XRD measurements had shown that an intermediate compound phase exists in crystalline mixtures, the dihydrate $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ [191]. This compound was also identified in the determination of the equilibrium phase diagram of water/hydrogen peroxide [187], indicating that when solutions approach equilibrium, there is competition between the formation of three phases: water ice, H_2O_2 ice, and the dihydrate. This dihydrate phase was subsequently identified using infrared spectroscopy [192]. The temperatures at which the dihydrate formed in those experiments (140–200 K) were like those on the warmer icy satellites of Jupiter; see also [193, 194].

3.1.2 Supercooling of Hydrogen Peroxide

The complete mapping of the freezing point in the H_2O_2 - H_2O system is complicated by the fact that hydrogen peroxide (like water or hydrazine) has a tendency to supercool when the temperature is lowered gradually, and no nucleation sites are provided. H_2O_2 solutions with any H_2O_2 concentration are capable of supercooling, but the phenomenon is most frequently observed with solutions above 50% H_2O_2 where supercooling of 10 to 50 °C below the generally accepted freezing point is not uncommon [195, 196].

The deuterium isotopomer of H_2O_2 , D_2O_2 , is even more prone to supercooling and assumes a highly viscous, glassy state at temperatures as low as 194 K = -79 °C (dry ice) or even 88 K = -185 °C (LN_2).

A water solution containing 45.5 to 87 mass-% H_2O_2 was found to form a glass when immersed in liquid oxygen at 90 K [197]. The boundary between crystallization and glass formation at 45.5 mass-% is very sharp and corresponds to the eutectic point of H_2O and H_2O_2 , while the boundary at 87 mass-% is less marked with a leeway of ~5 mass-% and coincides with the change in the slope of the melting point versus concentration curve for quickly frozen solutions. A D_2O solution containing 80 mass-% D_2O_2 was also found to form a glass in liquid oxygen, with no evidence of subsequent crystallization.

3.1.3 Freezing Point Diagrams of Binary Hydrogen Peroxide Mixtures

3.1.3.1 Freezing Point Diagrams of Solutions of Solids in Hydrogen Peroxide

Hydrogen peroxide is a good solvent, as good as water, and will form solutions with many inorganic salts. The objective of dissolving oxidizing salts in H_2O_2 is to lower the freezing point, increase the density, and improve its performance as a rocket propellant. One must be careful not to dissolve any combustible salts or organic compounds in HTP, or the mixtures may become detonable.

Solutions of inorganic oxidizing salts in H_2O_2 have been proposed as liquid propellant oxidizers. The addition of salts lowers the freezing points and the vapor pressure of H_2O_2 . Some of these solutions of ammonium salts in H_2O_2 can also be used as monopropellants. Freezing point diagrams of several binary and ternary systems involving H_2O_2 (PERSOL, OXSOL, PERHAN) will also be described in *Encyclopedia of Oxidizers*, chapters "Nitrate Oxidizers" and "Hydroxylammonium Salts". A powerful and low-freezing oxidizer called PERSOL-1 can be obtained by dissolving ammonium nitrate (AN) in hydrogen peroxide/water mixtures [198, 199]. The freezing point diagram of the ternary system AN/ H_2O_2 / H_2O is shown in Figure 4.

One preferred composition of PERSOL-1 contains 55.6% AN, 22.2% H_2O_2 , and 22.2% H_2O . This blend freezes at 276 K (3 °C) and has a density of 1.361 g/cm³. It can serve as an oxidizer for bipropellant or hybrid rocket propellant combinations. Monopropellants can be formulated by emulsifying this oxidizer with hydrocarbons

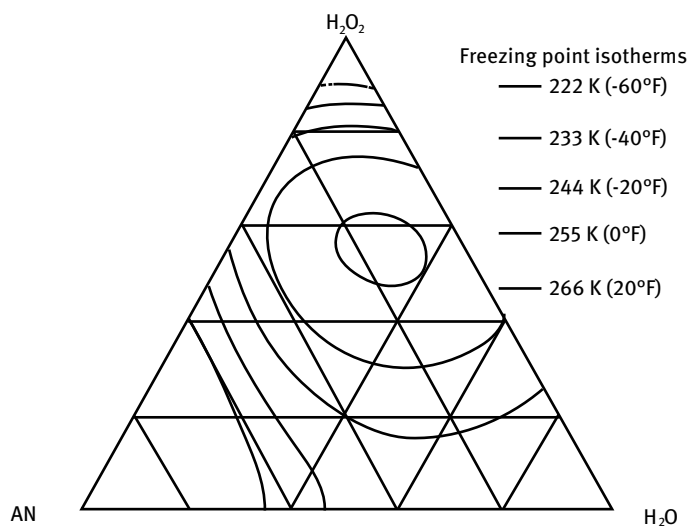


Figure 4: Freezing point isotherms diagram of ternary $\text{H}_2\text{O}_2/\text{H}_2\text{O}/\text{AN}$ oxidizer solutions also called PERSOL-1. (Reproduced and modified from [199].)

or by dissolving amine nitrate salts such as alkylammonium nitrate or alkanolammonium nitrates having one, two or three carbon atoms. Instead of AN, hydrazinium nitrate (HN) can be dissolved in H_2O_2 to form a mixture called “PERSOL-2” [200]. The freezing point diagram of the $\text{HN}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ system is illustrated in Figure 5. One

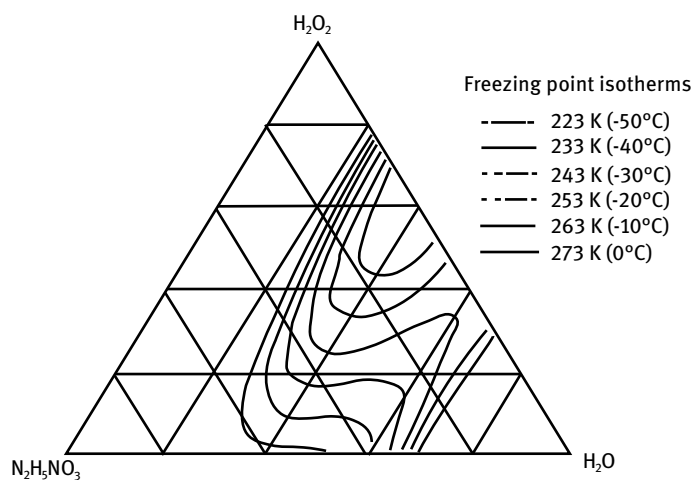


Figure 5: Freezing point diagram of $\text{HN}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ system. (Reproduced and modified from [200].)

would hesitate to mix hydrazine compounds and hydrogen peroxide. It is known that hydrogen peroxide and free hydrazine or hydrazine hydrate react instantly in a hypergolic manner, but the hydrazine molecule appears to be stabilized against such an attack by protonizing it and forming the hydrazinium(1+) ion. When looking at PERSOL-2 type oxidizers, there is still some concern that the strong oxidizer H_2O_2 might attack the fuel cation N_2H_5^+ , leading to hydrogen azide as an unwanted byproduct of reaction.

A very elegant, alternate way to represent freezing point data such as those in the triangular chart above is to display them as a 3-D color-coded graph (Figure 6) [201].

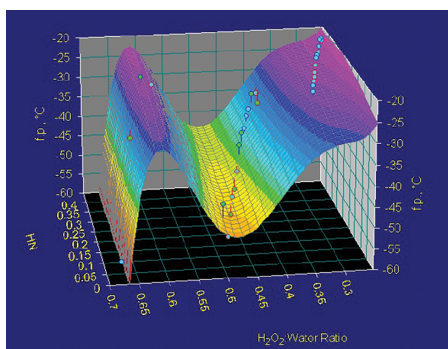


Figure 6: Freezing point diagram of $\text{HN}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ system. (From [201].)

Many salts form hydrates containing water of crystallization. Similar “hydrates” are formed with hydrogen peroxide instead of water in the sphere of hydration, except they are called *peroxidates*. Covalently bonded chemical adducts are formed from hydrogen peroxide and inorganic nitrates such as AN, sodium nitrate, potassium nitrate, ammonium dinitramide, or combinations thereof. These chemical adducts are referred to as *peroxidates* or persalts. They may be used as oxidizers in propellants, explosives, and pyrotechnics [202]. They represent hydrogen peroxide in solid form at room temperature, similar to crystalline hydrates. These adducts can also be used to produce low water content liquid hydrogen peroxide in a distillation tower. For instance, AN has a higher affinity to hydrogen peroxide than to water. The preferred H_2O_2 :AN molar ratio is 1:1, but discrete adducts with lower and higher H_2O_2 contents may also be formed. DSC thermograms indicated the formation of several different poly-peroxidates. On heating of the 1:1 adduct, four endotherms occurred at 327.09, 363.88, 403.97, and 434.26 K (53.94, 90.73, 130.82, and 161.11 °C). The 1:1 adduct is a solid at room temperature and starts to decompose at 423 K (150 °C). In a heated $\text{AN}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixture the water will distill off first, leaving the solid peroxidate behind. The solid can then be slowly decomposed under vacuum to release anhydrous hydrogen peroxide vapors that sublime and can be condensed in a cold trap. Similar, but less strongly hydrated salts can be obtained from hydrogen peroxide and sodium nitrate or potassium nitrate.

The freezing points (also called crystallization points) of AN solutions in 3% H_2O_2 (top curve) and 35% H_2O_2 (bottom curve) are shown in Figure 7. (It would be much more useful to have the AN diagram for 90% or 70% HTP instead of 3 and 35%.)

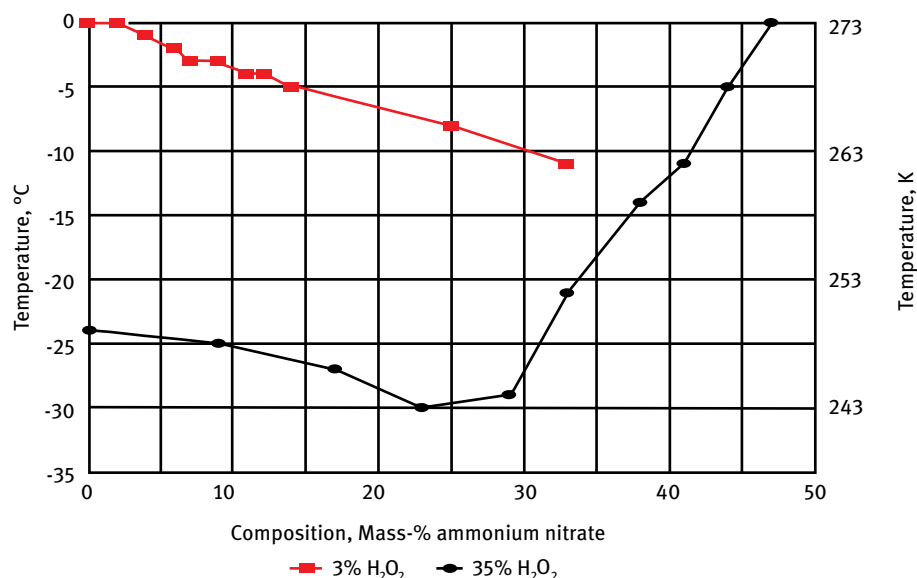


Figure 7: Freezing point of H_2O_2 /AN mixtures. (Chart created by Schmidt 2020, based on data from [202].)

A low-freezing oxidizer mixture containing 55% H_2O_2 , 39% ammonium nitrate, and 6% water was thoroughly characterized in drop weight impact sensitivity, cap sensitivity, boosted detonability, card gap sensitivity, and adiabatic compression sensitivity tests at room temperature and even at elevated temperature [203]. It was concluded that addition of AN to HTP does not worsen its sensitivity to mechanical and hydrodynamic shock and to adiabatic compression.

The density, viscosity, and freezing point diagram of ammonium nitrate solutions in HTP were measured. Ammonium nitrate in H_2O_2 forms a eutectic containing 46% AN [204].

In an effort to reduce the melting or glass transition temperature and to increase stability and to prevent aging without ruining the oxygen balance, ammonium nitrate or ammonium dinitramide was dissolved in hydrogen peroxide with purities from 60 to 80% [205, 206]. Such oxidizer solutions enable low operation temperatures far below 233 K (-40°C). They were tested as hypergolic propellants in combination with an energetic ionic liquid (EIL) based on AMIM DCA as fuel including appropriate cata-

lysts enhancing hydrogen peroxide decomposition. Hypergolic lab-scale ignition tests resulted in very short ignition delay times comparable to hypergolic combinations currently in operation.

The solubilities of perchlorate salts of alkali metals and alkaline earth metals at 273 K (0 °C) in anhydrous hydrogen peroxide are: LiClO_4 62.3, NaClO_4 42.12, KClO_4 3.52, RbClO_4 4.73, CsClO_4 15.34, $\text{Mg}(\text{ClO}_4)_2$ 70.1, $\text{Ca}(\text{ClO}_4)_2$ 97.7, and $\text{Sr}(\text{ClO}_4)_2$ 113.3 mass-% [207]. The solvates $\text{Ca}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}_2$ and $\text{Sr}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}_2$ were obtained as crystalline solids. LiClO_4 and $\text{Mg}(\text{ClO}_4)_2$ solvates could not be characterized due to their instability. The other perchlorates did not form solvates.

The $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ system was studied at 293 K (20 °C) to determine the optimum conditions for the preparation of anhydrous H_2O_2 by using anhydrous $\text{Mg}(\text{ClO}_4)_2$ (known as a very effective adsorbent for water vapor) as a desiccant [208]. Equilibrium solid phases are $\text{Mg}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}_2$ ($n=2, 4, 6$). The pure H_2O_2 can be obtained by vacuum heating of $\text{Mg}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}_2$ solutions at 293 K (20 °C). At $\text{Mg}(\text{ClO}_4)_2$, H_2O ratios corresponding to hexa- or tetrahydrates, 80–97% H_2O_2 was obtained, and anhydrous H_2O_2 was obtained for ratios corresponding to the dihydrate. The H_2O_2 yield was 94–97%.

3.1.3.2 Freezing Point Diagrams of Liquid/Liquid Mixtures with Hydrogen Peroxide

Hydrogen peroxide is readily miscible with inorganic and many organic liquids. The reason for adding other liquids to HTP would be to lower its freezing point, increase the specific impulse as a monopropellant, or improve the hypergolic ignition characteristics with organic fuels. If these added liquids are combustible fuels, the mixtures may be detonable. Other liquid additives that change the pH of H_2O_2 may destabilize it simply due to the change in pH. The destabilizing effect of KOH (a solid, not a liquid) on H_2O_2 was investigated after a tank with such a solution intended to be used in a chemical laser exploded during storage. Therefore, such mixtures should not be prepared in large quantities unless they are thoroughly characterized. There is an account of a not very well documented accident in WWII Germany where a mixture of HTP and ethanol (or methanol?) was transported and exploded. Despite this catastrophe, H_2O_2 /ethanol mixtures continue to be evaluated as rocket propellants. Shortly after 1935, a very serious accident occurred in Germany where physicists working for German Army Command tried to develop a more energetic H_2O_2 monofuel, but the propellant exploded and killed three people [209].

In the hydrogen peroxide/nitric acid binary system, the addition of HNO_3 to H_2O_2 would lower its freezing point of H_2O_2 and make the oxidizer hypergolic with many fuels with which H_2O_2 by itself might not otherwise react. Electrical conductivity measurements indicate a minimum at the formation of a peracid which is not capable of ionizing.

The freezing point of $\text{H}_2\text{O}_2/\text{CH}_3\text{OH}$ mixtures is shown in Figure 8 in comparison to those of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ mixtures. A difficulty was encountered with methyl alcohol beyond 51.5% H_2O_2 because the liquid froze to a glass [210].

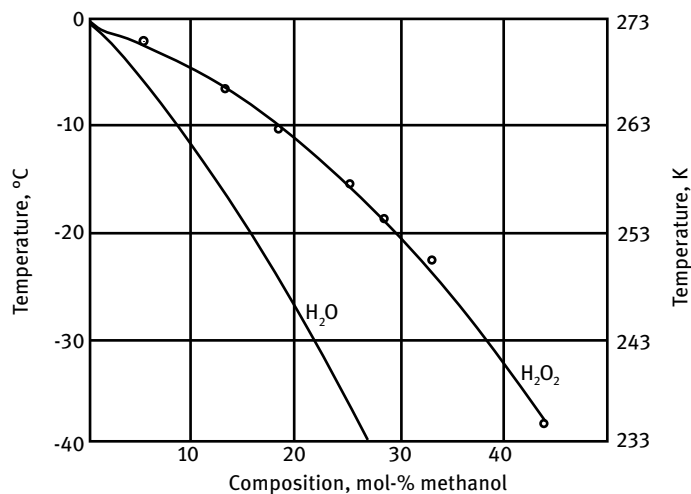


Figure 8: Freezing point of hydrogen peroxide/methanol mixtures in comparison to water/methanol mixtures. (Reprinted and modified from [210], with permission from © 1929 American Chemical Society; permission conveyed through RightsLink.)

The freezing point diagrams of mixtures of hydrogen peroxide with many organic polar solvents have been investigated.

Instead of using the more volatile methanol or ethanol as freezing point depressants in formulating a monopropellant more energetic than plain HTP, alcohols and diols with low vapor pressure have been tested as freezing point depressing fuels for HTP. One such mixture contained 67.8% H_2O_2 , 6.6% diethylene glycol, and 25.6% water, and it was thoroughly characterized in drop weight impact sensitivity, cap sensitivity, boosted detonability, card gap sensitivity, and adiabatic compression sensitivity tests at room temperature and even at elevated temperature [211].

3.1.4 Hydrogen Peroxide Phase Transitions under Very High Pressure

The pressure-induced phase transition and chemical decomposition of hydrogen peroxide and its mixtures with water at pressures up to 50 GPa were studied using confocal micro-Raman spectrometry and synchrotron X-ray diffractions [212]. The X-ray results indicated that pure H_2O_2 crystallizes into a tetragonal structure ($P4_12_12$), the same structure previously found in pure H_2O_2 at low temperatures. The tetragonal phase (H_2O_2 -I) is stable to 15 GPa, above which it transforms into an orthorhombic structure (H_2O_2 -II) over a relatively large pressure range between 13 and 18 GPa. The phase I $\rightarrow$ II transition pressure decreased in diluted H_2O_2 to around 7 GPa for the 41.7% H_2O_2 and 3 GPa for the 9.5% H_2O_2 , based on measurements of the splitting of the $\nu_s(\text{O}-\text{O})$ stretching mode. Above 18 GPa, H_2O_2 -II gradually decomposed to a mixture of H_2O and O_2 , with complete decomposition at around 40 GPa for pure and 45 GPa

for the 9.5% H_2O_2 . Upon pressure unloading, H_2O_2 also decomposed to H_2O and O_2 mixtures, occurring at 2.5 GPa for pure and 1.5 GPa for the 9.5% mixture. At H_2O_2 concentrations below 20%, decomposed mixtures formed oxygen hydrate clathrates at around 0.8 GPa (just after H_2O melts). The compression data of pure H_2O_2 and the stability data of the mixtures indicated that the high-pressure decomposition is likely due to the pressure-induced densification, whereas the low-pressure decomposition may be related to the heterogeneous nucleation process associated with H_2O_2 melting.

3.2 Boiling Point of Hydrogen Peroxide

The boiling point of aqueous hydrogen peroxide solutions depends on the hydrogen peroxide concentration (Table 3). If hydrogen peroxide solutions are concentrated by boiling away the water, the boiling point of the remaining solution will gradually increase. The boiling point of 100% H_2O_2 is 425 K (152°C), substantially higher than that of water.

Table 3: Atmospheric pressure boiling points of hydrogen peroxide solutions.

Hydrogen peroxide concentration		Temperature	
Mol fraction	Mass-%	°C	K
0.0	0	100.0	373.1
0.1	17.34	103.0	376.1
0.2	32.07	106.9	380.0
0.3	44.73	111.5	384.6
0.4	55.73	116.7	389.8
0.5	65.37	122.3	395.4
0.6	73.90	128.2	401.3
0.7	81.50	134.0	407.1
0.8	88.31	139.7	412.8
0.9	94.44	145.1	418.2
1.0	100.00	150.2	423.3

Data source: [4]

3.2.1 Sublimation of Solid Hydrogen Peroxide

Sublimation of H_2O from $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ ice mixtures may be one mechanism explaining how H_2O_2 becomes enriched in the ice crust of planetary bodies. The growth of thin films of crystalline H_2O_2 and $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ (dihydrate) in ultrahigh vacuum by distilling an aqueous solution of hydrogen peroxide was investigated using IR reflectance spectroscopy and UV-visible reflectance [213]. The three different crystalline phases: water,

dihydrate, and hydrogen peroxide, have very different sublimation rates, making sublimation a viable method to isolate the less volatile component, crystalline H_2O_2 . Using infrared (IR) spectroscopy and thermogravimetric analysis (TGA), the isothermal decomposition of the metastable $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ was examined at 151.6 K. This decomposition occurs by fractional distillation through the preferential sublimation of water, which leads to the formation of pure hydrogen peroxide [214].

3.3 Critical Constants of Hydrogen Peroxide

The critical point conditions for hydrogen peroxide can only be predicted by vapor pressure and density calculations and are not accessible to experimental verification due to incipient decomposition (Table 4).

Table 4: Critical point property data of hydrogen peroxide.

Critical temperature, T_c		Critical pressure, p_c			Source	Year	References
K	°C	MPa	atm	bar			
730	457	21.614	214		Scatchard, Kavanagh, and Ticknor	1952	[215]
728	455			220	Nikitin et al.	1995	[216]

The critical temperatures and the critical pressures of aqueous solutions with mass fractions of hydrogen peroxide from 0 to 0.9 were measured using a pulse-heating method applicable to thermally unstable substances [216]. The critical temperature and the critical pressure of pure hydrogen peroxide were then determined by extrapolation. The uncertainty assigned by NIST Thermodynamics Research Center to the Nikitin critical point data was ± 15 K and ± 20 bar [217].

3.4 Density and Compressibility of Hydrogen Peroxide

3.4.1 Density of Hydrogen Peroxide and Hydrogen Peroxide Solutions

The density of pure hydrogen peroxide as a function of temperature and the density of aqueous H_2O_2 solutions as a function of H_2O_2 concentration and temperature are summarized in this section. Some of the tables overlap in their coverage, and the data have not yet been consolidated. Measurement of the density is one of the simplest methods to obtain approximate numbers for the hydrogen peroxide concentrations. A commonly accepted number for the density of 100% H_2O_2 at 298 K is 1.4425 g/cm^3 .

The sample of pure H_2O_2 used for the density determination listed in Table 5 was purified and concentrated by distillation to 30%, evaporation to 90%, and then by fractionated crystallization to 100% H_2O_2 [218].

Table 5: Density of pure hydrogen peroxide.

Temperature		Density
K	°C	g/mL
261.02	−12.13	1.4774
263.35	−9.80	1.4751
264.77	−8.38	1.4733
266.92	−6.23	1.4705
270.30	−2.85	1.4674
272.62	−0.53	1.4638
273.25	+0.10	1.4631
274.35	1.20	1.4617
276.15	3.00	1.4597
278.70	5.55	1.4570
281.45	8.30	1.4541
285.75	12.60	1.4490
288.45	15.30	1.4465
293.05	19.90	1.4419

Data source: [218].

Table 6 is a compilation of density data for hydrogen peroxide solutions, gathered from different literature sources. One of the better density determinations for 0–100% H_2O_2 at 273 K was performed by [219, 220] as shown in Table 7. Another more recent set of data for a wider temperature range agrees quite well with the 273 K data above. Only the 273 K data are shown in Table 8. From these data the density at five different temperatures can be calculated as a function of the H_2O_2 concentration by using the following polynomial equation

$$\rho = a + bw + cw^2 + dw^3$$

where ρ is the density in g/cm^3 , and w is the weight fraction of H_2O_2 , and a , b , c , and d are the temperature-dependent coefficients listed in Table 9.

Table 6: Density of liquid and solid hydrogen peroxide.

Concentration	Temperature		Density	Source	Year	References
Mass-%	°C	K	g/cm³			
Liquid						
100	0	273	1.471	Laporte	1960	–
100	20	293	1.447			
100	40	313	1.425			
100	60	333	1.404			
100	80	353	1.380			
100	100	373	1.351			
98	25	298	1.431			
80	0	273	1.3589	Huckaba and	1948	[219]
85	0	273	1.3858	Keyes		
90	0	273	1.4136			
95	0	273	1.4421			
100	0	273	1.4709			
80	25	298	1.3339	Kubaschewski	1950	[194]
85	25	298	1.3600	and Weber		
90	25	298	1.3867			
95	25	298	1.4142			
100	25	298	1.4425			
Solid						
~100	–4.45	268.7	1.6434	Laporte	1960	–
~100	–7.45	265.7	1.6437			
~100	–20.0	253.15	1.713			

Table 7: Densities of hydrogen peroxide solutions at 273 K = 0 °C.

Mass-% H ₂ O ₂	Measured density, ρ , g/cm ³
0.000	0.9998
9.657	1.0379
19.979	1.0803
40.009	1.1660
59.171	1.2539
71.354	1.3139
80.023	1.3590
89.379	1.4100
95.987	1.4483
96.228	1.4493
96.282	1.4499
99.479	1.4681
99.605	1.4685
100.0	1.4709 ^a

^a Extrapolated value

Data source: [219]; also listed as Ref. 19 in Schumb

Table 8: Density of hydrogen peroxide solutions at 273 K = 0 °C.

Mass-% H ₂ O ₂	Density ρ , g/cm ³
0.0	0.9999
7.36	1.0291
17.14	1.0690
24.36	1.0987
33.23	1.1370
44.62	1.1860
55.69	1.2373
65.07	1.2822
74.96	1.3321
83.27	1.3759
91.55	1.4221
96.65	1.4517

Data source: [221]

Table 9: Coefficients for polynomial equation relating density to weight percent hydrogen peroxide.

Temperature		Coefficients			
°C	K	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
0	273	0.9998	0.39939	0.01758	0.05470
10	283	0.9997	0.36790	0.06208	0.02954
25	298	0.9970	0.34672	0.06995	0.02885
50	323	0.9880	0.31382	0.09402	0.01910
96	369	0.9612	0.27652	0.11956	—

Data source: [221]

Another equation based on curve-fitted data from six different sources expresses the density as a function of both concentration and temperature from 273 to 466 K (from 0 to 193 °C = 32 to 379 °F) over a concentration range of 60 to 100 mass-% H₂O₂ [7]:

$$\rho = 1.0479 + 2.455 \times 10^{-3} W + 1.781 \times 10^{-5} W^2 - 6.76 \times 10^{-4} t - 2.4 \times 10^{-7} t^2 - 3.98 \times 10^{-6} Wt$$

where ρ is the density in g/cm³, W is the mass-% H₂O₂, and t is the temperature in °C. Figure 9 gives the density of H₂O₂ solutions as a function of H₂O₂ concentration and temperature.

The densities of binary solutions of H₂O₂ and H₂O from 273 K (0 °C) down to their respective freezing points were measured by a dilatometric method [222]. An extrapolation of the density plot gave a value of 1.4730 g/mL for the density of pure liquid H₂O₂ at 273 K (0 °C). When measuring the volume changes during solidification, it was found that solutions containing less than 45 mass-% H₂O₂ expanded on freezing, and that this effect was decreasing with increasing concentration. The reverse was true of

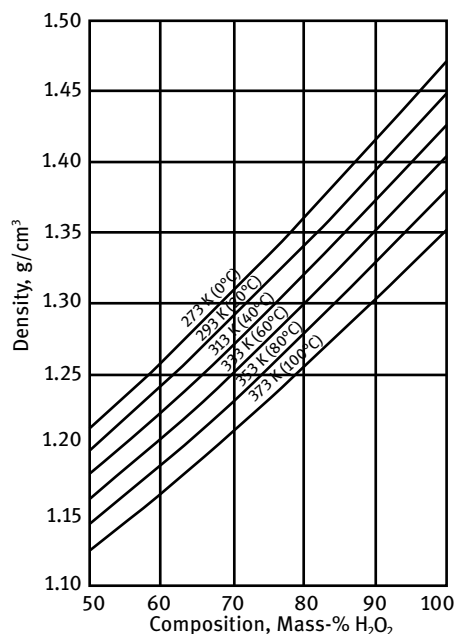


Figure 9: Density of aqueous H₂O₂ solutions. (Redrawn based on Laporte Chem. data.)

solutions containing over 65% H₂O₂. Observations on supercooling indicated that no solid solutions were formed between the two components.

In this book, we have collected mostly the density data for H₂O₂ solutions of practical interest containing more than 50% H₂O₂. If one plots the density as a function of H₂O₂ concentration over the entire range of compositions, one will notice that there are two areas where the linearity of the curve changes a little, one between 20 and 30% H₂O₂ and one between 70 and 80% H₂O₂ (Figure 10). This slight undulation is not evident in other published density data, which assume a simpler shape (Figure 11). This deviation from a straight line relationship is possibly caused by cluster formation at certain stoichiometries.

Figure 11 shows the density of hydrogen peroxide/water mixtures as a function of hydrogen peroxide content at 273 and 291 K (0 and 18 °C), but the function was drawn as an almost straight, slightly concave line [194].

Volumetric and calorimetric data were used to calculate the excess functions for mixtures of water and hydrogen peroxide over the entire concentration range, also in comparison with those for the corresponding deuterium isotopomer compounds [223]. A maximum in the excess-volume curves, presumably related to the formation of the compound H₂O₂•2H₂O, persists in the liquid mixtures over an appreciable temperature range above the melting point of H₂O₂. New density determinations were carried out on mixtures of heavy water and deuterium peroxide at 273 and 293 K (0 and 20 °C), and the effect of deuterium peroxide on the temperature of maximum density of heavy

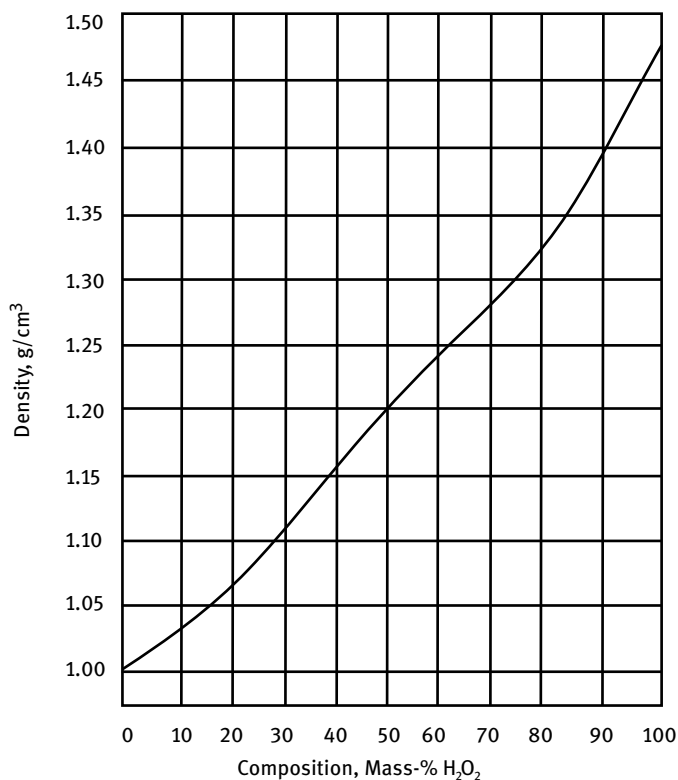


Figure 10: Density of hydrogen peroxide-water mixtures. (Republished and modified from [9], with permission of © 1999 Royal Society of Chemistry; permission conveyed through Copyright Clearance Center Inc.)

water was measured and compared with that of deuterated alcohols. It was concluded that the structure of liquid water is easily penetrated by hydrogen peroxide molecules.

It is well known that water is one of the few liquids that expand on freezing. The question is now: “How will mixtures of water and hydrogen peroxide behave on freezing?” This is an important question because containers in which solutions with lower concentrations of hydrogen peroxide are transported and stored may rupture if allowed to freeze accidentally in cold climates.

A set of curves for the density of HTP at concentrations between 84 and 89 mass-% and temperatures between 273 and 303 K (0 and +30 °C) was constructed to aid in the analysis of H₂O₂/H₂O mixtures [224].

The density of H₂O₂/H₂O mixtures at 295.7 K (22.6 ± 1.2 °C) can be expressed by the equation [225]:

$$\rho_0 = A + Bx + Cx^2$$

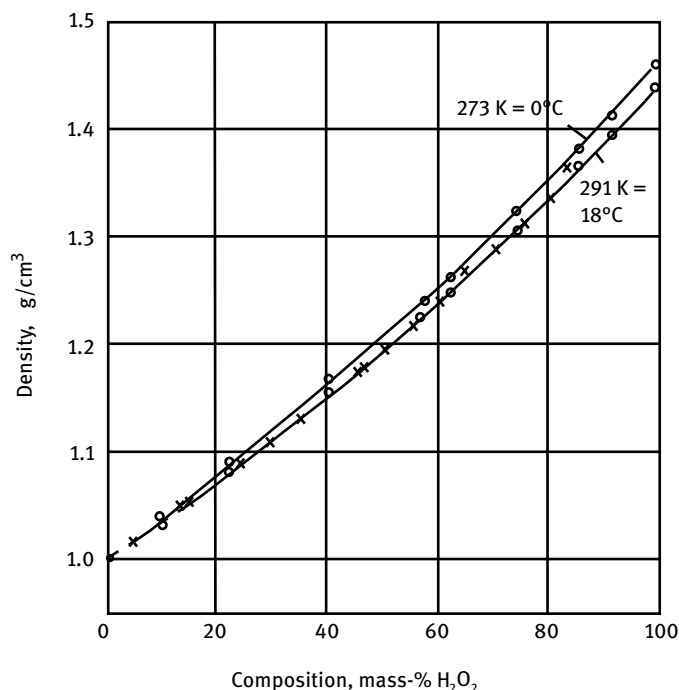


Figure 11: Density of hydrogen peroxide-water mixtures at 273 and 291 K. (Reproduced and modified from [194], with permission from © 1950 Wiley VCH GmbH.)

where ρ_0 is the density in g/cm³, x is the mass-% H₂O₂, and A, B, and C are constants: $A = 0.9991 \pm 0.0001$, $B = (3.369 \pm 0.003) \times 10^{-3}$, and $C = (1.058 \pm 0.003) \times 10^{-5}$.

The density of H₂O₂/H₂O solutions has been determined experimentally for temperatures in the range 273–269 K (0–96 °C), but the great difficulties in measuring densities at higher temperatures with incipient gas evolution makes it necessary to use calculation methods and extrapolate [226].

3.4.2 Coefficient of Thermal Expansion of Hydrogen Peroxide

The coefficients of thermal expansion taken from some old manufacturers' literature and listed in Table 10 do not match the average coefficients of thermal expansion calculated from curve-fitted data of measured densities taken from six different sources and illustrated in Figure 12.

Table 10: Coefficient of thermal expansion of hydrogen peroxide.

Concentration	Coefficient of thermal expansion $\times 10^4, ^\circ\text{C}^{-1}$				
Mass-% H_2O_2	Temperature range, $^\circ\text{C}$				
	0–20	20–40	40–60	60–80	80–100
60	6.8	7.2	7.5	8.0	8.8
70	7.1	7.4	7.7	8.2	9.0
80	7.4	7.5	7.8	8.3	9.4
90	7.7	7.6	7.9	8.5	9.9
100	8.1	7.7	7.9	8.8	10.6

Data source: Laporte Chem. Co.

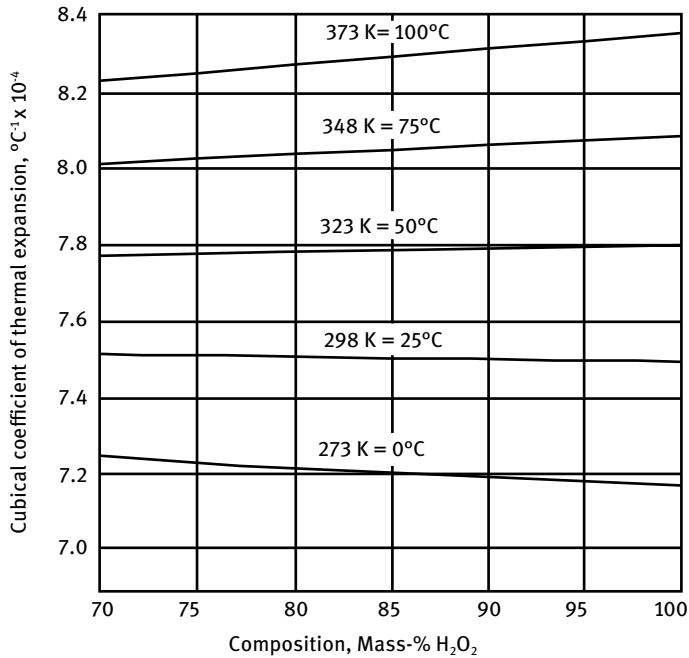


Figure 12: Coefficient of thermal expansion of hydrogen peroxide. (Reproduced and modified from [7].)

3.4.3 Compressibility of Hydrogen Peroxide

Adiabatic compressibility data are usually derived from velocity of sound measurements in liquids. The adiabatic compressibility of H_2O_2 solutions was calculated from experimental density and sonic velocity data covering a temperature range of 276.6 to 306.6 K (3.5 to 33.5 $^\circ\text{C}$ = 38.3 to 92.3 $^\circ\text{F}$) and a concentration range of 0 to 93.4 mol-%

(0 to 96.5 mass-%) [227]. These data were used to plot the adiabatic compressibilities of propellant-grade H_2O_2 solutions shown in Figure 13. Although no experimental data have been reported on the isothermal compressibility of H_2O_2 , the adiabatic compressibility, density, and heat capacity data were used to calculate an isothermal compressibility of $26.514 \times 10^{-12} \text{ cm}^2/\text{dyn}$ ($26.865 \times 10^{-6} \text{ atm}^{-1}$) for 100% H_2O_2 at 293 K ($20^\circ\text{C} = 68^\circ\text{F}$).

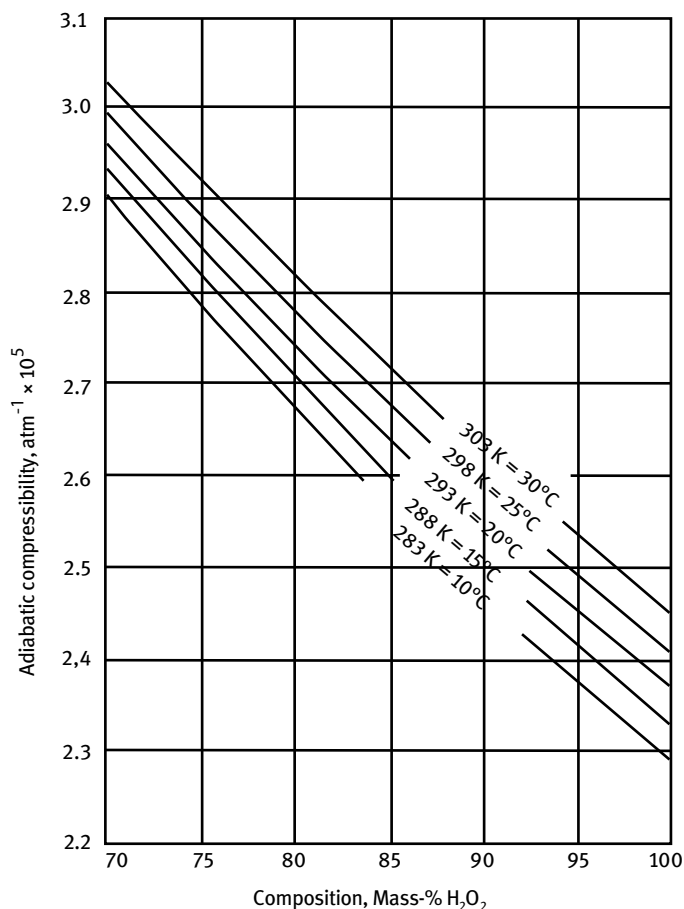


Figure 13: Adiabatic compressibility of hydrogen peroxide. (Reproduced and modified from [7].)

3.4.4 Velocity of Sound in Hydrogen Peroxide

The sonic velocity was measured for a temperature range from 276.6 to 306.6 K (3.5 to $33.5^\circ\text{C} = 38.3$ to 92.3°F) and a concentration range of 0 to 93.4 mol-% H_2O_2 (0 to 96.5 mass-%) [227, 228]. The unusually low compressibility of hydrogen peroxide was

explained by assuming a three-dimensional network of molecules held together by hydrogen bonding. These data were later used to plot the velocity of sound of propellant-grade H_2O_2 solutions shown in Figure 14.

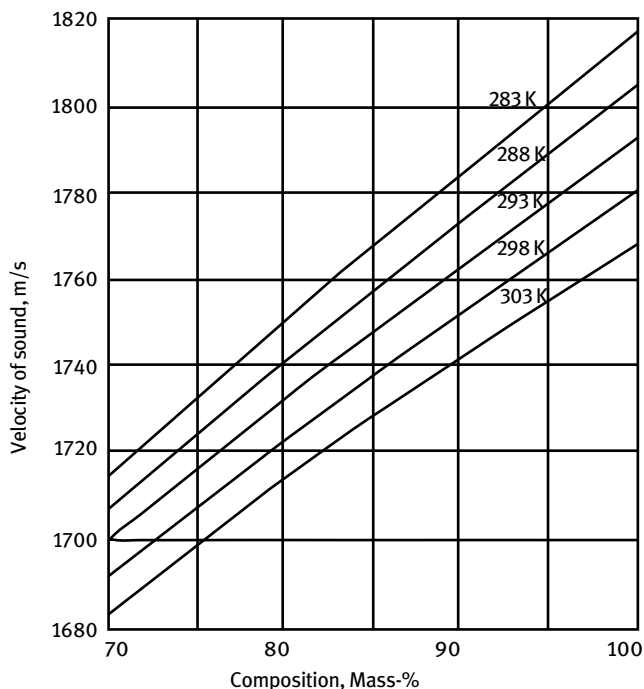


Figure 14: Velocity of sound of hydrogen peroxide solutions. (Based on data from [227].)

The velocity of sound of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixtures was measured over the entire range of compositions [225]. The mean and standard deviation of the temperatures at which the sound speed data were taken was $295.7 \pm 1.2\text{ K}$ ($22.6 \pm 1.2^\circ\text{C}$). To represent the sound speed data at any composition, the corrected values of sound speed were least-squares fit to the analytic (sigmoid) form

$$c_0 = \frac{(A + Dx^B)}{(1 + x^B)}$$

where c_0 is the velocity of sound in $\text{mm}/\mu\text{s}$, x is the mass-% H_2O_2 divided by C , and A , B , C , and D are fitting parameters. The resultant parameter values are $A = 1.488 \pm 0.004 \text{ mm}/\mu\text{s}$, $B = 1.636 \pm 0.183$, $C = 105.8 \pm 29.5$, and $D = 2.090 \pm 0.153 \text{ mm}/\mu\text{s}$. The experimental data and the fitted curve are shown in Figure 15; see also [229].

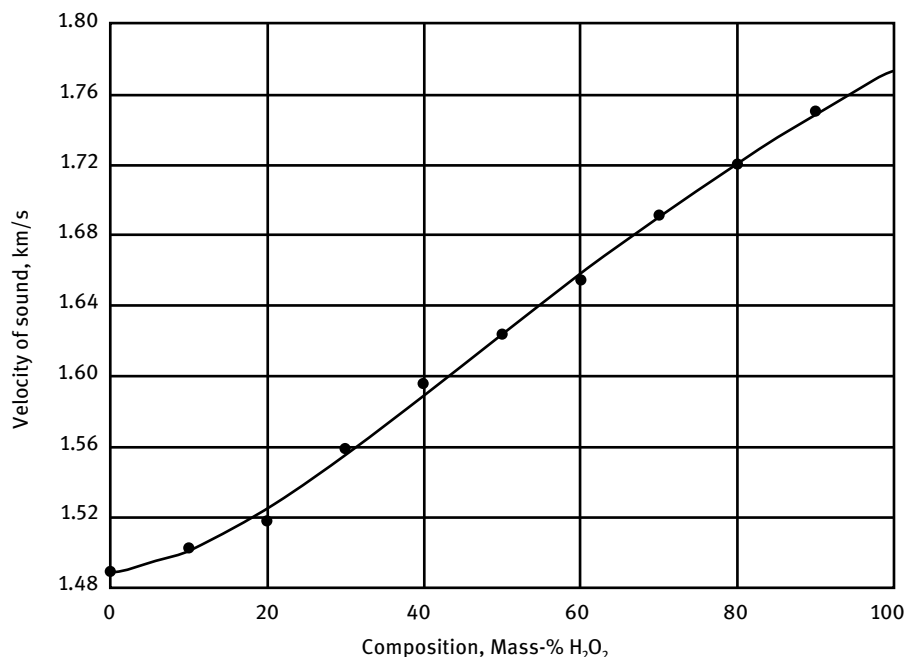


Figure 15: Velocity of sound in H₂O₂/H₂O mixtures at 295.7 K (22.6 °C). (Chart created by Schmidt 2020, based on data from [225].)

3.5 Vapor Pressure and Vapor Phase Composition of Hydrogen Peroxide Solutions

The determination of the vapor-pressure of pure hydrogen peroxide is important because the data makes possible the calculation of the latent heat of evaporation and Trouton's constant, the physical properties which are of particular interest when compared with the corresponding ones for water. The experimental difficulties which must be overcome in the measurement of the vapor pressure of hydrogen peroxide are that at high temperatures hydrogen peroxide decomposes when in contact with glass or mercury. A mercury manometer cannot be used directly because of the immediate decomposition that takes place when peroxide vapor comes into contact with the mercury surface, the latter being attacked and covered with scum, which makes accurate pressure readings impossible. One of the very first vapor pressure determinations for H₂O₂ gave the equation

$$\log p = - \frac{0.05223 \times 48530}{T} + 8.843$$

where p is the pressure in mm Hg, and T is the temperature in kelvin, a molecular latent heat of evaporation of 11.610 kcal/mol, and a Trouton's constant of 27.3, showing that hydrogen peroxide is associated in the liquid phase, similar to water whose Trouton's constant is 26.2 [230].

Total vapor pressure and vapor composition data for hydrogen peroxide solutions are listed in Table 11; see also Figure 16.

Table 11: Total vapor pressure and vapor composition of hydrogen peroxide solutions.

Temperature		Total vapor pressure, mm Hg				Vapor composition, mol fraction H ₂ O ₂		
°C	K	Mol fraction H ₂ O ₂ in liquid phase				0.70	0.80	0.90
0	273	0.856	0.583	0.404	0.272	0.202	0.352	0.600
10	283	1.83	1.30	0.915	0.642	0.224	0.381	0.626
20	293	3.66	2.64	1.89	1.36	0.238	0.397	0.640
25	298	5.09	3.71	2.69	1.95	0.247	0.407	0.648
30	303	6.99	5.14	3.77	2.77	0.255	0.417	0.656
40	313	12.8	9.55	7.14	5.36	0.272	0.435	0.671
50	323	22.4	17.0	12.9	9.90	0.287	0.452	0.684
60	333	37.8	29.1	22.5	17.5	0.302	0.468	0.696
70	343	61.8	48.2	37.8	29.8	0.316	0.482	0.707
80	353	97.8	77.2	61.3	49.1	0.329	0.495	0.716
90	363	150	120	96.5	78.2	0.342	0.508	0.725
100	373	226	182	148	121	0.354	0.519	0.733
110	383	331	269	221	182	0.365	0.530	0.740
120	393	474	389	322	269	0.376	0.540	0.747
130	403	666	552	460	387	0.386	0.549	0.753
140	413	919	767	645	546	0.396	0.558	0.758
150	423	1247	1048	887	755	0.405	0.566	0.763

Data source: [215]

Curve fitting of data obtained by Scatchard, Kavanagh, and Ticknor [231] led to the following vapor pressure equation for pure H₂O₂, valid for the range from 333 to 363 K (60 to 90 °C)

$$\log p = 44.5760 - 4025.3/T - 12.996 \log T + 0.0046055T$$

where p is the pressure in mm Hg, and T is the absolute temperature in K.

The vapor pressure of hydrogen peroxide is difficult to determine experimentally, since incipient decomposition causes formation of oxygen that increases the measured pressure above the liquid sample. For this reason, vapor pressure measurements

rarely go to temperatures exceeding 340 K (70 °C). According to [232], one can derive a vapor pressure equation by curve fitting data to the Clausius-Clapeyron equation:

$$\log p_D = 24.594655 - 3375.1/T - 5.23700 \log T$$

where p_D is the vapor pressure in mm Hg, and T is the absolute temperature in K.

Charts were presented for the vapor pressure of hydrogen peroxide from 278 to 433 K (40 to 320 °F) [233]. A copy of such a chart is shown in Figure 16.

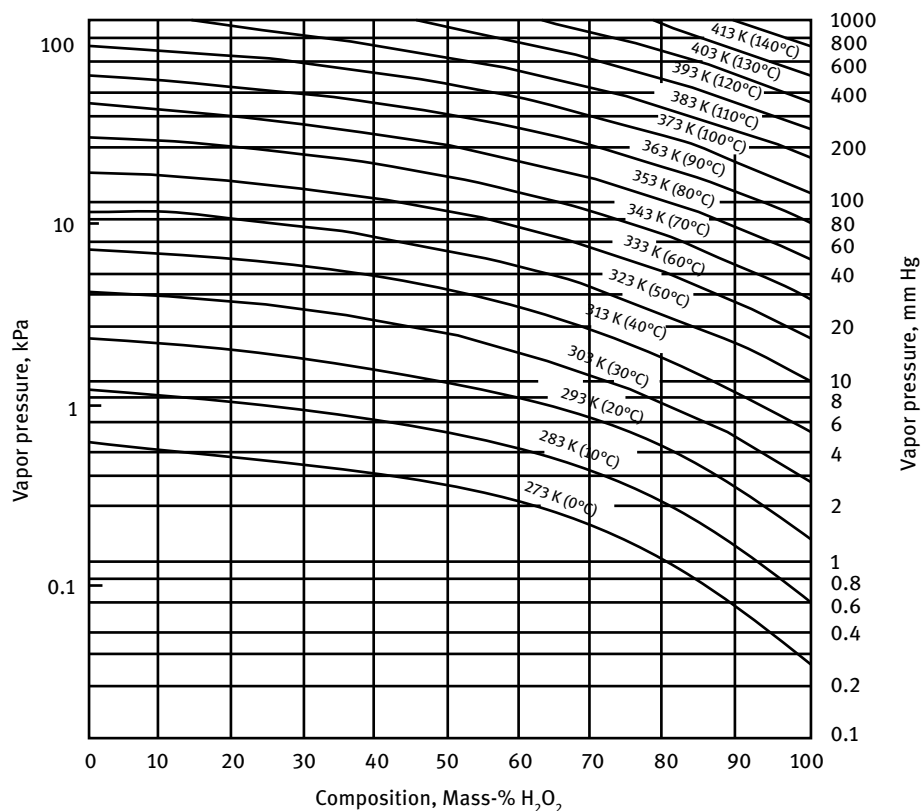


Figure 16: Total vapor pressure of aqueous hydrogen peroxide solutions. (Reproduced and modified from Laporte Chem. Co.)

Because the boiling points of water and hydrogen peroxide are so far apart ($\Delta T = 50^\circ\text{C}$), it is relatively easy to achieve H_2O_2 concentration by simple distillation. A fractionating column would certainly help achieve more effective separation and

reduce carryover of water. The vapor phase diagram of the $\text{H}_2\text{O}_2\text{-H}_2\text{O}$ system needs to be known in order to design a distillation system. Figure 17 shows the vapor phase composition diagram for two pressures: 30 mm Hg and 760 mm Hg.

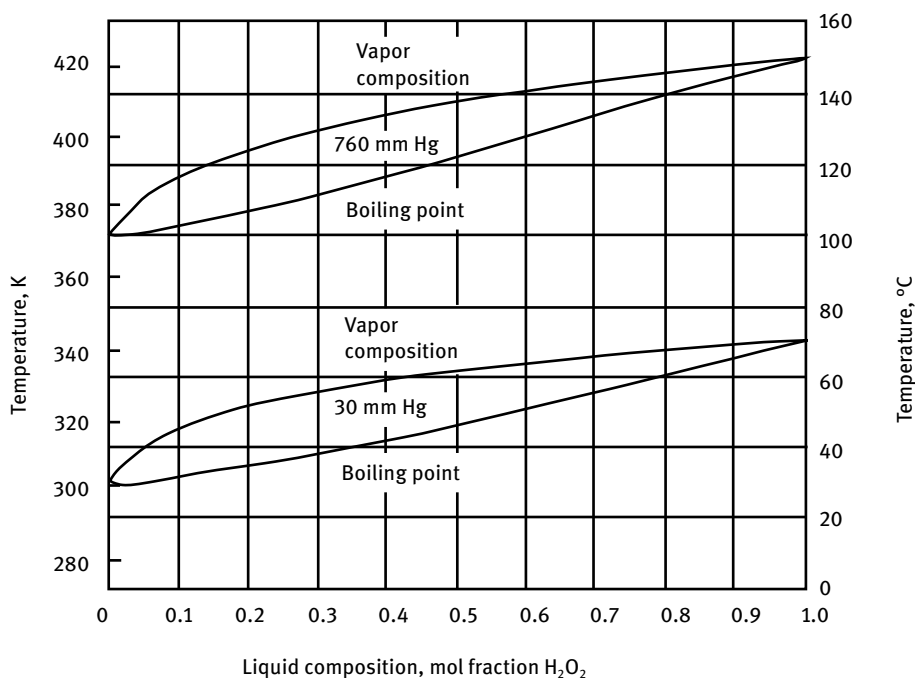


Figure 17: Vapor phase composition diagram of the $\text{H}_2\text{O}_2\text{-H}_2\text{O}$ system. (Reproduced and modified from [4].)

We do not provide the numerical data on which Figure 17 is based. It may suffice to just give the boiling points of $\text{H}_2\text{O}_2\text{-H}_2\text{O}$ mixtures at atmospheric pressure as already summarized in Table 3 at the beginning of this chapter.

The total vapor pressures of binary mixtures of H_2O_2 and H_2O were measured by a static method at 303, 318, and 333 K (30, 45, and 60 °C) over the entire range of compositions [234]. The vapor-pressure composition curves exhibit a large negative deviation from Raoult's law. The activities of H_2O and H_2O_2 in their solutions were calculated based on the polarity of the two pure liquids. These data are important for the design of distillation apparatus for the concentration of H_2O_2 solutions; see also [235].

Available experimental data of the pressure dependence of temperature of non-equilibrium boiling of rapidly heated aqueous solutions of hydrogen peroxide

were used to determine the pressure(P)-temperature(T)-concentration(x) relationship [236]. A correlation was obtained for a solution under conditions of phase equilibrium (saturation surface in three-dimensional space of variables P , T , and x) in a wide range of states, including the critical state. The surface obtained was used to calculate the equilibrium composition of vapor above the equilibrated liquid as a function of x and T by solving the Duhem equation.

In continuation of this work, the dependences of total pressure and equilibrium composition of vapors on temperature and mol fraction of hydrogen peroxide in solution were calculated for a H_2O_2 - H_2O two-component two-phase system [237]. It was assumed that the relaxation to concentration equilibrium in gas at the surface of the solution would be attained quite rapidly compared to the half-life of hydrogen peroxide. Three independent approximate methods were used to calculate the total pressure, but two of these methods did not use the ideal gas approximation for the vapor phase. Approximation formulas express the dependence of pressure and composition of gas on relative concentration of hydrogen peroxide in solution and on temperature. Total pressure curves were given for the entire range of compositions at temperatures of 373, 423, 473, 523, and 573 K. Small deviations of phase diagrams from one another implied that any of three approximations may be used for the calculation of total pressure $P(x, T)$ in the $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ system. Error limits of calculations were estimated. The simplest method for the calculation of total pressure was a method that was based on the closeness of the thermodynamic properties of water and hydrogen peroxide: the $P(x, T)$ function was determined by interpolation using formulas for lines of phase equilibrium of $P(T)$ of individual components.

3.6 Viscosity of Hydrogen Peroxide

3.6.1 Viscosity of Liquid Hydrogen Peroxide

Early literature described the appearance of pure hydrogen peroxide as a “syrupy consistency”. This is not supported by current data (Table 12) showing that pure H_2O_2 is not much more viscous than pure water.

Figure 18 is a graphical compilation of viscosity data for 90 and 98% hydrogen peroxide collected from four different sources and combined by Anderson [183].

3.6.2 Viscosity of Hydrogen Peroxide/Water Mixtures

The viscosity of hydrogen peroxide solutions as a function of H_2O_2 concentration is not a linear function but goes through a minimum and a maximum as illustrated in Figure 19, which shows the viscosity at three different temperatures. The S-shape of

Table 12: Viscosity of 90 and 98% hydrogen peroxide.

Concentration	Temperature			Viscosity			References
Mass-% H ₂ O ₂	K	°F	°C	mPa s	centipoise	lb _f ft ⁻¹ s ⁻¹ × 10 ³	
90	273	32	0	1.887	1.887	1.268	[238]
90	273	32	0	1.872	1.872	1.258	
90	293	68	20	1.260	1.260	0.847	[238]
90	298	77	25	1.156	1.156	0.777	
90	323	122	50	0.803	0.803	0.540	
90	323	122	50	0.801	0.801	0.538	[7]
90	373	212	100	0.479	0.479	0.322	[7]
90	398	257	125	0.402	0.402	0.270	[7]
90	423	302	150	0.362	0.362	0.243	[7]
90	436	326	163	0.311	0.311	0.209	[7]
98	273	32	0	1.839	1.839	1.236	[238]
98	273	32	0	1.812	1.812	1.218	
98	293	68	20	1.252	1.252	0.841	[238]
98	293	68	20	1.250	1.250	0.840	[183]
98	298	77	25	1.156	1.156	0.777	
98	303	86	30	1.068	1.068	0.718	[183]
98	313	104	40	0.920	0.920	0.618	[183]
98	323	122	50	0.816	0.816	0.548	
98	323	122	50	0.812	0.812	0.546	[183]
98	333	140	60	0.724	0.724	0.487	[183]
98	343	158	70	0.645	0.645	0.433	[183]
98	353	176	80	0.583	0.583	0.392	[183]
98	358	185	85	0.555	0.555	0.373	[183]

the curve is particularly distinct at 273 K (0 °C). The shape of the curve is difficult to explain. Compound or hydrate formation as it is observed with anhydrous hydrazine and water does not occur in the H₂O/H₂O₂ liquid system. Both H₂O and H₂O₂ liquids by themselves are heavily associated due to hydrogen bonding and cluster formation.

Numerical data for viscosity data at two different temperatures are summarized in Table 13.

Similar viscosity data measured at 273 K and 291 K (0 and 18 °C) were measured already almost 100 years ago [218] and were included in Table 14. It was then that the S-shape of the viscosity curve was first noted.

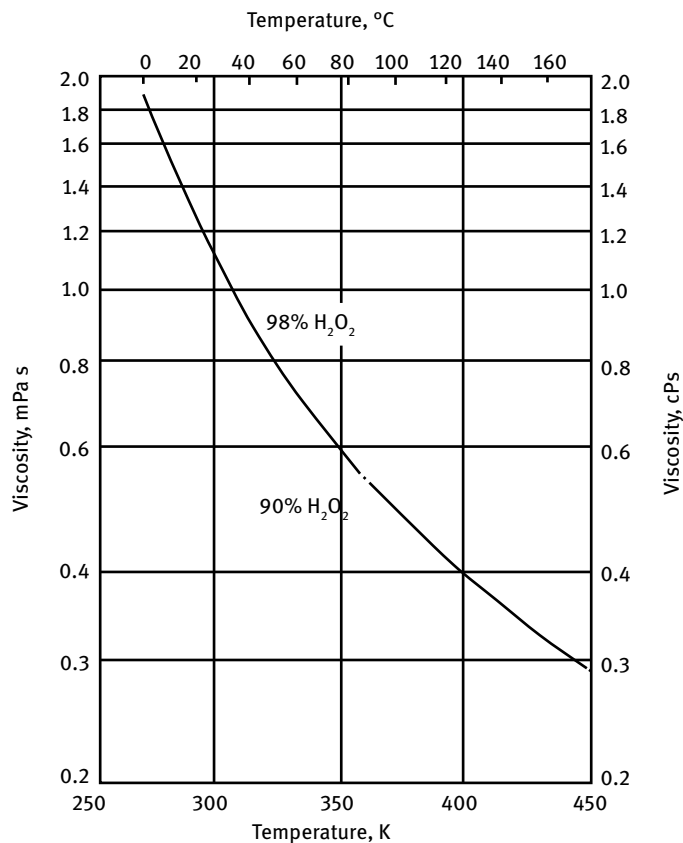


Figure 18: Viscosity of 90 and 98% hydrogen peroxide. (Reproduced and modified from [183].)

3.6.3 Viscosity of Hydrogen Peroxide Vapor

The viscosity of hydrogen peroxide vapor is an important parameter in the heterogeneously catalyzed decomposition of H_2O_2 in chemical reactors. The vapor of undecomposed H_2O_2 has to diffuse toward the catalyst surface, and its flow is impeded by a flow of decomposed H_2O_2 (i.e., H_2O and O_2) in the opposite direction.

The viscosity of vapor mixtures of highly polar H_2O_2 and H_2O containing up to 65 mol-% H_2O_2 was measured by a capillary flow method at 1 atm total pressure and a temperature of 443 K (170 °C) [240]. The method of determining viscosity used was that of measurement of the pressure drop occurring upon flowing hydrogen peroxide vapor through a capillary tube at constant temperature. The viscosity of anhydrous H_2O_2 vapor at 443 K (170 °C) was found to be 144 μPs by extrapolation. Studies were

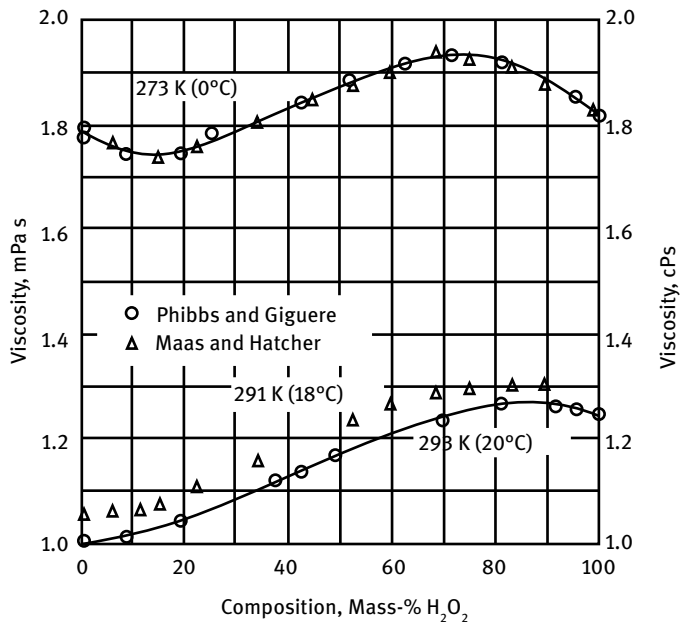


Figure 19: Viscosity of hydrogen peroxide-water mixtures. (Reproduced and modified from [4].)

Table 13: Viscosity of liquid hydrogen peroxide solutions at 273 and 293 K (0 and 20°C).

Composition Mass-% H ₂ O ₂	Viscosity, mPa s		Viscosity, centipoise	
	At 273 K = 0°C	At 293 K = 20°C.	At 273 K = 0°C	At 293 K = 20°C
0.00	1.792	1.005 ^a	1.792	1.005 ^a
8.68	1.746	1.011	1.746	1.011
19.06	1.746	1.045	1.746	1.045
25.11	1.783		1.783	
37.33		1.120		1.120
42.72	1.844	1.140	1.844	1.140
49.08		1.170		1.170
51.93	1.884		1.884	
62.37	1.917	1.219	1.917	1.219
69.78		1.234		1.234
71.55	1.933		1.933	
81.21	1.919	1.266	1.919	1.266
91.76		1.262		1.262
95.75	1.854	1.259	1.854	1.259
100.00	1.819	1.249	1.819	1.249

^a In line with a more recent revision of the water viscosity at 20°C from 1.005 to 1.002 cPs, since water was used to calibrate the instrument, all data above should be reduced by 0.3%
Data source: [238], also listed as Schumb's Ref. 29 in Schumb Table 11

Table 14: Viscosity of hydrogen peroxide solutions.

H ₂ O ₂ Concentration Mass-%	Temperature		Viscosity η	
	°C	K	mPa s	cPs
50	18	291	1.23	1.23
90	18	291	1.34	1.34
90	0	273	1.860	1.860
90	25	298	1.153	1.153
98	0	273	1.810	1.810
98	25	298	1.155	1.155
100	0	273	1.798	1.798
100	25	298	1.156	1.156

Data source: Becco product literature and [239]

also made at 473 and 513 K (200 and 240 °C) to provide a basis for estimating the effect of temperature. An all-glass apparatus made it possible to produce vapors containing less than 1 mol-% of dioxygen, and it was demonstrated that this low oxygen concentration did not affect the precision of measurements. The viscosity can be represented by the equation

$$\mu = 134 + 0.35(t - 100) - 14y$$

where μ is the viscosity in μ Ps, t is the temperature in °C, and y is the mol fraction of H₂O₂. This equation is recommended for the calculation of the viscosity of vapor mixtures of H₂O₂ and H₂O over the temperature range of 373 to 573 K (100 to 300 °C) and is believed to have a precision of $\pm 2\%$.

3.7 Surface Tension of Hydrogen Peroxide

Density, surface tension, and viscosity measurements of highly concentrated hydrogen peroxide are difficult to perform due to the interference of tiny bubbles formed during the decomposition of the highly concentrated material. The surface tension data for H₂O/H₂O₂ mixtures for two different temperatures are summarized in Table 15.

The data from Table 15 are plotted in Figure 20.

Table 16 is more convenient because it contains data for even degree Celsius numbers. Most likely it was obtained by interpolating the Phibbs and Giguere data, since it also uses the same two temperatures.

Similar surface tension measurements at 273 and 291 K (0 and 18 °C) were measured already 100 years ago [218]. The units of the measurements reported there should be dyn/cm and not dyn.

Table 15: Surface tension of hydrogen peroxide solutions at 273 K and 293 K (0 °C and 20 °C).

Composition Mass-% H ₂ O ₂	Surface tension,			
	mN/m		dyn/cm	
	At 273 K = 0 °C	At 293 K = 20 °C	At 273 K = 0 °C	At 293 K = 20 °C
0.00	75.65	72.75	75.65	72.75
17.05	76.36	73.41	76.36	73.41
26.31	76.95	74.12	76.95	74.12
37.33	77.69	74.67	77.69	74.67
49.76	78.41	75.68	78.41	75.68
64.33	79.62	76.65	79.62	76.65
71.55	80.48	77.36	80.48	77.36
84.12	81.92	78.61	81.92	78.61
95.75	82.93	79.87	82.93	79.87
100.00	83.3 ^a	80.4 ^a	83.3 ^a	80.4 ^a

^a Extrapolated value, precision: +/- 0.05 dyn/cm; 1 dyn = 10⁻⁵ N
Data source: [238]

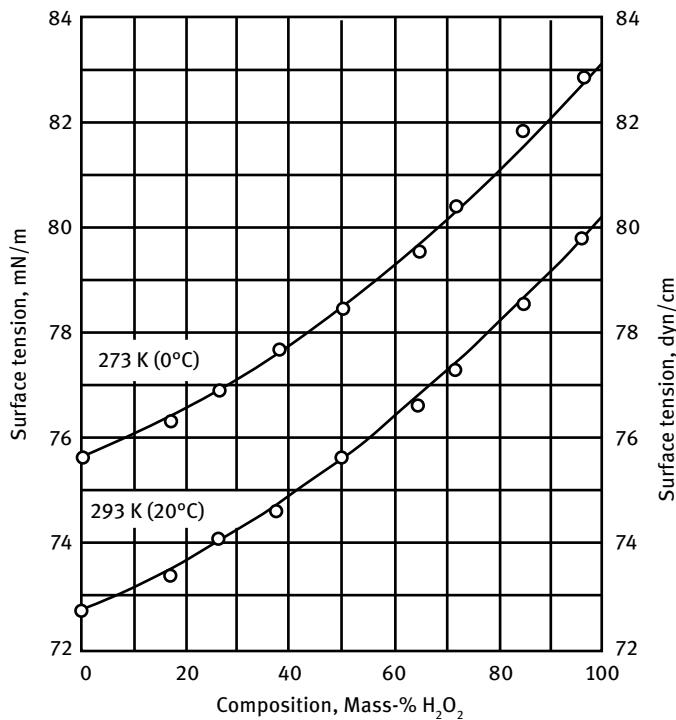


Figure 20: Surface tension of hydrogen peroxide-water mixtures. (Reproduced and modified from [4].)

Table 16: Surface tension of hydrogen peroxide solutions.

H ₂ O ₂ concentration	Surface tension, dyn/cm		Surface tension, mN/m	
Mass-%	At 273 K = 0 °C	At 293 K = 20 °C	At 273 K = 0 °C	At 293 K = 20 °C
50	78.55	75.65	78.55	75.65
60	79.34	76.45	79.34	76.45
70	80.20	77.30	80.20	77.30
80	81.16	78.25	81.16	78.25
90	82.15	79.24	82.15	79.24
98		80.20		80.20
100	83.25	80.30	83.25	80.30

Data source: Laporte Chemicals Ltd. and [27]

3.8 Thermal Conductivity of Hydrogen Peroxide

The thermal conductivity of hydrogen peroxide is listed in Table 17. The only measured thermal conductivity data for high-strength H₂O₂ found in the literature as second-hand information are referenced by Anderson [183] as shown in Table 18.

Table 17: Thermal conductivity of hydrogen peroxide.

State	Temperature		λ	
	°C	K	cal cm ⁻¹ s ⁻¹ °C ⁻¹	W cm ⁻¹ K ⁻¹
Liquid	25	298	0.0014	0.0059
Vapor	200	473	0.00007	0.00029

Data source: Laporte Chemicals Ltd. and [27]

Table 18: Thermal conductivity of hydrogen peroxide and water.

Concentration	Thermal conductivity, λ					
Mass-% H ₂ O ₂	BTU h ⁻¹ ft ⁻¹ °F ⁻¹		cal s ⁻¹ cm ⁻¹ °C ⁻¹ × 10 ³		W m ⁻¹ K ⁻¹	
Temperature, °F	32	77	32	77	32	77
Temperature, K	273	298	273	298	273	298
98.2	0.321	0.339	1.327	1.401	0.555	0.587
50.0	—	0.347	—	1.434	—	0.601
0.0	0.324	0.353	1.339	1.459	0.561	0.611

Data source: [183]

Calculated/extrapolated thermal conductivity data for 98% HTP are summarized in Table 19, and data for 98% HTP and water are graphed in Figure 21 for a very wide temperature regime, up to very close to the critical point, including temperatures where HTP is sure to decompose. The critical point of hydrogen peroxide is not only critical in the sense of merging liquid and vapor states but is also critical in terms of its explosion hazard. The thermal conductivity behavior of hydrogen peroxide between its normal boiling point and its critical point may be similar to that of water.

Table 19: Thermal conductivity data for 98% HTP, measured and extrapolated.

Temperature			Thermal conductivity		
K	°F	°C	BTU h ⁻¹ ft ⁻¹ °F ⁻¹	cal s ⁻¹ cm ⁻¹ °C ⁻¹ × 10 ³	W m ⁻¹ K ⁻¹
273	32 ^a	0	0.321	1.327	0.555
277	40	4.4	0.323	1.334	0.559
298	77 ^a	25.0	0.339	1.401	0.587
300	80	26.7	0.343	1.419	0.594
322	120	48.9	0.364	1.506	0.630
344	160	71.1	0.384	1.590	0.665
366	200	93.3	0.401	1.657	0.694
389	240	115.6	0.413	1.707	0.715
411	280	137.8	0.421	1.741	0.729
433	320	160.0	0.426	1.761	0.737
455	360	182.2	0.427	1.764	0.739
477	400	204.4	0.424	1.755	0.734
500	440	226.7	0.420	1.736	0.727
544	520	271.1	0.404	1.670	0.699
566	560	293.3	0.392	1.622	0.678
589	600	315.6	0.378	1.562	0.654
611	640	337.8	0.361	1.493	0.625
633	680	360.0	0.342	1.413	0.592
993	720	382.2	0.319	1.320	0.552
1033	760	404.4	0.295	1.219	0.511
1122.6	849.5 ^b	454.1	0.144	0.595	0.249

^a measured data

^b critical point

Data source: [183]

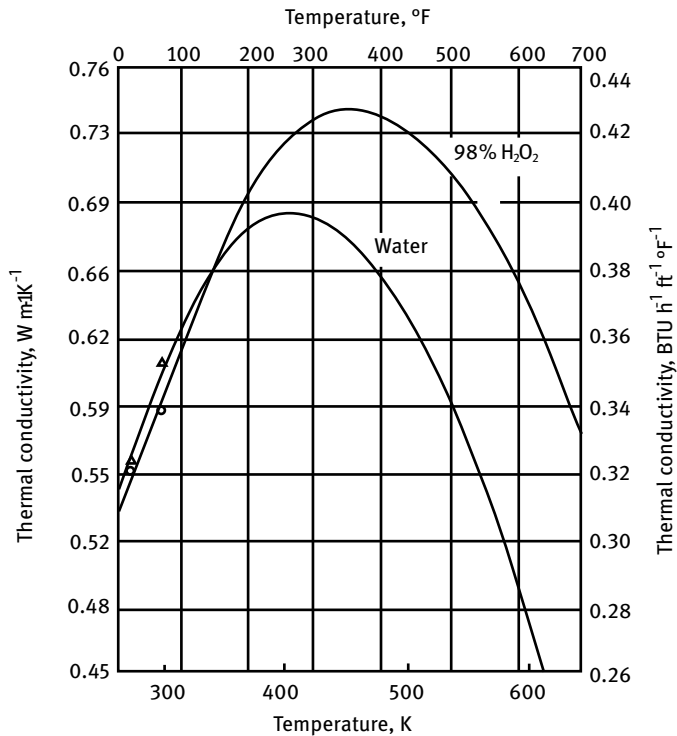


Figure 21: Thermal conductivity of 98% hydrogen peroxide and water. (Reproduced and modified from [183].)

3.9 Heat Transfer Coefficient of Hydrogen Peroxide

Hydrogen peroxide has very good heat transfer properties, which make it suitable as a coolant in regeneratively cooled rocket engines, as long as the flow velocity is kept up high enough, and as long as the heat soaking back after engine shutdown does not overheat the residual liquid in the cooling channels. Heat transfer tests with 98% H₂O₂ were carried out in CRES-316 tubes [241–243]. The threshold of explosive decomposition is also dependent on the type of the wall material because some metals may act as catalysts and will lower the threshold beyond which a thermal runaway situation will destroy the engine.

Contrary to other liquids, hydrogen peroxide does not have a range of nucleate boiling heat transfer. Once a certain heat flux is exceeded, the incipient decomposition immediately leads to a film boiling heat transfer situation. The heat transfer coefficient of 98% H₂O₂ is illustrated in Figure 22. Under the conditions of this test, the curve ends abruptly at 550 cal cm⁻² s⁻¹ because the cooling capacity disappears as the wall burns out.

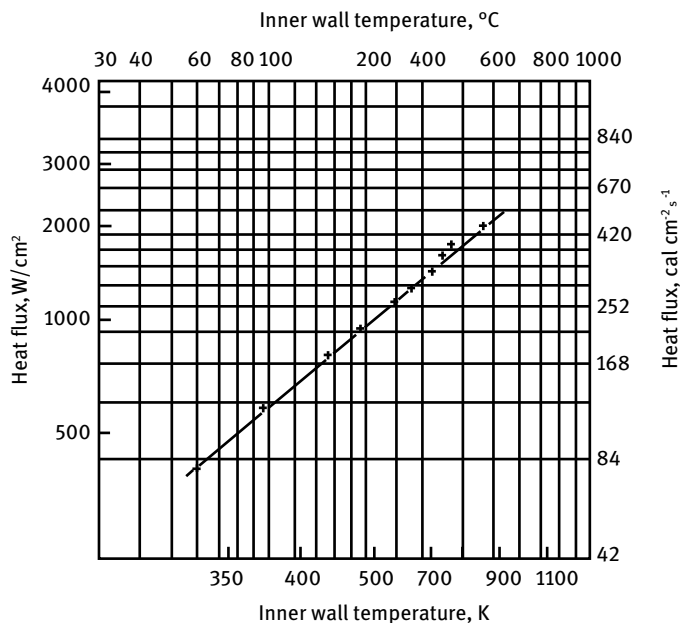


Figure 22: Heat transfer to 98% H_2O_2 at 47.5 at and 20.5 m/s flow velocity. (Reproduced and modified from [242].)

Due to the good heat transfer properties of 90% H_2O_2 , this oxidizer has been used as a regenerative coolant in the North American Aviation AR-2 rocket engine (see *Encyclopedia of Hypergolic Bipropellant Combinations*) which was used in piloted jet fighters to give them a fast escape in critical situations.

Experimental heat transfer studies on 90% H_2O_2 solutions indicated that a high flux heat transfer, usually associated with boiling, was obtained from a 347 stainless steel surface to liquid 90% H_2O_2 as a result of the H_2O_2 decomposition [244]. This decomposition, which simulates film boiling by the liberation of gas bubbles at the heat transfer surface, is accelerated with each temperature increase of the surface. Under the conditions studied, heat transfer rates were obtained that could not be explained by forced convection and/or boiling heat transfer alone. Figure 23 illustrates the magnitude of this effect in terms of heat flux as a function of surface temperature.

Figure 24, based on the same set of data, shows the heat flux as a function of temperature difference between the heater wall and the liquid.

An extension of these studies to high fluid velocities and moderately high temperature differences showed that at high flow rates and high Reynolds numbers (where decomposition is limited by the short liquid residence time), the resultant heat transfer data agreed with that expected for forced convective heat transfer [245]. It was found that heat fluxes as high as $11.75 \text{ BTU in.}^{-2} \text{s}^{-1}$ (at liquid velocities of 80 ft/s) could

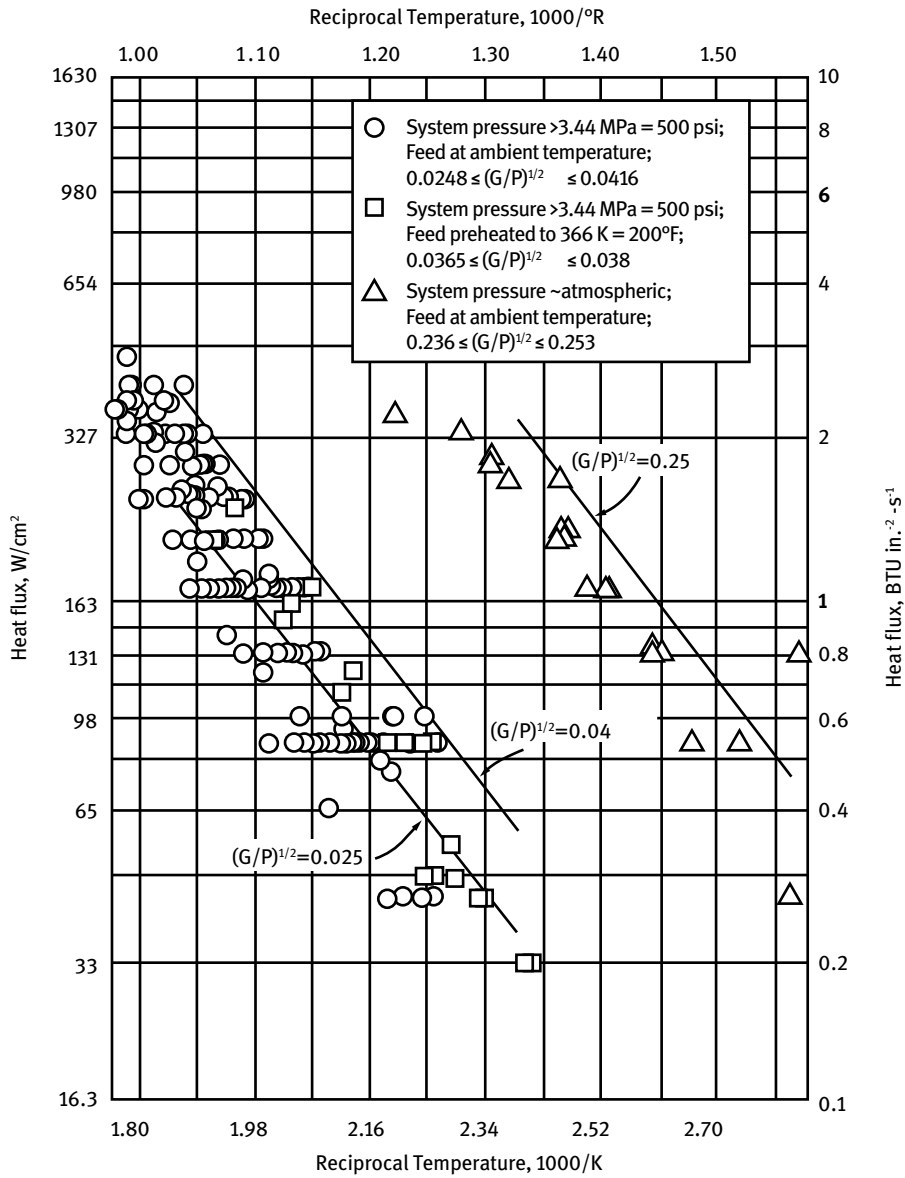


Figure 23: Heat flux to 90% hydrogen peroxide at low flow velocities as a function of surface temperature T_s . (Reprinted and modified from [245].)

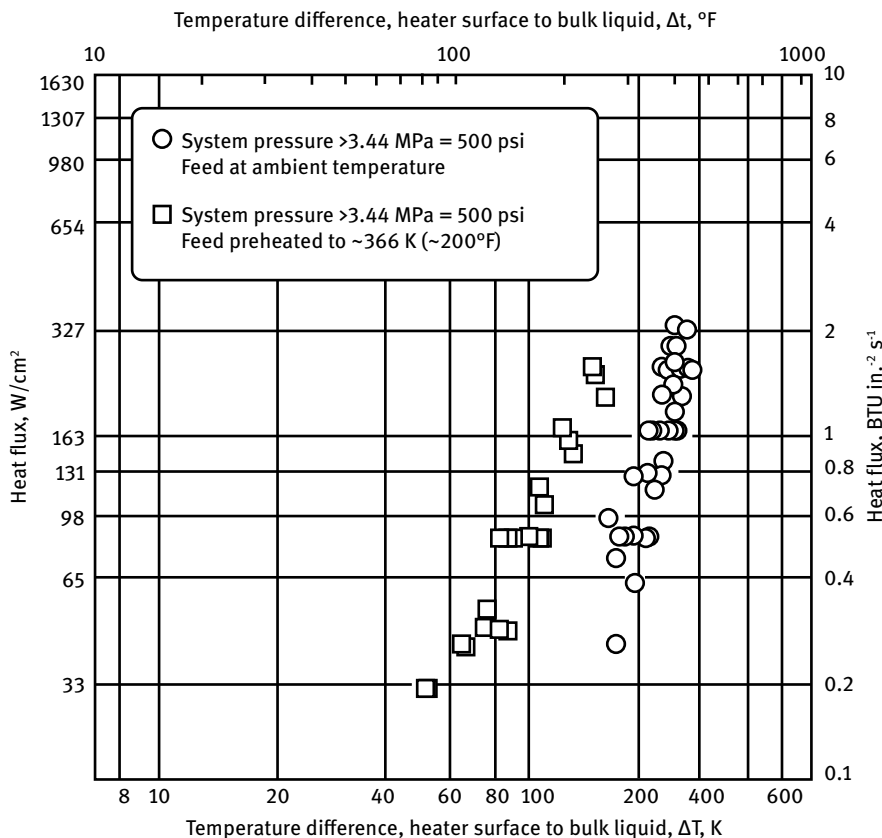


Figure 24: Heat flux to 90% hydrogen peroxide as a function of temperature difference between the heater wall and the liquid. (Reprinted and modified from [245].)

be obtained with 90% H_2O_2 without complication by decomposition of the hydrogen peroxide. A least-squares fit of the heat transfer data obtained on 90% H_2O_2 resulted in the following expression:

$$(N_{\text{Nu}})_f = 0.0287(N_{\text{Re}})_f^{0.8}(N_{\text{Pr}})_f^{\frac{1}{3}}$$

which is the least-squares fit of the heat transfer data graphed in Figure 25.

In unpublished studies by Pratt & Whitney, heat transfer measurements in the forced convective region of both 90 and 98% H_2O_2 were reported. They were later reported also by McCormick at FMC and repeated by Constantine and Cain [246]. Peak heat fluxes of $7.80 \text{ BTU in.}^{-2} \text{s}^{-1}$ were measured for 90% H_2O_2 at fluid velocities of 41.3 ft/s. The results obtained for the peak heat flux of 98% H_2O_2 at 4.83 MPa (700 psia) and 20.3 m/s (66.8 ft/s) are shown in Figure 26.

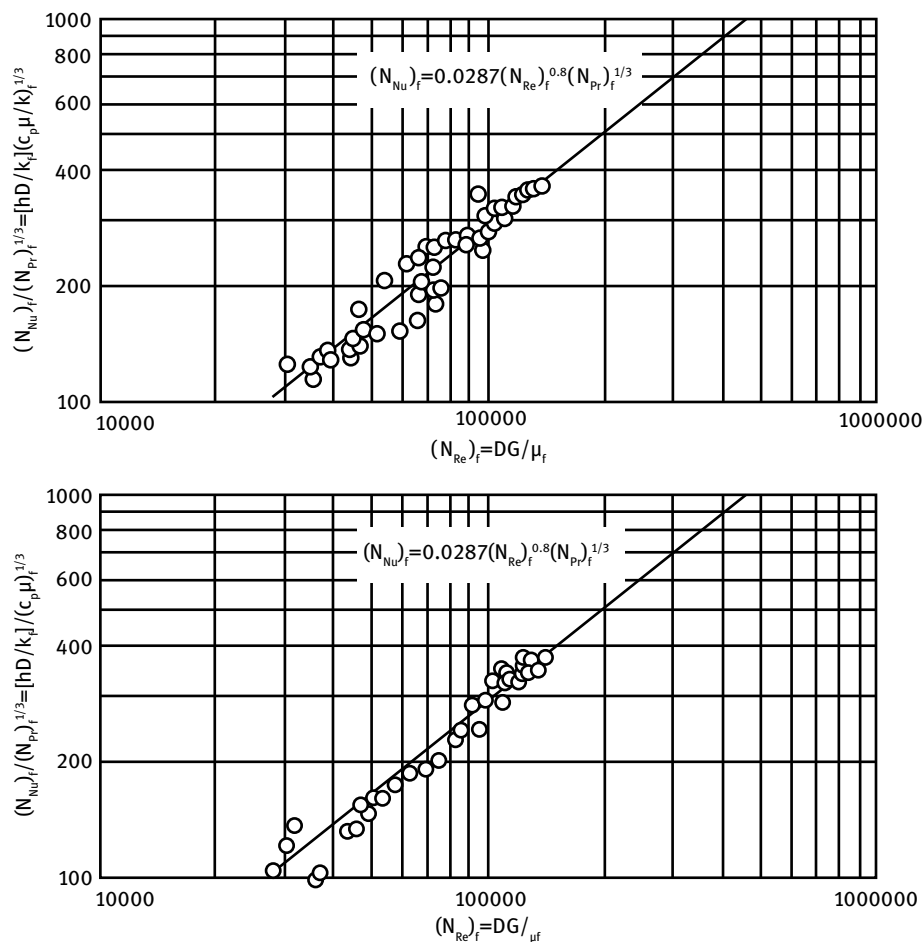


Figure 25: Heat transfer to 90% hydrogen peroxide

Heat transfer to water (for comparison)

Heat transfer to liquid 90% hydrogen peroxide in comparison to that to water. (Reprinted and modified from [244])

The correlation of the data in 98% H_2O_2 (Figure 27 and 28), respectively, indicated better agreement of the data with the Dittus-Boelter relationship. The Dittus-Boelter equation is:

$$\text{Nu}_D = 0.023 \text{Re}_D^{0.8} \text{Pr}^n$$

where D is the inside diameter of the circular duct, Pr is the Prandtl number and $n = 0.4$ for the fluid being heated. It has been suggested, however, that some of the apparently low heat transfer coefficients may be due to scaling (oxidation) of heat transfer surfaces, creating a low conductivity barrier.

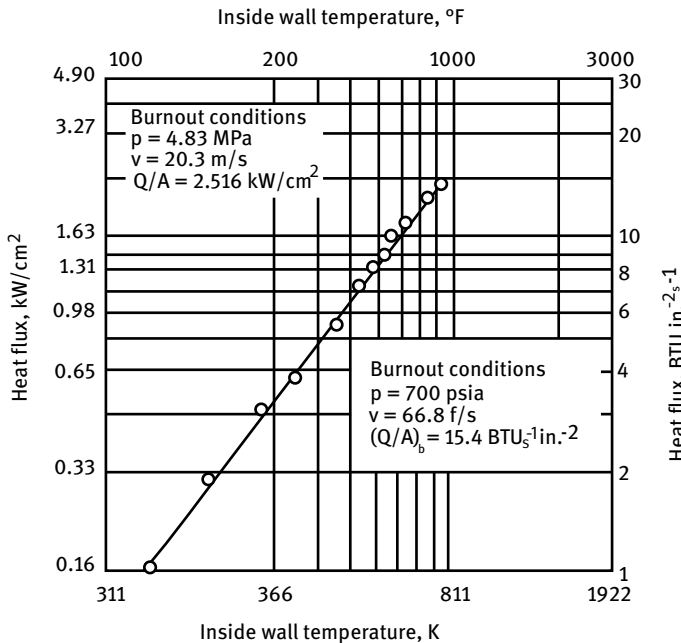


Figure 26: Heat flux versus inside wall temperature during heat transfer to 98% H₂O₂. (Reproduced and modified from Pratt & Whitney, as referenced by Constantine and Cain [246].)

The correlation illustrated in Figure 28 is based on the Sieder-Tate equation for the convective region in the form:

$$\text{Nu}_b = 0.027 \text{Re}_b^{0.8} \text{Pr}_b^{1/3} \left(\frac{\mu_b}{\mu_w} \right)^{0.14}$$

where Nu is the Nusselt number, Re is the Reynolds number, Pr is the Prandtl number, and μ is the viscosity. The results of this equation are shown as a solid line. The subscript b designates the properties at the bulk temperature, and the subscript w designates the properties at the wall temperature.

A study at Aerojet on the use of 98% hydrogen peroxide for regeneratively cooled rocket engines reported that during 18 experimental tests, heat fluxes up to 7.8 kW/cm^2 ($48.2 \text{ BTU in.}^{-2} \text{ s}^{-1}$) were achieved [247]. Some of these high-pressure heat-transfer experiments were conducted with both 90 and 98% H₂O₂. Electrically heated 4.8 and 6.3-mm (3/16 and 1/4-in.) diameter Inconel 718 and 4.8-mm (3/16-in.) diameter stainless steel test sections were used at pressures of 5.86 and 32.4 MPa (850 and 4700 psi) and at coolant velocities of 7.62 to 60.35 m/s (25 to 198 ft/s) and feed temperatures from 289 to 389 K (60 to 240 °F). Thirteen of these tests were burnout tests, in which the burnout or ultimate heat flux was evaluated in electrically heated round tubes by increasing the heat flux in increments, at a fixed flow rate and at fixed pressure con-

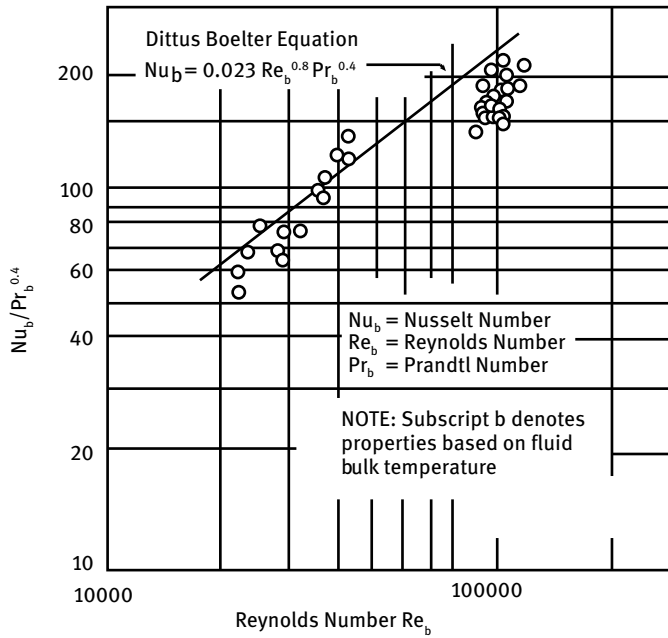


Figure 27: Correlation of Nusselt number versus Reynolds number during heat transfer to 98% H_2O_2 ; convective heat transfer region. (Reproduced and modified from Pratt & Whitney, as referenced by Constantine and Cain [246].)

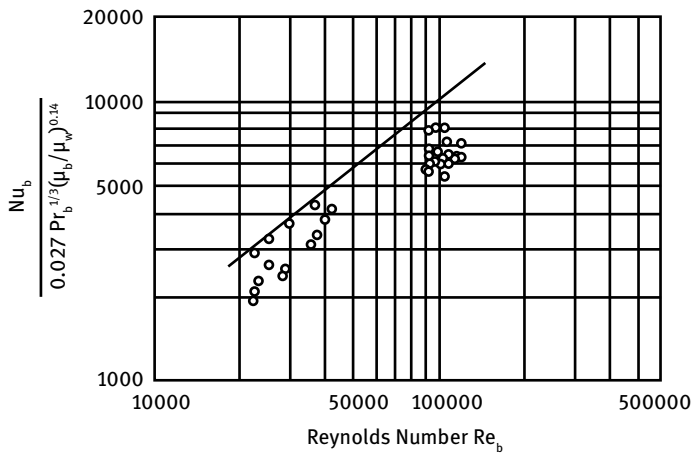


Figure 28: Correlation of heat transfer to 98% H_2O_2 with Sieder-Tate equation; convective heat transfer region. (Reproduced and modified from Pratt & Whitney, as referenced by Constantine and Cain [246].)

ditions, until failure of the tube occurred. It was found that the heat flux at burnout (under the conditions tested) was directly proportional to the fluid velocity by the relationship:

$$\text{heat flux} = 0.21 \times \text{velocity}$$

These results indicated good correlation of heat flux and fluid velocity with the studies of Sanborn et al. [244] and [245]. The remaining 11 of the 98% H_2O_2 tests were extended-duration tests in which a constant heat-flux level was maintained for durations up to 10 min. During these tests, no appreciable difference in heat transfer could be associated with feed temperature, and no detectable decomposition was evident. Four similar tests with 90% hydrogen peroxide indicated no discernible differences from the results of the 98% H_2O_2 tests. Titration of the peroxide after short-duration testing indicated that little or no H_2O_2 decomposition had occurred in the test section. The short-duration burnout tests showed that the maximum burnout heat flux is directly proportional to coolant velocity and is insensitive to coolant pressure. As in the studies of Sanborn et al. [244] and [245], the Dittus-Boelter correlation was found to represent the data more closely than either the Colburn or Sieder-Tate relationships (Figure 29). The straight line in Figure 29 is represented by the equation

$$\text{Nu} = 0.023 \text{Re}_f^{0.8} \text{Pr}_f^{0.4}$$

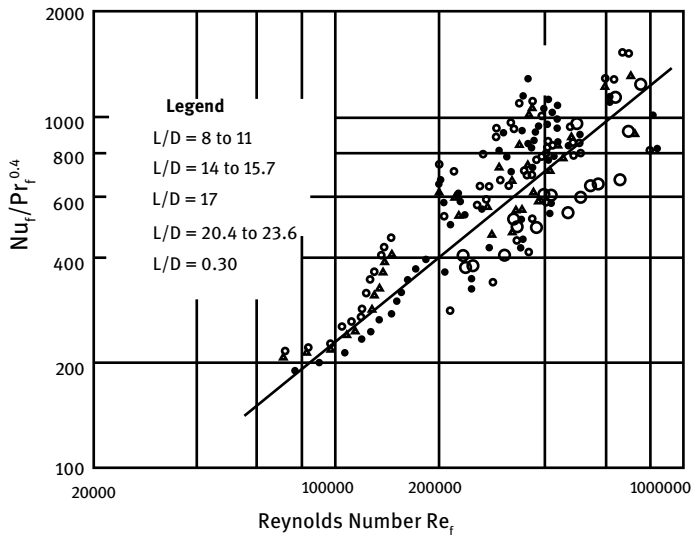


Figure 29: Raw forced convection heat transfer data for 98% H_2O_2 based on film properties, entered into a graph with least square fit of Dittus-Boelter equation. (Reproduced and modified from [247].)

The Dittus-Boelter equation, where the subscript b indicates properties for the temperature of the bulk of the fluid,

$$\text{Nu}_b = 0.023 \text{Re}_b^{0.8} \text{Pr}_b^{0.4}$$

would yield a conservative estimate of heat-transfer coefficients for 98% H_2O_2 and was recommended for design purposes. Long-duration tests conducted at velocities of 15.24 to 45.72 m/s (50 to 150 ft/s) with Inconel 718 tubing indicated that the long-duration burnout heat flux is degenerated to about 65% of that demonstrated in short-duration tests. Titration of the peroxide after these tests indicated that minor H_2O_2 decomposition had occurred. It was concluded that 98% H_2O_2 would be an excellent regenerative coolant in rocket engine systems. The long-duration burnout problem at high pressure can be avoided by limiting the design burnout heat flux to about 65% of the short-duration burnout point. A potential transient cooling problem could exist during the shutdown of a regeneratively cooled engine.

The results of all these studies have shown that hydrogen peroxide has coolant properties comparable to those of water. Of course, the difficulty in its use as a regenerative coolant lies in the limited stability of the H_2O_2 at higher temperatures. As a result, various bulk liquid temperature limits have been suggested and established in the use of H_2O_2 as a regenerative coolant. These limits range from established maximum allowable temperatures of 380 K (225 °F) (with a 58 °C = 105 °F rise over inlet temperature) to suggested operating limits of 394 K (250 °F) (with red line conditions at 408 K = 275 °F); see also [248].

A MEMS microrocket engine using 98% liquid hydrogen peroxide and JP7 as propellants uses its propellants to regeneratively cool the combustion chamber and the nozzle. Although JP-7 has been proven to be an effective coolant under such conditions, hydrogen peroxide becomes unstable at high temperature and may explode, thus adding a critical constraint to the cooling scheme. To address this issue, heat transfer experiments in 95 μm inside diameter, 4 mm long, electrically heated stainless steel microtubes have been performed to define the stability limit and explosion condition associated with 98% hydrogen peroxide thermal decomposition [249]. Tests were conducted whereby heat transfer to the hydrogen peroxide was increased until an explosion occurred. For each test, prior to the explosion, an experimental forced convective heat transfer coefficient was obtained and compared to standard empirical correlations. Experimental results indicated that 98% hydrogen peroxide has limited cooling capacity for a regeneratively-cooled rocket engine. Independently of pressure and mass flow, results showed that a local fluid temperature of approximately 423 K (150 °C) consistently led to an explosion in stainless steel microtubes. In addition, standard macroscale heat transfer correlations were found to significantly underestimate the heat transfer rates obtained experimentally. Instead, a correlation developed for forced convective heat transfer in microtubes was derived and provided a more accurate estimate.

3.10 Refractive Index of Hydrogen Peroxide

Refractive index data are available for the entire concentration range from 0 to 100% H_2O_2 , but we are mostly interested in data for the upper concentration range. Table 20 gives the refractive index for the sodium D-line for hydrogen peroxide solutions in the range from 50 to 100% H_2O_2 . Similar data for a different temperature are in Table 21. Because refractive index can be measured even with relatively cheap refractometers accurately to the fourth place behind the decimal point, some tables give the conversion from refractive index to H_2O_2 concentration in increments of 0.2% H_2O_2 . We deemed the following table (Table 20) with 1% H_2O_2 increments sufficiently accurate for everyday use in a rocket propellant test site. One of our tables is for measurements at 293 K (20 °C), whereas tables in other sources (Schumb, Table 42, pages 269–270) are for 298 K (25 °C); 298 K (25 °C) may be more practical because in a laboratory it is easier to warm the sample to 298 K (25 °C) than to cool it to 293 K (20 °C) if the lab is located in a warm climate. On the other hand, 298 K (25 °C) is more likely to cause problems with bubble formation.

Other sources give the refractive index for light with other wavelengths, but we restrict ourselves to data that were obtained with the sodium D line (589 nm).

Table 20: Refractive index n_D^{20} of hydrogen peroxide solutions.

Mass-% H_2O_2	n_D^{20}	Mass-% H_2O_2	n_D^{20}	Mass-% H_2O_2	n_D^{20}
50	1.3671	67	1.3802	84	1.3943
51	1.3678	68	1.3810	85	1.3952
52	1.3686	69	1.3818	86	1.3961
53	1.3693	70	1.3826	87	1.3969
54	1.3701	71	1.3834	88	1.3978
55	1.3708	72	1.3842	89	1.3986
56	1.3716	73	1.3851	90	1.3995
57	1.3723	74	1.3859	91	1.4004
58	1.3731	75	1.3867	92	1.4013
59	1.3739	76	1.3876	93	1.4021
60	1.3747	77	1.3884	94	1.4030
61	1.3755	78	1.3892	95	1.4039
62	1.3762	79	1.3901	96	1.4048
63	1.3770	80	1.3909	97	1.4057
64	1.3778	81	1.3918	98	1.4066
65	1.3786	82	1.3926	99	1.4075
66	1.3794	83	1.3935	100	1.4084

Data source: Laporte Chem. and [27]

Table 21: Refractive index n_D^{25} of hydrogen peroxide solutions.

Mass-% H_2O_2	n_D^{25}	Mass-% H_2O_2	n_D^{25}
50	1.3661	75	1.3854
51	1.3668	76	1.3862
52	1.3675	77	1.3870
53	1.3683	78	1.3878
54	1.3690	79	1.3886
55	1.3698	80	1.3894
56	1.3705	82	1.3911
57	1.3712	83	1.3920
58	1.3719	84	1.3928
59	1.3727	85	1.3937
60	1.3734	86	1.3945
61	1.3742	87	1.3954
62	1.3750	88	1.3962
63	1.3758	89	1.3971
64	1.3766	90	1.3980
65	1.3774	91	1.3988
66	1.3782	92	1.3997
67	1.3790	93	1.4006
68	1.3798	94	1.4014
69	1.3806	95	1.4023
70	1.3814	96	1.4032
71	1.3822	97	1.4041
72	1.3830	98	1.4049
73	1.3838	99	1.4058
74	1.3846	100	1.4067

Data source: [251]

A 1943 publication [250] gave the refractive index for the C-, F-, and G-lines of hydrogen and the Na D line, first for pure H_2O_2 ($n_D^{20} = 1.4087$) and then over the whole range of concentrations in 0.2-% increments at four different temperatures (289, 293, 297, and 301 K = 16, 20, 24, and 28 °C), but the data were later revised. Previous values for the n_D of pure and aqueous H_2O_2 were revised owing to errors in analysis and in temperature control. The best value for anhydrous H_2O_2 now is $n_D^{25} = 1.4067 \pm 0.0001$, and it has an average temperature coefficient of $3.4 \times 10^{-5} \text{ °C}^{-1}$, as shown in [251].

For rocket applications, the main interest is in HP above 65% H_2O_2 , and we have not included refractive index data for H_2O_2 solutions below 50%. However, if one plots the included refractive index data for H_2O_2 solutions below 50%, one will notice that the curve has a kink (“dogleg”) and a change in slope between 20 and 40 mass-% H_2O_2 .

Hydrogen peroxide as a ligand in metal salts, replacing water of crystallization, alters the refractive index of these adducts [252].

3.11 Spectroscopic Properties of Hydrogen Peroxide

The absorption spectra of hydrogen peroxide are summarized in detail in this chapter because the spectroscopic properties of hydrogen peroxide are the basis of analytical methods and lead to a better understanding of the energy content and causes for decomposition of this unstable molecule. It is the energy content that makes this chemical useful as a rocket propellant. Understanding the molecular structure is important in explaining processes that lead to its formation (e.g., in quenching an O_2/H_2 flame) and its decomposition (thermal or catalytic processes). The excited states in a molecule, measured by absorption of infrared or ultraviolet energy, are just one step prior to dissociation (or even explosion), and the threshold of dissociation of H_2O_2 must be known in order to use it safely. There are several processes that lead to the natural occurrence of H_2O_2 . One of the typical methods for a spectroscopist is to compare spectra of hydrogen peroxide H_2O_2 to spectra of the isotope-substituted deuterium peroxide D_2O_2 . Isotope substitution is often helpful in identifying specific molecular vibrations in a molecule and the absorption frequency of spectra associated therewith. Therefore, we carry references to D_2O_2 , although it is not used as a rocket propellant. The search for higher (potentially more energetic) polyoxides H_2O_3 and H_2O_4 is also supported by spectroscopic evidence of the short-lived existence of these molecules.

Reactions of alkaline hydrogen peroxide with chlorine give atomic oxygen in an excited state that can power a chemical laser. Although no hydrogen peroxide is involved in the lasing, transitions between molecular energy levels of such processes releasing atomic oxygen need to be understood, based on the spectra of hydrogen peroxide summarized in this chapter.

3.11.1 IR and Raman Spectra of Frozen Hydrogen Peroxide

Spectra of hydrogen peroxide in the frozen state show the strong interaction of hydrogen bonds that are responsible for the high freezing point of this chemical. Isolating H_2O_2 molecules in a solid matrix of an inert, frozen, IR-transparent material will eliminate the interaction between adjacent molecules and result in sharper spectra.

The IR absorption between 2.5 and 25μ of thin films of pure frozen H_2O_2 has been measured at 4 and 80 K [192]. Two types of spectra were observed, one crystalline and the other amorphous. It was shown that the molecular spectrum of ordinary ice is not crystalline but vitreous. The spectra of frozen mixtures of H_2O_2 and H_2O deposited simultaneously from the vapor indicated large shifts of the intermolecular vibrations in the crystalline dihydrate, $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. The principal intermolecular force constant in crystalline H_2O_2 was calculated to be $0.24 \times 10^5 \text{ dyn/cm}$.

The infrared spectrum of crystalline and vitreous hydrogen peroxide was studied from 300 to 4000 cm^{-1} , and a normal coordinate analysis of the tetragonal crystal with four molecules/unit cell showed that the hydrogen bonds are only slightly weaker than in H_2O , but the O—H line widths due to hydrogen bond broadening are only 80 cm^{-1}

[253]. From the coupled motion of the torsion and the high-frequency libration, the torsional frequency in the gas was estimated to be about 230 cm^{-1} .

Comparing the far IR spectra of H_2O_2 and D_2O_2 in the solid states, the absorption spectra of hydrogen and deuterium peroxides in the crystalline and glassy states were measured in the far IR down to 50 cm^{-1} [254]. All the lattice vibrations predicted by the group theory on the basis of the known structure of the crystal have been observed, but some previous assignments of the internal torsion and the high-frequency libration had to be revised. The new data confirmed that in the crystal, the H_2O_2 molecules are trapped in a strained configuration. The samples were always obtained first as glasses that showed no definite low-frequency bands. With deuterium peroxide two distinct metastable phases could often be observed.

A systematic investigation of the vibrational spectra of the hydrogen peroxide crystal and its deuterated analog over the range $4000\text{--}50\text{ cm}^{-1}$ has been carried out using both IR and Raman spectroscopy [255]. Mixtures of the two isotopic species up to approximately 95% deuteration were studied to identify the fundamentals of the hybrid molecule, HDO_2 . Single crystals of hydrogen peroxide oriented along two of the three crystallographic axes were examined in the Raman effect with polarized laser light. The O—H stretching bands were remarkably narrow in the Raman spectra: $\Delta\nu = 20\text{ cm}^{-1}$ at 80 K (-193°C) compared to about 80 cm^{-1} in the IR. Nearly all the O—H stretching components predicted by the factor group analysis were observed, but a satisfactory identification of all components of the OOH deformation modes could not be achieved. The O—O stretching frequency in D_2O_2 (872 cm^{-1}) was slightly higher than in H_2O_2 , (871 cm^{-1}) contrary to expectations. The hydrogen bonds in the H_2O_2 crystal appeared somewhat less strong (by about 10–15%) than those in ice. The low-temperature crystal $\text{H}_2\text{O}_2\text{-I}$ has a characteristic, intense O—O stretching mode at 880 cm^{-1} at 263 K. In addition, it has eight relatively strong lattice phonons and four O—H vibrons at 263 K. Two of the OH stretching modes at 3332 and 3198 cm^{-1} are strong, but the other two are weak side bands. The normal mode analysis found that the force constant of the O—H stretching mode in $\text{H}_2\text{O}_2\text{-I}$ is less than that of water ice, which implicates a weaker hydrogen bond strength in $\text{H}_2\text{O}_2\text{-I}$ than in ice.

3.11.2 Matrix-Isolated Hydrogen Peroxide

Isolating H_2O_2 molecules in a solid matrix of an inert, frozen, IR-transparent material will eliminate the interaction due to hydrogen bonding between adjacent molecules and result in sharper spectra.

Matrix-isolation spectra of the system $\text{H}_2\text{O}_2:\text{N}_2$ obtained in the region $4000\text{--}300\text{ cm}^{-1}$ at 4.2 K were free of complications due to association or over-all rotation [256]. The most unusual feature of these spectra was the band system at 385 and 350 cm^{-1} in the torsional region. This main band at 385 cm^{-1} was exceedingly broad for a matrix spectrum. These bands were then assigned to the $n = 0 \rightarrow 1$ and $1 \rightarrow 2$ torsional transitions.

The infrared spectrum between 4000 and 200 cm^{-1} of polycrystalline D_2O_2 at 83 K (-190°C) corresponded to that of H_2O_2 indicating that the crystal structure and coupling for each of the six normal modes are the same in D_2O_2 as in H_2O_2 [257]. At temperatures near 173 K (-100°C) the crystal spectra of both H_2O_2 and D_2O_2 changed with time on CsI and CsBr cold windows. The greatest change observed was that the crystal bands arising from torsion disappeared and were replaced by two other bands about 100 cm^{-1} lower in frequency. Also, the bands in the stretching and bending regions lost their fine structure and shifted to lower frequency, indicating that the peroxides actually dissolved into the salt windows without decomposition at these low temperatures. The spectra of H_2O_2 and D_2O_2 matrix isolated in argon and nitrogen at about 8 K showed that the most interesting features of these spectra are the extraordinarily broad bands in the torsional region, ν_4 , in both nitrogen and argon as the matrix.

The Raman spectra of solid hydrogen peroxide and deuterium peroxide were measured by the matrix-isolation technique in solid argon at 10 K [258]. The first three symmetric fundamentals were observed for peroxide monomers only. Correlation with existent infrared spectra lead to a reassignment of the latter in terms of hydrogen-bonded polymers. Some spectroscopic features and diffusion experiments suggested the existence of cyclic dimers, favored structurally. The products from a microwave discharge in D_2O vapor and argon were also examined by the same technique in infrared and Raman. Besides water and peroxide, some ozone and DO_2 radicals were found, as well as the unstable polyoxides, D_2O_3 and D_2O_4 ; the latter two, however, only at very small concentrations.

3.11.3 IR and Raman Spectra of Liquid Hydrogen Peroxide

The absorption spectrum of 99.6% pure liquid H_2O_2 has a wide diffuse band with a maximum at 10110 $\text{\AA}$. This represents a shift of 400 cm^{-1} from the frequency of the corresponding band of H_2O_2 vapor [259]. A low-temperature dihydrate phase was identified using infrared spectroscopy [192]. The low-resolution wide-band IR spectrum of liquid H_2O_2 is presented in Figure 30.

A high-dispersion study of the OH bands of hydrogen peroxide in the photographic infrared revealed the rotational structure of the two hybrid bands at 10283.68 and 10291.08 cm^{-1} [261]. The small moment of inertia of hydrogen peroxide was found to be $2.786 \times 10^{-40} \text{ g cm}^2$, while the harmonic mean of the two larger moments of inertia was found to be approximately $33.9 \times 10^{-40} \text{ g cm}^2$. The planar *cis* configuration was ruled out spectroscopically, and it was concluded that hydrogen peroxide exists in a non-planar form.

The IR absorption spectrum of H_2O_2 was reexamined in the region from 1.5 to 25 μm and compared to that of D_2O_2 [262]. Figure 31 shows IR absorption spectra of hydrogen peroxide solutions with three different concentrations in the range between 0.9 and 2.1 μm .

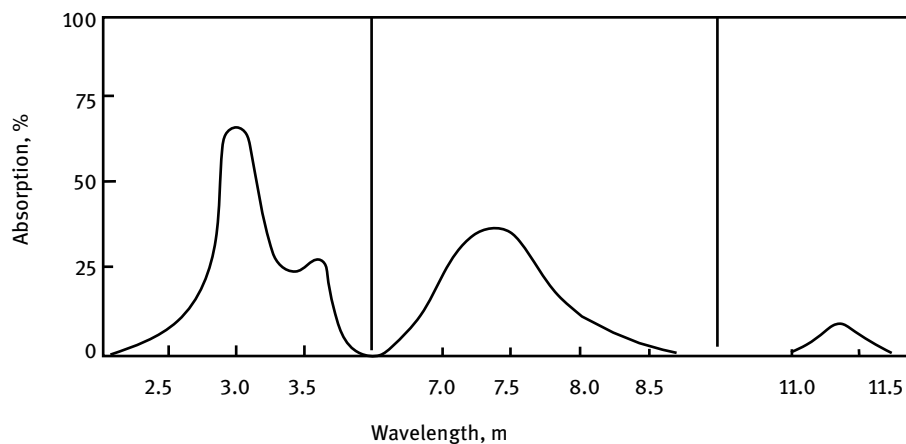


Figure 30: Infrared spectrum of liquid hydrogen peroxide. (Republished and modified from [260], with permission of © 1950 American Institute of Physics; permission conveyed through Copyright Clearance Center Inc.)

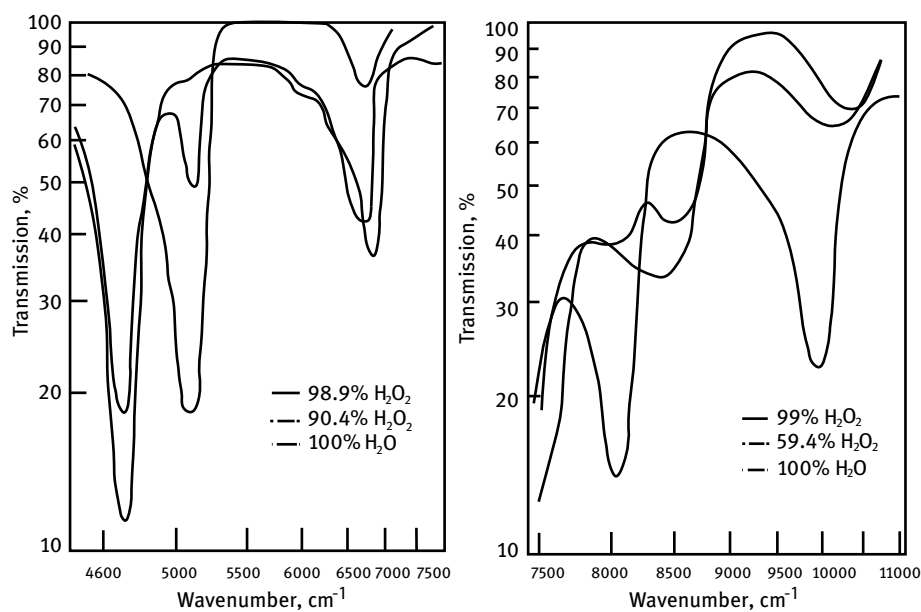


Figure 31: Infrared absorption spectra of aqueous hydrogen peroxide solutions. (Republished and modified from [262], with permission of © 1955 Canadian Science Publishing; permission conveyed through Copyright Clearance Center, Inc.)

A pair of well-resolved perpendicular bands arising from torsional oscillation of the OH groups was found centered about 460 and 575 cm^{-1} . The overtone band at 3.8 μm is a hybrid with prominent rotational structure and some indications of doubling. The vapor bands of D_2O_2 are quite different in appearance from those of H_2O_2 . Four new overtone bands were observed in liquid H_2O_2 . The infrared spectrum of D_2O_2 was measured for the first time in the solid and vapor states. The vapor bands were quite different in appearance from those of H_2O_2 . One of the fundamentals, the asymmetric O—D stretching at 2661 cm^{-1} , was resolved sufficiently to allow calculation of the rotational constants of the isotopic molecule. The O—O stretching vibration at 11 μ was too weak to be located definitely in the spectra of the gaseous peroxides. The bond distances and angles were given as $r(\text{O—O})$, $1.49 \pm 0.01 \text{ \AA}$; $r(\text{O—H})$, $0.97 \pm 0.01 \text{ \AA}$; $\alpha(\text{OOH})$, $100^\circ \pm 2^\circ$.

The IR absorption of thin films of pure H_2O_2 between 2.5 and 25 μm has been measured at 4 and 80° K [263]. Two types of spectra were observed, one crystalline and the other amorphous. The results were discussed in terms of hydrogen bonding and disorder with reference to the case of water ice. It was shown that the molecular spectrum of ordinary water ice is not crystalline but vitreous. The spectra of frozen mixtures of H_2O_2 and H_2O codeposited simultaneously from the vapor indicated large shifts

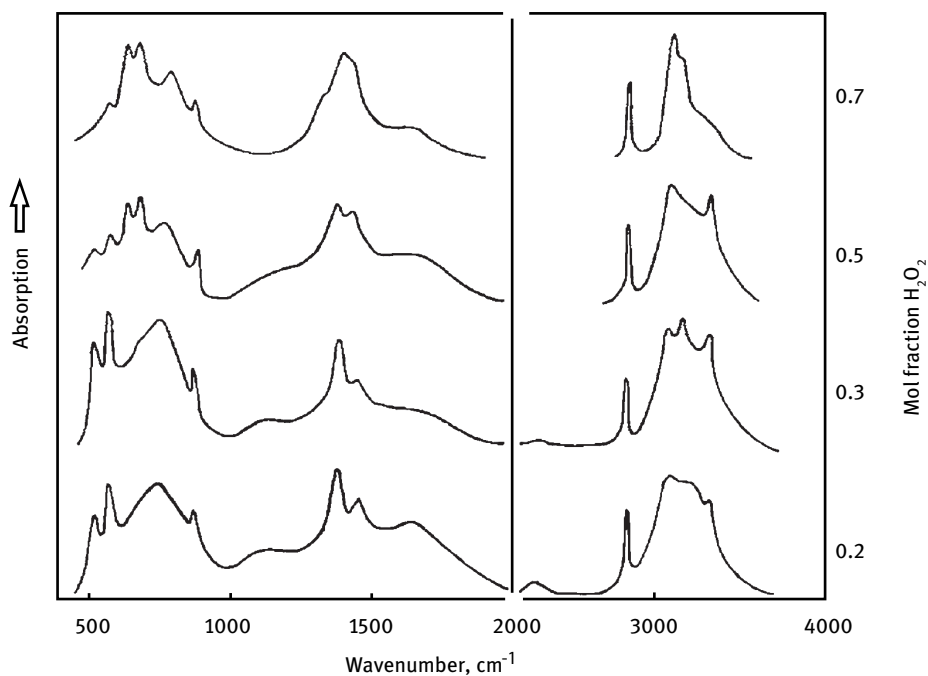


Figure 32: Infrared spectra of crystalline mixtures of H_2O - H_2O_2 at 80 K (note the change of scale at 2000 cm^{-1} .) (Reproduced and modified from [263], with permission from © 1969 Elsevier; permission conveyed through RightsLink.)

of the intermolecular vibrations in the crystalline dihydrate, $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. Important changes take place in the spectra of both H_2O and H_2O_2 crystals when these compounds are deposited together. Whereas the internal vibrations were little affected (except for ν_4 of H_2O_2), the intermolecular frequencies underwent large downward shifts: from 850 to 765 cm^{-1} for ν_{R} of H_2O and from 656 to 535 cm^{-1} for ν_{A} of H_2O_2 (Figure 32). The new bands with lower frequencies are characteristic of the crystalline dihydrate $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ since they were the most intense in mixtures having intermediate compositions in the neighborhood of $\chi = 0.3$, while the crystalline bands of both pure components became weaker.

Raman spectra of liquid 99.5% H_2O_2 were obtained at 303 and 233 K ($+30^\circ$ and -40°C) and compared with the spectrum of 90% D_2O_2 at 233 K (-40°C), revealing three bands not previously reported [264], Figure 33. Their assignment to molecular vibrations, together with that of the previously known bands, helped to clarify the structure of these molecules. Raman spectra were also obtained for aqueous solutions at 303 and 233 K (30° and -40°C) over the entire range of concentrations. The results indicated that the addition of hydrogen peroxide to water leads to more extensive hydrogen bonding and an increased degree of order in the solutions; see also [265].

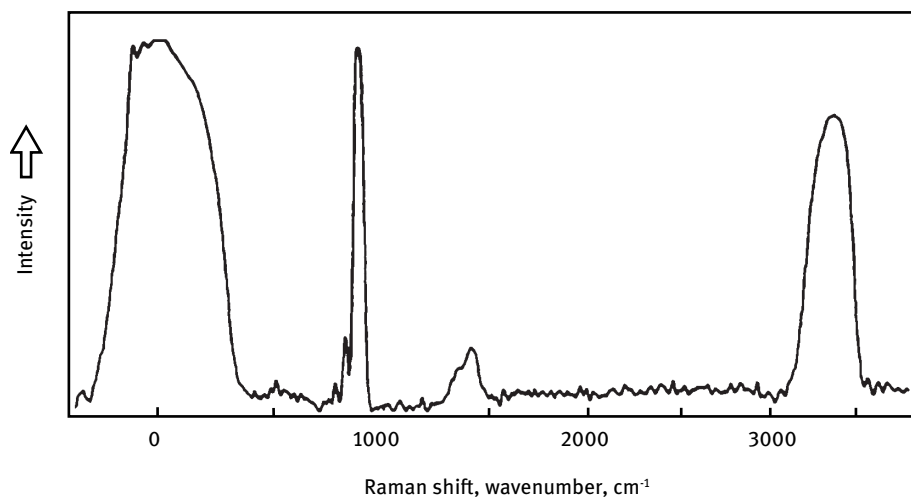


Figure 33: Raman spectrum of liquid hydrogen peroxide at 233 K, normal exposure. (Reproduced and modified from [4].)

3.11.4 IR Spectra of Hydrogen Peroxide Vapor

The absorption spectrum of hydrogen peroxide vapor was examined under low dispersion in the range $2\text{--}15\text{ }\mu\text{m}$ [260]. Four bands were observed at 3590 , 2630 , 1255 , and 877 cm^{-1} . The spectrum of the liquid also was measured between 2 and $21\text{ }\mu\text{m}$, and it showed five bands at about 3400 , 2780 , 1350 , 880 , and 550 cm^{-1} . The last

one, which seemed very diffuse, was presumably the torsional oscillation of the OH groups; as such it corresponds to a potential energy barrier of the order of 16.7 kJ/mol (4 kcal/mol). Under high dispersion, the second harmonic O—H frequency was found to consist of two identical hybrid bands at 7036.6 and 7041.8 cm⁻¹, of which the rotational constant for the ground state was in perfect agreement with that already found for the third harmonic band. The explanation given previously for the doublet character of the vibrational levels of hydrogen peroxide was further substantiated by these results. Based on interpretation of both vibrational and rotational data, the O—H distance in hydrogen peroxide appears to be slightly greater than that in water.

A complete vibrational analysis of hydrogen peroxide, using the IR spectral data of other authors, made use of symmetry coordinates [266]. The amplitude factors corresponding to each of the six normal modes of vibration were calculated. While some theories stated that there can be no flow of energy between the normal modes, other hypotheses assumed that there is a flow of energy between the normal modes of the molecule, some of which lead to dissociation.

3.11.4.1 Near IR Spectrum of Hydrogen Peroxide Vapor

Hydrogen peroxide IR absorption bands obtained with better than 0.2 cm⁻¹ resolution demonstrated both doubling due to internal rotation and effects due to the inertial asymmetry [267]. The ground-state rotational constants were found to be: $A' = 10.068$ cm⁻¹, $B'' = 0.8740$, and $C'' = 0.8384$. These parameters indicated a wide dihedral angle for H₂O₂, as shown in the following structure parameters: O—O bond = 1.475 Å, O—H bond = 0.950 Å, dihedral angle $\alpha = 119.8^\circ$, and OOH $\alpha = 94.8^\circ$. The constants were applied to the microwave data for H₂O₂ and the deuterated species. The ground-state splitting was found to be 11.44 cm⁻¹, and this number, used with torsion at 317 cm⁻¹, gave the barriers hindering internal rotation. They were $V_{cis} = 1300$ cm⁻¹ and $V_{trans} = 300$ cm⁻¹. Spectra of the O—H stretching fundamental region between 3480 and 3720 cm⁻¹ with many Q-branch lines and in the OOH bending fundamental region between 2510 and 2800 cm⁻¹ were shown in high-resolution detail.

Vibrational overtone predissociation spectroscopy, which detects the products of a unimolecular reaction initiated by overtone vibration excitation as a function of wavelength, is a method of studying highly vibrationally excited and readily decomposable molecules like H₂O₂. Spectra obtained by varying the excitation laser wavelength while keeping the probe laser tuned to interrogate a single product state, mirror the overtone vibration absorption spectrum of those molecules that decompose into the detected quantum state. Using this dual-beam technique to detect individual rotational states of •OH fragments from hydrogen peroxide excited in the regions of the third to the fifth •O—H stretching overtone (4νOH, 5νOH, 6νOH) revealed coarse and fine vibrational structures in the spectrum [268]. A statistical model of the unimolecular decomposition in combination with the vibration-torsion model of the absorption spectrum can explain the dependence of the overtone vibrational predissociation spectra on the rotational state of the •OH product.

The dissociation lifetimes during the overtone-induced dissociation of hydrogen peroxide were found to be on the order of picoseconds and comparable with statistical lifetimes, although energy redistribution is not complete [269]. It was concluded that overtone vibrational excitation features are negligibly lifetime-broadened by reaction.

Population inversion by supersonic expansion is a common technique in gas dynamic lasers (GDL). It would be nice if H_2O_2 by itself (without addition of alkali, chlorine, and iodine) could be used to drive a GDL. Vibrational overtone excitation spectra of both bound and predissociative states of hydrogen peroxide molecules cooled in a supersonic expansion were measured by detecting the decomposition product following excitation of an overtone vibration [270]. Spectra of bound states were obtained by a two-photon excitation technique in which a second photon excites the molecule from its bound vibrational overtone state to a dissociative state. The features in the bound state ($4\nu\text{OH}$) spectrum are 0.08 to 0.13 cm^{-1} wide, reflecting small inhomogeneous broadening, but those to the predissociative state ($6\nu\text{OH}$) are $1.5 \pm 0.3\text{ cm}^{-1}$ wide. This width corresponds to a lifetime of about 3.5 ps . Spectra of predissociative states were measured by detecting the decomposition product following excitation of an overtone vibration and compared to spectra of bound states obtained by a two-photon excitation technique in which a second photon excited the molecule from its bound vibrational overtone state to a dissociative state.

The infrared spectrum of hydrogen peroxide can be successfully analyzed by assuming that the low-frequency torsional motion is adiabatically separable from the higher frequency stretching and bending motions in the molecule. This can be done by studying the coupling of torsion and OH overtone vibrations in hydrogen peroxide by high level *ab-initio* calculations [271]. The *trans* barrier and equilibrium torsional angle were calculated as a function of OH stretch and averaged overtone local-mode wave functions.

The absorption spectra of vapors of concentrated hydrogen peroxide/water mixtures (without a carrier gas) were characterized at wavelengths from 1390 to 1470 nm using a near-infrared diode laser [272]. Low pressures in a flow-through cell were used to examine spectral features near the Doppler-broadened limit. An advantageous portion of the spectra near 1420 nm containing several distinct H_2O_2 peaks and one well-known H_2O peak (for calibration) was identified, and the cross-sections of these peaks were determined. These cross-section values can be used to measure vapor-phase concentrations of H_2O_2 in propulsion, atmospheric chemistry, and sterilization applications; see also [273].

3.11.4.2 Far IR Spectra of Hydrogen Peroxide

In one of the first studies to extend the range of measurements to longer wavelengths, the absorption of H_2O_2 between 15 and 150 cm^{-1} was examined with a grating spectrometer with 0.3 to 0.5 cm^{-1} resolution [274]. One interpreter of the strong lines (a series of doublets) proposed that H_2O_2 is a nearly symmetric top with the K levels split by the hindered rotation potential barrier [275]; see also [267].

The torsional oscillation between the two OH groups of the hydrogen peroxide molecule was investigated by measuring the far-infrared absorption spectrum of the molecule [276]. A 1-m-focal-length vacuum grating monochromator was used to scan the region from 15 to 700 cm^{-1} with an average resolution of 0.3 cm^{-1} . A steady stream of H_2O_2 vapor was passed through the flow cell to avoid the interference from water formed as a decomposition product of H_2O_2 . The observed spectrum contained seven perpendicular-type bands of which only the Q branches were resolved. The centers of the seven bands were at 11.43, 116.51, 198.57, 242.76, 370.70, 521.68, and 557.84 cm^{-1} . These bands result from transitions between different states of the internal rotation, and their identification now makes it possible to assign the internal-rotation energy levels for the first five excited states. Relative to the torsional ground state, these levels occur at 11.43, 254.2, 370.7, 569.3, and 775.9 cm^{-1} . These data support a theory of internal rotation in the hydrogen peroxide molecule for use in the analysis of the far-infrared spectra. The rotational states were compared to those derived from microwave spectra.

The rotational barriers in the deuterium peroxide D_2O_2 molecule were investigated from the far-infrared absorption of the vapor and compared to those previously obtained for H_2O_2 [277]. A 1-m focal-length vacuum grating spectrometer was used to scan the region from 20 to 400 cm^{-1} with an average resolution of 0.4 cm^{-1} . Seven perpendicular-type hindered-rotation bands characterized by prominent Q branches and unresolved P- and R-branch structure were observed in the spectrum. The band centers were located at 1.88, 42.3, 123.5, 136.8, 206.7, 250.9, and 302.6 cm^{-1} . From these data, it was determined that, relative to the ground state, the first five excited hindered-rotation states are at 1.88, 208.6, 250.9, 387.7, and 511.2 cm^{-1} . A theory of internal rotation, developed for an earlier application to the far-infrared spectrum of hydrogen peroxide, was then applied to the D_2O_2 spectrum. For this potential function, the *cis* and *trans* potential barrier heights are 2470 and 377 cm^{-1} , respectively, and the potential minima are 110.8° from the *cis* configuration. These parameter values are similar to the corresponding H_2O_2 values of 2460 cm^{-1} , 386 cm^{-1} , and 111.5°.

Using high-resolution Fourier transform spectra (resolution: 0.002 cm^{-1}), it was possible to measure the relative intensities of lines in the far-infrared spectrum of H_2O_2 in the 25–400 cm^{-1} spectral region [278]. The value of the dipole moment obtained from the fit of the observed intensities was then scaled to the value obtained from Stark effect measurements. A synthetic spectrum of the far infrared band of H_2O_2 was generated for comparison, using the dipole moment determined in this work for the line intensities and the parameters and the Hamiltonian matrix for the line positions. In addition to the ($\Delta n = \pm 1$, $\Delta K a = \pm 2$) torsional-rotational resonances within the ground vibrational state, which are usually observed for H_2O_2 , the Hamiltonian model explicitly takes into account both the vibration-rotation resonances involving the ground state and the $\nu_3 = 1$ vibrational state and the “staggering” effect which is due to the *cis* potential barrier.

3.11.4.3 IR Spectra of Decomposing Hydrogen Peroxide

The hydroperoxyl radical $\text{HOO}^\bullet$ formed in decomposing hydrogen peroxide can be identified not only by EPR and photoionization spectroscopy but also through its infrared spectrum [279].

3.11.5 Microwave Spectra of Hydrogen Peroxide

At the far end of the infrared spectral range, absorption spectra overlap with microwave spectra. Both are used to characterize the hydrogen peroxide molecule. In special applications, microwave heating can be used to ignite hydrogen peroxide by itself or in combination with combustible fuels.

Nine absorption lines of H_2O_2 and one hundred absorption lines of D_2O_2 and HDO_2 have been observed in the microwave frequency region using a flow system for sampling to overcome the decomposition of the peroxide at low vapor pressure [280], Table 22. An analysis of the microwave spectrum of H_2O_2 , using a symmetric top approximation, revealed that it is necessary to invoke hindered internal rotation to explain the experimental data. Using a sinusoidal approximation for the hindering potential yields a rotational barrier height of about 113 cm^{-1} . From Stark effect calculations, a dipole moment of 2.26 Debye units was obtained.

Table 22: Microwave absorption spectrum of hydrogen peroxide vapor.

Line	Frequency, Mc/s	Remarks
1	14829.5 ± 0.2	Quadratic Stark effect $J^* = 1$
2	37517.6 ± 0.2	Quadratic Stark effect $J^* = 2$
3	22054.5 ± 0.2	Quadratic Stark effect $J^*_{\min} = 7$, $ D = 1$
4	27639.6 ± 0.2	Quadratic Stark effect $J^*_{\min} = 7$, $ D = 1$
5	11072.4 ± 0.5	Quadratic Stark effect probably high J
6	35916 ± 2	Quadratic Stark effect high J , $ D = 1$
7	390333 ± 2	Probably high J
8	39495 ± 2	Probably high J
9	39790 ± 2	Probably high J

All lines are of medium or strong intensity, except 5, 6, and 7, which are relatively weak

Data source: [280]

Despite the excellence of theoretical models and the large amount of IR data that were available as of 1969, none had undergone the rigorous test offered by the high resolution of microwave spectroscopy. Until then, only two transitions of the ground vibrational state of HOOH had been measured and positively identified in the microwave region. Fifty rotational transitions of HOOH in the ground vibrational state have been measured in the millimeter-wave region from 60 to 300 kilomegacycles per second (kMc/s) and compared to similar measurements with DOOD [281]. Analysis of these transitions provided a complete set of values of the rotational constants and the accu-

rate value of $342\,885.0 \pm 2.0$ Mc/s for the doublet splitting of the ground-state vibrational levels by internal barrier tunneling. The rotational constants in the Hamiltonian for the semirigid-rotor model with an internal axis of rotation are (in megacycles per second): $\nu_{01,2}^{01,2} = 276208.0 \pm 2.0$, $\nu_{03,4}^{03,4} = 275912.7 \pm 2.0$, $\beta_{01,2}^{01,2} = 25662.1 \pm 2.0$, $\beta_{03,4}^{03,4} = 25673.7 \pm 2.0$, $\gamma_{01,2}^{01,2} = 542.96 \pm 0.5$, $\gamma_{03,4}^{03,4} = 476.64 \pm 0.5$. The dihedral angle of the OH bonds was found to be $120^\circ 1' \pm 15'$ for the lower level and $116^\circ 7' \pm 15'$ for the upper level of the ground-state doublet. Analysis of the millimeter-wave spectrum of HOOH provided a value of 342885.0 ± 2.0 Mc/s for the splitting of the ground vibrational state via the barrier tunneling mechanism.

The millimeter and submillimeter wave spectra of hydrogen peroxide have been extended to include the first excited torsional state, $n = 1$ [282]. The 135 newly assigned rotational transitions within the $n = 1$ torsional state ranged from $Ka = 2$ to 9 and up to $J = 30$. Sixty-seven new observations in $n = 0$, which included rotational quantum numbers up to $J = 47$ and $Ka = 5$, supplemented the previously measured 349 torsional ground state transitions.

3.11.6 UV Spectra of Hydrogen Peroxide

Hydrogen peroxide and peroxyacetic acid play an important role in the smog formation in the polluted atmosphere. Under the influence of sunlight in the atmosphere, hydrogen peroxide both forms and decomposes, and during its brief lifetime reacts with other species in the atmosphere, forming more persistent smog contributors such as peroxyacetic acid or peroxyntiric acid. The significance of peroxyntiric acid formation in photochemical smog has been the subject of many publications. Peroxyntiric acid would be a good rocket propellant oxidizer but is unfortunately too unstable for that application. Not only on Earth but also on other planets and some of their moons may the photochemical formation of and photolysis of hydrogen peroxide play an important role. The strong ultraviolet radiation on the surface of Mars most likely causes a high content of hydrogen peroxide in the ice in the polar caps. Traces of hydrogen peroxide have been detected in the Martian atmosphere. The photochemical production of hydrogen peroxide has been proposed previously as the primary mechanism for the oxidizing nature of the surface of Mars. The UV spectra of hydrogen peroxide are also of interest for UV-sterilization of drinking water.

It is extremely difficult to obtain clean UV absorption spectra of H_2O_2 vapor because the labile chemical photolyzes and decomposes before the recording of a spectrum is finished, and the spectrum becomes contaminated by decomposition products. Hydrogen peroxide UV spectra must be taken in flow cells where the supply of analyte is constantly renewed.

Although other investigators stated that they were unable to observe a sharp cut in the absorption spectrum of hydrogen peroxide vapor [283], it was later shown that there is a rather abrupt increase of the absorption coefficient at $1920\text{ \AA}$ [284]. It is doubtful that the dissociation energy of hydrogen peroxide can be derived from its

absorption spectrum. However, it seems possible that the photochemical decomposition of hydrogen peroxide gives an upper limit for its dissociation energy. There is no sharp cut of the absorption coefficient in the region of 2000 to 2100 Å. The absorption of hydrogen peroxide, with and without presence of water vapor, was measured at room temperature and slightly higher temperature. Because the beam of UV that is supposed to analyze the H_2O_2 vapor also decomposes the chemical, a steady stream of fresh, undecomposed H_2O_2 vapor must be flowed through the absorption cell in the spectrometer. The supply of liquid 100% pure hydrogen peroxide was kept in a quartz vessel evaporator at constant temperature. The quartz vessel was connected with one end to the absorption cell made of quartz, which was 190 cm long and 3 cm wide. The other end of the cell led to a liquid air-cooled trap and then to a vacuum pump. The hydrogen peroxide vapor flowing through the cell was collected in the cooling trap and then analyzed.

The ultraviolet absorption spectra of H_2O_2 in water and D_2O_2 in heavy water between 3000 and 4000 Å were measured at various concentrations [285]. Both peroxides showed slight but real deviations from Beer's law at high concentrations. Replacement of H by D shifts the absorption continuum by about 390 cm^{-1} towards shorter wave lengths. The shift is of the same order as that predicted from the difference in zero-point energy of the two isotopic materials.

The absorption coefficients of hydrazine and hydrogen peroxide between 1200 and 1400 Å were determined with a 2.5 Å bandwidth monochromator [286]. The absorption cross sections of hydrogen peroxide vapor in the wavelength range from 195 to 350 nm were determined at 296 K [287]. The absorption cross sections of neutral aqueous solutions of hydrogen peroxide were also measured in the same wavelength range to obtain calculated photodissociation coefficients of atmospheric hydrogen peroxide.

A superposition of ultraviolet absorption measurements published by ten different authors is shown in Figure 34. The shape of the curve relating the extinction coefficient to the wavelength in Figure 34 seems to be parabolic. Over a considerable range of wavelengths near the visible range the curve might be represented by a linear relationship on a semilogarithmic plot. It was suggested that a maximum in the absorption curve may well exist at wavelengths much shorter than those that have been investigated.

The UV spectra of frozen solutions of 17.5-M solutions of H_2O_2 in water at 265–320 nm were obtained as the difference between the spectrum of this solution and that of water, both frozen with liquid nitrogen [288]. The spectra of liquid and solid solutions of 17.5-M H_2O_2 in water were identical in this region.

The UV absorption cross sections of H_2O_2 vapor were determined over the wavelength range 210–350 nm at 296 K [289]. At the longer wavelengths, the gas-phase absorptivities were significantly larger than the corresponding values in the condensed phase. The atmospheric H_2O_2 photodissociation rate for overhead sun at the Earth's surface was estimated as $\sim 1.3 \times 10^{-5}\text{ s}^{-1}$.

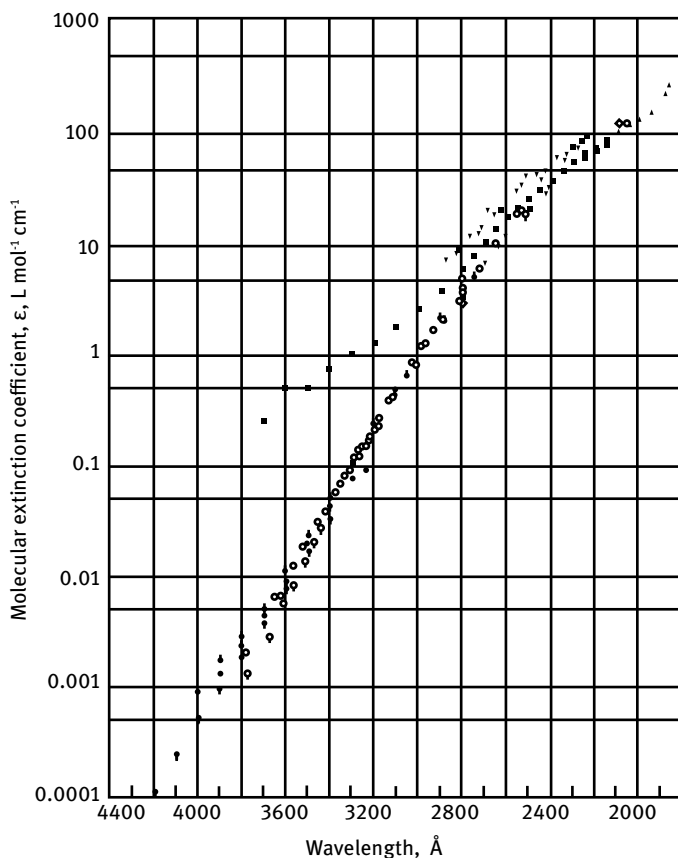


Figure 34: Comparison of ultraviolet absorption molecular extinction coefficients of hydrogen peroxide vapor and solutions. (Reproduced and modified from [4].)

Note: The identification of the authors responsible for the different symbol data points in this figure has been removed. It is irrelevant for our application.

Ab-initio calculations at the SCF and CI levels were performed in order to assign the vibrational structure of the UV spectrum of hydrogen peroxide and explain the potential energy surfaces of the lower excited states [290]. The theoretical intensity curve including the vibrational excitations was then calculated using the harmonic oscillator potential model, and several new assignments of the vibrational levels of the UV spectrum were proposed.

Near-ultraviolet and visible absorption cross sections of H_2O_2 were measured using incoherent broadband cavity-enhanced absorption spectroscopy [291]. The highly sensitive measurements spanned the range of 353–410 nm and extended electronic absorption cross sections by 60 nm to absorption cross sections below $1 \times 10^{-23} \text{ cm}^2$

molecule⁻¹. The data now enables one to calculate photolysis rate constants for H₂O₂ and hydroxyl radical ([•]OH) production rates in the lower troposphere. See also [292].

In pure solutions, hydrogen peroxide concentrations can be determined directly from the optical absorbance. The molar extinction coefficients of H₂O₂ solutions in the ultraviolet at four different wavelengths of 245, 240, 235, and 230 nm are [293]:

$$245 \text{ nm} = 0.0308 \pm 0.0003$$

$$240 \text{ nm} = 0.0394 \pm 0.0002$$

$$235 \text{ nm} = 0.0500 \pm 0.0006$$

$$230 \text{ nm} = 0.0624 \pm 0.0013$$

3.12 X-Ray Photoelectron Spectra of Hydrogen Peroxide

The He I photoelectron spectrum of hydrogen peroxide showed a splitting of 1.0 eV between the first two bands due to the oxygen non-bonding orbitals [294]. CNDO/2 and *ab-initio* calculations on hydrogen peroxide indicated that the non-bonding orbital splitting as well as the orbital assignment depend largely upon the dihedral angle between the two halves of the molecule [295]. The photoelectron bands may be assigned to the $4b\{n - (O)\}$, $5a\{n + (O)\}$, $4a\{\sigma(O-O)\}$, $3a\{\sigma + (O-H)\}$, and $3b\{\sigma - (O-H)\}$ orbitals in this order, where the + and - combinations indicate symmetric and anti-symmetric combinations with respect to the C₂ axis. These orbital assignments were supported by consideration of a sum rule concerning vertical ionization energies.

Ab-initio calculations at the SCF and CI levels were performed to calculate the potential energy surfaces and stable conformations of the first two ionic states of hydrogen peroxide (H₂O₂⁺) [296]. The lowest ionic state 2B was found to be most stable in the *trans* conformation. The second lowest state is the 2A state and it is stable in the *cis* conformation. The agreement between a theoretical intensity curve and a measured photoelectron spectrum was satisfactory.

Photoionization spectroscopy can identify not only the undissociated H₂O₂, but also one of its fragments, the hydroperoxyl radical HO₂[•] [297].

3.13 Nuclear Magnetic Resonance Spectra of Hydrogen Peroxide

The NMR transverse relaxation time T_2 of aqueous H₂O₂ solutions depends on the rate of exchange of the spin-bearing protons between H₂O₂ and H₂O molecules. For pulse separations exceeding the inverse exchange rate, this value becomes a constant, depending only on proton exchange time and magnetic field strength. This exchange time depends in a non-analytical way on the concentration of H₂O₂ and on the pH value. Thus, a measurement of T_2 and pH allows the inversion of the data for the non-invasive quantitative determination of the H₂O₂ concentration [298].

3.14 Electron Paramagnetic Resonance Spectra of Hydrogen Peroxide Decomposition

Electron paramagnetic resonance studies were carried out in a rapid flow mixing chamber in order to determine the rate constants for some dozen initiation and propagation reactions of these highly transient intermediate species, many of which are free radicals [299].

3.15 Dielectric Constant of Hydrogen Peroxide

The dielectric constant (also called dielectric strength) of pure H_2O_2 is less than that of water at all temperatures. The dielectric constant of H_2O_2 - H_2O mixtures goes through a maximum at 65 mass-% H_2O_2 as illustrated in Figure 35. For this reason, the dielectric constant is not suitable as an analytical tool to measure the concentration of H_2O_2 in binary H_2O_2 / H_2O mixtures (using the refractive index would be a better choice). The dielectric constant changes moderately steeply between 70 and 100 mass-% H_2O_2 , where it drops from 82 to 73 [300].

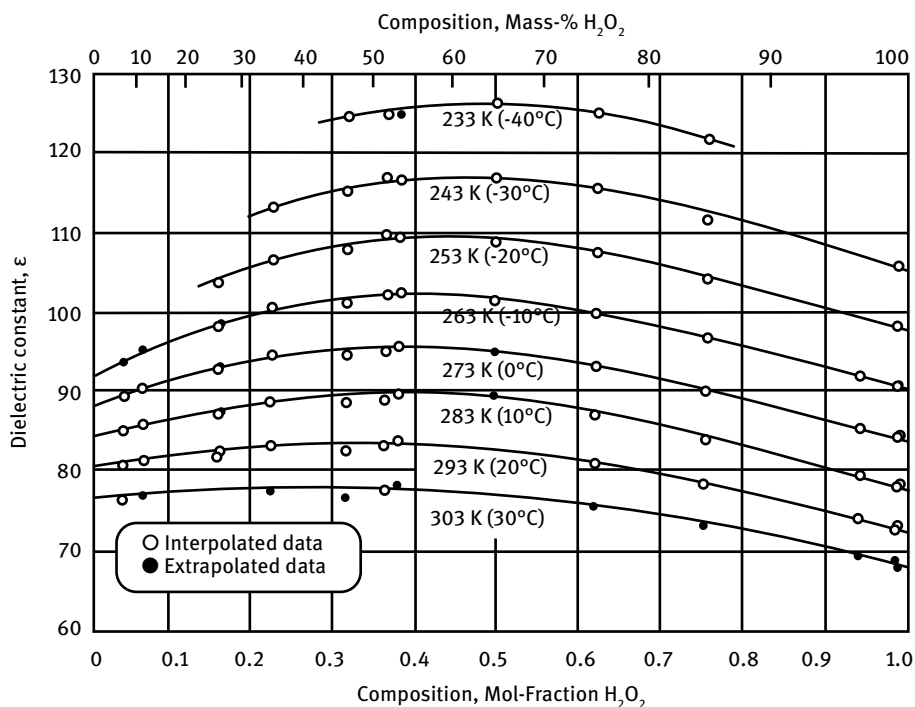


Figure 35: Dielectric constant of hydrogen peroxide/water mixtures at various temperatures. (Reproduced and modified from [4].)

The dielectric constant of pure H_2O_2 as a function of temperature can be calculated from the following curve-fitted equation

$$\varepsilon = 84.2 - 0.62t + 0.0032t^2$$

where ε is the dielectric constant (dimensionless), and t is the temperature in $^{\circ}\text{C}$. Dielectric constant data for three different H_2O_2 concentrations, all near or above 90%, are given in Table 23.

Table 23: Dielectric constant of hydrogen peroxide solutions.

Temperature		H_2O_2 concentration, mass-%		
$^{\circ}\text{C}$	K	90% H_2O_2	98% H_2O_2	100% H_2O_2
-30	243	111		106
-20	253	103		98
-10	263	95		91
± 0	273	89		85
+10	283	82		79
+20	293	77	74	73
+30	303	72		69

Data source: Laporte Chem. and [27]

Hydrogen peroxide, like hydrazine or water, has a tendency to supercool when cooled to below the freezing point. The molecular structure of supercooled liquids has been studied by measuring the relaxation time and dielectric constants [301].

3.16 Dipole Moment of Hydrogen Peroxide

The dipole moment of H_2O_2 is 2.26×10^{-18} esu (Schumb, page 314). The non-zero dipole moment rules out the linear chain trans form and the planar trigonal configuration of the hydrogen peroxide molecule and speaks in favor of the skewed configuration (see the discussion on molecular structure in Section 3.20 below).

The electric moment of hydrogen peroxide was found to be 2.13×10^{-18} in dioxane [302]. Comparative measurements made on the electric moment of water in the same instrument gave 1.90×10^{-18} in dioxane. Measurements made with both water and hydrogen peroxide in ether gave lower values for their electric moments.

The dipole moment of H_2O_2 is in good agreement with a symmetrical formula for the molecule with an angle of 110° between the O and H atoms and free rotation of the two OH groups around the O—O axis [303].

From microwave spectra and Stark effect calculations, a dipole moment of 2.26 Debye units was obtained [304]; see also [305, 306].

3.17 Electrical Conductivity of Hydrogen Peroxide

Hydrogen peroxide is a very weak electrolyte, and the amount of autodissociation is like that of water. Since the electrical conductivity of water is also very low, it requires extremely pure water to determine the natural conductivity that is due only to autodissociation and not affected by dissolved electrolytes.

Like water, hydrogen peroxide is a very good solvent, favoring dissociation of many dissolved electrolytes, many introduced as contaminants, in all ranges of concentration.

Because so many metals catalyze the decomposition of hydrogen peroxide, it is difficult to find electrode materials for electrochemical methods that will not cause decomposition of the H_2O_2 sample. Tin electrodes have been used for various laboratory experiments of electrical conductivity.

Because the electrical conductivities of pure H_2O_2 and pure water are not very different, and because the measurements are so easily disturbed by contaminants (stabilizers) commonly found in hydrogen peroxide, electrical conductivity measurements are not suitable as an analytical method to quickly determine H_2O_2 assay in propellant samples in the field. Using the refractive index would be a more reliable method.

Electrical conductivity in the $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ system goes through a maximum at 50 mass-% H_2O_2 , as illustrated in Figure 36, which is a composite of data obtained from three different sources. These measurements were made on freshly distilled H_2O_2 samples. Roth and Shanley [307] measured a specific conductance of $3.9 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ for the purest H_2O_2 sample they were able to obtain.

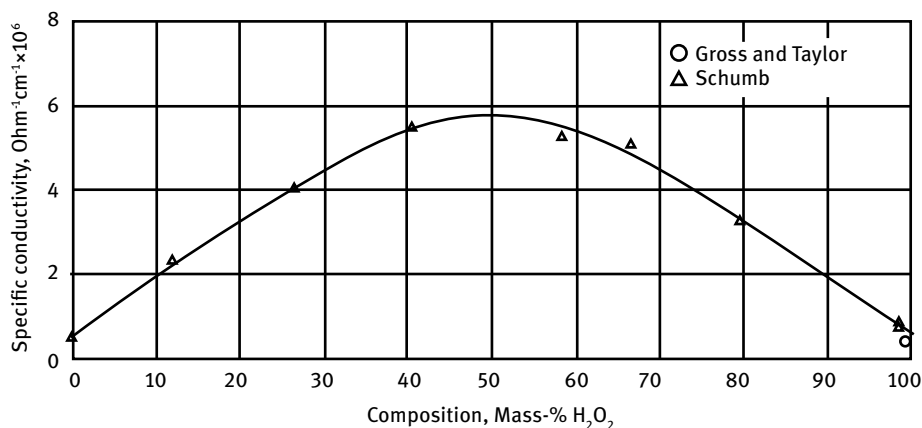


Figure 36: Specific conductance of hydrogen peroxide/water solutions at 298 K. (Reproduced and modified from [4].)

The specific conductance of hydrogen peroxide solutions with H₂O₂ concentrations above 80 mass-% is tabulated in Table 24.

Table 24: Specific conductance of hydrogen peroxide/water solutions at 298 K.

Mass-% H ₂ O ₂	Electrical conductivity at 298 K = 25 °C, Ω ⁻¹ cm ⁻¹ × 10 ⁻⁶	Source	Year	References
100	0.5	Bloom and Brunsvold	1957	[239]
98	0.8			
90	1.9			
99.9	0.39	Roth and Shanley	1953	[307]
98.5	0.82	Schumb	1949	[308]
80	3.4			

Measurements reported by the Laporte Laboratory in England showed a “flat maximum” in the curve of conductivity versus concentration extending over an appreciable range of concentration. This was not confirmed in later measurements, where samples of Becco 90% H₂O₂ were evaporatively redistilled at low pressure. The concentrated solutions were diluted with triply distilled “conductivity water” to the desired concentrations. Measurements of the specific conductivity were made at 288 K (15°C) in a conductivity cell with tin electrodes. The results of these measurements are indicated in Figure 37, which does not indicate any pronounced “flat maximum”, although the change in specific conductivity for the range 33–60 mass-% H₂O₂ is only from 4.0 to

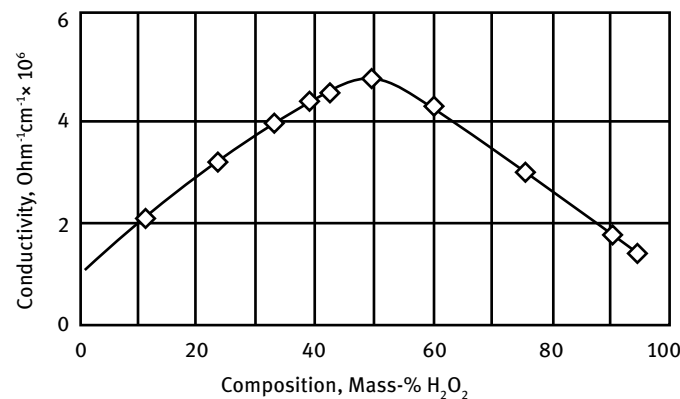


Figure 37: Electrical conductivity of hydrogen peroxide/water solutions at 288 K. (Reproduced and modified from [309].)

$4.5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. These results indicate that the form of the curve originally presented [308] is correct, although the maximum values in the vicinity of 50% H_2O_2 may be revised downward slightly.

Solutions of hydrogen peroxide in nitric acid are unstable when the concentration of the latter is greater than 50% HNO_3 . The conductivities of nitric acid solutions with <50% HNO_3 in water and water-peroxide mixtures have been determined, and the results indicated the formation of one or more unstable peroxides or peracids that are apparently incapable of ionizing [310].

Commercial as-received 90% H_2O_2 had an electrical conductivity of 11.5 μMHO . Purification by crystallization and a single distillation brought the conductivity down to 1.8 μMHO [311].

3.18 Magnetic Susceptibility of Hydrogen Peroxide

When a substance is placed in a magnetic field, the intensity of the field that passes within the substance may be either larger or smaller than the intensity of the field in the space surrounding the substance. A quantity called *permeability* is defined, which is a measure of the tendency of a magnetic field to pass through a substance as compared to the tendency to pass through a vacuum. Substances, such as oxygen, which are more permeable than a vacuum and in which a magnetic field becomes concentrated are termed *paramagnetic*. Substances, such as water and hydrogen peroxide, which are less permeable than a vacuum and in which a magnetic field is weakened are termed *diamagnetic*. Paramagnetic substances possess a permanent magnetic moment and are attracted to the more intense region of an inhomogeneous magnetic field, whereas diamagnetic substances acquire an induced magnetic moment when placed in a magnetic field and tend to be expelled from an inhomogeneous field. Hydrogen peroxide, like water, is diamagnetic.

When exposed to a strong magnetic field, both water and hydrogen peroxide were displaced in the same direction, that is, expelled from the field. Taking $K_{\text{H}_2\text{O}}$ as 7.2×10^{-7} and K_{air} as 0.25×10^{-7} , $K_{\text{H}_2\text{O}_2}$ was to have a value of 8.8×10^{-7} , as calculated in [312]. Thus, hydrogen peroxide is diamagnetic, and that to a greater extent than water.

Schumb 1953, [4], Ch. 5, p. 105–109 evaluated data for magnetic susceptibility of H_2O_2 solutions and nearly anhydrous H_2O_2 from four different sources and singled out the data for the magnetic susceptibility of pure H_2O_2 at 291 K (18 °C) measured by Gray and Farquharson [313, 314] as the most reliable set of data:

$$\chi_{\text{m}} = -(16.73 \pm 0.20) \times 10^{-6} \text{ cgs-units/mol}$$

Only a few updates to this data set have been published in the interim. A graph comparing the magnetic susceptibility data from different sources is shown in Figure 38.

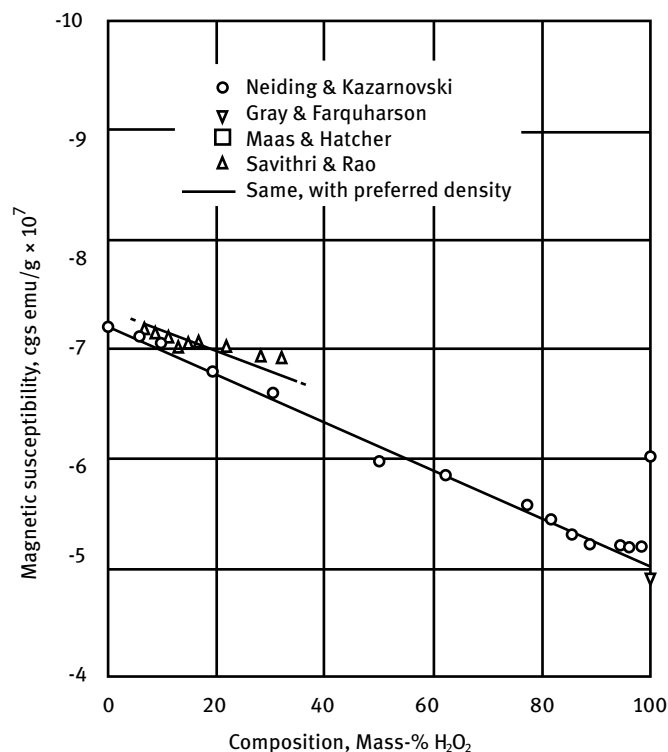


Figure 38: Comparison of magnetic susceptibility of hydrogen peroxide data from four different sources. (Reproduced and modified from [4].)

If one assumes that susceptibility is a linear function of the composition of H₂O₂/H₂O solutions and with no indication of a real deviation from linearity at hand for H₂O₂/H₂O solutions, the following equation was obtained by least squares fit from the data of Neiding and Kazarnovskii:

$$\chi_g \times 10^6 = -0.724 + 0.218w$$

where χ_g is the magnetic susceptibility in cgs-units/g and w is the mass fraction of H₂O₂. This equation is off by 0.004 cgs units/g for pure water, which closely represents the quoted precision of the data. Therefore, 0.004 might be reasonably added to the values calculated by the equation above. The mass susceptibility of a diamagnetic substance is, according to theory, independent of temperature.

3.19 Thermodynamic Properties of Hydrogen Peroxide

The most reliable sets of thermodynamic data for hydrogen peroxide are those available on the NIST Standard Reference Data Program Online Databases Chemistry – WebBook, which are updated periodically, and which have been downloaded and included in our summary of data. The other set of standard thermodynamic data for H_2O_2 vapor is in the JANNAF tables. There are some older summaries on the thermodynamic properties of H_2O_2 [315].

The thermodynamic properties of H_2O_2 and D_2O_2 were evaluated by a statistical method [316]. The partition function for the internal rotation was obtained from the summation of experimental internal rotational energy levels. The enthalpies of formation ΔH°_f (298.15 K) of $\text{H}_2\text{O}_2(\text{L})$ and $\text{H}_2\text{O}_2(\text{G})$ were reported as $-(44.88 \pm 0.02)$ and $-(32.54 \pm 0.04)$ kcal/mol, respectively. The enthalpy of formation ΔH°_f (298.15 K) for $\text{D}_2\text{O}_2(\text{L})$ was derived as $-(47.00 \pm 0.04)$ kcal/mol. From this ΔH°_f $\text{D}_2\text{O}_2(\text{L})$ 298.15 K value and the enthalpy of vaporization of $\text{D}_2\text{O}_2(\text{L})$, $\Delta H^\circ_{\text{evap}}$ (298.15 K) = (12.51 ± 0.05) kcal/mol, the enthalpy of formation at 298.15 K for $\text{D}_2\text{O}_2(\text{G})$ was obtained as $-(34.49 \pm 0.09)$ kcal/mol.

Partition functions of both rotational modes (hindered internal rotation and overall rotation) of the H_2O_2 molecule were considered to calculate the thermodynamic functions (internal energy, enthalpy, Helmholtz free energy, Gibbs free energy, and entropy) for a hydrogen peroxide gas of weakly interacting particles close to local thermodynamic equilibrium at temperatures above 300 K [317]. In such a gas, the functions may be obtained from the relationships of Gibbsian statistical mechanics.

3.19.1 Heat Capacity of Hydrogen Peroxide

3.19.1.1 Heat Capacity of Frozen Hydrogen Peroxide

The heat capacity of crystalline H_2O_2 , 99.97% pure, between 12 K and the melting point was determined with a low-temperature adiabatic calorimeter. The only anomaly in the heat capacity measurements was the absorption of 1.3 cal/mol at 216.8 ± 0.15 K, the lower eutectic temperature of H_2O - H_2O_2 solutions.

3.19.1.2 Heat Capacity of Liquid Hydrogen Peroxide

Heat capacity (specific heat) data of hydrogen peroxide and hydrogen peroxide solutions are summarized in Table 25.

Heat capacities were determined for $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixtures over the entire range of compositions for two temperature intervals starting at 298 K [318]. It was difficult to obtain accurate data at the upper end of the temperature range due to incipient decomposition. Table 26 gives smoothed data of the average heat capacities for $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixtures.

Table 25: Heat capacity (specific heat) of hydrogen peroxide and hydrogen peroxide solutions.

Phys- ical state	H ₂ O ₂ concen- tration	Temperature (range)		Heat capacity (specific heat), c_p		Source	Year	References
		Mass-%	K	°C	$\text{cal g}^{-1} \text{°C}^{-1}$	$\text{J g}^{-1} \text{°C}^{-1}$		
Solid	100		193	−80	0.2932	1.227	Anonymous, Laporte Chemicals Ltd.	1960 [27]
Solid	100		213	−60	0.3165	1.324		
Solid	100		233	−40	0.3398	1.422		
Solid	100		253	−20	0.3631	1.519		
Solid	100		263	−10	0.3748	1.568		
Solid	100		273	±0	0.3865	1.617		
Solid	100		263–253	−10 to −20	0.41 ± 0.02	1.71 ± 0.08	Foley and Giguere	1951 [184]
Liquid	100		273–299	0–26	0.6276	2.626		
Liquid	95		273–299	0–26	0.6442	2.695		
Liquid	90		273–299	0–26	0.6600	2.761		
Liquid	85		273–299	0–26	0.6760	2.828		
Liquid	80		273–299	0–26	0.6921	2.896		
Liquid	70		273–299	0–26	0.7252	3.034		
Liquid	60		273–299	0–26	0.7570	3.167		
Liquid	50		273–299	0–26	0.7900	3.305		
Liquid	100		273–298	0–25	0.632 ± 0.003	2.644 ± 0.013		
Liquid	50		273–333	0–60	0.803	3.360	Foley and Giguere	1951 [184]
Liquid	60		273–333	0–60	0.769	3.217		
Liquid	70		273–333	0–60	0.733	3.067		
Liquid	80		273–333	0–60	0.698	2.920		
Liquid	90		273–333	0–60	0.663	2.774		
Liquid	100		273–333	0–60	0.628	2.628		

Earlier heat capacity determinations for pure H₂O₂ gave 21.35 cal °C^{−1} mol^{−1} = 0.6276 cal °C^{−1} g^{−1} [319]; see also [188, 320].

The practically most important hydrogen peroxide concentration for rocket applications is 90% H₂O₂. Heat capacity and other thermodynamic data for 90% H₂O₂ solutions are listed in Table 27.

Charts were presented for liquid and vapor heat capacities of hydrogen peroxide from 255 to 478 K (0 to 400 °F) [233].

Table 26: Smoothed data of the heat capacities for H₂O₂/H₂O mixtures.

H ₂ O ₂ , Mass-%	Mol fraction H ₂ O ₂	Avg. molecu- lar mass	Heat capacity c_p			
			cal g ⁻¹ °C ⁻¹		J g ⁻¹ K ⁻¹	
			Temperature interval			
			25–45 °C	25–60 °C	25–45 °C	25–60 °C
0	0	18.02	0.998	0.998	4.176	4.176
10	0.056	18.92	0.945	0.946	3.954	3.958
20	0.117	19.89	0.904	0.908	3.782	3.799
30	0.185	20.98	0.869	0.873	3.636	3.653
40	0.261	22.2	0.835	0.838	3.494	3.506
50	0.346	23.56	0.8	0.803	3.347	3.360
60	0.443	25.11	0.765	0.769	3.201	3.217
70	0.553	26.86	0.731	0.733	3.059	3.067
80	0.679	28.88	0.696	0.698	2.912	2.920
90	0.827	31.25	0.681	0.663	2.849	2.774
100	1	34.02	0.626	0.628	2.619	2.628

Data source: [318]

3.19.1.3 Heat Capacity of Hydrogen Peroxide Vapor

The vapor phase heat capacity of H₂O₂ can be calculated from the Shomate equation:

$$C_p^\circ = A + BT + CT^2 + DT^3 + ET^{-2}$$

where A, B, C, D, and E are constants, and T is the absolute temperature in K divided by 1000. The coefficients are listed in Table 28. The same coefficients (and others) are used for formulas expressing the standard enthalpy of formation and the standard entropy of the vapor (Section 3.19.2 and 3.19.6). These equations were curve-fitted from data covering a range from 298 to 1500 K.

It was suggested that anomalies in the properties of supercooled water reflect the approach to a thermodynamic singularity in the vicinity of 228 K (–45 °C), and an attempt has been made to separate the total heat capacity of water into “anomalous” and “normal” components [321, 322]. The basis for such a separation is extrapolation to zero solute content of C_p of binary aqueous solutions from which the low-temperature anomalies have disappeared. The low temperature molar C_p isotherms of two closely related systems based on the second components H₂O₂ and N₂H₄ (N₂H₅OH) are very unusual. The extrapolations to zero solute of C_p isotherms in the two systems yielded similar but not identical “normal” components for pure water. The corresponding alternative sets of “anomalous” C_p components versus temperature data, when best-fitted to the singular point equation

$$C_{p(\text{anom})} = A(T/T_s - 1)^{-\gamma},$$

yield the same T_s value, 226 K.

Table 27: Thermodynamic data for 90% hydrogen peroxide solutions.

Temperature		Heat capacity		Entropy		Excess enthalpy, ($\Delta H_f - \Delta H_{298}$)				Enthalpy of formation		
K	°C	cal g ⁻¹ °C ⁻¹	J g ⁻¹ K ⁻¹	cal g ⁻¹ °C ⁻¹	J g ⁻¹ °C ⁻¹	cal/g	J/g	BTU/lb	cal/g	J/g	BTU/lb	
Solid												
200	-73	0.309	1.293	0.281	1.176	-127.7	-534.30	-229.86	-1658	-6937	-2984	
220	-53	0.333	1.393	0.309	1.293	-121.28	-507.44	-218.3	-1660	-6945	-2988	
240	-33	0.358	1.498	0.338	1.414	-114.38	-478.57	-205.88	-1662	-6954	-2992	
260	-13	0.392	1.640	0.366	1.531	-106.92	-447.35	-192.46	-1663	-6958	-2993	
263.3	-9.8	0.417	1.745	0.368	1.540	-105.59	-441.79	-190.06	-1662	-6954	-2992	
Liquid												
263.3	-9.8	0.664	2.778	0.680	2.845	-23.11	-96.69	-41.59	-1580	-6611	-2844	
280	7	0.664	2.778	0.714	2.987	-12.03	-50.33	-21.63	-1575	-6590	-2835	
290	17	0.663	2.774	0.735	3.075	-5.4	-22.59	-9.72	-1573	-6581	-2831	
298.1	25	0.663	2.774	0.755	3.159	0	0.00	0	-1571	-6573	-2828	
300	27	0.663	2.774	0.759	3.176	1.22	5.10	2.2	-1571	-6573	-2828	
310	37	0.663	2.774	0.781	3.268	7.86	32.89	14.15	-1568	-6561	-2822	
320	47	0.663	2.774	0.802	3.356	14.48	60.58	26.06	-1566	-6552	-2819	
330	57	0.663	2.774	0.822	3.439	21.11	88.32	38	-1564	-6544	-2815	
340	67	0.664	2.778	0.842	3.523	27.74	116.06	49.93	-1561	-6531	-2810	
350	77	0.664	2.778	0.861	3.602	34.38	143.85	61.8	-1539	-6439	-2806	
360	87	0.664	2.778	0.880	3.682	41.02	171.63	73.84	-1557	-6514	-2803	
370	97	0.664	2.778	0.898	3.757	47.66	199.41	85.79	-1555	-6506	-2799	
380	107	0.665	2.782	0.916	3.833	54.31	227.23	97.76	-1552	-6494	-2794	
390	117	0.666	2.787	0.933	3.904	60.96	255.06	109.73	-1550	-6485	-2790	
400	127	0.667	2.791	0.950	3.975	67.62	282.92	121.72	-1548	-6477	-2786	

Data source: [7]

Table 28: Constants for vapor phase thermodynamic data of hydrogen peroxide.

Coefficient	Value
A	34.25667
B	55.18445
C	-35.15443
D	9.087440
E	-0.422157
F	-149.9098
G	257.0604
$H = \delta H^\circ_{f,298}$	-136.1064

From [32]

3.19.2 Enthalpy of Formation of Hydrogen Peroxide

Enthalpy of formation data of hydrogen peroxide are listed in Table 29.

Table 29: Enthalpy of formation of hydrogen peroxide.

Concen- tration	Physical state	Enthalpy of formation ΔH^f_{298}			Source	Year	References
Mass-% H ₂ O ₂		kcal/Mol	kJ/Mol	cal/g			
100	liquid	−44.84	−187.6		Giguere	1950	[323]
100	vapor	−32.30	−135.1				
100	vapor	−32.53	−136.11		http://webbook.nist.gov/ chemistry/ (Chase) Data last reviewed in December, 1960	1998	[324]
100	liquid	−44.86	−187.7	−1319	PEPCODED.DAT	1990	[325]
100	vapor	−32.59	−136.34	−958	PEPCODED.DAT	1990	[325]
100	liquid	−44.88	−187.78	−1319	CEAGUI	1998	[326]

$M = 34.0147 \text{ g/mol} = 29.399 \text{ mol/kg}$

3.19.2.1 Enthalpy of Formation of Hydrogen Peroxide Vapor

The vapor phase excess enthalpy above the standard enthalpy of formation $\Delta H^\circ_{f,298}$ of H₂O₂ can be calculated from the Shomate equation:

$$H^\circ - H^\circ_{298.15} = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{\tau} + F - \Delta H^\circ_{f,298}$$

where A, B, C, D, E, and F are constants, and τ is the absolute temperature in K divided by 1000. The coefficients are the same as those listed in Table 28. The same coefficients (and others) were used for a formula expressing the heat capacity of the vapor (Section 3.19.1.3). These equations were curve-fitted from data covering a range from 298

Table 30: Thermodynamic properties of hydrogen peroxide vapor.

Temperature K	C_p $\text{J mol}^{-1} \text{K}^{-1}$	S° $\text{J mol}^{-1} \text{K}^{-1}$	$-(G^\circ - H^\circ_{298.15})/T$ $\text{J mol}^{-1} \text{K}^{-1}$	$H^\circ - H^\circ_{298.15}$ kJ/mol
298.	43.07	232.9	233.0	-0.02
300.	43.20	233.2	233.0	0.07
400.	48.65	246.4	234.8	4.68
500.	52.51	257.7	238.2	9.74
600.	55.50	267.6	242.3	15.15
700.	57.92	276.3	246.6	20.83
800.	59.90	284.2	250.8	26.72
900.	61.55	291.3	254.9	32.79
1000.	62.95	297.9	258.9	39.02
1100.	64.17	304.0	262.7	45.38
1200.	65.27	309.6	266.4	51.85
1300.	66.30	314.9	269.9	58.43
1400.	67.33	319.8	273.3	65.11
1500.	68.42	324.5	276.6	71.90

Data source: [33]

to 1500 K, according to [327]. The data in Table 30 were obtained from the same source and are consistent with the equation(s) above and below.

The thermodynamic functions of H_2O_2 vapor were calculated by Giguere [323] over the range from 298.16 to 1500 K based on structural data from the literature and determinations of the IR and Raman frequencies. The enthalpy of formation ΔH , the free energy of formation ΔF , and equilibrium constants at temperatures up to 1500 K were calculated for the formation of gaseous H_2O_2 from its elements, the decomposition of gaseous H_2O_2 into water vapor and oxygen, and the decomposition of H_2O_2 vapor into two hydroxyl-free radicals.

3.19.2.2 Enthalpy of Formation of Hydrogen Peroxide/Water Mixtures

In first approximation, enthalpies of formation of hydrogen peroxide/water mixtures could be calculated assuming additive behavior and neglecting the heat of mixing, which is small among compounds with similar molecular structure.

Enthalpies of formation for three hydrogen peroxide/water mixtures (50, 70, 90% H_2O_2) listed in the popular PROPEP/NEWPEP/GUIPEP Thermochemical Equilibrium program for the calculation of theoretical specific impulse of rocket propellants were unfortunately incorrect, and the mistake has persisted for almost 20 years. The three incorrect numbers shown in the PEPCODED.DAT 1986 file (-1927, -1684, and -1439 cal/g) should be replaced by the corrected numbers published a few years later. The correct enthalpies of formation for the three hydrogen peroxide/water mixtures were published in a very useful tutorial, and correction for NEWPEP and are -2556, -2070, and -1571 cal/g [328]. The number for the 90% H_2O_2 solution, -1571 cal/g, matches correctly with the number from Table 27 above.

3.19.3 Heat of Fusion of Hydrogen Peroxide

Enthalpies of the fusion data of solid hydrogen peroxide are summarized in Table 31.

Table 31: Enthalpy of fusion of hydrogen peroxide.

Temperature	cal/g	cal/Mol	kJ/Mol	Source	Year	References
K °C						
At the melting point	87.84	2987 ± 3	12.498	Giguere et al.	1954	[188]
At the melting point	85.83 ± 0.18	2919.5 ± 6.1	12.215	Foley and Giguere	1951b	[184]
For comparison: enthalpy of fusion of water						
273	0	79.72	1436.3	6.0095		
Molecular mass = 34.0147 g/mol = 29.399 mol/kg						

3.19.4 Heat of Vaporization of Hydrogen Peroxide

The heat of vaporization at the normal boiling point is 47.11 kJ/mol (11.26 kcal/mol = 331.2 cal/g) ([215], Ref. 26 in Schumb, page 231 and 304). From measurements of heat of vaporization of mixtures, those of pure H₂O₂ and D₂O₂ were calculated as 51.63 and 52.34 kJ/mol (12.34 and 12.51 kcal/mol), respectively [319]. The heat of vaporization of H₂O₂ at different temperatures is summarized in Table 32.

Table 32: Enthalpy of vaporization, 100% H₂O₂.

Type of data*	Temperature			$\Delta H_{\text{Evap.}}$		Source	Year	References
	°C	K	°F	kcal/mol	kJ/mol			
Calculated	-17.8	255.3	-0	12.778	53.463	Simkin and Hurd	1957	[232]
Calculated	4.4	277.5	40	12.547	52.497			
Calculated	26.7	299.8	80	12.313	51.518			
Calculated	49	322.1	120	12.076	50.526			
Calculated	71	344.1	160	11.834	49.513			
Calculated	93	366.1	199	11.579	48.447			
Calculated	116	389.1	241	11.31	47.32			
Calculated	138	411.1	280	11.026	46.133			
Calculated	160	433.1	320	10.724	44.869			
Calculated	182	455.1	360	10.397	43.501			
Calculated	204	477.1	399	10.025	41.945			
Measured	0	273.1	32	12.5917 ± 0.006	52.684	Foley and Giguere	1951b	[184]
Measured	25	298.1	77	12.330	51.59			

* Calculated from vapor pressure curve or measured

Table 33: Heat of vaporization of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixtures.

Concentration, mass-% H_2O_2	cal/g solution				J/g solution			
Temperature, °C	0	25	45	60	0	25	45	60
Temperature, K	273	298	318	333	273	298	318	333
0	596.0	582.1	571.2	563.9	2494	2436	2390	2359
10	576.1	563.4	552.9	545.4	2410	2357	2313	2282
20	556.0	543.5	533.4	526.4	2326	2274	2232	2202
30	535.3	523.8	514.3	507.1	2240	2192	2152	2122
40	514.1	503.1	494.1	487.4	2151	2105	2067	2039
50	492.8	482.2	473.7	467.3	2062	2018	1982	1955
60	470.3	460.4	452.0	446.0	1968	1926	1891	1866
70	447.5	437.8	430.0	424.1	1872	1832	1799	1774
80	423.5	414.1	406.5	401.3	1772	1733	1701	1679
90	397.8	388.8	383.1	376.6	1664	1627	1603	1576
100	370.9	362.7	356.3	351.3	1552	1518	1491	1470

Data source: [318]

The heat of vaporization of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixtures at four different temperatures was calculated from vapor pressure data over the entire range of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ compositions (Table 33).

3.19.5 Heat of Solution and Heat of Dilution of Hydrogen Peroxide

The mixing of pure hydrogen peroxide with water and the dilution of H_2O_2 solutions with additional amounts of water are usually exothermic. The effect of dilution is mildly exothermic (negative ΔH) for all concentrations above 294 K (21 °C). Some dilution processes below this temperature are endothermic. It is important to know the exact enthalpy of formation of H_2O_2 solutions if one wants to calculate the theoretical performance of H_2O_2 solutions to be used in a steam generator or rocket engine. Simply assuming additive behavior of the enthalpies of formation of the two ingredients H_2O_2 and H_2O will result in substantial errors. It was noticed 20 years ago that even a very popular theoretical rocket performance calculation computer program had incorrect enthalpy data for 50, 70, and 90% H_2O_2 in its ingredients data base.

To clarify the nomenclature, the term *heat of solution* or *heat of mixing* is applied only if one starts out with 100% H_2O_2 and adds various amounts of pure water. The term *heat of dilution* is appropriate, for instance, if one takes a 90% H_2O_2 solution and adds more additional water, e.g., in order to lower the flame temperature of a rocket engine.

All solution or dilution processes with hydrogen peroxide and water are exothermic when carried out above 294 K. Strangely enough, performing these operations at lower temperature has little thermal effect or is even endothermic. This is probably

an effect of breaking up the water clusters as one approaches the point of the highest density of water at 277 K. Hydrogen peroxide does not have a density maximum in the liquid range as water does. The heat capacities of the two liquids and their mixtures diverge in the same area.

In tabulating heats of solution and heats of dilution, there are two numbers that the experimenter will need to predict the exothermicity of the process and to correct for non-additive behavior of the enthalpies of formation in binary mixtures. The two numbers are **(1)** the integral heat of solution for the process of mixing anhydrous H_2O_2 with H_2O to form a solution with a given H_2O_2 concentration, and **(2)** the heat of dilution to infinite dilution.

In addition to using heat of dilution and heat of solution data for calculating the enthalpy of formation of H_2O_2 solutions (which are needed for many rocket performance calculations), the numbers are also needed to calculate the energy requirements for an industrial peroxide distillation and concentration plant. It takes energy to separate H_2O_2 and H_2O from their mixtures.

Table 34: Heats of dilution of hydrogen peroxide solutions in water at two different temperatures.

Temperature		H_2O_2 concentration		Heat of dilution, per mol H_2O_2	
$^{\circ}\text{C}$	K	Initial Mass-%	Final Mass-%	cal/mol	J/mol
26.9	300	98.7	89.7	-146.9	-614.6
26.9	300	98.7	88.9	-156.7	-655.6
26.9	300	98.7	79.4	-295.6	-1237
26.9	300	98.7	71.0	-406.1	-1699
26.9	300	98.7	62.0	-502.0	-2100
26.9	300	98.7	54.9	-575.4	-2407
26.9	300	98.7	50.3	-618.3	-2587
26.9	300	98.7	49.6	-627.4	-2625
26.9	300	98.7	42.8	-668.3	-2796
26.9	300	98.7	30.1	-736.1	-3080
26.9	300	98.7	14.0	-773	-3234
26.9	300	98.7	5.3	-803	-3360
0	273	98.7	86.0	-195	-815.9
0	273	99.4	70.2	-417.3	-1746
0	273	99.4	60.5	-515.1	-2155
0	273	98.7	46.3	-593.6	-2484
0	273	99.4	45.9	-597.3	-2499
0	273	99.4	38.1	-669.4	-2801
0	273	99.4	37.2	-669.9	-2803
0	273	99.4	19.7	-671.9	-2811
0	273	99.4	19.1	-671.6	-2810
0	273	24.5	9.3	42.2	176.6

Data source: [319]

Since the heat of dilution or heat of solution can be either endothermic or exothermic, the sign preceding the number can be either positive or negative. By convention, if the system is giving off heat to its environment, the process is exothermic, and the polarity of the enthalpy is negative. In using heat of dilution data, one must be careful to use the proper prefix (positive or negative); see also [194].

Table 34 gives the data that were also used to draw the graph in Figure 39.

Figure 39 shows that at lower temperatures the dilution of certain H_2O_2 solutions can become an endothermic process (based on data by [319] = Schumb's Ref. 79).

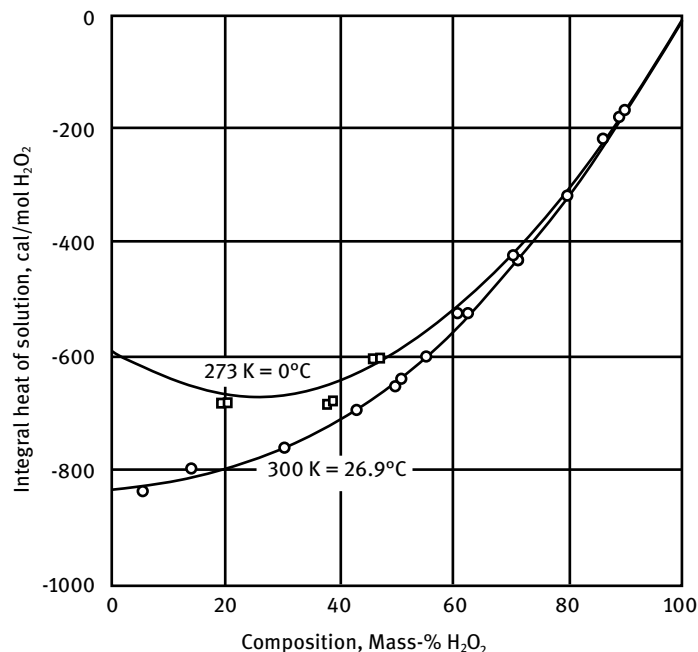


Figure 39: Integral heat of solution of hydrogen peroxide in water. (Reproduced and modified from [2].)

Table 34 gives only raw experimental data, but the integral heats of solution that are derived therefrom by interpolation and summarized in Table 35 are more useful.

The heat of **mixing** of H_2O_2 in H_2O at 298 K (25°C) and infinite dilution is -3427 J/mol (-819 cal/mol) [329]. The heat of mixing of H_2O_2 is $-3427 \pm 8 \text{ J/mol}$ ($-819 \pm 2 \text{ cal/mol}$), but that of D_2O_2 is $-3376 \pm 8 \text{ J/mol}$ ($-807 \pm 2 \text{ cal/mol}$).

Graphical representations of the heat of mixing of propellant-grade H_2O_2 - H_2O solutions were plotted from smoothed data given by [318]. These data agreed quite well with previous experimental data. Figure 40 was drawn using data from earlier publications based on data from Giguere and Carmichael [318].

Table 35: Integral heat of solution and heat of dilution to infinite dilution for hydrogen peroxide and water.

H ₂ O ₂ concentration	Integral heat of solution per mol H ₂ O ₂ , at 300 K (26.9 °C)		Integral heat of solution per mol H ₂ O ₂ , at 298 K (25 °C)		Heat of dilution to infinite dilution, per mol H ₂ O ₂ at 298 K (25 °C)	
Mass-%	cal/mol H ₂ O ₂	J/mol H ₂ O ₂	cal/mol H ₂ O ₂	J/mol H ₂ O ₂	cal/mol H ₂ O ₂	J/mol H ₂ O ₂
0 (infinite dilution)	-830	-3473	-813	-3402	0	0
10	-818	-3423	-805	-3368	-8	-33
20	-795	-3326	-785	-3284	-27	-113
30	-759	-3176	-752	-3146	-61	-255
40	-707	-2958	-703	-2941	-110	-460
50	-640	-2678	-636	-2661	-177	-741
60	-548	-2293	-545	-2280	-268	-1121
70	-440	-1841	-438	-1833	-375	-1569
80	-310	-1297	-310	-1297	-503	-2105
90	-161	-674	-160	-669	-653	-2732
100	0	0	0	0	-813	-3402

Data source: [2] page 243, Table 29

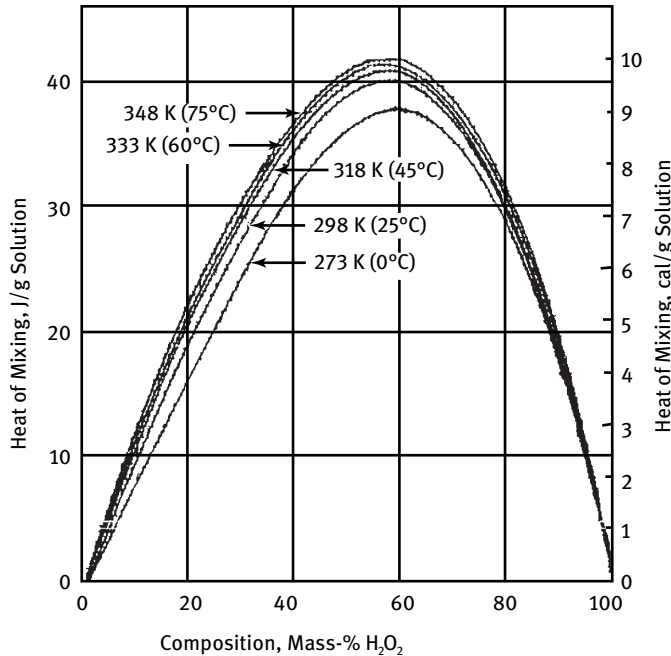


Figure 40: Heat of mixing of hydrogen peroxide and water. (Reproduced and modified from [246], based on data from [318].)

3.19.6 Entropy of Hydrogen Peroxide

One of the first measurements of the entropy of H_2O_2 as an ideal gas at 1 atm and 25 °C gave $55.76 \pm 0.12 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1} = 233.3 \pm 0.5 \text{ J mol}^{-1} \text{ K}^{-1}$ [188], as listed in Table 36. Comparison of this value with a recalculated statistical entropy leads to a value of $3.5 \text{ kcal/mol} = 14.6 \text{ kJ/mol}$ for the height of a hypothetical single barrier hindering internal rotation in the molecule. It was concluded that H_2O_2 does not consist of two tautomeric modifications.

Table 36: Entropy of hydrogen peroxide.

State	Temperature	Entropy		Source	Year
	K	$\text{cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$	$\text{J mol}^{-1} \text{ K}^{-1}$		
Vapor at 101 kPa = 1 bar	298.15		232.95	[324]	1960
Vapor at 101 kPa = 1 bar	298.15		234.542	[330]	2003
Ideal gas at 101 kPa = 1 bar	298	55.76 ± 0.12	233.3 ± 0.5	[188]	1954

The vapor phase standard entropy of formation of H_2O_2 can be calculated from the Shomate equation:

$$S^\circ = A \ln(\tau) + B\tau + C\tau^2/2 + D\tau^3/3 - E/(2\tau^2) + G$$

where S is the entropy in $\text{J mol}^{-1} \text{ K}^{-1}$, A , B , C , D , E , and G are constants, and τ is the absolute temperature in K divided by 1000. The coefficients are listed in Table 28. Some of these coefficients (and others) were used earlier for a formula expressing the heat capacity or the enthalpy of formation of the vapor (Section 3.19.2.1). These equations were curve-fitted from data covering a range from 298 to 1500 K.

The structural, spectroscopic, and thermochemical properties of $\text{H}_2\text{O}_2(\text{G})$ were re-examined and recalculated, and revised ideal gas thermodynamic tables were published [330]. The revisions were based on new spectroscopic information and made use of improved calculational methods. Compared to previous calculations, the entropy at 298.15 K (Table 37) is unchanged for H_2O_2 , but the high-temperature values

Table 37: Ideal gas thermochemical properties of hydrogen peroxide H_2O_2 at standard state pressure and temperature.

$T, \text{ K}$	$C_p,$ $\text{J K}^{-1} \text{ mol}^{-1}$	$S^\circ,$ $\text{J K}^{-1} \text{ mol}^{-1}$	$[G^\circ - H^\circ(\text{Tr})]/T,$ $\text{J K}^{-1} \text{ mol}^{-1}$	$H^\circ - H^\circ(\text{Tr}),$ kJ mol^{-1}	$\Delta H_f^\circ,$ kJ mol^{-1}	$\Delta G_f^\circ,$ kJ mol^{-1}	$\log K_f$
298.15	42.416	234.542	234.542	0.000	-135.880	-105.681	18.515

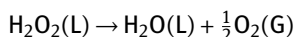
Data source: [330]

($T > 4000\text{ K}$) are significantly different. The original publication contains tabulated data for up to 6000 K , which is, of course, useless because H_2O_2 will long have decomposed before it reaches that temperature.

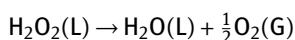
3.19.7 Heat of Decomposition of Hydrogen Peroxide

The ability to decompose exothermically is one of the properties that makes hydrogen peroxide useful in steam generators for turbine drives and rocket engines.

The enthalpy of decomposition has been measured experimentally and can be calculated from tabulated data. The generally accepted enthalpy of decomposition in accordance with the equation



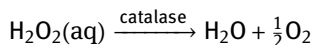
is $-98.70 \pm 0.08\text{ kJ/mol} = -23.59 \pm 0.02\text{ kcal/mol}$ and was derived from tabulated thermodynamic data. Experimental calorimetric determinations gave a value of $-98.07 \pm 0.12\text{ kJ/mol} = -23.44 \pm 0.03\text{ kcal/mol}$ [331]. Preliminary determinations of the heat of the reaction



catalyzed by Pt black at 273 K (0°C) and at various concentrations between 12.50 and 100% H_2O_2 in H_2O , gave $-98.49 \pm 0.17\text{ kJ/mol} = -23.54 \pm 0.04\text{ kcal/mol}$, a value slightly more exothermic than those found by previous authors [332].

For quick data lookup, although not very accurate, Figure 41 may suffice. The top line is for H_2O_2 going to liquid water and dioxygen, and the bottom line is for H_2O_2 going to steam and dioxygen. Note that by thermodynamic convention, the heat of decomposition is a negative number, but it is shown in Figure 41 as a positive number.

When we discuss enthalpy of decomposition of hydrogen peroxide, we usually think in terms of rocket engines operating on high concentrations of H_2O_2 and high temperatures. Only few of us realize that this reaction, catalyzed by enzymes, takes place continuously in our bodies, although fortunately with much lower H_2O_2 concentrations but with measurable heat output. The enthalpy of decomposition of hydrogen peroxide by catalase (EC 1.11.1.6) has been determined calorimetrically in isotonic saline solutions at 298 K (25°C) [293]. The value for the ΔH of decomposition for the reaction



was determined to be 100.4 kJ/mol ($24.0 \pm 0.3\text{ kcal/mol}$) at 298 K (25°C) in a closed reaction vessel.

When comparing the heat of decomposition as a function of H_2O_2 concentration, as the concentration of H_2O_2 in solution increases, there is less water to absorb the heat

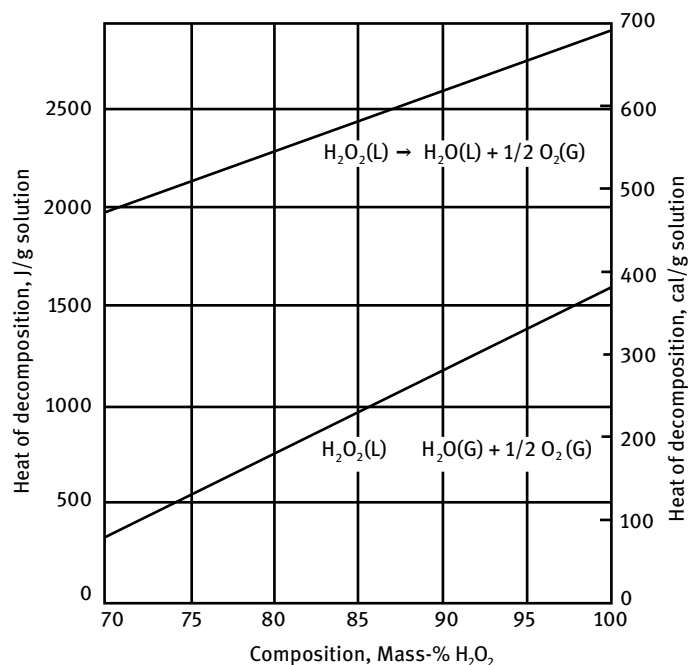
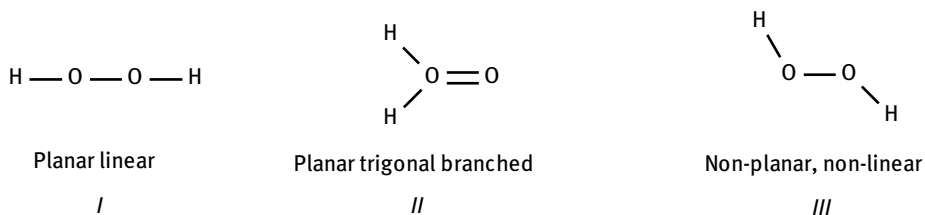


Figure 41: Heat of decomposition of hydrogen peroxide. (Reproduced and modified from [7].)

of decomposition. The heat of decomposition increases, and the heat of evaporation decreases. A crossover occurs at 63–64% H₂O₂ where rapid, accelerated decomposition becomes self-sustaining, the decomposition generates dry steam, and the concentration of H₂O₂ in the residual decomposing solution can increase because water evaporates first.

3.20 Molecular Structure of Hydrogen Peroxide

Various aspects of the molecular structure of the hydrogen peroxide molecule have already been discussed in the section on spectra of hydrogen peroxide. Much of what we know about the molecular structure of H₂O₂ and its isotope analog has been derived from spectrographic measurements, sometimes supplemented by computational chemistry of this relatively simple molecule. Because hydrogen peroxide has a dipole moment and a very large dielectric constant, the molecule must be unsymmetrical. Of the three possible structures of H₂O₂



the structure with the O—O peroxide bond has been shown by molecular spectroscopy to be the correct structure. The unsymmetrical structure II has sometimes been called “water oxide”.

The molecular structure of hydrogen peroxide was the subject of avid debates among numerous early investigators for many years. Three possible structures have been suggested over the years. From dipole moment determinations on H_2O_2 in solution, Linton and Maass favored structure II, whereas Theilacker, arguing from dipole moment and parachor data, favored structure I. In 1934, Penney and Sutherland, based on quantum-mechanical calculations, proposed that structure III, in which the azimuthal angles (φ and θ) are both about 100° , should be more stable than either the *cis* or *trans* configuration ($\varphi = 0$ or 180°). Furthermore, this structure not only predicted a value of the dipole moment in good agreement with that determined by Linton and Maass, but it also correctly accounted for the Raman lines. Later theoretical work confirmed this configuration.

The O—O—H bond angle of unstrained oxygen bonds is usually 100° . This results in three possible conformations of the H—O—O—H molecule and eliminates a straight-chain, axisymmetrical planar molecule. Infrared spectra as a function of temperature reveal the thawing of the rotational degree of freedom around the O—O axis. As long as free rotation exists, the *cis* and *trans* isomers or the skewed form cannot be isolated as individual compounds. The minimum-energy configuration is the skewed chain molecule. This is similar to the hydrazine molecule, which can also exist in *cis* and *trans* configurations, but the least-energy state is in the skewed configuration. The energy of the molecule as a function of rotation around the O—O axis shows minima and maxima depending on the *cis*, *trans*, and skewed positions of the two H atoms. The dihedral (azimuthal) angle ϕ describing the angle between the two planes in which the H atoms are lying shows an energy minimum at 100° , the most likely skewed configuration. For a *cis* configuration, the angle would be 0° and for a *trans* configuration, the angle would be 180° . The O—O—H angle is of the order of 110° , like that of water. For water, the measured bond angle is 104.45° . The OH groups undergo either free rotation, hindered rotation, or torsional oscillation, depending upon the heights of the barrier of the hindering potential. Evidence of hindered rotation or torsional oscillation was found in the rotational fine structure of infrared spectra. Extensive investigations of the IR and Raman spectra of the H_2O_2 molecule have confirmed these configurations. Bond energies [333], force constants and moments of inertia have been calcu-

lated from these spectra. Similar calculations were performed to identify the weakest bonds in the molecule, the breakage of which is most likely to initiate a decomposition chain reaction.

The structural parameters of the H_2O_2 molecule are illustrated in Figure 42.

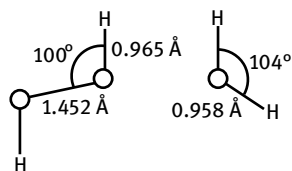


Figure 42: Structural parameters of the H_2O_2 molecule in comparison to H_2O
Distances in ångström = 10^{-10} m

It was stated above that the linear $\text{H}-\text{O}-\text{O}-\text{H}$ structure is the most likely structure for H_2O_2 . However, compounds with the unsymmetrical structure $\text{O}=\text{OH}_2$ (planar trigonal or pyramidal) have been claimed to exist as short-lived intermediates.

If it was not for the hydrogen bonding that connects H_2O_2 molecules in the condensed phase, H_2O_2 would have a boiling point like that of ethane. The high boiling point and high melting point of H_2O_2 and H_2O is the result of strong hydrogen bonding in the condensed phase. This is also expressed in the shift of IR absorption spectra when comparing spectra for the vapor and for the liquid. The Trouton constant for H_2O_2 is $111 \text{ J/mol} = 26.6 \text{ cal/mol}$, and it is similar to that of water ($109 \text{ J/mol} = 26.1 \text{ cal/mol}$), typical for associated liquids. Theoretically, for non-associated liquids, the Trouton constant should be $87.8 \text{ J/mol} = 21 \text{ cal/mol}$.

In reviewing the literature on the physical properties of hydrogen peroxide, one inevitably stumbles across many references to the deuterium isotopomer D_2O_2 and the hybrid HDO_2 . These compounds are not used as rocket propellants, and we would not mention them here if it was not for their utility in explaining the unique properties of H_2O_2 by comparing spectra and electronic properties. The substitution of H with D changes the natural frequencies and absorption characteristics of bond vibrations and helps the spectroscopist in the assignment of the absorption bands to certain parts of the molecule. The same applies to any other molecule in which hydrogen has been replaced with deuterium, but the $\text{H}_2\text{O}_2/\text{D}_2\text{O}_2$ system has been exceptionally well studied. The isotope effect is most distinct in low-molecular mass molecules such as H_2O , H_2O_2 , or NH_3 . D_2O_2 forms and accumulates as an unwanted byproduct in heavy-water cooled nuclear reactors.

Another type of nuclear reactor carries the fissionable uranium not in metallic or oxide form as a solid but dissolved in an aqueous solution, which becomes critical only as it circulates through the core of the radiation-shielded neutron source. In this solution, hydrogen peroxide (or deuterium peroxide, depending on the solvent) forms and decomposes with unequal speed, potentially leading to accumulation of H_2O_2 or D_2O_2 in the circulating water and altering its corrosive behavior [334].

Collisional activation, charge reversal, and six different neutralization-reionization mass spectrometric experiments with $[\text{H}_2\text{O}_2]^+$ radical cations and $[\text{H}_2\text{O}_2]^-$ radical anions were performed in order to probe the often disputed existence of neutral water oxide, $\text{H}_2\text{O}=\text{O}$, the long sought after tautomer of hydrogen peroxide, HOOH in the unsymmetrical structure II that has sometimes also been called “water oxide” [335]. Experiments together with *ab-initio* calculations indicated that $\text{H}_2\text{O}=\text{O}$ is a local minimum on the $[\text{H}_2\text{O}_2]$ potential-energy surface, and the elusive molecule seems to be formed as a transient upon neutralization of the corresponding radical cation H_2OO^+ in the gas phase. Even if it could be stabilized, it is doubtful that it would be a better rocket propellant than $\text{H}-\text{O}-\text{O}-\text{H}$; see also [336].

3.20.1 Rotational Barrier Energies in Hydrogen Peroxide

The infrared spectra of H_2O_2 are characterized by the band splitting caused by an internal rotation barrier along the axis of the $\text{O}-\text{O}$ bond. There is a vast amount of literature that deals with the energetics of internal rotation and their effect on the spectral and thermodynamic properties of this molecule. We have tabulated some of this literature in Table 38 because it is closely related to the energetics of H_2O_2 decomposition. Internal rotation can take place only as long as the $\text{O}-\text{O}$ bond is strong enough to hold the molecule together. Rotational barrier measurements and calculations are important to assess the stability of the hydrogen peroxide molecule and to determine the threshold where the molecule begins to decompose once internal vibrations and rotations become so vigorous that the chemical bonds can no longer hold the molecule together. For this reason, this chapter, although highly theoretical, is included in a book on rocket propellants.

There are many other dumbbell-shaped molecules where the two halves of the molecule rotate around the connecting axis, with or without rotational barriers. Hydrogen peroxide has frequently been compared to these other molecules, including ethane C_2H_6 , hydrazine N_2H_4 , disulfane H_2S_2 , and some containing more than two different atoms, such as methanol CH_3OH , hydroxylamine NH_2OH , and methylamine CH_3NH_2 . The publications listed in Table 38 are also useful in determining rotational barriers and energy levels in these other molecules; many of those are also used as rocket propellants. This information helps us to understand the peculiar properties of the hydrogen peroxide molecule that make it so attractive as a rocket propellant.

3.20.2 Computational Methods for Characterization of the Hydrogen Peroxide Molecule

The hydrogen peroxide molecule has unique properties that give it a high energy content that makes it suitable as a rocket propellant. While many parameters needed for the evaluation of H_2O_2 as a rocket propellant need to be determined experimentally, there has been a substantial effort to predict those parameters from theoretical calculations. Hydrogen peroxide is a relatively simple molecule, and many computational

Table 38: Literature on internal rotation, rotational barriers, bond energies, vibrational constants, and force constants in hydrogen peroxide.

Author(s)	Title	Source
Internal rotation, rotational barriers		
Davidson, R. B., and L. C. Allen	Rotational barriers in hydrogen peroxide	J. Chem. Phys. 55 , 519–527 (1971)
Dreizler, H.	Group theory of torsion rotation spectra of H ₂ O ₂	Z. Naturforsch. A21 , 1628–1632 (1966)
Dunning, T. H., and N. W. Winter	Hartree-Fock calculation of barrier to internal rotation in hydrogen peroxide	Chem. Phys. Lett. 11 , 194–195 (1971)
Dunning, T. H., and N. W. Winter	Theoretical determination of the barriers to internal rotation in hydrogen peroxide	J. Chem. Phys. 63 , 1847–1855 (1975)
Fink, W. H., and L. C. Allen	Origin of rotational barriers; Part I	J. Chem. Phys. 46 , 2261–2275 (1967)
Fink, W. H., and L. C. Allen	Origin of rotational barriers; Part II	J. Chem. Phys. 46 , 2276–2284 (1967)
Giguere, P. A., and I. D. Liu	Thermodynamic functions of hydrogen peroxide considering internal rotation	J. Am. Chem. Soc. 77 , 6477–6479 (Dec 1955)
Guidotti, C., et al.	Barriers to the internal rotation and observables of the ground state for hydrogen peroxide	Theor. Chim. Acta 27 , 55–62 (1972)
Halonen, L.	Overtone and combination stretching vibrational bands of hydrogen peroxide, ethene, and propadiene	J. Chem. Phys. 86 , 3115–3126 (1987)
Hirota, E.	Rotational structure of the infrared absorption spectrum of hydrogen peroxide vapor	J. Chem. Phys. 28 :5, 839–845 (1958); https://doi.org/10.1063/1.1744280
Khachkuruzov, G. A., and I. N. Przhivalskii	Molecular constants of hydrogen peroxide; Part VII: Parameters of internal rotation potential function	Opt. Spectrosc. 44 , 194–196 (1978)
Khachkuruzov, G. A., and I. N. Przhivalskii	Structural parameters of hydrogen peroxide	Optics and Spectroscopy 46 :5, 1034–1034 (1979)
Lee, J. S.	Accurate structure and torsional barrier heights of hydrogen peroxide	Chem. Phys. Lett. 359 , 440–445 (2002)
Lowe, J. P., and R. G. Parr	Internal rotation in hydrogen peroxide; Simple electrostatic model	J. Chem. Phys. 43 , 2565–2566 (1965)
Luo, X., and T. R. Rizzo	Rotationally resolved vibrational overtone spectroscopy of H ₂ O ₂ at chemically significant energies	J. Chem. Phys. 93 , 8620–8633 (1990)

Table 38: (continued)

Author(s)	Title	Source
Palke, W. E., and R. M. Pitzer	On the internal rotation potential in H_2O_2	J. Chem. Phys. 46 , 3948–3950 (1967)
Pederson, L., and K. Morokuma	Ab-initio calculation of the barriers to internal rotation of CH_3CH_3 , CH_3NH_2 , CH_3OH , N_2H_4 , H_2O_2 , and NH_2OH	J. Chem. Phys. 46 , 3941–3947 (1967)
Ranck, J. P., and H. Johansen	Polarization functions and geometry optimization in ab-initio calculations of the rotational barriers in hydrogen peroxide	Theor. Chim. Acta 24 , 334–345 (1972)
Rodwell, W. R., N. R. Carlsen and L. Radom	Theoretical studies of the effect of electron correlation on the geometry and barriers to internal rotation in hydrogen peroxide	Chemical Physics 31 :2, 177–186 (1978); CA 89 , 80465
Veillard, A.	Distortional effects on the internal rotation in hydrogen peroxide	Chem. Phys. Lett. 4 , 51–52 (1969)
Zuelicke, L., and H. J. Spangenberg	Calculation of the internal rotation hindrance potential of hydrogen peroxide	Theor. Chim. Acta 5 , 139–147 (1966)
Bond energies		
Giguere, P. A.	On the O—O bond energy in hydrogen peroxide	Can. J. Res. B B28 , 485–491 (1950)
Giguere, P. A.	The O—O bond energy in hydrogen peroxide	Can. J. Res. B B28 , 17–20 (1950)
Glockler, G., and G. Matlack	O—O bond energy in hydrogen peroxide	J. Chem. Phys. 14 , 504–505 (1946)
Lindeman, L. P., and J. C. Guffy	Determination of the O—O bond energy in hydrogen peroxide by electron impact	J. Chem. Phys. 29 , 247–248 (1957)
Sawyer, D. T.	Reevaluation of the bond-dissociation energies (DHdbe) for H—OH , H—OOH , H—O— , H—O— , H—OO— and H—OO	J. Phys. Chem. 93 , 7977–7978 (1989)
Simon, A., and M. Morchand	Raman spectrum of alkaline hydrogen peroxide solution and dissociation energy of the O—O bond	Z. Anorg. Allgem. Chem. 262 , 192–211 (1950)

Table 38: (continued)

Author(s)	Title	Source
Vibrational constants, force constants		
Botschwina, P., W. Meyers, and A. Semkov	Force constants and equilibrium geometries in hydrogen peroxide and other small molecules containing a hydroxyl group	Chem. Phys. 15 , 25–34 (1976)
Camy-Peyret, C., et al.	Torsion-vibrational interaction in hydrogen peroxide: first high-resolution observation of n_3	J. Mol. Spectrosc. 155 , 84–104 (1992)
Carpenter, J. E., and F. Weinhold, F. II: Natural bond orbital analysis	Torsion-vibration interactions in hydrogen peroxide; Part II: Natural bond orbital analysis	J. Phys. Chem. 92 , 4306–4310 (1988)
Chin, D., and P. A. Giguere	The torsional oscillation frequency of hydrogen peroxide	J. Chem. Phys. 34 , 690–691 (1961); This is only a short note! J. Mol. Spectrosc. 171 , 91–112 (1995)
Cook, W. B., et al.	Torsion-rotational energy levels, hindering potential, and inertial parameters of the first excited vibrational state of the anti-symmetric O—H stretch in hydrogen peroxide	
Khachkuruzov, G. A., and I. N. Przhivalskii	Molecular constants of hydrogen peroxide; Part I: Vibrational constants of H_2O_2	Opt. Spectrosc. 33 , 237–242 (1972)
Khachkuruzov, G. A., and I. N. Przhivalskii	Molecular constants of hydrogen peroxide; Part II: Vibrational constants of D_2O_2	Opt. Spectrosc. 33 , 786–787 (1972)
Khachkuruzov, G. A., and I. N. Przhivalskii	Molecular constants of hydrogen peroxide; Part V: Force constants	Opt. Spectrosc. 36 , 304–308 (1974)

chemists have used it as a benchmark to test the accuracy of their calculation methods and molecular models. This type of computational chemistry is useful to explain physical properties of existing molecules, and it is also useful in predicting physical properties of theorized, even more energetic molecules that so far exist only on paper and are waiting to be discovered. Similar calculations have been performed for many other rocket propellants. In the case of hydrogen peroxide, a relatively simple molecule, these calculations were relatively easy but challenging due to the ability of the two halves of the molecule to rotate or oscillate around the O—O axis of the molecule. Often, these calculations were performed side-by-side with actual spectral measurements and were often cited as a confirmation and proof of the correctness and accuracy of assumptions about energy levels in the molecule. One objective of these theoretical calculations is to determine the threshold of energy at which the molecule begins to break apart, starting an exothermic reaction. It is this exothermic reaction that enables hydrogen peroxide and other energetic molecules to act as monopropellants. This computational method can be applied to hydrogen peroxide and other dumbbell-shaped molecules like hydrazine or hydroxylamine [337].

The electronic structure of the hydrogen peroxide molecule in three different configurations, namely the *cis*, the *trans*, and the non-planar or skew forms, were calculated using Linear Combination of Atomic Orbitals (LCAO)-Molecular Orbital (MO)-Self-Consistent Field (SCF) approximations [338]. All the electrons were considered except those of the K-shell of the oxygen atoms. The orbitals of these atoms are essentially of the sp^3 hybrid type. It was shown that the skew form of the molecule with an azimuthal angle Φ of about 120° is the most stable, due mainly to conjugation of the σ_5 and σ_6 orbitals of the oxygen atoms with the other molecular orbitals. On the contrary, in the *cis* and *trans* forms these two orbitals are non-bonding. The predictions were compared to measured values of the ionization potentials, and the dipole moment and the predicted dipole moment, 2.05 D, agreed well with the experimental data.

A similar study of the electronic structure of the hydrogen peroxide molecule by a LCAO-SCF quantum chemical method gave a dipole moment of 2.71 D [339].

Equilibrium structure and barriers to internal rotation of hydrogen peroxide were accurately determined with a Hartree-Fock (HF) method and Rayleigh-Schroedinger perturbation theory [340]. The computed bond lengths [$R(\text{OO}) = 1.451 \text{ \AA}$, $R(\text{OH}) = 0.967 \text{ \AA}$] and angles [$\angle(\text{OOH}) = 99.3^\circ$ and $\angle(\text{HOOH}) = 119.3^\circ$] were in good agreement with experiment while near HF values lead to a false structure [$R(\text{OO}) = 1.390 \text{ \AA}$, $R(\text{OH}) = 0.943 \text{ \AA}$, $\angle(\text{OOH}) = 102.9^\circ$, $\angle(\text{HOOH}) = 111.2^\circ$].

Infrared intensities for the fundamental vibrations of H_2O_2 were predicted using atomic polar tensors obtained from *ab-initio* quantum mechanical calculations employing a 4-31G basis set [341]. The absolute intensities calculated quantum mechanically for H_2O_2 were compared to the previously reported intensities for H_2O_2 obtained by transferring a hydrogen atomic polar tensor to H_2O_2 from H_2O . These comparisons enabled estimates to be made for the infrared intensities of H_2O_2 as

follows: $A_1 = 14.5$ km/mol, $A_2 = 0.91$ km/mol, $A_3 = 0.058$ km/mol, $A_4 = 123$ km/mol, $A_5 = 46.2$ km/mol, and $A_6 = 101$ km/mol.

A series of *ab-initio* calculations of the internal structure of the HOOH molecule give us a better understanding of the forces that hold the molecule together and the energy levels it goes through as it rotates, oscillates, gets excited, and, eventually, breaks apart, releasing energy that can be used for rocket propulsion. Calculation of the oscillator strengths and optical rotatory strengths are part of this process [342]. Such *ab-initio* calculations can also be combined with traditional density-functional theory (DFT) methods. Comparison with experimental data and also with results from *ab-initio* methods (HF and correlated levels) showed a good performance of non-local density functional methods for the description of the hydrogen peroxide geometry, especially the torsion angle τ , when basis sets of sufficient quality were used. Different density functionals were then used in order to study *cis* and *trans* rotational transition states [343].

The potential energy surfaces for the singlet and triplet H_2O_2 molecular system were studied by using various methods suitable for examining most of the species and reaction paths on the H_2O_2 potential energy surfaces [344]. The hydrogen abstraction reaction $\text{O} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \cdot\text{OH}$ has a small or no energy barrier, suggesting this pathway may have relevance to the astrochemical formation of hydrogen peroxide in extraterrestrial environments.

The argument about the possible existence of a structural isomer of H_2O_2 has received new ammunition with the completion of *ab-initio* calculations [345]. *Ab-initio* molecular electronic structure theory was applied in an investigation of the oxywater-hydrogen peroxide isomerization. Oxywater, hydrogen peroxide, and the transition state connecting them have been located using a self-consistent-field configuration interaction including all single and double excitations and coupled cluster with single and double excitations methods with several basis sets. A classical barrier to isomerization of 5.7 kcal/mol has been predicted at the highest level of theory. Although these *ab-initio* predictions could be decreased by 1 or 2 kcal/mol, it was suggested that there can be little doubt that oxywater is a genuine minimum of the H_2O_2 potential energy hypersurface; see also [346–352].

The relative intensities of absorption bands of H_2O_2 in the far IR region can be calculated using a weak coupling of the vibrational, torsional, and rotational motions [353]. The contribution to the absorption band intensities due to a change of the rotational state of the molecule can be calculated using the 3j-symbols technique.

Highly accurate *ab-initio* variational calculations of the rotation-vibration energy levels of H_2O_2 in its electronic ground state used a recently computed potential energy surface and the variational nuclear-motion programs WARV4, which uses an exact kinetic energy (EKE) operator, and Trove, which uses a numerical expansion for the kinetic energy [354]. The Trove calculations were performed for levels with high values of rotational excitation, J up to 35. The calculations of the rovibrational energy levels reproduced the observed levels with a standard deviation of about 1 cm, simi-

lar to that of the $J = 0$ calculation as the discrepancy between theory and experiment for rotational energies within a given vibrational state is substantially determined by the error in the vibrational band origin. Minor adjustments were made to the *ab-initio* equilibrium geometry and to the height of the torsional barrier. Using these data and correcting the band origins using the error in $J = 0$ states lowers the standard deviation of the observed calculated energies to only 0.002 cm for levels up to $J = 10$ and 0.02 cm for all experimentally known energy levels, which extended up to $J = 35$.

3.20.3 Dimer and Polymer Association in the Vapor Phase

Hydrogen peroxide, like water, is strongly associated in the liquid phase through hydrogen bonds, allowing it to exist as a liquid at room temperature. Experimental vapor density measurements at 365 K ($92^\circ\text{C} = 165.6^\circ\text{F}$) showed that H_2O_2 is not associated in the vapor state [210].

The experimental investigation of the temperature dependence of the degree of association of pure liquids, water and hydrogen peroxide in the vapor phase has been supported by theoretical investigations in this direction. The possibility of using various methods for calculating the entropy of vapor formation of non-associated liquids, like water and hydrogen peroxide has been considered [355], including the use of the Hildebrand rule as made more rigid by Pitzer. The latter method does not however, lead to any improvement in the results since it is necessary to use values for the volume of the associated liquid, which inevitably introduces errors into the calculation. The results of calculating the temperature dependence of the monomer content was in good agreement with literature data of over the entire temperature range.

In the vapor above hydrogen peroxide/water mixtures, the two molecules form clusters of two or more molecules. High levels of *ab-initio* MO theory were used to calculate the structures, binding energies, vibrational frequencies and equilibrium constants of hydrogen peroxide-water dimers in the vapor phase [356]. The geometries of the different possible conformers were optimized and five different stationary points on the potential-energy surface were characterized, but only two were minima. The global minimum corresponded to a five-membered ring, where both monomers behave simultaneously as proton donors and proton acceptors. In the second minimum, which was about $9.2\text{ kJ/mol} = 2.2\text{ kcal/mol}$ higher, the hydrogen peroxide monomer behaved as a proton acceptor, while water behaves as a proton donor.

The same method was used to calculate the structures, binding energies, vibrational frequencies and equilibrium constants of hydrogen peroxide dimers in the absence of water [357]. Five different stationary points were found at this level, but only two of them were minima. The geometries of these two minima were refined, and their vibrational frequencies showed a sizeable red shift of the stretching vibrations of the proton donors. The global minimum corresponded to a six-membered ring having C_i symmetry; whereas, the second minimum is a five-membered ring, which lies about

1.1 kcal/mol above the global one. The formation of the latter implies a considerable enhancement of the dipole moment.

Hydrogen peroxide molecular clusters tend to form hydrogen-bonded cyclic and cage structures along the lines expected of a molecule, which can act as a proton donor as well as an acceptor. Results of density functional theory (DFT) and HF calculations suggest the formation of stable helical structures for larger clusters [358].

3.20.4 Molecular Structure of Frozen Hydrogen Peroxide

Hydrogen peroxide crystallizes into a tetragonal structure of $\text{H}_2\text{O}_2(\text{I})$, space group $D_4^4 - P4_12_12$ with four molecules in the unit cell, at -0.41°C and ambient pressure. The unit cell parameters were found to be $a = 4.06 \text{ \AA}$, $c = 8.00 \text{ \AA}$ at 253 K from single crystal XRD studies [359]. The observed density was 1.71 g/cm^3 at 253 K. Each oxygen atom has two close approach distances of $2.78 \text{ \AA}$ and two longer ones of $2.90 \text{ \AA}$, resulting in a very compact crystal. The nature of the hydrogen bonds formed in this crystal are also of interest, both in view of the unusually high density (1.70 g/cm^3) and in comparison to those formed in water ice, where the distance is given as $2.76 \text{ \AA}$.

Neutron studies revealed more information about the molecular structure of H_2O_2 : The O—O bond distance $d(\text{O—O})$ is $1.453 \pm 0.007 \text{ \AA}$ and $d(\text{O—H})$ is $1.008 \pm 0.005 \text{ \AA}$ (after correction for the thermal motion) [360]. The O—O—H and dihedral angles are $102.7 \pm 0.3^\circ$ and $90.2 \pm 0.6^\circ$, respectively. An infinite helix is formed through the network of O—O bonds around the fourfold screw axes along the c-axis.

The dihedral motion, O—H rotational with respect to O—O in H_2O_2 , has a very small energy barrier, 2.5 kcal/mol , resulting in high flexibility of H_2O_2 molecules.

If liquid H_2O_2 is subjected to very high pressures in a diamond anvil cell, it freezes at 1.5 GPa and ambient temperature into a tetragonal structure $P4_12_12$, $Z = 4$, denoted as $\text{H}_2\text{O}_2\text{-I}$ [361]. This is the same transition that has previously been reported in this material at 253 K. The unit cell parameters at 6.3 GPa are $a = 3.759 \text{ \AA}$, $c = 7.397 \text{ \AA}$, and $V = 15.74 \text{ cm}^3/\text{mol}$, representing 21% compression from that at ambient pressure. $\text{H}_2\text{O}_2\text{-I}$ has been found to transform into a high-pressure phase $\text{H}_2\text{O}_2\text{-II}$ at 7.5 GPa. One of most interesting results from this study was the discovery of the phase transition from tetragonal $\text{H}_2\text{O}_2\text{-I}$ to $\text{H}_2\text{O}_2\text{-II}$ near 7.5 GPa. The crystal structure of $\text{H}_2\text{O}_2\text{-II}$ appears to be an orthorhombic structure $Pmmn$. The infinite helix formed around the fourfold screw axis in $\text{H}_2\text{O}_2\text{-I}$ is deformed by possible partial disordering of the proton. The information suggested that $\text{H}_2\text{O}_2\text{-II}$ is denser and has stronger hydrogen bonds than $\text{H}_2\text{O}_2\text{-I}$. Both $\text{H}_2\text{O}_2\text{-I}$ and $\text{H}_2\text{O}_2\text{-II}$ were found to be stable chemically at high pressures, but they decompose into oxygen and H_2O at the onset of melting. The high stability of H_2O_2 at high pressure is probably due to a large kinetic barrier associated with decomposition.

3.21 Electron Impact Ionization and Mass Spectrometry of Hydrogen Peroxide

An investigation was made to determine the conditions of the reactions of hydroperoxyl and hydroxyl radicals and oxygen atoms in the presence of hydrogen peroxide [362]. For detection by positive ion beam mass spectroscopy, the radicals must be ionized to HO_2^+ and OH^+ by collision with electrons. The same ions are produced by dissociation of hydrogen peroxide induced by collision with electrons having an energy greater than the appropriate appearance potential. The appearance potentials of the ions HO_2^+ , OH^+ , and O^+ formed by dissociation of H_2O_2 were therefore investigated and are listed in Table 39.

Table 39: Appearance potentials of hydrogen peroxide ions or fragments in mass spectrometry

Ion or fragment	Appearance potential, eV
H_2O_2^+	12.1 ± 0.3
HO_2^+	16.1 ± 0.4
OH^+	16.0 ± 0.3
O^+	$>18.9 \pm 0.4$

Previous estimates of 13.6 eV for the ionization potential of the hydroxyl radical were confirmed. The ionization potential of hydrogen peroxide is 12.1 ± 0.3 eV. The minimum heat evolved in the formation of HO_2 from H and O_2 is equal to the ionization potential of HO_2 , which is 235 ± 9 kcal or 46 kcal assuming $I(\text{HO}_2) = 12.2$ eV. The appearance potential of OH^+ from H_2O_2 is less than that from H_2O (18.7 eV). For HO_2^+ , the observed appearance potential of 16.1 eV then equals the sum of the ionization potential of HO_2 , the H—OOH bond dissociation energy, and any kinetic or excitational energy of the dissociation products.

The appearance potentials of H_2O_2 electron bombardment fragments were determined from a plot of the logarithm of the ion current versus the electron accelerating voltage [363]. The peak intensities were corrected based on the assumptions that H_2O_2 does not make a 32 peak (O_2^+), and that there is not a rearrangement peak at mass 18 (H_2O^+). The dissociation energy for the O—O bond was found from the equation:

$$A(\text{OH}^+) = D(\text{HO—OH}) + I(\text{OH})$$

where A = appearance potential, D = dissociation energy, and I = ionization potential of the species indicated in parentheses. Assuming $D(\text{H—OH}) = 5.06$ eV gives $D(\text{HO—OH}) = 200 \text{ kJ} = 47.8 \pm 3 \text{ kcal}$, which is in fair agreement with $217 \text{ kJ} = 52 \text{ kcal}$ obtained from thermochemical measurements.

Several reactions have the ability to produce HO_2 radicals: **(1)** reaction of H with O_2 , **(2)** reaction of H with H_2O_2 , **(3)** reaction of O with H_2O_2 , **(4)** reaction of OH with H_2O_2 , **(5)** photolysis of H_2O_2 , and **(6)** low-power electrical discharge in H_2O_2 . Mass

spectrometric analysis for the purpose of identification and determination of thermochemical energies of HO_2 showed that the low-power electrical discharge in H_2O_2 provided the most intense and convenient source of HO_2 radicals [364].

The measured values are: ionization potential of HO_2 , $I(\text{HO}_2) = 11.53 \pm 0.02 \text{ eV}$, and appearance potential $A(\text{HO}_2^+) = 15.36 \pm 0.05 \text{ eV}$ with an estimated absolute accuracy of $\pm 0.1 \text{ eV}$. The derived bond dissociation energies D thermochemical energies are: $D_0(\text{H}-\text{OOH}) = 370 \text{ kJ/mol} = 88.4 \pm 2 \text{ kcal/mol}$, $D_0(\text{H}-\text{O}_2) = 192 \text{ kJ/mol} = 45.9 \pm 2 \text{ kcal/mol}$, $\Delta H^\circ_{\text{OOH}}(\text{HO}_2) = 23.8 \text{ kJ/mol} = 5.7 \pm 2 \text{ kcal/mol}$ for the values at 0 K; and $D(\text{H}-\text{OOH}) = 374.9 \pm 8.4 \text{ kJ/mol} = 89.6 \pm 2 \text{ kcal/mol}$, $D(\text{H}-\text{O}_2) = 197.1 \pm 8.4 \text{ kJ/mol} = 47.1 \pm 2 \text{ kcal/mol}$, and $\Delta H^\circ_{298}(\text{H}-\text{O}_2) = 20.9 \pm 8.4 \text{ kJ/mol} = 5.0 \pm 2 \text{ kcal/mol}$ for the corresponding values at 298 K (25°C). Ion-molecule reactions, which are negligible in normal operation of mass spectrometers, were shown to be a potentially serious source of interference in studies of HO_2 with conventional mass spectrometers.

4 Chemical Properties of Hydrogen Peroxide

The most pronounced chemical properties of hydrogen peroxide are its thermal instability and its oxidizing capability. In many chemical reactions in the analytical laboratory and in the chemical process industry, hydrogen peroxide is preferred as a clean oxidizer because it does not leave any residues. One must keep in mind, however, that towards very strong oxidizers (such as potassium permanganate) hydrogen peroxide acts as a reducing agent, and it is converted to elemental dioxygen.

When dozens of drums of concentrated hydrogen peroxide that were impounded by the victorious Allied Forces at the end of WWII in Germany were shipped across the Atlantic to the United States for further analysis and to support the post-war launches of A-4 (V-2) rockets under the supervision of the US Army, the drums brought with them the dubious reputation of containing an unstable chemical that had caused many drums to explode unexpectedly. Those reports were mostly based on happenings at the mobile V-1 launch sites during WW-II, where the pistons in catapults that launched the air-breathing “buzz-bomb” cruise missiles were powered by a steam generator fed with coinjected hydrogen peroxide and calcium permanganate solutions.

Several publications dealing with hydrogen peroxide in the years from 1946 to 1949 reflect the effort of the US chemical industry to come up to speed in making, storing, selling, and shipping this energetic chemical [365–367]. These publications are now only of historical interest.

4.1 Miscibility, Solubility, and Solvent Properties of Hydrogen Peroxide

4.1.1 Miscibility

Hydrogen peroxide is a hydrophilic, polar, protic solvent and is miscible with all other protic solvents. It dissolves in aprotic solvents such as diethyl ether to a greater extent than water.

Hydrogen peroxide is miscible in all proportions with water, methanol, ethanol, isopropanol, ethyl cellosolve, acetone, or pyridine. One must remember, however, that most mixtures of concentrated hydrogen peroxide with organic compounds are potentially detonable and many will even autoignite on standing or on contact. The miscibility of hydrogen peroxide with other organic liquids is generally greater (wider) than that of water.

In addition, hydrogen peroxide is more soluble than water in several organic liquids. Table 40 lists the number of grams of 90% hydrogen peroxide that will dissolve in 100 grams of the listed solvents at room temperature [367]. The corresponding numbers for water are listed for comparison. Looking at mixtures of hydrogen peroxide with organic solvents, one must remember that all these mixtures are potentially detonable (*Encyclopedia of Monopropellants*, chapter “Hydrogen Peroxide”). In spite of this hazard, mixtures of hydrogen peroxide with alcohols have been tested as rocket propellants, sometimes with catastrophic results.

Table 40: Miscibility of hydrogen peroxide with organic solvents.

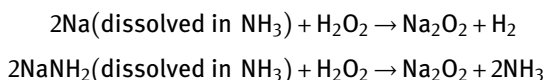
Organic solvent	g of 90% H ₂ O ₂ per 100 g of solvent	g of water per 100 g of solvent
Dimethyl phthalate	28	1.6
Diethyl phthalate	2.5	1.0
Ethyl acetate	4	3.5
Aniline	4	3.5

Data source: [367]

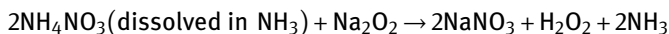
Ammonia gas will dissolve in hydrogen peroxide similarly to how it will dissolve in water, but there is concern that such solutions will decompose or explode spontaneously. If the solutions were stable enough, they would make a good monopropellant. Maybe it must be kept cold all the time.

At temperatures below 243 K (−30 °C) and with more than 30% H₂O₂, hydrogen peroxide forms stable solutions in liquid ammonia. In liquid ammonia as a solvent, H₂O₂ behaves like a weak acid. Reactions of H₂O₂ with sodium amide or sodium metal dissolved in liquid ammonia lead to formation of sodium peroxide, which is not soluble

in liquid ammonia [368]:



In solutions of ammonium nitrate NH_4NO_3 in liquid ammonia, the AN would act as a Bronsted acid and when reacted with a suspension of finely ground Na_2O_2 , anhydrous H_2O_2 can be generated and separated from the excess ammonia solvent and the NaNO_3 residue by fractionated distillation:



It was suggested that this might be a method to make anhydrous H_2O_2 starting with less concentrated H_2O_2 . It is an omission that this publication ignores the formation of a $\text{H}_2\text{O}_2 \bullet \text{NH}_3$ adduct like NH_4OH .

4.1.2 Hydrogen Peroxide as a Solvent for Solid Compounds

Hydrogen peroxide is a polar solvent, and many salts and other neutral solid compounds are soluble in hydrogen peroxide (as long as they do not react with it or destabilize it).

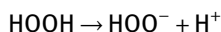
It was common practice to dissolve potassium hydroxide in hydrogen peroxide solutions in order to use this solution as a working fluid in chemical lasers Airborne Laser – Chemical Oxygen Iodine Laser (ABL-COIL) for making atomic oxygen. It was known that H_2O_2 is less stable in alkaline than in acidic solutions, but it was thought that the material was safe to store. This casual attitude changed when a large tank with basic hydrogen peroxide exploded (Section 7.8). The physical properties of basic hydrogen peroxide solutions had been summarized [369], but the safety properties were lacking. New methods developed for preparing mixed-base hydrogen peroxide for use in the ABL-COIL include mixing and simultaneously cooling the mixture with liquid nitrogen [370]. The temperature had to be maintained below 280 K (7°C). Dissolving the alkali metal hydroxides in hydrogen peroxide solutions is a very exothermic process. About 50 kJ (12 kcal) of heat are released per mol base added. Instead of KOH, mixtures of KOH, NaOH and LiOH can be used. Typically, the molar ratio of $[\text{H}_2\text{O}_2]$ to $[\text{OH}]$ was about 1.15.

Solid oxidizers like ammonium nitrate or ammonium dinitramide are readily soluble in hydrogen peroxide, and such solutions have been evaluated as oxidizers that have a lower freezing point and higher density than plain hydrogen peroxide. Instead of dissolving AN in water, a more powerful oxidizer called PERSOL-1 can be obtained by dissolving AN in hydrogen peroxide/water mixtures [198, 371]. PERSOL-1 contains 55.6% AN, 22.2% H_2O_2 , and 22.2% H_2O . This blend freezes at 276 K (+3°C) and has a density of 1.361 g/cm³. The freezing point diagram of the

ternary system AN/H₂O₂/H₂O will be shown in *Encyclopedia of Oxidizers*, chapter “Nitrate Oxidizers”. Many of these solutions do not have sharp freezing points but instead have glass transition points. The ignition delays of solutions of AN or ADN in HTP with an ionic liquid fuel, 1-allyl-3-methylimidazolium dicyanamide, were measured [372].

4.2 Autodissociation Constant of Hydrogen Peroxide

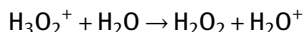
The acid constant of the reaction



is 1.78×10^{-12} at 293 K (20 °C). The $\text{p}K_{\text{a}}$ is 11.75. Other sources give $\text{p}K_{\text{a}}$ as 11.65 ± 0.10 . The heat of dissociation is 34.3 kJ/mol = 8.2 kcal/mol. As a weak acid, hydrogen peroxide forms salts with various metals, which usually hydrolyze when dissolved in water. Hydrogen peroxide is a much weaker base than water, but it can still form adducts with very strong acids. The strong superacid HF/SbF₅ forms unstable salts containing the H₃O₂⁺ ion.

There are two types of dissociation constants for hydrogen peroxide: those in aqueous solution and those of dissociation in the vapor phase. The one in aqueous solution goes to ionic species and is reversible, and dissociation in the gas phase often goes to free radical species as intermediate fragments of the irreversible decomposition process.

In the reaction



the equilibrium lies over on the right because H₂O₂ is a weaker base and a stronger acid than H₂O. The reaction enthalpy of this proton exchange is $\Delta H = -17.57 \pm 5.02$ kJ/mol = -4.2 ± 1.2 kcal/mol [373]. The $\text{p}K_{\text{a}}$ value of H₂O₂ dissociation is 11.75 ± 0.02 , which corresponds to a dissociation constant of $1.78 \pm 0.1 \times 10^{-12}$ at 20 °C. The enthalpy of reaction ΔH is 34.3 kJ/mol = 8.2 kcal/mol, the entropy of reaction ΔS is 107.5 J mol⁻¹ K⁻¹ = 25.7 cal mol⁻¹ °C⁻¹, and the free energy ΔG of the reaction is 66.1 kJ/mol = 15.8 kcal/mol.

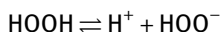
Glass electrodes can give accurate pH measurements even in non-aqueous solvents like hydrogen peroxide. The standard potential of glass electrodes in H₂O/H₂O₂ mixtures was measured over the entire range of compositions [374]. Thus, if the dissociation of a weak acid and the pH of a solution of its sodium salt in a solvent mixture are known, the ionic product of the solvent can be calculated directly from the equation:

$$\text{p}K'_{\text{M}} = 2\text{pH} - \text{p}K'_{\text{A}} - \log c_{\text{A}^-}$$

where $\text{p}K'_{\text{M}}$ is the negative logarithm of the ionic product of the solvent medium, pH is the pH of the solution of the sodium salt, $\text{p}K'_{\text{A}}$ is the negative logarithm of the dissoci-

ation constant of the acid, and c_{A^-} is the concentration of the anions from the sodium salt of the acid. The ionization constants of H_2O/H_2O_2 mixtures were measured by titration of sodium hydroxide or piperidine with perchloric acid in the mixed solvents and measuring the pH at the equivalence point. The pK of the solvent is twice the value of the pH at the equivalence point. The pK_a as a function of the H_2O_2 content of the solvent goes through a minimum [375].

Autodissociation of hydrogen peroxide in aqueous solution results in formation of H^+ and HOO^- ions:



The equilibrium constant

$$K = [H^+][HOO^-]/[HOOH]$$

is 2.4×10^{-12} at room temperature. Hydrogen peroxide is a stronger “acid” than water. The pH of a 90% aqueous solution is near 4.9 (even in the absence of phosphoric acid, which is sometimes added as a stabilizer). In spite of the more acidic pH, the corrosive action of H_2O_2 is only moderate, but the materials of construction must be selected very carefully (Section 5). Alkali metal peroxides will hydrolyze in water and release hydrogen peroxide and form a solution of alkali metal hydroxide in water. Such alkaline solutions of hydrogen peroxide are not very stable.

Upon dilution with conductivity quality pure water, the pH of several H_2O_2 samples from different sources increased from 0 to 5 when the samples were diluted from 90 to 10% H_2O_2 [376].

4.3 Adduct and Compound Formation in Aqueous Solutions

Hydrogen peroxide can form several adducts and compounds in aqueous solutions. Some of these may be of interest as rocket propellants. One must be careful when mixing an oxidizer like hydrogen peroxide with a fuel like ammonia. The potential explosive hazard of such mixtures is unexplored.

Dry ammonia was passed into anhydrous hydrogen peroxide kept at 273 K (0 °C). The gas dissolved readily and, after a considerable amount had gone into solution, white crystals formed. These were filtered off and dried with filter paper; analysis showed that they had a composition corresponding to $NH_3 \cdot H_2O_2$ [312].

Thermal analysis of the system NH_3 - H_2O_2 - H_2O showed the existence of two compounds: $NH_3 \cdot 3H_2O_2 \cdot 6H_2O$ with a melting point of 244.3 K (−28.8 °C) and another with a melting point of 258 K (−15 °C), which is probably $(NH_4)_2O_2 \cdot 2H_2O$ [377]. Two eutectic points were observed at 218.65 K (−54.5 °C) (0.7% NH_3) and 239.75 K (−33.4 °C) (12.5% NH_3).

A compound called *ammonium hydroperoxide* may have formed when thin films were successively condensed from the vapors of H_2O_2 and NH_3 on NaCl plates at

93.1 K (−180 °C) [378]. A reaction took place between the solids when the temperature was allowed to rise to 195 K (−78 °C). The IR spectrum showed the 1630-cm^{−1} and 1450-cm^{−1} bands of the NH₄⁺ ion and the O—O stretching band at 836 cm^{−1}. A new band at 1100 cm^{−1} was attributed to a bending mode of the O₂H[−] ion.

It was found that the peroxide remained stable and the ammonia unoxidized when in contact at low temperatures, that is, below 273 K (0 °C). A saturated solution of gaseous ammonia in 99.5% H₂O₂ was allowed to warm to room temperature, but when it was agitated, the solution exploded [379].

4.4 Reactions of Hydrogen Peroxide

For rocket propulsion applications, the most important reactions of hydrogen peroxide are the monopropellant catalytic decomposition reactions and the autoignition with a few select fuels in hypergolic bipropellant combinations. Technical applications of catalytic decomposition reactions will be discussed in *Encyclopedia of Monopropellants*, chapter “Hydrogen Peroxide”, regardless of whether they involve academic studies in the laboratory or actual flight hardware. The effects of inadvertent contaminants on the slow decomposition of H₂O₂ are discussed in Section 4.5.5 on storability.

4.4.1 Redox Reactions of Hydrogen Peroxide

Hydrogen peroxide is unusual in that it can be both an oxidant and a reducing agent, depending on the nature of the compounds it is reacting with.

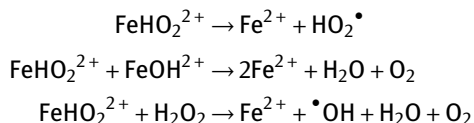
A very unusual phenomenon was observed during reactions of hydrogen peroxide with chromate in a weakly acidic medium at elevated temperature and at high initial concentration of hydrogen peroxide. Oscillatory periodic changes of pH occurred during the chromate-catalyzed decomposition of hydrogen peroxide in a weakly acidic medium at elevated temperature and at high initial concentration of hydrogen peroxide [380]. In a closed system, there were only two or three periods, but sustained oscillation occurred in a continuous stirred tank reactor (CSTR). In closed systems, the oscillating temperature exhibited a maximum (up to 15 °C increase), but in a CSTR, sustained oscillation occurred at a constant stationary temperature.

4.4.1.1 Reactions of Hydrogen Peroxide with Iron Ions

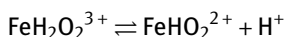
Iron ions are ubiquitous and may be leached from steel vessels or steel components (valves, fittings) that the liquid comes into contact with. Iron contamination accelerates the decomposition of H₂O₂ during storage. Reactions of H₂O₂ with Fe²⁺ or Fe³⁺ ions result in a series of reactions that have been examined very thoroughly because they generate free •OH radicals as an intermediate (Fenton reagent). Such free radicals can serve as initiators for free radical chain reactions such as polymerizations,

calibration of an electron spin resonance (ESR) instrument, and in a biologic system of living cells, they may induce cancer. They are also effective in destroying organic contaminants in industrial waste streams.

The reaction of Fe^{3+} with H_2O_2 proceeds via the following three initial steps [381]:



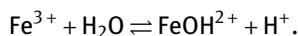
which occur after the preequilibrium



At 298 K (25°C) and ionic strength 0.45, the rate constant (k) of the first reaction is $1.6 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$, and the activation energy (E_a) is $92 \text{ kJ/mol} = 22 \text{ kcal/mol}$; the rate constant for the second reaction is $k = 5.0 \text{ L mol}^{-1} \text{ s}^{-1}$, $E_a = 50 \text{ kJ/mol} = 12 \text{ kcal/mol}$, and the rate constant for the third reaction is $k = 2 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$. When these rate constants and the proposed (ion-free radical) mechanism were applied to published data, they agreed well with the experimental values. A rate law of the catalytic decomposition of H_2O_2 was derived that at $[\text{Fe}^{3+}] : [\text{H}_2\text{O}_2]$ ratios of equal to or greater than 1 follows the equation

$$-d[\text{H}_2\text{O}_2]/dt \approx [\text{Fe}^{3+}][\text{H}_2\text{O}_2]^{1.5}/([\text{H}^+] + K)$$

where K is the equilibrium constant for



Peroxy complexes where H_2O_2 is temporarily included in the sphere of hydration of the iron(III) ion are intermediates in the iron-catalyzed decomposition of H_2O_2 [382, 383]. Similar peroxy complex intermediates are formed in the reactions of H_2O_2 with chromate [384, 385] or molybdate ions [386, 387].

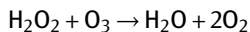
Here, we are mostly interested in reactions of H_2O_2 with iron compounds as an unwanted reaction leading to accelerated decomposition of HTP during storage if it becomes contaminated by iron leached from the wall of storage containers or flow system components (plumbing, valves, pumps, filters). We are also interested in catalytic iron compounds (dissolved iron compounds in a solvent) that can be squirted into a decomposition chamber as a liquid catalyst simultaneously with H_2O_2 , causing instant controlled decomposition and initiation of combustion where H_2O_2 is used as an oxidizer in bipropellant rocket engines.

4.4.2 Reaction Mechanisms of H_2O_2 Reactions with Other Inorganic Species

Hydrogen peroxide can react with many other compounds. The reactions of prime interest are those that promote instant decomposition or lead to hypergolic ignition of

two (or more) reactants, as will be discussed in more detail in a later volume of this series where we deal with bipropellants.

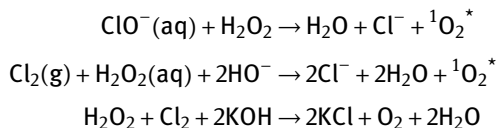
Attempts to synthesize a higher peroxide by reaction of H_2O_2 with ozone instead resulted in decomposition of ozone and H_2O_2 acting as a reducing medium:



This is a reaction proceeding via free radical intermediates. Attempts to identify semistable associate complexes in the O_3 and H_2O_2 system by computational chemistry using time-dependent density functional theory found four complexes as semistable structures of $\text{O}_3\text{-H}_2\text{O}_2$ [388]. Natural bond orbital analysis and quantum theory of atoms in molecules were employed to elucidate the interaction characteristics of the $\text{O}_3\text{-H}_2\text{O}_2$ complexes. Two different intermolecular interactions were predicted that aid in the formation of complexes, namely: conventional $\text{O}\cdots\text{H}$ hydrogen bond and $\text{O}\cdots\text{O}$ contact. The hope of synthesizing a powerful, heretofore unknown oxidizer by reaction of H_2O_2 and O_3 is fading.

4.4.2.1 Reaction Mechanisms of H_2O_2 Reactions with Halogens

The reaction of H_2O_2 with chlorine and alkali and subsequent reactions with iodine are key steps in the operation of chemical oxygen iodine lasers (COIL). The laser is fed with gaseous chlorine, molecular iodine, and an aqueous mixture of hydrogen peroxide and potassium hydroxide (or $\text{KOH}/\text{NaOH}/\text{LiOH}$). The COIL output wavelength is $1.315\mu\text{m}$, the wavelength of transition of atomic iodine.

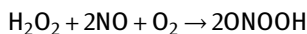


Because the oxygen thus formed is released in an excited state as singlet Δ oxygen (as indicated by the asterisk) and because spontaneous transition of excited oxygen to the triplet Σ ground state is forbidden by quantum mechanics, the excited atomic oxygen has a spontaneous lifetime of about 45 min. This allows the singlet Δ oxygen to transfer its energy to the iodine molecules injected to the gas stream which are nearly resonant with the singlet oxygen, so the energy transfer during the collision of the particles is rapid. The excited iodine then undergoes stimulated emission and lases at $1.315\mu\text{m}$ in the optical resonator region of the laser. The COIL has four primary parts: oxygen generator, gain generator (or resonator), pressure recovery system, and storage tanks that hold all the chemicals needed to operate the laser. Directed energy from the laser weapon would heat the incoming threat missile body, causing overpressure and/or stress fracture, which would destroy the hostile missile. The COIL was planned to be mounted on an aircraft and flown at high altitudes to detect, track, and destroy threat missiles in the boost phase, but the Airborne Laser program was eventually canceled in 2008; see also [389].

4.4.2.2 Reactions of H₂O₂ with Nitrogen Oxides

Reaction of H₂O₂ with NO

The reaction of H₂O₂ with NO in alkaline solutions will form peroxonitrites



This reaction may occur *in vivo*, since both H₂O₂ and NO are formed in various metabolic and nerve conduction processes. The anion is stable, but the free acid will decompose to nitrate with a rate of 1.3 s⁻¹ at 298 K.

The addition of fresh or decomposing H₂O₂ (a source of hydroxyl-free radicals) to stack gases from fossil fuel burning power plants is one of the methods suggested to clean up the stack gases by quickly oxidizing NO to NO₂, which is then removed by conventional DeNO_x processes [390].

Reaction of H₂O₂ with NO₂ or N₂O₄

The reaction of H₂O₂ with NO₂ is one of the key reactions in atmospheric smog formation under the influence of ultraviolet light from the sun. The reaction in the presence of water may lead to pernitric acid. Subsequent reactions with organics lead to peracetic acid, a nasty irritant.

4.4.3 Reactions of H₂O₂ with Organic Compounds

4.4.3.1 Reactions of H₂O₂ with Organic Amines

Mixtures of H₂O₂ with organic amines could potentially be used as monopropellants that are more energetic than H₂O₂ by itself (if they do not autoignite or explode during mixing). The freezing points of mixtures of 98% H₂O₂ with a selection of organic aliphatic, aromatic, and heterocyclic amines were determined [210]. The H₂O₂ and the amines formed adducts with peritectics and showed one or two eutectics. In several cases, the adducts could be isolated and showed stoichiometric composition of 2:1, 3:1 or 4:1 adducts. It was found that the peroxide remained stable and the amine unoxidized, as long as they were kept at low temperatures, that is, below 273 K (0 °C). If the solutions were allowed to warm up to room temperature, some of the amines caused decomposition of the peroxide, with oxidation of the amine to the nitro compound. Piperidine was the most active in producing decomposition and when warmed to room temperature, the heat of the reaction was enough to accelerate it progressively until the peroxide decomposed with **explosive** violence. The monobutylamine with the tertiary carbon atom attached to the nitrogen was the most stable of the amines tried, no decomposition took place. No crystals could be formed at the higher concentrations of the organic base since the mixture froze to a glass once the first eutectic had been passed. Even if they do not autoignite, these mixtures are **detonable**.

4.4.3.2 Reactions of H_2O_2 with Organic Amides

The reaction of H_2O_2 with urea produces urea peroxohydrate, CAS RN [124-43-6], which is industrially important as a solid form of hydrogen peroxide and can be used as topical disinfectant, mouthwash, and chemical oxidant. The optimum conditions for preparing urea peroxide were obtained as follows: molar ratio of hydrogen peroxide to urea 1.2; reaction temperature 298 K (25 °C); reaction time 30 min; mass ratio of stabilizer to urea 0.2%. Salicylic acid is suitable as a stabilizer [391].

4.4.3.3 Reactions of H_2O_2 with Ketones

The use of dilute H_2O_2 and/or acetone to clean laboratory equipment is common, but it has been shown to be potentially hazardous due to reactions of H_2O_2 with organic solvents that can form explosive peroxides. Mixing concentrated H_2O_2 and acetone with an acid catalyst is known to form the shock and friction sensitive explosives triacetone triperoxide (TATP) and diacetone diperoxide (DADP). When studying the potential formation of explosive peroxides when mixing dilute H_2O_2 and acetone solutions, the conclusion of these experiments was that when mixing dilute solutions, such as less than 3% H_2O_2 and 7% acetone, the solutions are unlikely to form significant amounts of TATP or DADP [392]. In the presence of an acid catalyst, hundreds of parts per million of organic peroxides can be formed. Although TATP is relatively insoluble in water, it is soluble at roughly the 15 ppm level and higher for acetone and H_2O_2 solutions, thus any acetone peroxides that are formed without an acid catalyst should remain soluble in the aqueous cleaning solution. If they were to precipitate, that would be a hazard.

4.5 Slow Homogenous Decomposition in the Liquid Phase

The following discussion of the decomposition of hydrogen peroxide in the liquid phase and in the vapor phase is restricted to decomposition as it relates to storage and handling. The controlled and deliberate decomposition of hydrogen peroxide such as in monopropellant rocket engines and gas generators will be discussed in *Encyclopedia of Monopropellants*. Many decomposition mechanisms (predominantly those based on homogeneous or heterogeneous catalysts) are suitable for the design of igniters for H_2O_2 rocket engines.

Unless a droplet of hydrogen peroxide is suspended in a weightless condition in outer space, where it will not be in contact with a container wall, it is very difficult to study the stability of H_2O_2 under terrestrial conditions in a gravity field without interfering effects from contact with the wall. Any contact with a wall is likely to alter the results of homogeneous liquid decomposition measurements. Flasks and tanks used for storage stability experiments have always been meticulously cleaned and passivated to minimize wall effects.

Methods for measuring the rate of decomposition of HTP are described in Section 4.7. Homogeneous decomposition rates for pure HTP in the absence of contaminants or stabilizers reported in the literature vary widely, depending on the source of the pure or ultrapure H_2O_2 and on the experimental conditions, such as the container material and exclusion of light and other stimuli.

4.5.1 Effect of Water Content on Slow H_2O_2 Decomposition in the Liquid Phase

Most other unstable compounds (e.g., hydroxylamine free base) may be relatively stable in aqueous solution and become increasingly unstable when the solution is more concentrated or when all water is removed to obtain the compound in the anhydrous state. In the case of hydrogen peroxide, the opposite may be the case, and a contradictory observation has been made repeatedly that the highly purified H_2O_2 is more stable than 70–90% aqueous solutions.

This unusual phenomenon has sometimes been used to test the compatibility of large hydrogen peroxide containers by exposing them not to high concentration hydrogen peroxide (for which they were intended) but to lower concentration hydrogen peroxide, as this would be a more stressing test of the compatibility and cleanliness of the tank. If the tank does not show excessive reactivity with low concentration hydrogen peroxide solutions, the compatibility should improve as the concentration increases. This is somewhat counterintuitive in that it suggests that very high concentrations of hydrogen peroxide, such as 98% or anhydrous hydrogen peroxide, are more stable than 90 or 70% and, therefore, potentially safer to store. Different explanations have been offered for this dependency, such as hydrogen peroxide and water forming clusters in which the H_2O_2 molecule is more stressed. It is unlikely that changes in surface tension can have any effect on H_2O_2 stability in solutions.

One must differentiate if one compares stability of solutions from which water has been removed, allowing accumulation of stabilizer in the less volatile residue or solutions (dilutions) made by adding ultrapure water to ultrapure, near 100% H_2O_2 . In the latter case, not only the H_2O_2 is diluted, but also the stabilizer concentrations decreased proportionally. In some cases, 98% H_2O_2 may be more stable than 90% H_2O_2 because, depending on the concentrating process used, the contaminants may be removed during the last concentration step, or the stabilizer may accumulate in the residue.

On the other hand, it is surprising to learn that when 90% unstabilized H_2O_2 was diluted with doubly distilled, very pure water under extremely clean conditions, the dilute solutions decomposed at a faster rate than the concentrated stock solution. This observation seems to counter what one intuitively would expect from concentrated energetic materials and their solutions.

4.5.2 Effect of Temperature on Slow Decomposition in the Liquid Phase

Data for the rate of decomposition of HTP as a function of temperature are listed in Table 41.

Table 41: Effect of temperature on decomposition of 90% hydrogen peroxide.

Temperature			Approximate rate of decomposition
K	°C	°F	
	30	86	1% per year
	66	151	1% per week
	100	212	2% in 24 h
	140	284	Decomposes rapidly with boiling

Data source: [367]

Commercial 90 and 98% hydrogen peroxide, maintained at 213 K (−60 °C) in the solid state, decomposed at a rate of less than 1 ppm per day [393]. As this was the order of magnitude of detection of decomposition in the equipment used at that time, it was believed that under these conditions high strength hydrogen peroxide can be considered stable and storable (less than 0.1% decomposition in 3 years).

Stability characteristics of concentrated hydrogen peroxide solutions have been studied at 323 to 373 K (50 to 100 °C) over the range 70 to 90 weight-% hydrogen peroxide in both the absence and the presence of stabilizers [308]. A temperature of 323 K (50 °C) proved satisfactory for the accuracy of the gas evolution method used to determine the rate of decomposition of peroxide samples. Previous reports [367] of high stability for very pure hydrogen peroxide at concentrations of 85 to 90% were confirmed. The temperature coefficient of the rate of decomposition of unstabilized H_2O_2 solutions was determined for the intervals 323 to 333 K (50 to 60 °C) and 333 to 343 K (60 to 70 °C) as 2.2 ± 0.1 , which is believed to be approximately applicable over any 10 °C range between 323 and 373 K (50 and 100 °C). Methods of preparing the surface of Pyrex[®] containers for use with concentrated hydrogen peroxide were developed, which make it possible to obtain reproducible measurements of the uncatalyzed decomposition rate. Pure aluminum and pure cast tin were found to be suitable materials of construction. Vigorous agitation was without appreciable effect on the measured rate of decomposition of 85% unstabilized hydrogen peroxide. The importance of pH on rate of decomposition was emphasized by measurements with and without added catalytic ions of known concentrations of ferric or cupric ion in 85 to 90% hydrogen peroxide at 323 K (50 °C) and on the required concentrations of stabilizers to counteract such catalytic action; see also [394, 395].

In the range between 343 and 363 K (70 and 90 °C), the rate of decomposition of highly pure, unstabilized H_2O_2 increases by a factor of 2.2 for every 10 °C increase in temperature. This temperature dependence agrees quite well with the rule-of-thumb

for many chemical reactions that the rate doubles for each 10° increment of temperature increase.

In some cases, 98% H_2O_2 may be more stable than 90% H_2O_2 because, depending on the concentrating process used, the contaminants may have been removed along with water during the last concentration step, or the non-volatile stabilizer may have accumulated in the residue. Depending on the storage conditions, decomposition rates of 1%/year must be assumed as acceptable for 98% H_2O_2 . The same material may lose 2%/day if it is stored at 373 K (100°C).

The measured decomposition rate of 0.014%/day at 323 K (50°C) for commercial 70% H_2O_2 [396] agreed well with previously published data since it lies between minimum reported values for stabilized and unstabilized hydrogen peroxide [308]. It was concluded that the peroxide used in these tests must have been a stabilized commercial grade. However, no chemical tests for the presence of stabilizers were made. Figure 43 is a plot of the decomposition rates calculated from oxygen evolution volumes versus temperature, derived from measurements at up to 408 K (135°C). The slope of the graph equals the log of the temperature coefficient a . A value of 2.08 was measured for a in this work illustrated in Figure 43.

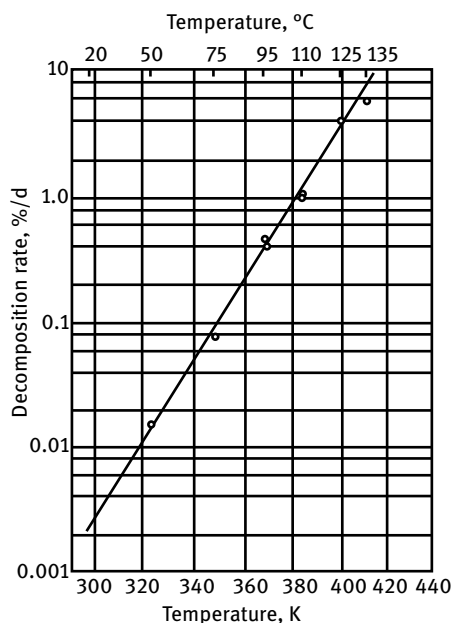


Figure 43: Decomposition rate of 70% commercial grade hydrogen peroxide. (Reproduced and modified from [396].)

The exothermic decomposition process of H_2O_2 was examined by an adiabatic calorimetric method in order to better understand explosion accidents caused by H_2O_2 [397]. It was shown that the initial exothermic temperature for 30 mass-% H_2O_2 was 307.65 K (34.5°C), with the reaction heat being 301 J/g, the maximum self-heating

rate 35 °C/min, and the maximum explosion pressure per unit mass 1.7 MPa/g. It was also contemplated that timely cooling of a tank of decomposing H₂O₂ can prevent an explosion.

Thermal stability of 10, 20, 31, and 45 mass-% H₂O₂ (obtained from MGC Pure Chemical Taiwan, containing not specified stabilizers) was tested by differential scanning calorimetry (DSC) [398]. To build up a comprehensive kinetic model, various tests were conducted with heating rates of 1, 2, 4, and 10 °C/min, respectively. The experimental curves showed that H₂O₂ decomposition has one exothermic peak, and it may start to decompose below 320–354 K (47–81 °C). The activation energy and total heat of decomposition for three heating rates are summarized in Table 42.

Table 42: The thermokinetic parameters of 10, 20, and 31 mass-% H₂O₂ decomposition, as determined by DSC.

H ₂ O ₂ , mass-%	Heating rate, °C/min	<i>E_a</i> , kJ/ mol	<i>ΔH</i> , J/g
10	2	102.3	192.4
20	2	337.0	421.0
31	2	256.3	703.5
10	4	306.2	269.1
20	4	94.7	409.8
45	4	98.4	887.3
10	10	232.2	470.6
31	10	166.0	838.8
45	10	156.5	1078.5

Data source: [398]

There are plenty of data for activation energy of H₂O₂ decomposition at low to moderate concentrations (20–40% H₂O₂), but data are lacking for 70% and higher H₂O₂ concentrations (because they are more difficult to determine).

In a DSC with stainless steel sealed crucibles, the onset of decomposition of a commercial 50% H₂O₂ solution was at 340.5, 358.9, and 359.4 K (67.4, 85.8 and 86.3 °C) with heating rates of 3, 5, and 7 °C/min. [399]. The activation energy was 77.1 kJ/mol.

4.5.3 Effect of pH on Slow Decomposition in the Liquid Phase

The rate of decomposition of H₂O₂ is pH dependent. In alkaline solutions, the decomposition proceeds faster by several orders of magnitude than in acidic solutions. One industrial accident was caused by sudden decomposition of hydrogen peroxide in a caustic solution used in a chemical oxygen-iodine laser (COIL) test facility [400, 401].

A study of the role of pH on stability showed that a broad maximum in stability existed over a pH range of 0 to –2.5 (Figure 44).

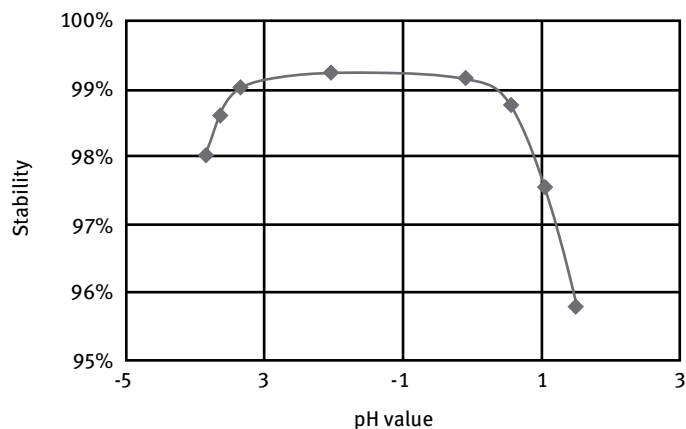


Figure 44: Stability of 98% H_2O_2 as a function of pH. (Reproduced and modified from [402].)

The homogeneous decomposition of H_2O_2 in the absence of catalysts is dependent on the pH. H_2O_2 solutions are generally more stable in acidic solutions and less stable in alkaline solutions. In alkaline solutions, the autodissociation equilibrium



is shifted toward the right with the formation of HOO^- ions, which are unstable and accelerate the decomposition. Aqueous solutions of sodium peroxide are short-lived and decompose as soon as the sodium peroxide has dissolved. Strongly acidic additives (with the exception of phosphoric acid) accelerate the decomposition of HTP.

Exothermic decomposition of hydrogen peroxide due to contaminants has caused many industrial explosions. In one accident, H_2O_2 was mixed with H_2SO_4 in a vacuum tank truck, and an explosion occurred at that moment. The cause of the accident was that H_2SO_4 accelerated the decomposition of H_2O_2 and led to a runaway reaction. Runaway temperature explosion often occurs after an induction period. The thermal decomposition reaction of 20 mass-% H_2O_2 mixed with low (0.1, 0.5 or 1.0 N) or high concentrations of 96 mass-% H_2SO_4 was measured using DSC and a commercial instrument called Vent Sizing Package 2 (VSP2) [403]. Thermokinetic data, such as exothermic onset temperature (T_0), heat of decomposition (ΔH_d), pressure rise rate (dP/dt), and self-heating rate (dT/dt) were measured. The “piranha” solution (Caro’s acid solution), which is used to remove organic residues from semiconductor wafer substrates, has caused many accidents. In a printed circuit board manufacturing process, hydrogen peroxide mixed with sulfuric acid was used as the microetch chemical for copper surface roughening. The typical recipe is a 3:1 mixture of H_2SO_4 (96 mass-%) with H_2O_2 (20 mass-%). In this series of experiments, 30 mL of 20 mass-% H_2O_2 were mixed 10 mL of 0.1, 0.5, and 1.0 N H_2SO_4 . In another set of experiments, 2, 4, and 6 mL of 20 mass-% H_2O_2 were mixed with small amounts of 96 mass-% H_2SO_4 . When H_2O_2

solutions were acidified with small concentrations of H_2SO_4 , the reaction rate was observed to decrease to slower than that of pure, unadulterated 20 mass-% H_2O_2 . With gradually increasing concentration of acid, the rate increased to a reaction rate that was still slower than that of pure H_2O_2 , depending on the concentration of H_2SO_4 . When the H_2O_2 was mixed with concentrated H_2SO_4 , a violent reaction occurred immediately.

Hydrogen peroxide and hydrochloric acid are used in the semiconductor chip manufacture to clean silicon wafers. Inadvertent mixing has caused several accidents. Like the action of sulfuric acid, hydrochloric acid catalyzes the exothermic decomposition of H_2O_2 into oxygen and water.

Two-phase behavior in vessels, pressure relief valves, and vent piping is an important consideration in the design of chemical process equipment and associated safety relief systems. In order to investigate vapor-liquid two-phase flow behavior and proper size of venting systems, 12-N HCl was mixed with 30 mass-% H_2O_2 in different volume ratios from 1:15 to 1:2 [404].

In the 1980s, the accelerating rate calorimeter (ARC) allowed new advances in thermal hazard analysis, because it could record temperature and pressure data more accurately within the region of a self-decomposition reaction under approximately adiabatic conditions. Although ways to keep adiabatic conditions may be similar, test cell (bomb) and sensitivity are not the same in ARC as in other adiabatic calorimeters, such as Vent Sizing Package 2 (VSP2). Still, the operating procedures (heat-wait-search = H-W-S) are all the same. Vent Sizing Package 2 was used to separate catalytic and self-decomposition reactions for hydrogen peroxide in the presence of hydrochloric acid [405]. The standard operating procedure is a H-W-S cycle to find the onset temperature of a specific runaway reaction whose heat rate is equal to or greater than $0.05^\circ\text{C}/\text{min}$. The H-W-S operating method can only show the self-decomposition reaction. When HCl concentration decreases, the first catalytic reaction can be readily differentiated from the following second self-decomposition reaction. An improved operating procedure was used to find the slow first step catalytic reaction of hydrogen peroxide in the presence of hydrochloric acid. In these two reactions, the HCl concentration decreased with the activation energy of the first catalytic reaction and then increased with the activation energy of the second self-decomposition reaction. The temperature at which the catalytic and self-decomposition reactions intersect in the experiment operated by the improved method is the onset temperature of the experiment operated by the standard operating procedure. By the improved operating procedure, the duration of the first catalytic reaction increased while HCl concentration decreased.

The reactions of hydrogen peroxide in the presence of hydrochloric acid were studied by using an RSST adiabatic calorimeter [406]. The experimental data obtained from the RSST included the transient temperature profile, the transient pressure profile, the transient temperature variation profile, the transient pressure variation profile, and the heat of reaction. This violent reaction and the accumulation of heat and

non-condensable gas increase temperature and pressure in this reaction and lead to runaway reaction and overpressurization in a closed vessel. It was necessary to estimate kinetic parameters at various volumetric ratios of H_2O_2 to hydrochloric acid. Hydrogen peroxide with 30 mass-% H_2O_2 and hydrochloric acid with 37 mass-% HCl from Merck Co. were used without further purification and mixed in volumetric ratios of hydrogen peroxide to hydrochloric acid of 15:1, 7:1 or 4.33:1 for a total sample volume of 8 mL. It was concluded that the catalytic decomposition reaction of high concentration H_2O_2 by hydrochloric acid is a “non-tempered hybrid system”. The criteria of stability and runaway temperature with varying volumetric ratios of H_2O_2 to hydrochloric acid can be evaluated from their kinetic parameters and ambient temperatures. The critical ignition and quenching temperatures can be predicted based on geometric factors of the reacting vessel and heat loss to the environment.

At a pH value equal to 9, the decomposition rate of 30 mass-% H_2O_2 is highest, and this condition can lead to accidents [407].

In order to study the influence of pH on the thermal runaway reaction hazard of H_2O_2 , Vent Sizing Package 2 (VSP2) was used to analyze the thermal behavior of 27.5 mass-% H_2O_2 with different pH values of 1.8, 4, 5, 6, 7, or 8 under adiabatic conditions [408]. The time to the maximum reaction rate at 303 K (30 °C) under adiabatic conditions was obtained from the kinetics data. The results showed that as the pH value of H_2O_2 increased, the onset exothermic temperature decreased, and the time to the maximum reaction rate under adiabatic conditions got shorter and shorter, so the risk probability of thermal runaway increased significantly. When H_2O_2 is stored in the industrial conditions, there is a certain risk when the pH value is 6, and thermal runaway is almost inevitable when the pH value is more than 7.

Most of the bleaching of cellulose fibers and fiber products is done at high, alkaline pH, and the strength of hydrogen peroxide is quickly lost in the presence of metal ions. It was examined which metal ions are the most adverse and must be avoided to extend the life of the bleaching agent [409].

4.5.4 Wall Effects on Slow Decomposition in the Liquid Phase

There is a wide array of publications on the storage stability of hydrogen peroxide. It was extremely difficult to eliminate surface (wall) effects and measure the true homogeneous rate of decomposition of H_2O_2 .

Experiments at the Laporte laboratories in England, in which ground glass particles were mixed with H_2O_2 in small glass vessels in order to offer a large area of glass in contact with the H_2O_2 solution under test, indicated that the surface-to-volume ratio was without significant effect upon the observed decomposition rate. In an attempt to explore this process more completely, two sets of experiments were carried out at MIT [309]. In one, the rate of decomposition of 90% H_2O_2 was measured in the usual way with a Pyrex[®] gas evolution flask filled with different volumes of the solution. The flasks used for this purpose were round 250 mL flasks with flattened bottoms but an essentially round end with a radius near 4 cm. The surface area exposed was calcu-

lated from measurements of the height of the liquid in the flask. The volume of liquid was determined by weighing the amount of H_2O_2 of known concentration and density added to the flask. The variation of S/V ratio possible under these conditions was 0.8 to 1.5 cm^{-1} . It was found that the rate was the same when the flasks were half or totally full. Experiments with 40, 100, or 200 glass rods added to the flask and S/V ratios of 0.8 to 7 cm^{-1} at 323 K (50°C) led to the conclusion that the rate of decomposition is independent of the surface-to-volume ratio. If the procedure of adding more and more surface were carried far enough, the slope of the decomposition rate curve would decline to the horizontal, meaning that the rate of decomposition would be independent of the surface-to-volume ratio.

In another experiment, the primary objective was to study the homogeneous thermal decomposition in 100% H_2O_2 and arrive at a reasonable mechanism for the decomposition [410]. After spending a considerable effort to keep the experiments dust-free and make the quartz surfaces catalytically inactive, it was found that a homogeneous decomposition was still not achieved. Because of this result the work was not continued beyond the first stages of a kinetic study. In this study, spherical bulbs of fused quartz with a capacity of about 1 mL and weighing about 0.4 g were constructed from selected quartz tubing. The quartz vessels were cleaned and conditioned before use by the procedure recommended by Schumb. Hydrogen peroxide used in this work was purified by repeated recrystallization of concentrated 97.85% stabilizer-free material obtained from Buffalo Electric Co. The material was handled in quartz glassware under dust-free conditions. The hydrogen peroxide was purified by six crystallizations carried out in a closed system constructed in such a way that the H_2O_2 -enriched crystals always remained in the same flask. After crystallization, the material gave an analysis of 99.8% hydrogen peroxide by weight using a method of direct titration against potassium permanganate in dilute sulfuric acid solution.

A series of progress reports on early H_2O_2 characterization and the mechanism of autodecomposition work at MIT contains some of the information that was later included in a book by Schumb, Satterfield, and Wentworth [309, 376, 411–413]; see also [414].

There are some contradictions in these publications, but we have not attempted to referee the dispute. It is obvious that the rate of autodecomposition during storage of HTP is dependent on so many variables that it is difficult to make a comparison. Many early investigators failed to specify whether the HTP they tested contained a stabilizer, how much stabilizer, and which type(s) of stabilizer(s). One investigator [415] of early samples of HTP tested for storage stability reported that:

Commercial 90 and 98% hydrogen peroxide, maintained at -60°C in the solid state, decomposed at a rate of less than 1 ppm per day. As this was the order of magnitude of detection of decomposition in the equipment used it is believed that under these conditions high strength hydrogen peroxide can be considered stable and storable (less than 0.1% decomposition in 3 years).

Another series of stability tests on samples of commercial (stabilized) 90 and 98% hydrogen peroxide at 213, 243, and 273 K (−60, −30, and 0 °C) in Pyrex[®] glass showed that commercial grades of 98% and some commercial grades of 90% hydrogen peroxide available in the 1960s, maintained at 0 °C or below, can be considered stable and storable (decomposition rates below 1–0.5 ppm/d) [416]. These two quarterly reports were superseded by a more comprehensive final report [417]. That final report contains data on the low temperature 213, 243, and 273 K (−60, −30, and 0 °C) stability in Pyrex[®] glass of 90–100% hydrogen peroxide, on the effect of container surfaces on the stability of such peroxide in the 323–343 K (50–70 °C) temperature range, and on the mechanism of hydrogen peroxide decomposition. It was shown that carefully purified, or commercially stabilized, 90–100% hydrogen peroxide in Pyrex[®] glass at 213 to 273 K (−60 to 0 °C) was stable and storable, with less than 1 ppm per day (0.04% per year) decomposition. At higher temperatures, 323–343 K (50–70 °C), mildly irradiated Teflon fluorinated ethylene propylene (FEP) fluorocarbon as a container surface is exceedingly inert to high strength hydrogen peroxide, causing less than one-third of the peroxide decomposition of a passivated aluminum surface, and less than one-half of that of passivated Pyrex[®] glass. Using high purity (99.999% Al) aluminum instead of pure (99.95% Al) aluminum did not improve the quality of the passivating film of oxide formed on the surface. Studies of the sites of attack of hydrogen peroxide on aluminum surface, together with methods of following the mechanism of decomposition of hydrogen peroxide catalyzed by metal ions (both oxidizing and reducing) and radiation helped in the development of superior stabilization systems for hydrogen peroxide.

The rate of decomposition of 90 to 99% H₂O₂ at 323 K (50 °C) is proportional to the surface : volume ratio, based on experiments with Pyrex[®] vessels. The wall-catalyzed surface heterogeneous reactions are much faster than the homogeneous decomposition. Thus, the rate of decomposition in very large storage vessels is lower than in 55-gallon drums or smaller containers.

The container walls in the vapor phase that are not wetted by the liquid also contribute to the overall decomposition. The alkaline surface of common soda glass containers will catalyze the decomposition of H₂O₂. Coating the inside of a soft glass bottle with paraffin has greatly reduced the rate of decomposition of H₂O₂ solutions. Borosilicate glass like Pyrex[®] is less active than soda glass (“soft glass”) in this regard.

The question that is often raised is whether the storage stability of highly concentrated H₂O₂ is limited by dissolved contaminants or by contact with the walls of the tank material. Thus, in outer space in a zero-g state where in the absence of surface tension effects the hydrogen peroxide could float without being in contact with a wall, the storage stability might feasibly be improved. However, hydrogen peroxide has been used only in very few satellites, and no such space storage data are available. One genuine handicap in the space application of hydrogen peroxide is the need to vent the tank periodically to relieve the pressure caused by oxygen formation. It is

difficult to vent a tank in zero-g since some of the liquid may also inadvertently escape along with the gas/vapor phase.

4.5.5 Effect of Contaminants on Slow Decomposition in the Liquid Phase

The slow decomposition of H_2O_2 during storage of highly concentrated hydrogen peroxide is highly undesirable and has been investigated for many decades. It takes place even in high purity H_2O_2 and is catalyzed by traces of contaminants, suspended or dissolved, including ions of many transition metals such as Fe^{3+} , Cu^{2+} , Co^{2+} , Ni^{2+} , and metallic silver or platinum-group metals and their alloys (Section 4.10.2.1).

Table 43 gives a comparison of the effects of various metal salts dissolved in 90% H_2O_2 and heated to 373 K (100 °C). At a concentration of 0.1 mg/L, copper and chromium ion were the worst offenders.

Table 43: Effect of metal salt contaminants in 90% H_2O_2 .

Additive	Concentration, mg/L	% of original active oxygen lost during 24 h at 373 K (100 °C)
None		2
Copper	0.1	85
Copper	0.01	24
Aluminum	10	1
Iron	1.0	15
Chromium	0.1	96
Tin	10	2
Zinc	10	10

Data source: [367]

A wide range of contaminants, including 2-propanone, Fe_2O_3 , FeSO_4 , H_2SO_4 , HCl , HNO_3 , H_3PO_4 , NaOH , KOH , and LiOH was tested in a DSC for the decomposition of 10, 20, 31, and 45 mass-% H_2O_2 between 303 and 573 K (30 and 300 °C) in contact with a series of incompatible materials [418]. Most of the tests were performed with 31% H_2O_2 . The activation energy of the decomposition of unadulterated 31% H_2O_2 was $E_a = 336 \text{ kJ/mol}$.

A study of the effects of Fe^{3+} , Cr^{3+} , Ni^{2+} , and Mn^{2+} ions on the decomposition of 15% solutions of hydrogen peroxide in water showed that the ions Ni^{2+} and Mn^{2+} ions were ineffective in promoting decomposition, but Fe^{3+} and Cr^{3+} lead to significant decomposition at concentrations of 10 parts per million or greater [419].

The following tests were not really slow decomposition experiments because the 35% H_2O_2 solution was heated to 366–372 K (93–99 °C) to accelerate the process. The effect of nitric acid with and without additional iron or copper ions was determined by measuring the half-life time of 35% H_2O_2 under the test conditions [420]. The half-life time of H_2O_2 in 1.7-M HNO_3 at 366–372 K (93–99 °C) was 48000 s but decreased to 2800 s

in 4.1-M HNO_3 , 28 s in 8-M HNO_3 , and 0.3 s in 12-M HNO_3 . In the presence of 0.73 mg/L Fe^{3+} in 1.7-M HNO_3 , the half-life time of 3.4-M H_2O_2 was 36094 s but decreased steeply to 206 s at 95 mg/L and was down to 20 s at 1000 mg/L Fe^{3+} . Similarly, with Cu^{2+} ions, the half-life time of 3.4-M was 3208 s at 0.83 mg/L Cu^{2+} , 746 s at 108 mg/L, and 372 s at 1000 mg Cu^{2+} /L.

4.5.5.1 Effect of Iron Contaminants on Slow Decomposition in the Liquid Phase

The iron ion is the main contaminant that one would worry about when high purity H_2O_2 becomes inadvertently contaminated by contact with steel. In trying to improve storage stability of HTP, carefully controlled amounts of iron ion were added to HTP with and without the addition of stabilizers, and tests were performed to determine how much stabilizer is required to counteract (“neutralize”) the deleterious effect of iron ion contamination.

The catalytic decomposition of H_2O_2 by iron salts has been the subject of many investigations. The reaction has frequently been termed a ferric-ion catalyzed reaction in order to distinguish it from the reaction in which the ferrous ion is oxidized to a ferric ion by H_2O_2 without oxygen evolution; see also [421].

The catalytic effect of iron(III) perchlorate on the decomposition of H_2O_2 in aqueous solution has been studied at mol fractions of H_2O_2 up to 0.95 and at temperatures of 283, 298, and 313 K (10, 25, and 40 °C) [422]. The reaction is homogeneous, provided that the solution is kept sufficiently acidic, with a rate that was found to follow the expression

$$\frac{dX_p}{dt} = aX_p + bX_F^2$$

where X_F is the mol fraction of iron perchlorate, X_p is the mol fraction of hydrogen peroxide, and a and b are parameters dependent upon pH, temperature, and solvent composition. In concentrated solutions, both a and b are linear functions of $X_p/(1 - X_p)$. This was interpreted as arising from the replacement of molecules of water in the solvation shell of the ferric ion by molecules of peroxide to give ferric-peroxy complexes of the type $[\text{Fe}(\text{H}_2\text{O})_5(\text{H}_2\text{O}_2)]^{3+}$. The kinetics of the reaction most likely follow radical mechanisms.

The stabilizing effect of fluoride, sulfate, nitrate, phosphate, and pyrophosphate ions and sodium stannate was examined in $\text{H}_2\text{O}_2 + \text{H}_2\text{O}$ mixtures that were doped with iron(III) perchlorate as a catalyst [423]. Phosphate and pyrophosphate acted by precipitating inactive ferric salts from solution. No stabilizing effect was observed for nitrate ions. The other ions act in homogeneous solution by forming complexes with ferric ion. From the kinetic data the constants for complex formation were calculated, and it was shown that the presence of even one complex group in the coordination shell of the ferric ion was enough to make the ferric ion inactive. Sodium stannate yielded a colloidal solution, and its stabilizing effect is apparently the result of the adsorption of ferric ions on the colloidal particles. The stabilization showed a marked

time-dependence, and it seems probable that the catalytic ions become incorporated in the stannic-oxide lattice.

The fast thermal activity interpreter (FTAI) instrument was used to examine the chemical reactivity of commercially available 50% hydrogen peroxide at two different temperatures (303 and 313 K = 30 and 40 °C) both with and without contamination [424]. The results showed that at 303 K (30 °C) a small amount of rust (330 ppm) increased the reaction rate of 50% hydrogen peroxide already by a factor of 50. When the temperature was increased to 313 K (40 °C), the reaction rate was further increased by almost a factor of four. The implication for reactivity management is that at this contamination level most practical vessel sizes would require emergency venting capability. A safety evaluation was then performed to determine the emergency venting requirement for the safe transportation or storage of contaminated hydrogen peroxide. It was determined that for quantities of the material less than 33.4 L (5 gallons), conventional breather vents would be enough to accommodate the gas that evolved. However, for larger quantities, a safety relief device would be needed. For example, for a 1.5 m³ (400-gallon) tote bin at 313 K (40 °C) the required minimum vent area was estimated to be 27.7 cm² (4.3 in.²), corresponding to a minimum vent diameter of 5.8 cm (2.3 in.).

The adiabatic temperature increase of both closed and open systems and the pressure increase for closed systems were used as a measure of severity of the assessment criteria. The time to maximum rate (TMR_{ad}) may be an indicator for the probability of occurrence of a runaway reaction scenario. The results at 293 K (20 °C) showed that a small amount of Fe³⁺ (12.7 mg/L) reduced the TMR_{ad} of 30 mass-% H₂O₂ by almost a factor of 11 [425].

4.5.5.2 Effect of Non-ferrous Metal Contaminants on Slow Decomposition in the Liquid Phase

Many other metal ions other than ferrous and ferric ion are active catalysts in the decomposition of hydrogen peroxide and will accelerate the rate of gas and heat evolution and lower the temperature threshold beyond which the process becomes autocatalytic and results in a thermal runaway situation. One of the most active ions in this regard is copper. Although much of the work on the effect of contaminants on the stability of H₂O₂ reported in the literature has been carried out with intermediate concentrations (30–45% H₂O₂), the same contaminants would also wreak havoc in rocket-grade hydrogen peroxide (RGHP).

On the Metropolitan Expressway in Tokyo, a tank car exploded because it was carrying H₂O₂ in a compartment in which some copper(II) chloride (CuCl₂) accidentally remained. An experimental investigation in a reaction calorimeter of the catalytic activity of CuCl₂, in comparison to two other copper(II) compounds [nitrate: Cu(NO₃)₂ and copper sulfate: CuSO₄] and three iron(III) compounds [FeCl₃, Fe(NO₃)₃, Fe₂(SO₄)₃] revealed that during the experiments at 308 K (35 °C), 2 × 10⁻⁵ mol of copper compounds slowly reacted with H₂O₂ and generated a precipitate [426]. A 1 × 10⁻⁴ mol

solution of CuCl_2 produced a violent decomposition at 308 K (35°C). At 288 K (15°C), only a moderate heat release occurred. The iron compounds caused the H_2O_2 to decompose violently at all temperatures.

The effect of various concentrations of Cu^{2+} ion (added in the form of Cu(II)Cl_2 solutions) and initial temperature on the heating rate of 30% H_2O_2 was measured as part of an investigation into the explosion of a waste-liquid hauling truck in Japan [427]. The testing was done in a simple glass test tube with an immersed, Teflon-coated thermocouple. For Cu^{2+} concentrations at or below 0.02 mass-%, no cook-off occurred, and the heat was conducted away safely. For Cu^{2+} concentrations of 0.04, 0.05, 0.075, 0.115, 0.144, and 0.172 mass-%, a cook-off spike occurred within 100 to 5 min. When the Cu^{2+} concentration was over 0.25%, the mixture spattered immediately on adding the ion. For the intermediate concentration, 0.075 mass-% Cu^{2+} , the energy of activation in the range from 298 to 308 K (25 to 35°C) was 32.3 kJ/mol.

In continuation of these tests, other contaminants in addition to copper ion were tested [428]. In order to avoid any interfering catalytic effects, glass vessels were used, whereas VSP2, RSST, and ARC use metal vessels. Moreover, as the runaway reaction was confirmed visually, a considerable quantity of hydrogen peroxide was used, as opposed to <1 g sample sizes in DSC, VSP2, RSST, and some ARC tests. The concentration of slightly more than 30 mass-% H_2O_2 was adjusted by diluting 35 mass-% of hydrogen peroxide (Wako Chemicals Co. Ltd., stabilizer-free grade) with distilled water. Then, a calculated amount of aqueous solution containing a known contaminant was added to the H_2O_2 solution, so that the final concentration of H_2O_2 was exactly 30 mass-%, and a desired concentration of metal ion obtained. Iron, copper, or chlorine ions accelerated the runaway reaction, but nickel, potassium, sulfate, and nitrate ions had little effect. CuCl_2 accelerated the decomposition more slowly than the iron compounds. The color of the hydrogen peroxide solution changed to dark brown, and suspended particles were gradually produced when the CuCl_2 blue solution was added. After the runaway reaction ended, these particles disappeared, and the color of the solution returned to be blue. The same brown particles were also found in the case of $\text{Cu(NO}_3)_2$ and CuSO_4 .

4.5.5.3 Effect of Organic Contaminants on Slow Decomposition in the Liquid Phase

Incompatible organic contaminants can not only accelerate the decomposition of H_2O_2 in the liquid phase, but they can also result in the formation of detonable mixtures. The main concern is with organics that are introduced inadvertently from lubricants, sealants, or plasticizers in contact with HTP. On the other hand, some organic compounds, such as oxin or ethylene diamine tetraacetic acid (EDTA) are added to H_2O_2 deliberately as stabilizers.

The reaction of hydrogen peroxide with 2-propanone (acetone) leads to formation of triacetone triperoxide, a powerful explosive. Many accidents have occurred during the illicit preparation of this compound for clandestine (terrorist) purposes [418].

Differential scanning calorimetry (DSC) and Vent Sizing Package 2 (VSP2) were used to evaluate the thermal hazard of H_2O_2 mixed with 2-propanone (acetone) [429]. The results indicated that H_2O_2 is highly hazardous when mixed with 2-propanone as a potential contaminant. The time to maximum rate (TMR) was used as emergency response time in the chemical industries. Whereas TMR of H_2O_2 alone was calculated to be 70 min for runaway reaction (after T_0), the TMR of H_2O_2 /propanone mixtures was reported to be only 27 min. The critical temperature T_c of 20 mass% H_2O_2 was determined to be 389 K (116 °C).

The specific impulse of HTP as a monopropellant can be improved by dissolving alkanol fuels in the oxidizer. The storability of 90% HTP/alkanol mixtures with oxidizer: fuel ratios of 10, 30, and 50 was tested for 39 days at room temperature [430]. The active oxygen loss in methanol was much worse than that in ethanol. Some of these HTP/alcohol mixtures are detonable.

4.5.6 Effect of Container Materials on the Decomposition of Hydrogen Peroxide

The decomposition of H_2O_2 is catalyzed on the surface of many materials, including the surface of materials in which it is stored. Inevitably, this decomposition continues even in the absence of surface contact (assuming a drop of H_2O_2 is suspended in a zero-g lab in outer space), but at a slower rate.

The use of concentrated hydrogen peroxide as a rocket propellant requires a knowledge of its effect upon materials that are likely to be used as containers, gaskets, propellant lines, etc., and of its stability in the presence of such materials. The effects of such materials on the stability of concentrated hydrogen peroxide were summarized soon after concentrated hydrogen peroxide first became available [431].

In order to identify the effect of the reaction vessel material on the slow decomposition of liquid HTP, a series of experiments using several different materials at different surface: volume ratios were carried out [432, p. 179–184]. For vessels made of molybdenum glass, opaque quartz, and (to a lesser degree) Pyrex[®] glass, the surface: volume ratio was found to significantly affect the HTP decomposition rate. However, if the vessel was made from Teflon or optical grade quartz, the decomposition rate was very slow, the lowest ever observed, and it was no longer dependent on the S/V ratio. The rate of decomposition remained unchanged even if the S/V was increased by a factor of 3 to 4. It is assumed that under these conditions the decomposition of H_2O_2 is that taking place in the homogeneous liquid as opposed on the heterogeneous surface. For commercial grade HTP (94–97% H_2O_2), the thermal effect was 2.75 ± 0.13 kJ/g as determined by calorimetry. The liquid phase decomposition of H_2O_2 was found to be a first-order reaction as indicated by the straight line in Figure 11.6 on page 180 of [432]. If one plots the rate of heat evolution against the reciprocal temperature (with constant degrees of conversion), one can derive the activation energy and pre-exponential factor from the slope and intercept of the Arrhenius curve as shown in Figure 11.8 on page 181 of [432]. These data were obtained with 96% H_2O_2 in reaction

vessels made of Teflon or optical grade quartz. In this case, $E_{\text{act}} = 85.8 \text{ kJ/mol}$ and $k_0 = 4.5 \times 10^5 \text{ s}^{-1}$.

In Russia, where hydrogen peroxide continues to be used for a variety of rocket propulsion applications, it has become common practice to characterize different samples of HTP by a so-called *thermal stability index* (TSI). The TSI is defined as the amount of oxygen in cm^3 at standard temperature and pressure (STP) evolved from a sample of 50 mL HTP heated in a glass flask at 369 K (96°C) for 1 h. It was attempted to establish a correlation between the TSI and the kinetic constants of homogeneous HTP decomposition. The TSI did not influence the effective activation energy. In contrast, the pre-exponential factor in the expression for the rate constant increased linearly with the TSI. That indicates that the TSI is due to the homogeneous decomposition. Data obtained for various HTP samples with different initial TSI values can be plotted in Arrhenius coordinates as one straight line with a normalized TSI. Data obtained with two different methods, volumetric and calorimetric methods, fall on the same line as shown in Figure 11.11 on page 182 of [432]. The kinetic rate equation derived from these data is

$$k = 4.8 \times 10^5 \exp\left(-\frac{20800}{RT}\right)$$

where k is the rate constant in s^{-1} , and T is the temperature in kelvin. These experiments were then repeated for HTP in contact with various metals of construction. The highest rates of decomposition were observed for HTP in contact with niobium (=columbium) and nickel, and the lowest rates were observed on aluminum. The kinetic rates were then used to calculate the temperature at which the decomposition becomes self-accelerating under adiabatic conditions and results in a run-away reaction, which quickly leads to rupture of any container. The threshold temperature can be calculated using the Semenov theory equations.

4.6 Results of Long-Term Ground Storage Tests with HTP H_2O_2

There are numerous storage stability tests described in the literature, but it is difficult to bring them to a common denominator. The main reasons for differing results and results not reproducible at other organizations are the different passivation methods used for storage containers prior to filling them with HTP, and errors that may have slipped in during sampling and analysis. Alone the act of taking a grab sample from a storage test in progress is already apt to unwittingly introduce contaminants and alter the results. The volume:surface ratio and the climate of the environment where the hydrogen peroxide drums or spherical tanks are stored has a major effect on the rate of decomposition. For space applications, extrapolation from ground storage tests to in-space predicted useful life span has not been very accurate. In-orbit

reaction control systems using hydrogen peroxide have demonstrated space storability in excess of 2 years (with an estimated predicted storability of 5 years). Long-term in-space storability depends on a reliable method for venting excess gas pressure without spilling any liquid that would still be needed for the rest of the mission. Surface tension passive propellant management devices would allow liquid/gas phase separation in a zero-g environment, but they would add a lot of surface area and speed up decomposition of H_2O_2 . Spinning satellites or pre-venting propellant settling by use of a cold gas thruster system would be the only good phase separation method but takes a lot of extra weight.

Hydrogen peroxide ground storage tests were conducted during the 1950s and 1960s by most of the HTP manufacturers in the US to demonstrate the reliability and marketability of their product.

Four grades of Becco H_2O_2 were evaluated for storage in sealed storage containers: commercial 90% by weight H_2O_2 , propulsion-grade 90% by weight H_2O_2 , commercial 98% by weight H_2O_2 , and propulsion grade 98% by weight H_2O_2 , in 1-gallon capacity TFE Teflon bladders contained in mild steel test tanks at 293–294 K (70–72 °F) for 5 months, 322 K (120 °F) for 7 days, and 347 K (165 °F) for 72 h [433]. The bladders were not as compatible as desired due to the bleaching and crack development experienced with this dispersion-type Teflon. Tests showed that the oxygen loss from the H_2O_2 during storage can be decreased by improved passivation techniques, surface pretreatment techniques, and improved stabilizers. The most promising test results were obtained with the 98% propulsion-grade HTP containing phosphate stabilizer.

In parallel, storage tests were conducted by US Government agencies such as National Aeronautics and Space Administration (NASA), former National Advisory Committee for Aeronautics (NACA), Jet Propulsion Laboratory (JPL) and Air Force Research Laboratory (AFRL) to verify the storability claims advertised by the propellant suppliers. In between, propulsion system manufacturers ran their own storage and materials compatibility tests. It is impossible to summarize all that information and, in many cases, it is not worth being summarized and preserved for posterity.

The Shell Development Co., Emeryville, CA, a division of the HTP manufacturer Shell Chemical, conducted storage tests with HTP of different pedigree and attempted to purify HTP by passing it through an ion exchange resin. Samples of HTP that had been further purified by ion exchange, distillation, or recrystallization were placed in storage at 25 °C along with stabilized samples prepared under a previous contract [434–436]. Samples were stored in Aclar[®]-lined (a fluoropolymer film) vessels and tin-plated aluminum or steel vessels in addition to Pyrex[®] vessels for comparison of the relative activities of these surfaces toward decomposition of HTP. Two vessels of type 1260 aluminum previously in use with HP in storage were heat-treated with HTP in order to reduce their surface activity and were then refilled with HTP and returned to storage for several more years. Samples thus purified by ion exchange immediately prior to filling the 5-gallon storage containers were stored for over 1 year at 298 K and suffered active oxygen losses of less than 0.1%/year [166]. Pressure buildup during

extended storage of HTP in closed vessels (sealed storage with no pressure relief valve) is a major concern, and a hurdle that has not yet been mastered.

Outdoor covered storage of FMC propulsion grade 98 mass-% HTP at Aerojet Missile and Space Propulsion in 30-gallon as-received aluminum shipping containers (2.5 year storage time) resulted in an apparent decay of 1 to 1.5% concentration per year, measured by a comparison of three different assay methods, as shown in Figure 45. At the 2.5-year point, assay results ranged from 95.3 to 96.2 mass-%, down from the original as-received value of 98.9 mass-% HTP [437].

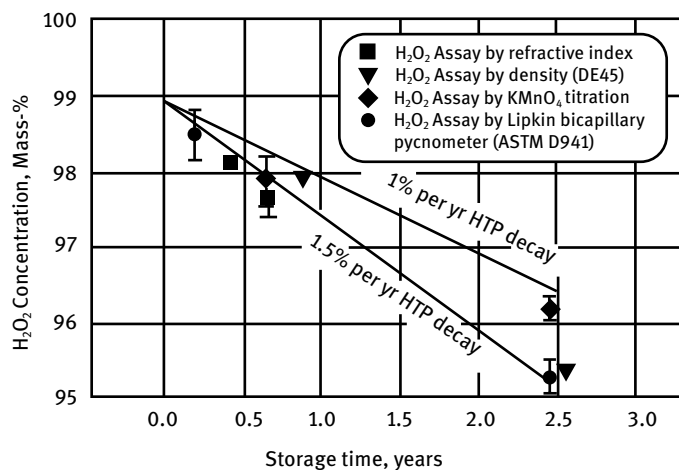


Figure 45: Decay of assay of 98 mass-% HTP as a function of storage time. (Reproduced and modified from [437].)

It has been reported [438] that in a single drum of 90% propellant-grade hydrogen peroxide which had been in storage at FMC for over 17 years, the concentration of this drum started at 90 to 91% and after 17 years was measured at approximately 84%, which is just less than 0.4% drop in concentration per year. This drum had been stored outdoors in the ambient conditions of Texas. In addition, a second set of drums containing 90% hydrogen peroxide had been in storage at 278 K (5 °C) for over 17 years and have been measured at 90.5%. This demonstrates that at 278 K (5 °C) essentially no measurable decomposition occurred over 17 years. Some of these tests may have to be repeated under carefully controlled conditions, also stating the amount of stabilizer used.

During the 1998–2001 time frame, NASA Stennis Space Center (NASA SSC) stored H₂O₂ in 55 and 30-gallon drums near the E-3 test facility. In April 2001, four drums of 98% concentration peroxide were discovered to be expelling their contents from vent holes and around the top clamping ring [439, 440]. Out of an abundance of caution, the contents of the drums were safely pumped into a disposal area and disposed of.

Seven additional drums were similarly disposed of when they were found to be suspiciously warm. The vendor-supplied drums were stainless steel with a polyethylene lining. These drums failed to meet long-term storage requirements. NASA Stennis Space Center discontinued use of polyethylene lined stainless steel drums for long-term storage. From then on, vendor container designs were reviewed, inspected, and approved by NASA SSC personnel prior to acceptance.

4.7 Experimental Methods to Determine H_2O_2 Decomposition Rates

The stability of hydrogen peroxide is normally defined by two parameters: AOL and a term called the *stability*. The AOL parameter is defined as a value based upon a test at a specific temperature and duration for a set of propellant properties (concentration, purity, and stabilizer content) and a specific material of construction with or without surface passivation. A common test is an elevated temperature test at 339 K (66 °C) for 1 week. This is a type of an accelerated exposure test.

The homogeneous decomposition rate of hydrogen peroxide can be measured in the temperature range 318–532 K using any of or a combination of the following techniques:

- gravimetry
- manometry ($T = 350\text{--}430\text{ K}$, $p = 0.1\text{--}5\text{ MPa}$)
- volumetry ($T = 318\text{--}350\text{ K}$, atmospheric pressure) using a *microdroplet device* (Method I) or an *automated volumetric device* (AVD) (Method II)
- microcalorimetry

As part of a program to determine the hazards of 4000-gallon tanks with 70% H_2O_2 in an external fire, three different methods for measuring short-term H_2O_2 decomposition rates were evaluated [396]: measurement of (1) the volume of oxygen evolved, (2) the weight loss, or (3) the change in peroxide concentration. The first proved to be the most satisfactory method. The very small weight changes observed made the second method marginal. The third method was unsatisfactory due in part to the small concentration changes experienced. Furthermore, an analytical precision of not less than 0.01% was required, and this was not obtainable. Both the second and third methods are more appropriate for long-term tests, or tests where large changes in concentration occur. The weight of the reaction tube was measured on an oversized analytical balance accurate to about 0.5 mg. Weight losses were usually under 100 mg, and rates calculated therefrom had an accuracy of only 5 to 10%. The peroxide concentration was determined by titration of a small sample or aliquot with standard 0.2N ceric ammonium sulfate. The precision of the analysis was 0.2% or better. However, this equated to a precision of only about $\pm 50\%$ in the calculated decomposition rate. Thus, the titration method is unsuitable with small changes in concentration of peroxide.

4.7.1 Gravimetric Methods

The simplest, but not the most accurate method for determining the storage stability of HTP in contact with candidate materials of construction is to weigh the flask, HTP, and sample coupon together before and after keeping it in a thermostatted bath for a known length of time and allowing the evolved oxygen to vent, causing a weight loss. Based on the results of such a test, the materials can then be classified as suitable for long-term exposure or suitable only for short-term exposure, such as in a transfer hose that gets rinsed out after each use.

A common AOL test method for testing for classification used a sample coupon 3 in. $\times$ 0.5 in. $\times$ 0.0625 in., which would be cleaned, treated, and processed as closely as possible to the actual material being used [438]. This coupon sample size has a surface to volume ratio of approximately 0.33 in.⁻¹ when tested in 75 mL of hydrogen peroxide, simulating the surface to volume ratio of a typical hydrogen peroxide drum. The sample is placed in a clean and passivated 100-mL glass flask and weighed to an accuracy of ± 0.01 g. Hydrogen peroxide of a known initial concentration C_1 is added to the flask, and the flask is weighed again to obtain M_1 . The flask neck is covered with a 10-mL beaker. The flask is placed in a constant temperature bath for specific test temperature and duration, such as 339 K (66 °C) for 1 week. At the end of the test, the flask is removed and cooled. The 10-mL beaker is removed, the flask and contents are weighed again, and the final concentration C_2 of the hydrogen peroxide is determined. The final hydrogen peroxide mass M_2 is obtained from the difference between the final mass of the flask, fluid, and sample from the initial dry mass of the flask and sample. The AOL is calculated as:

$$\text{AOL} = 100\% \times \frac{M_1 C_1 - M_2 C_2}{M_2 C_2}$$

After the AOL test, a sample of the final hydrogen peroxide is typically subjected to a stability test to see whether any leached contaminants have altered its stability in the absence of the coupon. A cleaned and passivated 50-mL volumetric flask is filled to 50 mL with hydrogen peroxide from the AOL test. The flask is weighed to ± 0.01 g, giving the initial mass M_1 . The flask is covered with a 10-mL beaker and immersed in a constant temperature bath at 373 K (100 °C) for 24 h. After 24 h, the flask is removed and allowed to cool. The 10-mL beaker is removed and the flask is reweighed to determine the final mass. The stability is defined as:

$$\text{Stability} = 100\% \times \frac{(50 \times \rho \times C \times 0.47) - (W_1 - W_2)}{50 \times \rho \times 0.47}$$

where ρ is the density of the hydrogen peroxide, and C is the concentration of the hydrogen peroxide at the beginning of the test. Both these methods are inaccurate because not only oxygen but also HTP vapor and water vapor will escape during the test and cause mass loss.

4.7.2 Manometric Methods

The pressure as a function of time can be measured by standard manometers installed on thermostatted closed containers containing hydrogen peroxide (Method III).

4.7.3 Volumetric Methods

If there is any doubt about the storage and thermal stability of HTP for a specific application, one can conduct an accelerated aging test at elevated temperature and measure the amount of oxygen formed. One method heats the sample to 373 K (100 °C) for 1 h and measures the amount of oxygen formed gasometrically.

This method can also be used to compare the efficiency of different stabilizers. Working with 90–99% H_2O_2 solutions, it was noticed that as one approaches 98% H_2O_2 , the effectiveness of stabilizers is diminished or even reversed [307]. It appears that above 98%, the heterogeneous reactions with walls and the autodecomposition of hydrogen peroxide prevail. A comparison of the accelerated manometric method with long-term standing tests in 20–50-L containers at 298 K and periodic H_2O_2 concentration analysis of grab samples showed that over a 150-fold range of decomposition rates, the correlation between the two methods was linear and was usually within a factor of 2. This was taken as a validation of the accelerated volumetric method.

An AVD consists of an automated gas burette with a compensation vessel that moves up and down via a reversible motor [432, there p. 175–176]. A U-tube gauge responding to the pressure change in the sealed system in which decomposition of the liquid takes place is used as a sensor. As gas collects in the system, the compensation vessel moves down and drags a recorder ink pen over a moving paper strip driven by a synchronous motor. When the burette is completely filled with gas (in the lowest position of the compensation vessel), an electric contact triggers the lifting of the compensation vessel by the reversible motor, while gas is released to ambient air through a check valve. At the uppermost position of the compensation vessel another electric contact stops the reversible motor. The curve registered on the paper is, thus, a series of zigzag lines from which the rate of gas evolution can be calculated.

Another device is the *microdroplet device*, which is based on displacement of an inert liquid from a small reservoir (sitting inside a large round-bottom flask) with an inserted capillary dip tube by gas evolved from a propellant sample in a closed 1-L flask kept at constant pressure and temperature. The small reservoir and the main flask share the vapor space. The change in the volume of the displaced liquid is identical to the volume of the evolved gas and is recorded as a function of time. The liquid displaced from the vessel connected to the reaction flask drops from a capillary into a collector dish sitting on a recording digital scale. The amount of gas evolved is determined by periodically weighing the collector dish (the density of the liquid is known, and it must be assumed that none of the evolved gas dissolves in the liquid and that the liquid density remains constant). In addition, one can count the number of droplets by placing the droplet path into the path of light from a light source to a photocell and

separately measure the mass of 10 or 100 droplets. High sensitivity was achieved by using perfluorinated liquids characterized by a low surface tension and forming very small droplets of a constant volume ($V = 10^{-3} \text{ cm}^3$) but ignoring evaporation losses from the perfluorinated liquid.

A method for volumetrically measuring oxygen evolution as a means to monitor peroxide stability in stationary storage tanks instead of immersing a thermocouple avoids any penetrations of the tank wall to insert temperature probes [441, 442]. Measuring liquid peroxide temperature to monitor peroxide stability has significant limitations. The bulk decomposition of 0.75%/week (dump limit) from 276 lb_m of 90% HTP in a large volume tank at 25 °C produces 30 mL of gas. This flow rate corresponds to an equivalent temperature rise of approximately 14 millidegrees C, which is difficult to measure reliably. Thus, if heat transfer were included, there would be no measurable temperature rise. Temperature changes from the surrounding environment and heat lost to the peroxide will also mask potential problems. The use of oxygen flow measurements provides a more sensitive technique for monitoring stationary tank contents and will provide an earlier indication of an abnormal decomposition when compared to relying on temperature rise measurements.

For measuring the rate of decomposition of commercial 70% H₂O₂ exposed to a bonfire, a Pyrex[®] reaction vessel supported in an insulated thermostatted water bath was connected through capillary tubing to a water-jacketed gas burette with a leveling bulb [396]. The reaction vessels were heavy wall Pyrex[®] tubes 9 in. long by 1 in. diameter. An integral upper tube 8 in. long by 0.4-in. outer diameter (OD) extending above the bath, permitted any escaping water vapor to condense and flow back. The volume of these tubes was 57 mL. The reaction tubes were cleaned by standing filled with concentrated nitric acid for 24 h or more, followed by thorough rinsing with distilled water. They were then preconditioned by standing with 70% hydrogen peroxide.

4.7.4 Calorimetric Methods

Calorimetric methods are suitable for the automatic measurement of the decomposition rates of hydrogen peroxide at ambient temperature [443], but it was not until the sensitivity of calorimeters was improved by several orders of magnitude that such methods actually found practical applications. An ultrasensitive heat measurement technique, isothermal microcalorimetry, was used at the NASA White Sands Test Facility to monitor the decomposition of hydrogen peroxide at near ambient temperatures [444, 445]. Isothermal microcalorimetry measures the heat flow from a reaction vessel into a surrounding heat sink. The microcalorimeter instrument was able to detect heat releases as small as 5 μW. Microcalorimetry is approximately 1000 times more sensitive than accelerating rate calorimetry or differential scanning calorimetry for measuring thermal events. The decomposition rates of hydrogen peroxide at the picomols⁻¹ g⁻¹ level have been measured showing the effects of stabilizers and peroxide concentration. Typical measurements were carried out in 12-mL samples with and without ma-

terial test coupons at 40 °C over a 24-h period. Three different hydrogen peroxide solutions were used in these studies: commercial samples of nominally 70 and 85% solutions provided by Solvay Interlox, Inc. or a 90% solution supplied by FMC Corp. Analysis by permanganate titration showed the solutions to contain 69.5, 82.6, or 89.5% H_2O_2 , respectively. Analysis by inductively coupled plasma-mass spectroscopy indicated a tin content of 1.9 mg/kg and 1.6 mg/kg, respectively for the Solvay materials. FMC 90% propellant-grade H_2O_2 contains 1 to 2.9 ppm tin. Phosphate and sulfate were present at less than 1 mg/kg in all samples as shown by ion chromatography. Portions of the Solvay samples were purified by vacuum distillation (<55 °C at approximately 1 mm Hg) in an all-glass/polytetrafluoroethylene (PTFE) rotary evaporator. The distillation raised the assays to 79.8 and 86.5% H_2O_2 . The distilled solutions showed less than 5 ppb tin (but tin is not volatile, how was it carried over?). The phosphate, sulfate, and nitrate concentrations, however, were only slightly lowered to less than 0.5 ppm. The purified materials were then stored in polyethylene containers. The bulk decomposition rate of 90% H_2O_2 at 298 K in the absence of incompatible storage tank materials was $21.8 \text{ picomols s}^{-1} \text{ g}^{-1}$. The bulk decomposition rate of 82.6% H_2O_2 at 298 K in the absence of incompatible storage tank materials was $5.9 \text{ picomols s}^{-1} \text{ g}^{-1}$. Materials tested in contact with various HTP concentrations were Haynes 214, Inco 600, Al-5254, Al-6061, CRES-304, tantalum, Tefzel, Kynar, FEP, and PTFE. PTFE was the most compatible material, and CRES 304 was the least compatible material. The decomposition rate data can be used to predict the pressure in a H_2O_2 -filled tank stored for a certain time at a constant temperature.

In continuation of these studies, Al-5254, a tank material, and CRES-316, a component (valve) material were tested in 90% HTP [446, 447]. The total volume of the samples in the microcalorimeter was approximately 20 mL. The background decomposition rate of HP in a passivated container was determined in triplicate at temperatures between 298 and 333 K (25 and 60 °C). These background heat rates were due to the decomposition of the HP on the surface of the glass container and bulk homogeneous decomposition. This background rate was normalized to the mass of peroxide. The average heat of decomposition rate per gram and the corresponding molar decomposition rate range from $21 \text{ picomols s}^{-1} \text{ g}^{-1}$ at 298 K (25 °C) to $300 \text{ picomols s}^{-1} \text{ g}^{-1}$ at 333 K (60 °C). Data for Al-5254, passivated CRES-316 and electropolished CRES-316 were measured at 298, 313, and 333 K (25, 40, and 60 °C) and the decomposition rates plotted versus $1/T$ on a semilogarithmic plot to obtain the activation energies from an Arrhenius plot. The results showed that Al-5254 was the best material, and passivated CRES-316 was the worst material, with electropolished CRES-316 being in between.

4.7.5 Optical Methods

An optical bubble detection technique was used to determine the stability margin of propellant-grade hydrogen peroxide (HTP) in run tanks by accelerating and visually

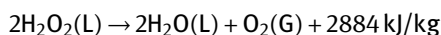
observing the decomposition of a small H_2O_2 sample in contact with a metal coupon, thus simulating the propellant/tank interface [448]. Small samples of 90% HTP were periodically withdrawn from a run tank over a 400-h period and introduced into a Petri dish containing a steel coupon similar to the tank material, but at elevated temperature. During the decomposition oxygen was given off, and bubbles were formed over the coupon surface. Measurements were then made with respect to bubble formation, size, and density over the metal coupon, and a suitable imaging technique was used to extract bubble density data from the video. The data were then compared to the observed stability in the run tank as measured by pressure rise. The data were used to derive a mass diffusion-controlled oxygen bubble growth model for hydrogen peroxide/metal interfaces.

4.7.6 Other Methods

A measurement of NMR transverse relaxation time T_2 and pH of aqueous H_2O_2 solutions allows a non-invasive *in-situ* quantitative determination of the H_2O_2 concentration [298, 449]. This method was applied to measure the time profile of the heterogeneously catalyzed H_2O_2 decomposition on catalyst pellets by monitoring the reactant concentration in the vicinity of the pellet or in a closed volume. This is a new method for contact-free and non-invasive on-line monitoring of H_2O_2 concentrations.

4.7.7 Kinetics of the Liquid-Phase Thermal Decomposition of Hydrogen Peroxide

The decomposition of hydrogen peroxide follows the overall global reaction



The theoretical adiabatic decomposition temperature for 100% H_2O_2 at 6.89 MPa (1000 psia) is 1275 K (1002°C).

4.7.7.1 Surface Effects on Liquid-Phase Thermal Decomposition of Hydrogen Peroxide

The surfaces of glass, quartz, and to a lesser degree, of Pyrex[®] glass, affect the rate of the thermal decomposition of liquid H_2O_2 [450]. The temperature dependence of the rate constant of the thermal decomposition of H_2O_2 is

$$k = 5 \times 10^5 \exp(-20800/RT) \text{ s}^{-1}$$

The rate of H_2O_2 decomposition increased with an increasing concentration of Fe^{3+} in the system, while the energy of activation of the decomposition was practically independent of the Fe^{3+} concentration. The H_2O_2 used in these studies was 96–97% obtained by vacuum distillation. It is assumed that it did not contain any stabilizers. The reaction vessel was optical quartz or Teflon. The temperature differential between the reaction vessel and a constant temperature bath was measured with thermocouples. The rising gas bubbles would stir the reacting mixture, there was no mechanical

stirrer. The kinetic constants were calculated from the differential thermograms. Initial experiments in molybdenum glass, opaque quartz, and Pyrex® showed a lot of scatter in the data. In optical quartz or Teflon, there was only a weak effect of the surface: volume ratio. Varying the surface: volume ratio by a factor of 3 to 4 did not affect the rate or activation energy data. Because iron ions are considered one of the main culprits in limiting the storage stability of HTP and iron can easily be leached from process equipment or storage tanks, the effect of iron ion addition on thermal stability of HTP was examined. The experimental conditions are summarized in Table 44.

Table 44: Effect of added iron³⁺ ion concentration in hydrogen peroxide decomposition experiments.

Sample No.	Fe ³⁺ concentration	Temperature range		Activation energy		Rate constant
	mass-%	K	°C	kJ/mol	kcal/mol	s ⁻¹
0	Original liquid	323–453	50–180	87.0	20.8	3.1×10^{-9}
1	10^{-5}	327–363	54–90	87.4	20.9	4.6×10^{-9}
2	5×10^{-5}	320–363	47–90	91.6	21.9	2.6×10^{-8}
3	1.3×10^{-4}	317–348	44–75	87.4	20.9	3.0×10^{-7}
4	5×10^{-4}	313.9–348.6	40.8–75.5	83.7	20.0	8.9×10^{-7}
5	1.5×10^{-3}	303–325.6	30–52.5	81.6	19.5	8.0×10^{-6}

Data source: [450]

The data from Table 44 are illustrated in Figure 46 and 47. The numbers on the lines in Figure 46 refer to the sample numbers in Table 44. As one can see, the slope of the Arrhenius curves remains pretty well the same. In a double-log plot in Figure 47, the log of the kinetic rate at 323 K increased linearly with the log of the iron ion concentration. If the catalytic action in the original HTP was due exclusively to Fe³⁺ contamination, its concentration would have been below 1.2×10^{-5} mass-%.

The rate of decomposition of stabilized 30 mass-% H₂O₂ on various materials was studied in 2-N NaOH and 1.95-N H₂SO₄ solutions at temperatures between 295 and 343 K (22 and 70 °C) [451]. These were not catalyst materials, but materials related to electrochemical synthesis of peroxides. A sample size of 0.5 g of the materials in powder form (<75 μm) was dispersed in 50 mL of 30% H₂O₂ in a flask in a thermostat, and the rate of gas evolution was measured volumetrically and entered into Arrhenius plots. The activation energies are summarized in Table 45.

If the pre-exponential factor was plotted against the activation energy, a linear relationship was observed. The rate of decomposition in 1.95-N H₂SO₄ solutions was an order of magnitude slower than in 2-N NaOH. The activation energies for reactions catalyzed by powders were significantly higher than those for solid body catalysts; see also [452].

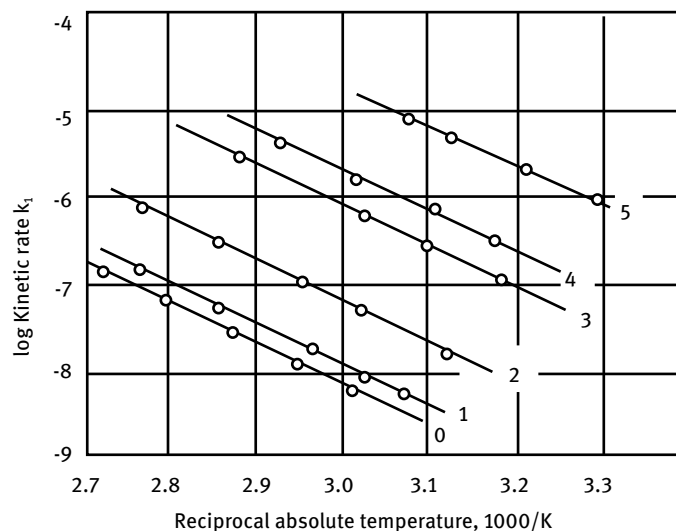


Figure 46: Arrhenius plot of kinetic rate of hydrogen peroxide decomposition for different iron ion concentrations. (Republished and modified from [450], with permission of © 1971 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

Legend: The numbers refer to the samples listed in the first column of the table above.

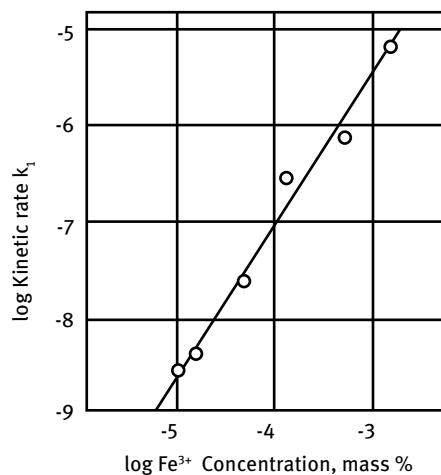


Figure 47: Kinetic rate of hydrogen peroxide decomposition as a function of iron ion concentration at 323 K. (Republished and modified from [450], with permission of © 1971 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

Table 45: Activation energies of H_2O_2 decomposition.

Material	Activation energy	
	kJ/mol	kcal/mol
TiC	112	26.65
Ti	110	26.2
Cr_3C_2	96	22.96
TiN	85	20.34
Activated carbon	36	8.656
For comparison (compact metals, not powders):		
Cd	40	9.5
Sn	37	8.8
Sb	34	8.2

Data source: [451]

4.8 Catastrophic Thermal Decomposition of Hydrogen Peroxide

Hydrogen peroxide is a very versatile reagent for many industrial processes, but it is very sensitive to impurities that can catalyze its decomposition violently and cause damage to equipment and personnel.

In investigating an accident, the adiabatic stability of 30% hydrogen peroxide was tested by an accelerating rate calorimeter (ARC) [453]. The measured data were modified by considering of thermal inertia factor of ARC. The results showed that the initial exothermic temperature for 30% hydrogen peroxide is 307.6 K (34.5 °C), with the maximum temperature being 519 K (246 °C), and the time to maximum self-heating rate was 100 min; see also [454–456].

In a critical review of several hydrogen peroxide explosion accidents, investigators sought to establish an evaluation model for its safe storage and transportation [425, 457, 458]. The runaway scenario that can serve as a basis for the assessment of the thermal risk is based on an adiabatic temperature increase and pressure rise of closed or insufficiently vented systems. Both closed and open systems were discussed. The time to adiabatic maximum rate (TMR_{ad}) was presented as the probability of occurrence of the scenario. Two examples both with and without contamination showed that at 293 K (20 °C) the severity of 30% H_2O_2 decomposition is critical, and a small amount of Fe^{3+} (12.7 mg/L) reduced the TMR_{ad} of 30% H_2O_2 by almost a factor of 11.

4.8.1 Chemiluminescence During Liquid-Phase Thermal Decomposition of Hydrogen Peroxide

Decomposition of hydrogen peroxide in water is accompanied by an ultraweak luminescence [459]. The quantum yield was approximately one photon per 10^{14} to 10^{16} transformation acts of hydrogen peroxide. The kinetics of luminescence and its depen-

dence on the reaction of hydrogen peroxide decomposition were investigated, and an attempt was made to identify the elemental reaction responsible for the most intense luminescence (even in the absence of luminol or other organics).

4.9 Stabilizers for Hydrogen Peroxide

We list stabilizers here mainly because they may interfere with some of the intended applications of stabilized HTP in rocket engines, predominantly monopropellant rocket engines. Many stabilizers will clog (“foul”) the catalyst bed or poison the catalyst (*Encyclopedia of Monopropellants*, chapter “Hydrogen Peroxide”). We have yet to find a stabilizer that will effectively stabilize the HTP to the same level of long-term storage stability as hydrazine and still not interfere with catalyst operation in a monopropellant engine. There are several types of stabilizers for liquid hydrogen peroxide and its aqueous solutions. One group of stabilizers seems to owe its activity to the complex-forming ability, which serves to sequester heavy metal ions from the solution; in this group, the pyrophosphates, fluorides, cyanides, and various organic substances such as 8-hydroxyquinoline and acetanilide may be mentioned. Another group of stabilizers are suspended colloidal solids, which owe their activity to adsorption powers. Substances such as freshly precipitated alumina and silica, hydrous antimony oxide, and hydrous tin(IV) oxide are effective to varying degrees in increasing the stability of hydrogen peroxide solutions. The degree of stabilization depends upon the nature of the catalyst, pH of the solution, temperature, and the main contaminant(s) present. Thus, the decomposing action of copper ion under certain circumstances is inhibited by tin(IV) oxide and less by pyrophosphate, while the opposite is true for chromium ions. Often, commercial hydrogen peroxide contains more than one type of stabilizer.

Stability is achieved by not just adding a single component but rather a “cocktail” of different chemicals that supplement each other. The primary hydrogen peroxide stabilizer is tin(IV) hydroxide supplied as stannate that forms colloidal stannic acid (hydrated stannic oxide, aq. SnO_2) particles. Normally the tin is added as an alkali metal stannate, such as sodium stannate trihydrate or potassium stannate trihydrate. Unfortunately, positively charged ions, such as calcium, magnesium, and aluminum tend to coagulate the sol and, consequently, remove the tin by settling or filtration. Negatively charged ions such as pyrophosphates and phosphates can be used as peptizing agents to improve the stability of colloidal stannic oxide. Numerous organic phosphonic acids may also be used as stabilizers. Those stabilizers act by chelating metal ions that catalyze or enhance the peroxide decomposition. However, some of these stabilizers undergo chemical changes in peroxide solutions that make them poor chelators for metals, and hence the stabilizing effect is dissipated with time. The phosphonic acids may include those with a nitrogen atom which is capable of being oxidized to an *N*-oxide, such as amino tris(methylenephosphonic acid) (ATMP) and

ethylenediaminetetra(methylenephosphonic acid) (EDTMP), or those not capable of being oxidized, for example 1-hydroxyethyl-1,1-diphosphonic acid (HEDP). In addition to these stabilizers, corrosion inhibitors to prevent hydrogen peroxide attack on metals during extended storage periods in metal tanks complete the recipe. Both nitrates and pyrophosphates play an important role in this respect. Acids are added as buffering agents and to adjust the pH value of the final product.

The catalytic action of dissolved homogeneous catalytic contaminants can be inhibited by the addition of complex-forming stabilizers, such as phosphoric acid, sodium dihydrogen phosphate, 8-oxyquinoline or barbituric acid. Phosphonic or aminophosphonic acids may also be used. Pyrophosphate is a peptizing agent that improves the stability of colloidal stannic oxide and also acts as a corrosion inhibitor [460].

A long list of stabilizers ($\text{Na}_4\text{P}_2\text{O}_7$, Na_3PO_4 , NaH_2PO_4 , H_3PO_4 (85%), H_2SO_4 , HNO_3 , NH_4NO_3 , NaNO_3 , KF , NH_4F , NH_4HF_2 , $\text{Al}(\text{OH})_3$, Al_2O_3 , MgO , SnO_2 , SnO , hexamethylenetetramine), added at concentrations of 100 ppm to 89.4–92% HTP in contact with 99.7% chemically pure soft aluminum coupons or stainless steel coupons was tested for up to 41 days at room temperature [365]. Acidic compounds, except for H_3PO_4 , caused accelerated HTP decomposition. The best results were obtained with sodium dihydrogenphosphate NaH_2PO_4 . Fluorides caused etching and weight loss of both the stainless steel and aluminum coupons. The best performing stabilizers were then tested at 323 K (50 °C) for up to 14 days at two different concentrations. Additions of 100 and 200 ppm of $\text{Na}_4\text{P}_2\text{O}_7$, sodium orthophosphate Na_3PO_4 , sodium dihydrogen phosphate NaH_2PO_4 , phosphoric acid H_3PO_4 , magnesium oxide MgO , or hexamethylenetetramine were evaluated as stabilizers for 89.3% HTP in contact with coupons of CRES-304 or Al52ST in glass flasks during storage at 323 K (50 °C) for up to 14 days, and HTP samples were taken after 1, 7, and 14 days and analyzed for peroxide assay. The best results were obtained with sodium dihydrogen phosphate NaH_2PO_4 in contact with stainless steel and with sodium orthophosphate Na_3PO_4 , in contact with aluminum. Hexamethylenetetramine caused rapid decay of HTP. The higher stabilizer concentration (200 ppm instead of 100 ppm) did not always improve storability and sometimes had the opposite effect. In two separate tests without contact with metal coupons, 89.8% HTP was heated with 100, 500, 1000, 5000, or 10000 ppm sodium orthophosphate Na_3PO_4 to 323 or 373 K (50 or 100 °C) for up to 14 days. The samples with 500 and 1000 ppm phosphate had totally decomposed after only 3 days at 373 K. The samples with 5000 ppm phosphate had totally decomposed after only 7 days at 323 K. The H_2O_2 content of the sample with 100 ppm Na_3PO_4 had dropped to 89.1% H_2O_2 after 14 days at 323 K and to 60.8% H_2O_2 after 14 days at 373 K.

Stabilizers can be dissolved or suspended in the liquid or attached to the walls of the container. Stabilizers cannot change the rate of the slow thermal decomposition of hydrogen peroxide, they can only minimize the adverse effects of contaminants acting as catalysts. The decomposition of H_2O_2 cannot be retarded by increasing the storage pressure either. HTP produced nowadays already has such a high grade of purity that

the addition of stabilizers appears unnecessary. In those cases, stabilizers are added mostly as a precaution against accidental introduction of contaminants at the user's site and after the material has left the manufacturing facility.

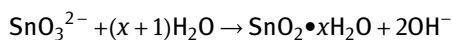
There are hundreds of patents with various stabilizer recipes, we list here only a few typical ones. As we explained before, some stabilizers may be tolerated by HTP decomposition catalysts, while others are active catalyst poisons.

A hydrogen peroxide solution having a pH of less than 4.5 was stabilized with about 0.02 to 0.1 g/L of 8-hydroxyquinoline, about 0.2 to 0.6 g/L of a compound selected from the group consisting of tetrasodium pyrophosphate and tetrapotassium pyrophosphate, and about 0.1 to 0.4 g/L of a compound selected from the group consisting of sodium stannate and potassium stannate and phosphoric acid sufficient to furnish the equivalent of about 0.1 to 0.2 g/L of anhydrous phosphoric acid [461].

It was found that the decomposition of HTP in contact with aluminum containing small amounts of heavy metals can be retarded by dissolving 3 mg/L aluminum ion in the form of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 35% H_2O_2 [462]. An aluminum 5652 coupon immersed in 35% H_2O_2 for 3 months caused the H_2O_2 to become contaminated with 10 mg/L of leached aluminum, but the aluminum content of the $\text{Al}(\text{NO}_3)_3$ -treated H_2O_2 remained unchanged. The active oxygen loss of the $\text{Al}(\text{NO}_3)_3$ -treated H_2O_2 was half of that of the untreated H_2O_2 .

4.9.1 Sodium Stannate as Stabilizer

Sodium stannate, 8-hydroxyquinoline ("oxine") and ammonium pyrophosphate/phosphate are the three main stabilizers for H_2O_2 and its aqueous solutions. Sodium stannate is added as $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ but will most likely hydrolyze in the H_2O_2 solution to form a colloidal hydrated tin(IV) oxide.



It has been suggested that this process takes several weeks before the stannate addition becomes effective. This freshly formed colloidal tin(IV) oxide has a large surface area, which absorbs ("scavenges") and deactivates catalytic ions such as Fe^{3+} . The colloid formation is pH-dependent. In 90% H_2O_2 , the stabilizing action of sodium stannate is at its best between pH 3.5 and 6. Some manufacturers will use a buffer to maintain a narrow pH range between 4 and 5. It will take 4–6 h after addition of sodium stannate for the stabilizing action to take effect. This also indicates that this is a solid-state reaction (adsorption) and not an ionic chelating/complexing effect. A $\text{SnO}_2 : \text{Fe}^{3+}$ ratio of 13 to 26 is required for stabilization of H_2O_2 containing more than 0.3 ppm Fe as a contaminant. Other sources suggested that this process (formation of the colloid suspension) takes several weeks before the stannate addition becomes effective. Any sludge that forms at the bottom of the tank after stabilizer addition must be separated from the stabilized HTP before it can be used as a rocket propellant.

Sodium stannate may hydrolyze and form a suspension of colloidal tin(II) oxide. Sodium stannate does not act as a complex former, but bad actors (metal ions) are adsorbed and deactivated on the surface of tin(II) hydroxide [hydrated tin(II) oxide] particles in suspension.

Instead of adding sodium stannate as an aqueous solution to the hydrogen peroxide to be stabilized, it has been proposed to first prepare a more concentrated solution of sodium stannate trihydrate in concentrated hydrogen peroxide and then add this solution to the hydrogen peroxide to be stabilized [463]. After this step, the pH will be adjusted with acid (e.g., citric acid or phosphoric acid).

A colloidal suspension of tin oxide can be produced by operating an electric arc discharge between two tin electrodes submerged under distilled water [464]. In a 24-h test at 373 K (100 °C), the active oxygen loss of a tin-stabilized 30% H_2O_2 sample with 20 ppm tin was an order of magnitude less than that of an untreated sample.

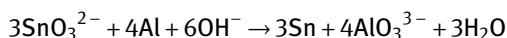
Sodium stannate hydrolyzes completely in 87% concentrated H_2O_2 solution to form a stable lyophobic sol of stannic acid [465, 466]. Precipitation of this sol results by a reduction in the concentration of the potential determining ion (OH^- or O_2H^-) or by the electrostatic adsorption of small quantities of polyvalent cations, e.g., Al^{3+} . In the presence of colloidal stannic acid, the hydrolysis equilibrium of this ion is automatically displaced towards the formation of a stable AlOH^{3+} ion which, by adsorption, neutralizes negative charges on the colloid. Adsorption of aluminum ions is the critical factor governing the stability of stannic acid sols in concentrated hydrogen peroxide solution stored in aluminum tanks [467]. Protection of the sol is afforded by orthophosphate and pyrophosphate ions, which are adsorbed and increase its tolerance for aluminum. Pyrophosphate, in addition, provides an alternative sink for aluminum ions, which are precipitated as aluminum pyrophosphate, AlHP_2O_7 .

The mechanism by which tin hydroxide sols are precipitated by aluminum ions explains the process by which sodium stannate stabilizes commercial H_2O_2 against decomposition catalysts such as the polyvalent ions, Fe^{3+} , Cr^{3+} , and Cu^{2+} . The hydrolysis equilibria of these ions are automatically adjusted to the formation of the stable FeOH^{2+} , CrO^+ , and CuOH^+ ions, respectively, which are strongly adsorbed on the stannic acid colloid and thereby deactivated [468, 469]. These catalytic ions may only be present in minute amounts in non-stabilized commercial hydrogen peroxide (pH ~4.5), mostly in the heterogeneous state. The equilibrium between the heterogeneous and homogeneous phase is disturbed sufficiently to permit the formation of ionic species that are subsequently deactivated by this process.

Stannic acid sols in concentrated hydrogen peroxide differ greatly in appearance and behavior from stannic acid hydrosols in water [470]. In water the sol particles are comparatively large, grow rapidly and are of a feathery appearance, whilst in hydrogen peroxide, the particles are small, compact, and show a distinct but much less pronounced tendency to increase in size with time. This aging process in hydrogen peroxide, which apparently consists of the aggregation of the smaller particles in a polydisperse system, takes place mainly during the first week after

preparation and results in a reduction of approximately 25% in the adsorptive power of the sol.

When tin-stabilized HTP is stored in aluminum containers, part of the tin in the colloid may be displaced by aluminum, causing the colloid to precipitate.



Aluminum strips suspended in 10 to 50 ppm Sn stannate-stabilized 90% H_2O_2 were covered within a few days of immersion with a gray deposit, and there was concern that this loss of stabilizer could cause the HTP to be more susceptible to contaminants. However, when the post-aluminum exposure HTP was challenged by the addition of a small amount of 0.1 ppm. of Fe^{3+} (as the sulfate) to each sample and heated to 323 K (50 °C), but there was sufficient stabilizer remaining even after some of it had been lost due to reaction with aluminum [471].

A decline in the stabilizing activity of sodium stannate induced colloid must be anticipated if the colloiddally suspended tin hydroxide is allowed to coagulate and precipitate [472].

Unstabilized >99% H_2O_2 used for the following tests would decompose in small borosilicate glass vessels at a rate of 0.5 to 1% year⁻¹ at 303 K (30 °C), 10% year⁻¹ at 339 K (66 °C), and 20% year⁻¹ at 373 K (100 °C). Sodium stannate in the form of $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ was added to 99% H_2O_2 at 0.7, 7, and 70 ppm and stability was tested at 303, 339, and 373 K (30, 66, and 100 °C) [307]. A precipitate formed in the 70 ppm solution at pH 3 and 4. The variation of the sodium stannate concentration in pure H_2O_2 was without significant effect on its stability, but lowering the pH had a marked and deleterious effect. Sodium pyrophosphate $\text{Na}_4\text{P}_2\text{O}_7$ was added to 99% H_2O_2 at 1, 10, and 100 ppm and stability was tested at 303, 339, and 373 K (30, 66, and 100 °C) and the pH was adjusted to either 3, 4, or 5. The effect of varying the temperature or the pH was more pronounced than varying the stabilizer concentration. It was concluded that conventional stabilizers, such as sodium stannate, sodium pyrophosphate, or 8-hydroxyquinoline do not improve the stability of 99+% H_2O_2 . The addition of acid will destabilize high-purity H_2O_2 .

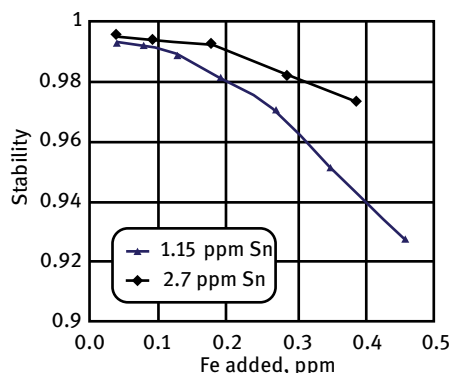
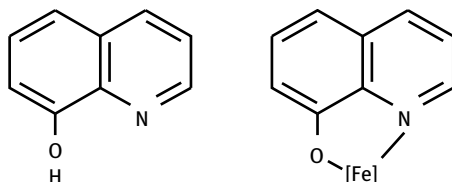


Figure 48: Reserve capacity of two different stannate stabilizer concentrations to neutralize an Fe^{3+} ion insult on the stability of 98% HTP. (Reproduced and modified from Huang, Yuan, and Pinsky [402].)

A study of the protective reserve capacity of added sodium stannate as a function of added iron ion contamination showed that stannate at 2.7 ppm Sn provided reserve stability (with no change in measured stability) up to 190 ppb of added Fe (Figure 48) [402].

4.9.2 8-Hydroxyquinoline (Oxine) as Stabilizer

8-Hydroxyquinoline is most often used in the form of its pyrophosphate salt. It is amphoteric and can form cations and anions. If iron is bonded as enolate on the —OH group in the 8 position, it is also coordinated with the neighboring nitrogen atom in the 1 position:



Oxine alone is not very active against iron contamination but in combination with pyrophosphate it constitutes an effective stabilizer. As most organic compounds, oxine is slowly oxidized by H_2O_2 in solution and may not provide the ultimate in long-term stability. The oxidation of oxine by H_2O_2 is catalyzed by Fe^{3+} ions. Addition of pyrophosphate complexes the Fe^{3+} and extends the life of oxine.

Hydrogen peroxide used by the Germans during World War II was usually 85% H_2O_2 and was stabilized with 8-hydroxyquinoline in the form of the pyrophosphate or mixed with sodium pyrophosphate. This organic stabilizer slowly oxidized, and in approximately 6 months it had effectively disappeared. This organic stabilizer is normally considered superior to stannate in protection against iron.

Since 8-hydroxyquinoline is a light fluffy powder and not immediately soluble in H_2O_2 , it tends to float on the surface of the liquid without wetting. This difficulty may be overcome by first dissolving the 8-hydroxyquinoline in aqueous alkali. The pH of the finished stabilized solution will be adjusted before shipping or storing it to compensate for the addition of the alkali.

4.9.3 Sodium Pyrophosphate as Stabilizer

Sodium pyrophosphate $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ by itself can stabilize H_2O_2 against iron contamination at concentrations up to 10 ppm Fe^{3+} . Like stannic oxide, it is less protective against copper contamination but still better than stannic oxide in this respect. Sodium dihydrogen phosphate and sodium hypophosphite NaH_2PO_2 is a less active stabilizer than sodium pyrophosphate.

4.9.4 Other Stabilizers and Combinations of Stabilizers

Combinations of stabilizers have been tested, and some combinations may exhibit benefactory synergism, where the stabilizing effect of the combination is better than the sum of that of the ingredients by themselves.

Passivation of container walls, in particular in aluminum containers, is a valuable step in minimizing storage stability problems with HTP. Cleaning and passivation methods are discussed in Section 5.3.4.

If a runaway decomposition of a hydrogen peroxide storage tank is imminent, and the contents cannot be drained and diluted fast enough, it has been suggested to add one part of 85% phosphoric acid solution to 100 parts of hydrogen peroxide [473].

A tin pyrophosphate formed by reaction of tin metal with phosphoric acid at 573 K (300 °C) for 1 h is a useful stabilizer.

A three-way stabilizer can be prepared by first preparing a solution of 0.1% $\text{Na}_2\text{Sn}(\text{OH})_6$, allowing it to age for 5 days, adding 0.5% 1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid and 1.1% $\text{Na}_4\text{P}_2\text{O}_7$ to the stannate solution, adjust the pH to 3.1 and using 1 part this stabilizer solution for every 100 parts of 35% H_2O_2 [474]. Standard stability tests at 373 K (100 °C) showed the thus stabilized H_2O_2 to lose less than 0.4% per 24 h.

Magnesium in strongly alkaline (pH > 9) solutions is capable of masking iron and retard the catalytic activity of colloidal iron hydroxides that would have formed in the absence of magnesium [475].

4.9.5 Stabilizers Acting as Catalyst Poisons

The most comprehensive study on the effect of stabilizers as catalyst poisons for hydrogen peroxide catalytic decomposition on a silver catalyst in a reactor with and without various stabilizers was conducted by the Naval Research Laboratory in 1958 [476]. A very high purity, unstabilized hydrogen peroxide that had been purified by a fractional freezing process served as the reference propellant. A 2-cm length of 20-mil pure silver wire immersed in 50 mL of HTP served as catalyst in a constant volume reactor, and the oxygen evolved was measured in a wet test meter. Only a few studies have illustrated the rate of silver loss during the decomposition of HTP as clearly as shown in this report. The small 2-cm length of silver wire lost 5 mg of silver, while the decomposition of (the slowly diluting) HTP generated 20 liters of gas. The effect of HTP concentration on the rate of silver loss was opposite to what would be expected: The initial rate of silver loss was faster in 90% HTP than in 99% HTP (although the maximum rates were similar). Also, the effect of temperature on the rate of silver loss was opposite to what would be expected: The initial rate of silver loss was faster at 293 K (20 °C) than at 358 K (85 °C). One explanation offered for this observation was that at the higher HTP sample temperature, the wire is enveloped by a cloud of gas (film boiling), while at lower temperatures the metal is in contact with the corrosive liquid (nucleate boiling). The rate of HTP decomposition and silver catalyst loss were

dependent on the concentration of stannate, phosphate, and aluminum ion. The effect of tin was dependent on aging, such that the effect was negligible one day after it was first added but became more pronounced with time. The increased silver loss due to the presence of aluminum was moderate. When phosphate was added to HTP in increments, the activity first increased. With concentrations above 2 mg/L, the inhibiting action masked the initial increase. Phosphate sharply increased the amount of silver that dissolved in the decomposing HTP. The catalyst activity was reduced by a factor of 50 when 4 mg/L phosphate was added to the propellant. Addition of aluminum ion or adjusting the pH was ineffective in mitigating the adverse effect of phosphate. Addition of lithium, magnesium, calcium, or barium cations had no effect on the rate of decomposition or the rate of silver loss. Sulfate or nitrate did not alter the activity of silver catalyst in the laboratory studies, but sulfate deposits would clog the rocket engine reactor.

Catalyst pack failures for heterogeneous systems have been reported with phosphate levels of only 0.5 ppm. Apparently, a phosphate level of only 15 ppm causes instant failure of the catalyst; see also [477].

4.10 Catalytic Decomposition of Hydrogen Peroxide

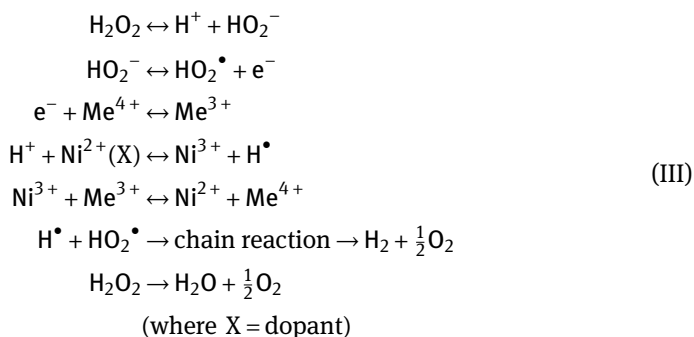
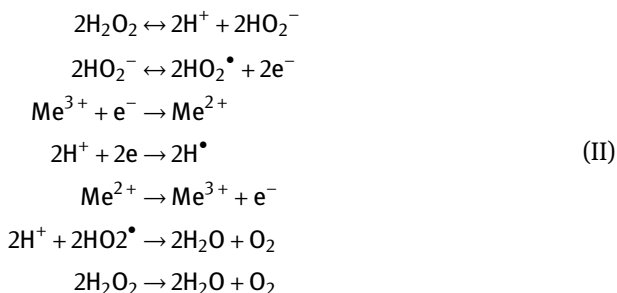
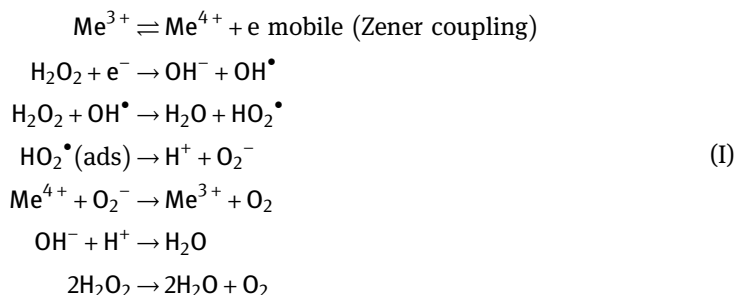
This chapter deals with the unwanted, slow decomposition of liquid H_2O_2 during storage as well the intentional decomposition of HTP achieved by bringing it into contact with catalysts. These catalysts can be heterogeneous, requiring surface contact between the liquid and the solid, or they can be homogeneous substances that are soluble in H_2O_2 or in the fuels brought into contact therewith.

All academic studies on the activity and durability of H_2O_2 decomposition catalysts are summarized here in *Encyclopedia of Oxidizers*, where chemists are likely to find the information they are looking for. The other information in *Encyclopedia of Monopropellants*, chapter “Hydrogen Peroxide Monopropellants”, is an engineer’s approach to the task of selecting flightworthy catalysts for engine designs on the drawing board and on the static rocket test stand. There is some overlap between these two sections, so if the information a reader is looking for cannot be found here, it is possible that they may find it in *Encyclopedia of Monopropellants*, chapter “Hydrogen Peroxide Monopropellants”.

One of the most complete summary reviews of catalysts for the decomposition of hydrogen peroxide in rocket engines was published in [478]. A thorough compilation of references like the one printed in that paper will make several of the following sections in this chapter unnecessary.

4.10.1 Reaction Mechanisms of Catalytic H₂O₂ Decomposition Reactions

A good correlation between the H₂O₂ decomposition activity and the δ -oxygen non-stoichiometries of non-stoichiometric doped metal oxides was found, especially for lanthanum perovskites. Hence, oxygen vacancies have been suggested to participate in the reaction. Various decomposition mechanisms have been suggested in the literature for the decomposition of H₂O₂ on transition metal (Me) oxide-based catalysts, which involve ions, free electrons, and free radicals. Me could be a metal like manganese or iron, which readily change states of oxidation. These mechanisms can be classified into the following three mechanisms (I), (II), and (III), where mechanism (III) involves a dopant metal:



The mechanisms (I) and (II) describe the decomposition on pure metal oxides and have some steps in common: **(1)** the initial surface oxidation or reduction of H_2O_2 molecules, and **(2)** the surface facilitation of the necessary electron mobilization to generate free radicals.

The mechanism (III) describes the decomposition on composite or doped or ternary metal oxide catalysts, also involving the steps **(1)** and **(2)**, and accounts explicitly for the chain reaction nature of the decomposition reaction propagation [479].

Many of the studies on catalysts for decomposition of hydrogen peroxide were carried out in dilute solutions, so as to avoid runaway situations and maybe even maintain isothermal conditions. Such studies in dilute solution may be only of limited value to a rocket designer, but they help us develop more active catalysts for the decomposition of hydrogen peroxide and other monopropellants in higher concentrations.

4.10.2 Catalysts for H_2O_2 Decomposition

4.10.2.1 Homogeneous Catalysts for Hydrogen Peroxide Decomposition

Homogeneous catalysts are discussed here first, not necessarily because they are the most important mode of H_2O_2 decomposition initiation, but because historically this appears to be the first method that was used practically. This method is rarely used in today's H_2O_2 energy systems, and this chapter is relatively short, much shorter than the subsequent chapter on heterogeneous catalysts for the composition of H_2O_2 . One main disadvantage of homogeneous catalyst injection is that for monopropellants, a second liquid must be stored in a separate tank, or the catalyst has to be soluble in a fuel in order to hypergolize it as soon as it comes into contact with H_2O_2 in a bipropellant engine. The need for pressurizing the second tank and metering the liquid catalyst in carefully controlled proportions in relation to the variable main H_2O_2 flow adds to the complexity of the system. Many aqueous catalyst solutions freeze or crystallize from a saturated solution as soon as the ambient temperature drops to cold season conditions. A potential advantage of homogeneous catalysts for decomposition HTP is that they are insensitive to stabilizers in the HTP that could otherwise foul heterogeneous packed catalyst beds.

A very comprehensive review of the reactions of hydrogen peroxide with catalysts in aqueous solutions was published in 1952 and included 132 references [480]. It includes detailed discussions of reactions of H_2O_2 with Fe^{2+} and Fe^{3+} ions, ferrocyanide and ferricyanide ions, copper compounds, Cu^{2+} ions, copper complexes, permanganate, chromate, molybdate, and tungstate.

Sodium iodide solutions were tested by FMC and the US Navy during the years after WWII for an intended torpedo propulsion system but were later replaced by silver screen catalysts. Operating times up to 10 h were demonstrated with a sodium iodide/90% HTP in comparison to 0.014-in. diameter silver wire woven into wire mesh in a H_2O_2 system.

The homogeneous catalysts used most often were aqueous solutions of alkali metal and alkaline earth metal permanganates: KMnO_4 , NaMnO_4 , $\text{Ca}(\text{MnO}_4)_2$ [365, 481, 482]. In the steam generator of the German A-4 rocket, additional decomposition of H_2O_2 was achieved by lining the reactor with bricks made of $\text{Ca}(\text{MnO}_4)_2$.

The solubilities of permanganate salts in water increase in the order $\text{KMnO}_4 < \text{NaMnO}_4 < \text{Ca}(\text{MnO}_4)_2$. Attempts to add the homogeneous permanganate catalysts to non-hypergolic fuels (alcohols, amines) as a means of hypergolization failed in most cases because the permanganate oxidizes the organic compounds. Other manganese compounds have also been tested for this purpose. As part of the “green” propellant effort in the 1990s numerous fuel-soluble catalysts were tested to initiate the decomposition of H_2O_2 in contact with otherwise non-hypergolic fuels. Although these are truly hypergolic propellants that should be discussed in another volume of this series, we summarize some of the homogeneous catalysts here regardless of whether they are used for initiating the decomposition of H_2O_2 by itself or in the presence of a fuel where the fuel is added to increase the specific impulse (Table 46).

Table 46: Fuel-soluble homogeneous catalysts for initiation of H_2O_2 decomposition or hypergolization of fuels.

Catalyst compound name	Chemical formula	Fuel	Catalyst concentration used, mass-%	References
Sodium nitroprusside = di-sodium pentacyano nitroso ferrate(II) dihydrate	$\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$	85% Hydrazine hydrate	1.07 g/L	[483, 484]
Iron(II) β -naphthalene sulfonate trihydrate “Naphferrol”	$\text{Fe}(\text{C}_{10}\text{H}_7\text{SO}_3)_2 \cdot 3\text{H}_2\text{O}$	Methanol	200 g/L	[483]

If the methanol/naphferrol solution is allowed to stand in contact with air, the salt will autoxidize, and the insoluble Fe(III) salt will precipitate from the solution.

Pentacyanonitrosoferrates are not suitable as fuel-dissolved catalysts for long-term storage since they may react with hydrazine or hydrazine hydrate used as fuels [484].

Two types of very small thrust chamber prototypes based on the homogeneously catalytic decomposition of hydrogen peroxide by an aqueous solution of iron(II) chloride have been fabricated by precision machining and silicon etching process [485]. One prototype had a conical nozzle with a throat diameter of 0.3 mm, while the other has a planar nozzle with a rectangular throat section of 0.04 mm $\times$ 0.2 mm. Controlled by two miniature electromagnetic valves, the thruster system could work in either continuous or pulse mode. In preliminary experiments on these prototypes, a smallest impulse per controlling pulse of less than 80 $\mu\text{N s}$ was obtained.

Ions of water-soluble permanganate catalysts probably do not act as such, but a reaction between permanganate and peroxide at high pH or a reaction between manganese(II) ion and alkali forms finely divided manganese dioxide, which then acts as a catalyst [486, 487]. No catalysis occurred until the solution was saturated with manganese(II) hydroxide. By using radioactive tracer methods, it was shown that no exchange takes place between manganese(II) ion and manganese(IV) dioxide in aqueous suspensions. However, as soon as hydrogen peroxide is added, a complete exchange of manganese takes place as both manganese(II) ion and manganese(IV) dioxide react with the hydrogen peroxide. Similar observations were made with mixtures of cobalt(II) ion and cobalt(III) hydroxide [488].

Some liquid catalysts have a nasty tendency to precipitate at the outlet to the injector, clogging the orifices and, thus, limiting their use for multiple engine restarts. Experiments have been carried out with several liquid catalysts, from which the rate of reaction and the tendency to form precipitates were compared against the benchmark catalytic agent, sodium permanganate [489–492]. The concentration of highly stabilized HTP used in these tests was between 81 and 86% H_2O_2 . It was found that, although exhibiting a reduced tendency to form precipitates, none of the candidate agents considered matched the reaction rate of sodium permanganate. Catalysts were injected with a syringe into 10–80% H_2O_2 in a closed vessel reactor, and the rate of oxygen evolution was measured as indication of catalyst activity. Sodium iodide gave a sustained decomposition but had a long startup delay. Iron(II) chloride tetrahydrate had no ignition delay and was capable of producing useful decomposition temperatures. After completing the closed vessel reactor tests, the candidate liquids were injected together with 83% H_2O_2 in a simple 100-N monopropellant thruster simulator, and the temperatures at various distances from the impingement point were measured as a function of time. The reactor was intended as the ignition source for a bipropellant engine with downstream injection of hydrocarbon fuels (*Encyclopedia of Non-hypergolic Bipropellant Combinations*, the chapter “Hydrogen Peroxide”).

Hydrogen peroxide (in much lower concentrations than those used in rockets) can also be decomposed by many organic enzymes, e.g., catalase, liver extract, saliva, or yeast. An enzyme in saliva causes the decomposition of dilute H_2O_2 solutions used as a mouthwash. These materials are very effective in decomposing dilute hydrogen peroxide but are sometimes destroyed by concentrated H_2O_2 before they can cause continued H_2O_2 decomposition.

The bombardier beetle activates a defense mechanism by mixing a solution containing hydrogen peroxide and hydroquinones with an enzyme solution in a bladder, causing instant decomposition of the mixture and rapid, oscillating ejection of the hot reacting mixture in a well-aimed jet to ward off potential predators [493], Figure 49.



Figure 49: Bombardier beetle discharging a jet of hydrogen peroxide / hydroquinone reaction products. (From [493])

4.10.2.2 Laboratory Test Methods for Catalysts with Liquid Hydrogen Peroxide

Before monopropellant decomposition catalysts advance to the level of rocket engine testing at high pressures, they are usually tested at atmospheric pressure in the laboratory. A variety of catalyst tests methods has been described in the literature, which have been used for all types of monopropellants, including hydrazine, hydrogen peroxide, and hydroxylammonium nitrate-based monopropellants (*Encyclopedia of Monopropellants*). Many of these machines have been patterned after hypergolic ignition delay test apparatus designs. The machines are usually readily converted from the use of one type of monopropellant to another.

There are several test methods for the evaluation of catalysts for the decomposition of hydrogen peroxide. Some are as simple as an open-air ceramic spot plate (or ceramic crucible) test with hydrogen peroxide administered by hand from an eye dropper, others are more sophisticated with temperature and pressure instrumentation. This most common test method is a “drop test”, where a drop of liquid propellant is added to a catalyst sample in a crucible, and the reaction is monitored with thermocouples or observed with high-speed video recording. The key parameter is the ignition delay from the moment of drop impingement to the first sign of an exothermic reaction.

Other catalyst test machines have immersed a single catalyst granule in a large excess of liquid (with agitation to enhance mass transfer) and measured the rate of gas evolution with a flow meter or a gasometer.

The best reproducible results are obtained with constant volume reactors instrumented for high-speed temperature and pressure recordings independent of operator skills in adding a droplet to a grain of catalyst.

Closed Bomb/Constant Volume Reactors

Silver granules (10–20 mesh), 4% Ag/ Al_2O_3 , and 1.6% Mn manganese oxide/ Al_2O_3 catalysts were tested with 30 and 50 mass-% hydrogen peroxide in a 170-mL constant vol-

ume instrumented batch reactor operating between vacuum and 2 bar [494–496]. The 100–200 mg catalyst sample could be repeatedly exposed to 10–100 μL propellant injected from a syringe. Between multiple tests, the exhaust products would be pumped off to vacuum. The reactor could simulate pulse mode operation of a monopropellant rocket engine but not the steady-state operating mode. Catalytic decomposition of 30 and 50 mass-% hydrogen peroxide was compared to that of anhydrous hydrazine (Ir/ Al_2O_3 catalysts) and XM46 (Pt/ Al_2O_3 catalysts) in the same reactor, based on the comparison of pressure, pressure rise rate, and temperature. In the presence of the silver catalyst, 50-% H_2O_2 decomposed starting at room temperature. For H_2O_2 the reactor did not need to be preheated to 403 K (130 °C) as with XM46. The ignition delay was 0.3 s for 50% H_2O_2 at 293 K (20 °C). The supported silver/ Al_2O_3 catalyst noticeably lost activity after only three injections.

A closed bomb reactor was used to assess the performance of catalysts for decomposition of high concentration hydrogen peroxide [497]. The catalysts had different chemical and geometrical characteristics and consisted of wire screens, metal foams, and coated or impregnated ceramic pellets. The apparatus was designed to measure the rate at which gas is evolved when hydrogen peroxide comes into contact with a catalytic material. Initial work used ceramic-pellet based carriers. The apparatus allowed a small quantity (typically 3 mL) of 87.5% hydrogen peroxide to be injected rapidly into a reaction chamber, which was allowed to exhaust into a sealed vessel. The aim was to identify the time delay between the introduction of the HTP and the end of the decomposition reaction, and thereby assess the catalyst activity. This was achieved mainly by monitoring the pressure and temperature rise in the sealed vessel. Catalysts tested included 0.5 mass-% Pd on Al_2O_3 , 0.5 mass-% Ru on Al_2O_3 , 0.5 mass-% Pt on Al_2O_3 , and 1 mass-% Pt on Al_2O_3 . The catalyst carriers for manganese oxide impregnation were γ -alumina with a surface area of 200–260 m^2/g and zirconia with a surface area of 95 m^2/g . The catalyst that achieved the highest ranking was a manganese oxide/zirconia catalyst.

Dynamic Flow Reactors

Different types of cellular ceramic-based catalysts for 87.5% hydrogen-peroxide decomposition at miniature scale with nominal mass flows of 0.3 g/s were tested in a flow reactor configuration similar to a propulsion application [498]. The test matrix included honeycomb monoliths with different channel geometries, densities, lengths, different carrier materials, and washcoating procedures, as well as different types of catalysts such as pellets and foams. There were 39 catalyst configurations with a total of 121 catalysts that were experimentally investigated based on their transient and stationary performance at design mass-flow levels of 0.3 g/s and a bed loading of 2.5 $\text{kg m}^{-2} \text{s}^{-1}$. The duration of the tests was typically 200 s to achieve steady-state operating conditions.

Gravimetric, Open Venting Methods

While the constant volume reactor measures the initial startup performance of a catalyst, the gravimetric open venting method is designed to assess lifetime [499]. This is achieved by measuring the change in mass of a 30% hydrogen peroxide solution as its decomposition is being catalyzed. A fixed volume (100 mL) of 30% hydrogen peroxide is held in a beaker placed on a digital readout balance. At time zero the catalyst with a known surface area is added into the beaker. As the 30% peroxide solution decomposes, oxygen and some water vapor are released leading to a reduction in mass, which is measured in 1-s intervals. The experiment is stopped after a fixed time or when the mass change is below 1% of the remaining mass. At this time, the pellets are removed, and the solution replaced with a fresh 100 mL of 30% hydrogen peroxide solution. The experiment is repeated until the catalyst is exhausted. The catalyst performance is judged on two parameters: the rate of mass change and the number of full cycles required to exhaust the catalyst.

Volumetric, Open Venting Methods

The easiest method to measure activity of catalysts is to place a small (20 mg) catalyst sample in a test tube in a glass vessel with multiple ports for injection of the liquid H_2O_2 from a pipette, thermocouples measuring liquid and gas temperature, a pressure relief valve, and the vent gas port through which gases and vapors leaving the vessel enter a condenser where steam and unreacted H_2O_2 are condensed out, and the non-condensable gases are metered through a flow meter. The quantity of H_2O_2 injected is selected such that it may take 60–100 s to consume all the propellant. This method has been used for characterizing candidate catalysts before advancing to reactor testing in a rocket engine [500]. Two types of samples were tested: powders and metal wires. Of the four powder catalyst samples tested, Mn_2O_3 was the most active catalyst powder followed by silver, MnO_2 , and MnO in order of decreasing activity. Four different 0.1 mm diameter metal wires of 150 mm length (gold, platinum, palladium, silver) were coiled to form spirals with a diameter of 5 mm and immersed in 10 g of H_2O_2 . In this experiment, silver showed the best activity and gold the worst, with platinum second and palladium third. However, in some experiments, the silver wire dissolved with time, indicating that its life as a catalyst could be limited.

Other Test Methods

One can also study the phenomena occurring at the H_2O_2 /catalyst interface by visual observation. (From a safe distance with a telescope). When observing H_2O_2 on the surface of a metallic catalyst (a silver tube with the potential of temperature conditioning by flowthrough water) with a telemicroscope, the visual appearance reminds one of nucleate or film boiling of a liquid on a hot surface [501]. The heat of decomposition of H_2O_2 is released in a thin layer on the surface of the catalyst. Decomposition of $\leq 45\%$ H_2O_2 releases individual bubbles, and with $\geq 60\%$ H_2O_2 the catalyst is enveloped in a steam bubble (a vapor barrier) and no longer in contact with the liquid. The maxi-

imum heat flux is achieved at 47% H_2O_2 , which is at the upper limit of nucleate boiling. If one plots the heat flux as a function of the temperature difference between the surface and the liquid, the maximum is at a ΔT of 55 K (100 °F) and occurs with 47% H_2O_2 . The heat transfer through the steam layer is very slow, like that in film-boiling heat transfer, so that the catalyst can become very hot. A new silver surface had to be in contact with HTP for 5–10 min before a constant rate of gas evolution was attained. In the presence of a large excess of liquid, the temperature of the silver tube never exceeded the boiling point of HTP. Some of the silver eroded and was carried away in the flowing H_2O_2 in the form of small particles, and the finely divided silver particles caused additional decomposition away from the surface.

Catalyst immersion tests at Purdue University totally immersed the 1-inch cubes of catalyst-coated Celcor monoliths in hydrogen peroxide with a concentration of <10 mass-% H_2O_2 and allowed it to react in a controlled environment [502]. A thermocouple was used to collect temperature data. At set time intervals, samples of the hydrogen peroxide were taken and examined in the refractometer. This allowed for the qualitative determination catalyst activity.

The only apparatus capable of testing hydrogen peroxide decomposition catalysts at elevated pressures is the apparatus designed at Purdue University. This catalyst immersion test apparatus simulated rocket chamber conditions more closely than a spot plate or Pino tester and consisted of a 5 cm diameter ID $\times$ 20 cm length, 25-mm wall thickness CRES-304 chamber with a propellant fill port and a vent orifice, containing 100 to 250 mL HTP, carrying five thermocouples and a pressure transducer and a movable catalyst holder on a rod that could be moved up and down by a pneumatically actuated piston [503, 504]. The lower liquid limit (100 mL) was to ensure that the catalyst would be fully wetted when immersed while the upper limit was dictated by the position of the fill valve. Initial testing was conducted with hydrogen peroxide and silver screen catalyst samples. The bottom of the chamber had an O-ring seal through which the rod slides up and down. At the beginning of the test, the catalyst mounted at the tip of the rod was in the vapor phase. The catalyst rod/holder was translated in the vertical direction by use of air pressure and a three-way pressure-loaded solenoid valve. Shop air was used as the pressure source for the air cylinder. When toggled, the valve acted to load one end of the air cylinder, while relieving the other end, raising or lowering the catalyst holder in the process. The valve was controlled remotely. Reaction started when the rod was moved down, and the catalyst was completely immersed in the liquid. The nominal operating pressure was <6.2 MPa (<900 psia). With an active catalyst, such as 18-mesh pure silver screen, a chamber pressure of 6 MPa was achieved within 5 s. Higher chamber pressures could be achieved by using smaller vent orifices. The temperature and pressure traces of the test (Figure 50 bottom and top) usually showed two phases, which differed in activity.

The slow Phase I continued until the liquid boiling point was reached. At atmospheric pressure 90% H_2O_2 has a boiling point of 414.4 K (286.2 °F). During testing, a dramatic change in flow attributed to boiling occurred at ~403 K (~265 °F). The low-

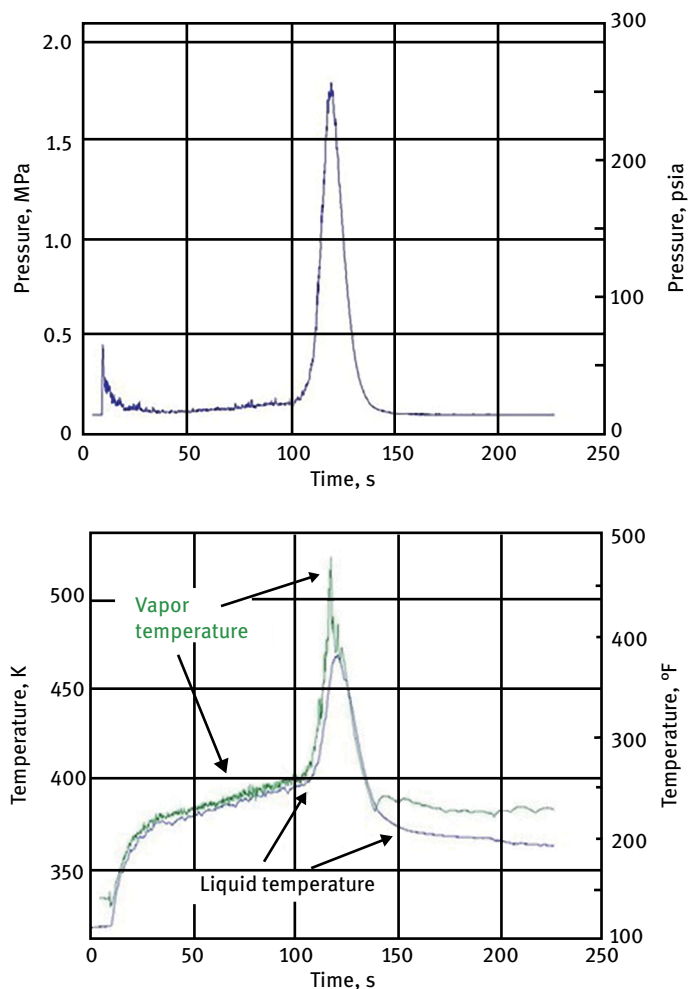


Figure 50: Pressure and temperature traces from a hydrogen peroxide/catalyst immersion test. (Reproduced and modified from [504].)

ered boiling temperature is associated with the lowered concentration due to H_2O condensation. Once the boiling point was reached, Phase II started, and the pressure and temperature inside the vessel rose rapidly, which typically took ~ 100 s. While the particular pressures and temperatures varied depending on the test parameters, the two-phase region behavior was exhibited in almost every test. The duration of Phase II reaction was limited by the amount of peroxide available. A constant pressure was not achieved in Phase II. The pressure rise simply ceased after all H_2O_2 had been consumed.

4.10.2.3 Heterogeneous Catalysts for Hydrogen Peroxide Decomposition

Heterogeneous catalysts for the decomposition of hydrogen peroxide (and most other monopropellants) can be elemental metals in various forms (wire, mesh, foil, pellets, spheres), active metals supported on ceramic carriers, metals cosintered or copressed with metal oxides (“cermets”), or metal oxides. Catalyst researchers have crisscrossed the periodic table of elements in search for metals and metal compounds that are active as catalysts for decomposition of HTP in rocket engines. This effort was very similar to the search for hydrazine decomposition catalysts. For hydrogen peroxide, initial efforts essentially very quickly boiled down to two heterogeneous catalysts: metallic silver and manganese dioxide.

It is unfortunate that many of the publications dealing with catalysts for the decomposition of hydrogen peroxide did not state the level and type of stabilizers in the hydrogen peroxide that they used for the catalyst activity experiments. Stabilizers may act as catalyst poisons. Only very few experimenters were smart enough to test their catalysts side-by-side with both a stabilizer-free hydrogen peroxide and a stabilized type of hydrogen peroxide.

Many of the studies of heterogeneous catalysts for H_2O_2 decomposition referenced here worked with relatively dilute solutions, too dilute to be of any interest as a rocket propellant. However, some of the kinetics derived from such studies apply to hydrogen peroxide decomposition in higher concentration solutions as well. Some of the studies dealt with premature H_2O_2 decomposition at the electrodes of fuel cells, which limits the useful life and energy storage capacity of fuel cells but is only of marginal interest for a rocket application. A short overview of catalyst design for hydrogen peroxide decomposition was published in 1961 [505].

FMC developed hydrogen peroxide decomposition catalysts under a series of US Air Force contracts in the 1960s and in support of laboratory work has done an exhaustive literature survey covering the literature between 1945 and 1965 [506]. This is a very useful introduction into this topic and should have been updated periodically. The main source of information was *Chemical Abstracts*. The literature survey with 394 references is nicely arranged by grouping the metals in the same order as in the periodic table of elements. That helps to bring out similarities in the vertical groups. The survey showed that silver and platinum were the most extensively investigated catalysts. Other major catalysts were palladium, copper, iron, cobalt, manganese, and their compounds. Various methods have been proposed to increase catalytic activity by additives that promote the parent activity of elements or compounds. Samarium nitrate-treated silver, cobalt-manganese oxide mixtures, ruthenium and its compounds, and silver-gold alloys were the most active catalysts reported; see also [507, 508].

For the selection of catalysts, it was proposed that the dependence of the adsorption γ of a standard series of organic substances on their ionization potentials (I) on the adsorbents be obtained first [509]. It was shown for the example of catalytic decomposition of hydrogen peroxide that adsorbents for which the maximum on the $\gamma =$

$f(I)$ curve coincides with the ionization potential of the starting compound undergoing transformation are active catalysts.

Activated charcoal would not be a good catalyst support for HTP applications in a rocket engine, because it would burn away like a hybrid fuel grain, but some grades of carbon black will catalyze the decomposition of hydrogen peroxide [510, 511]. Carbon-black filled elastomers (typical black rubber) or graphite bearings must be avoided if they come into contact with hydrogen peroxide liquid or vapor.

It is interesting to note that dissolved silver salts do not have a catalytic effect. As a solvent 90% H_2O_2 can be saturated with silver nitrate, and the solution remains stable. It has been noted that silver metal and silver(I) oxide dissolve somewhat in H_2O_2 , and that the decomposition ceases as soon as the solid catalyst is removed. The remaining leached silver ions have no effect on the H_2O_2 decomposition if the solution remains acidic or neutral. As soon as a trace of alkali is added and the pH is raised, a brown precipitate ($AgOH$ or AgO_2H) forms that is a very active catalyst.

This is only an incomplete sampling of the literature on the catalytic decomposition of hydrogen peroxide. There are so many papers on multi-element comparative evaluation of heterogeneous catalysts for decomposition of hydrogen peroxide that we had to arrange them in chronological order. Following the chronological multi-element list, there are sections dealing with only one specific element or its oxide(s) as H_2O_2 decomposition catalysts.

4.10.2.4 Supported Metal and Metal Oxide Catalysts

Platinum deposited on molecular sieves or zeolites may be suitable for selective oxidations of organic compounds with H_2O_2 in dilute solutions (such as the epoxidation of alkenes), but they do not stand up to the high temperatures in a rocket engine [512, 513].

Supported catalysts containing the oxides of silver, ruthenium, manganese, lead, vanadium, or chromium on a granular alumina or alumina-silica carrier were prepared and evaluated for their hydrogen peroxide decomposition activity in a stirred batch reactor [514–517]. Uniform active metal loading (g-atom per unit surface area) was to allow comparison of the different metals (or their oxides). Soluble salts of the metals [$AgNO_3$, $RuCl_3$, $Mn(NO_3)_2$, $KMnO_4$, NH_4VO_3 or $(NH_4)_2CrO_4$] were dissolved in water to obtain solutions at a defined concentration of 0.96 g-atom metal per liter. The carrier granules were soaked only once in half their bulk volume of solution for 4 h and then dried and weighed to determine the weight gain of undecomposed salt. The weight gain depended on the affinity of the carrier for the metal ions. Active metal oxide loading varied accordingly. The dried catalyst was calcined in air for 15 h and weighed to determine the metal oxide loading. In addition, the active metal loading was determined by extracting the catalyst with either concentrated hydrochloric acid or *aqua regia* for 24 h and analyzing the metal content in the extract by ICP. The carriers evaluated included four molecular sieves, five aluminas, three alumina/silicas with three different $Al_2O_3 : SiO_2$ ratios, and silica. The H_2O_2 decomposition activity

was determined in a batch reactor, which was a 50-mL spherical glass flask containing 20 mL of 70% stabilized hydrogen peroxide (FMC/SC grade). This reactor reminds us of the one used by the Shell Development Company in 1962 during the early development phase of a hydrazine decomposition catalyst that was later named Shell 405, and this historical event was the most successful catalyst development for rocket applications in a long time. FMC/SC 70 contained 63.9 mass-% H_2O_2 , 0.68 mg/L P, 2.01 mg/L Na, and 0.67 mg/L Sn. The solution was stirred with a magnetic stirrer and a glass-encapsulated thermocouple was inserted into the solution, and the time to max temperature was recorded. At time $t = 0$, a precise weight of catalyst was dropped into the hydrogen peroxide solution. Forty μL aliquots were withdrawn from the batch at defined time intervals, which were then analyzed for remaining H_2O_2 content by refractive index. In the immersion batch reactor, the most active catalysts were a ruthenium oxide/ Al_2O_3 catalyst, a commercial 1% Pt/ Al_2O_3 , and calcined potassium permanganate on mol sieve. It was learned that tetravalent manganese is more active than trivalent manganese as a catalytic agent, that base-promoted manganese exhibits lower weight loss during calcination than manganese alone, and that neutral silver is more catalytically active than silver oxide. It was planned to test the most active catalysts in a flow reactor that would more closely represent actual rocket engine operating conditions than a batch reactor. Catalysts based on molecular sieves may be suitable for selective oxidations of organic compounds with H_2O_2 in dilute solutions (such as the epoxidation of alkenes), but they do not stand up to the high temperature in a rocket engine.

The preparation of supported iridium catalysts for decomposition of hydrogen peroxide is described in [518]. In a method for preparing this hydrogen peroxide decomposition catalyst, the porous particulate carrier is impregnated with an organic solvent solution of H_2IrCl_6 , dried, calcined, and reduced. This catalyst is similar to Shell 405.

The oxides of silver, ruthenium, manganese, lead, vanadium, and chromium deposited on a commercially available molecular sieve, alumina, alumina/silica, and silica carriers were evaluated for the decomposition of rocket-grade HTP [519]. Soluble salts of the above cations were dissolved in water to obtain solutions at a defined metals concentration of 0.96 mol/L. Calcinations were performed in a furnace by roasting in air at above the known decomposition temperatures for 15 h. The finished catalysts were then tested in a batch reactor consisting of a 50-mL spherical glass flask containing 20 mL of 70% stabilized hydrogen peroxide (FMC/SC grade). The solution was stirred at a defined angular velocity with a magnetic stirrer and a glass-encapsulated thermocouple was inserted into the solution. At time $t = 0$, a precise weight of catalyst was dropped into the hydrogen peroxide solution. Forty microliter aliquots were withdrawn from the batch at defined time intervals, which were then analyzed by refractive index. A temperature record was also obtained for each experimental run. By plotting $-\ln [C_t/C_0]$ versus time, and knowing the catalyst molar metal loading, k' , the catalytic rate constant, was obtained for a variety of catalyst types. The rate constant was then normalized to the number of active catalyst metal atoms loaded onto the carriers

to generate k' . The most active catalysts were those containing ruthenium oxide and manganese oxides obtained by decomposition of potassium permanganate. Tetravalent manganese was found to be more active than trivalent manganese, and neutral silver was more catalytically active than silver oxide.

An assortment of metallic and supported catalysts for an 85% HTP decomposition chamber that was intended as an igniter for a hybrid rocket was investigated at the University of Surrey [520]. The effort was centered on a hydrogen peroxide hybrid rocket to be used as satellite kick stage. During Phase 1, between August 1994 and February 1995, a total of seven different catalyst pack configurations were tested:

- Type-1: maximum density silver-plated nickel gauze
- Type-2: maximum surface area silver-plated nickel gauze
- Type-2A: Type-2 catalyst, sintered for 30 min at 800 °C
- Type-3: KMnO_4 crystals
- Type-4: LCH 212
- Type-4A: LCH 212 plus Shell 405 in upper bed
- Type-5: silver-plated gauze provided by the US Air Force Academy
- Type-7: stacks of pure silver screen and stacks of very rough silver plated on a nickel screen

Note: What Surrey calls “LCH 212” is actually LCH-202 (from the author’s laboratory) that was salvaged along with Shell 405 catalyst from surplus Chevaline Peace Courage post-boost propulsion systems built by Rocket Research Company (RRC) for Bell Aerospace (Buffalo, NY) and Royal Ordnance in the UK that were cut open and the catalyst removed and diverted for other purposes. They also used it for N_2O decomposition.

The overall performance with the Type-4 catalyst was fair. Startup was relatively slow (accounting for the low average T_c) but the overall performance was consistent, and no wet starts were observed. On all runs, temperatures consistently reached nearly 873 K (600 °C). After the last test, the Type-4 catalyst was examined to reveal that the glossy black finish on the pellets had taken on a white discoloration over much of the surface. This was most likely due to oxidation of the iridium by the peroxide. Because of this rapid oxidation, LCH and Shell 405 had to be ruled out for long-term space applications. However, because of its consistent performance, a modified catalyst pack, Type-4A using both LCH and Shell was used for a hybrid ignition test. Nine 30-s tests and one 20-s test were conducted with the Type-7 catalyst with good results.

Five metallic and five metal oxide catalysts supported on 18–24 mesh granular alumina were prepared and evaluated by measuring the rate of gas evolution of a 30-mg catalyst sample in 2 mL of 80-% H_2O_2 [521]. The catalysts with various molar ratios were prepared by impregnating the alumina support with a metal salt solution. The impregnated catalysts were dried at 373–393 K (100–120 °C) for 12 h, and then calcined in a muffle furnace in air at 673–1073 K (400–800 °C) for 4 h. The total loading of the metal oxides was 3–25 mass-%. The activity of the metal catalysts in decreas-

ing order was $\text{Ir} > \text{Ru} > \text{Ag} > \text{Pt} > \text{Pd}$ and the activity sequence of metal oxide catalysts was $\text{MnO}_x > \text{CoO}_y > \text{FeO}_y > \text{PbO}$. MnO_x was the most active catalyst among these metal oxides. When doped with other elements, the activity of MnO_x could be enhanced. A catalyst designated M3 had the highest activity, which was near the activity of Ru, Ir, or Ag. As M3 was much cheaper than the noble metal catalysts, it was subsequently used for HTP decomposition reactor experiments and compared to an $\text{Ir}/\text{Al}_2\text{O}_3$ catalyst. The tests used two different catalysts in a smaller (19 mm D $\times$ 38 mm L) reactor with 50–80% HTP and a mass flow of 15–23 g/s and then the M3 only in a larger (196 mm D $\times$ 90 mm L) reactor with 92% HTP and demonstrated good startup and shutdown transients for a gas generator application. The mass flow was 758 g/s, and the chamber pressure was 1.58 MPa. The highest catalyst bed temperature was 1033 K (760 °C), and the gas temperature reached 1063 K (790 °C).

A patent [522] for transition metals (Mn, Ag, Ru, Pb, V, Cr or Co, or other transition metals or noble metals, such as Cu or Pt) oxides deposited on a porous catalyst base of either zeolite molecular sieves, porous alumina, silica or aluminosilicate, or high surface area ceramic materials all in the form of a porous monolith, a honeycomb or chunks, extrudate, pieces, pellets, spheres uses preparation methods of impregnation, drying and calcining similar to those described in an earlier patent by the same inventor [523].

Manganese oxides, palladium, platinum, ruthenium, and silver were deposited on $\gamma\text{-Al}_2\text{O}_3$ and Si-doped Al_2O_3 spheres, starting from different precursors during the impregnation phase [524]. Metal loadings on the ceramic substrates were evaluated by SEM/EDAX, and the activity of different catalysts in the decomposition of 30% H_2O_2 was measured in a laboratory apparatus. The platinum penetration extends down to 180 μm below the surface, about half of the pellet radius. The $\text{Pt}/\text{Al}_2\text{O}_3$ 2nd type (LR-59) catalyst was found to be the most active, showing an excellent repeatability and no appreciable poisoning.

Two different active metal impregnation techniques were used to prepare supported $\text{Pt}/\text{Al}_2\text{O}_3$ and Pt/SiC catalysts for HTP decomposition on spheres and granules of several alumina-based carriers (lanthanum doped alumina, bimodal δ -alumina and θ -alumina, silicon carbide, and α -alumina) with Brunauer Emmet Teller (BET) surface areas between 4 and 200 m^2/g [525]. The alumina supports, five different types, were in spherical form, manufactured by SASOL with diameters ranging from 0.6 to 2.7 mm. A granular silicon carbide support with an average diameter of 0.55 mm and a specific surface area lower than 1 m^2/g was also used, but platinum adhesion was unsatisfactory. Twelve catalysts with different carriers, different active metal loading, and different impregnation methods were prepared and tested. Chemical activity and thermal shock resistance of finished catalysts were measured, and SEM-EDAX measurements of the platinum load on the supporting surface were used to assess the effectiveness of the active metal deposition and monitor the catalyst degradation caused by 87.5% HTP decomposition. Two of the $\text{Pt}/\alpha\text{-Al}_2\text{O}_3$ catalysts, including $\text{Pt}/\alpha\text{-Al}_2\text{O}_3$ catalyst LR-III-39, showed high chemical activity and excellent thermomechanical strength, with

no signs of platinum loss because of hydrogen peroxide decomposition. High surface loads of platinum (44 mass-% on the surface) were achieved on the α - Al_2O_3 substrate despite its relatively low surface area ($4 \text{ m}^2/\text{g}$), successfully overcoming the limitations usually associated with active metal deposition on low surface area substrates. One of the catalyst impregnation methods may represent an effective alternative to the incipient wetness impregnation technique traditionally used for the synthesis of heterogeneous catalysts.

A commercial 0.6 mm diameter spherical γ - Al_2O_3 made by SASOL with a surface area of $170 \text{ m}^2/\text{g}$ was used as the support for a $\text{Pt}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ wash coat [526]. The as-received carrier was first sintered in air at 1373 K (1100 °C) for 1 h in order to obtain the desired crystal phase with a measured BET surface area of about $74 \text{ m}^2/\text{g}$. The second step consisted in the preparation of a sol/gel containing Ce/Zr in a 60-to-40 atomic ratio, starting from the corresponding nitrates in the presence of citric acid and following a procedure already described in the literature. The third step consisted in coating the Al_2O_3 spheres with the $\text{CeO}_2/\text{ZrO}_2$ sol/gel precursor by wet impregnation and absorption. After impregnation, the samples were calcined at 823 K (550 °C) for 6 h. The fourth step was the deposition of Pt by a modified ion exchange method using either an aqueous $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ solution or a H_2PtCl_6 solution in acetone. For some of the samples, the $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ platinum precursor solution was directly added to the Ce/Zr sol prior to coating it onto the alumina substrate, but the end results were discouraging. Finally, the samples were calcined at 773 K (500 °C) for 4 h and reduced in flowing H_2 at 673 K (400 °C) for 4 h. The final Pt loading was 6 to 10% by mass. Based on laboratory tests with 30% H_2O_2 , followed by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) and X-ray diffraction (XRD) examination, a sample with the designation CZ-11 which had been impregnated with a H_2PtCl_6 solution in acetone, resulting in a final Pt loading of 10% by mass, exhibited the best performance in terms of chemical activity and repeatability. The same catalyst was later used in a thruster test (*Encyclopedia of Monopropellants*, the chapter “Hydrogen Peroxide Monopropellants”).

A team from the University of Pisa, Italy, and ALTA S.p.A., Italy, developed a platinum catalyst that was then tested for durability in an actual flight-worthy thruster and analyzed by SEM-EDAX [527]. This is a nicely illustrated paper and shows excellent quality SEM images and EDAX scans of the catalyst before and after firing in the rocket engine.

Four different catalyst beds were evaluated under operational conditions representative of typical application in small monopropellant thrusters to characterize the resulting performance of the thrusters [528]. The catalyst beds were integrated in a reconfigurable flanged 6.5-N thruster prototype and tested at sea-level pressure. The catalysts consisted of platinum deposited on α - Al_2O_3 or $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2/\text{Al}_2\text{O}_3$ carriers. The preparation of this catalyst had already been described [526]. Two different substrates, respectively, indicated as 0.6/4 and 0.6/75 and produced by SASOL GmbH, have been used as catalyst carriers. The 0.6/4 support consisted of α - Al_2O_3 with a BET

surface area of $4 \text{ m}^2/\text{g}$, while the 0.6/75 substrate was a mixture of α and θ alumina, with a one-order-of-magnitude-higher BET surface area ($75 \text{ m}^2/\text{g}$). Three platinum catalysts, indicated as LR-III-97, LR-III-106, and LR-IV-11, were prepared using proprietary coating techniques. Another platinum catalyst, indicated as CZ-II-600, was prepared as reported by Romeo et al. [529]. The thruster was designed to operate with 5 g/s of 90% H_2O_2 at a nominal chamber pressure of 15 bar and $10 \text{ kg m}^{-2} \text{ s}^{-1}$ of bed loading (25 mm catalyst-bed diameter), developing a nominal thrust of 6.5 N. Three conical nozzles were used to change the bed loading and allow atmospheric operation of the thruster without nozzle flow separation at three values of mass flow rate (5, 17, and 28 g/s) and the same chamber pressure (15 bar). The main element of the thruster is the cylindrical casing, which was interfaced at the upstream end with a flanged connection to the thrust balance and at the aft end to a threaded nozzle. All beds showed high decomposition efficiencies, well in excess of 90%. In particular, two catalyst beds (indicated as LR-III-106 and CZ-II-600) were able to decompose up to 13 and 11 kg of 90% hydrogen peroxide (equivalent to 433 and 366 g of decomposed H_2O_2 per gram of catalyst) in 2500 and 2000 s of continuous thruster operation. They exhibited c^* efficiencies higher than 95%. The experimental results also indicated two main sources of catalyst degradation. In low-porosity catalysts, the decay of chemical activity affects the temperature efficiency and causes the flooding of the first portion of the catalytic bed, whereas highly porous catalysts experience thermal cracking and rupture of the carrier, which leads to excessive growth of the pressure drop across the catalytic bed. With the LR-IV-11 catalyst, there was a progressive increase in the pressure drop across the bed. However, the increase in the pressure drop did not affect the correct operation of the cavitating venturi, and therefore the thrust remained essentially constant. As in the case of LR-IV-11, the occurrence of excessive pressure losses, rather than the degradation of its catalytic activity, caused the termination of the run.

All-Metal Catalysts

Many of the studies on the effects of all-metal catalysts on dilute hydrogen peroxide solutions were done to develop electrodes for fuel cells. In fuel cells, electrodes should actively reduce hydrogen peroxide while current is drawn, but they should not decompose hydrogen peroxide during idle times. Other types of non-catalytic electrodes are needed for polarographic studies of H_2O_2 redox reactions and conductivity or pH measurement in H_2O_2 solutions.

A porous, cobalt-plated steel screen catalyst for the decomposition of hydrogen peroxide can be made by electroplating an iron or steel screen first with copper and then in a bath with sacrificial cobalt anodes to give a coating of 0.007 in. of cobalt [530]. The final coating is rough, porous, and fernlike. Its activity can be increased further by dipping it in hydrogen peroxide and allowing it to dry.

A study of the catalytic decomposition of acidic H_2O_2 solutions (10^{-4} to 10^{-1} M) in the presence of platinum, iridium, palladium, and gold showed that in H_2SO_4

solution, platinum, iridium, and palladium are catalytically active, but gold is not active [531]. The H_2O_2 decomposition is a first-order reaction with the following kinetic constants: $k = 6 \times 4 \times 10^{-5} \text{ s}^{-1}$ for platinum; $k = 1 \times 2 \times 10^{-5} \text{ s}^{-1}$ for iridium; $k = 0 \times 34 \times 10^{-5} \text{ s}^{-1}$ for palladium; all at 298 K (25°C) and referred to a 10 cm^2 metal surface. The surface of the electrode practically becomes covered by a monomolecular layer of oxide during the catalytic H_2O_2 decomposition in acid solution. The metal loses its catalytic activity when it cannot be covered by an adsorbed oxide layer, as when it forms complexes with the solution: for instance, Pt and Ir in HCl solutions or Au in H_2SO_4 solutions.

Silver and platinum metals are known as active catalysts for hydrogen peroxide reduction and decomposition, but their relative activities were not well known, and data were also lacking with respect to the relative rates of reduction and decomposition of H_2O_2 in contact with different catalysts and electrode materials. The rates of H_2O_2 reduction and decomposition at different electrodes that are catalytically active in these reactions and relatively corrosion-resistant in alkaline solutions were measured, including Ag, Au, Pt, and Pd, the alloy Pd-Ru, the surface Raney-nickel catalyst Ni-SRC, as well as Ni-SRC coated with an electrolytic palladium deposit, Pd/Ni-SRC [532].

Heterogeneity of the surface of metals of the copper group can be observed in the decomposition of hydrogen peroxide [533]. The distribution curves of the active centers with respect to their activation energy indicates that there are active centers with different activation energy on the surfaces of both single crystals and polycrystalline samples. The (100) faces, which are more closely packed, are characterized by lower activation energy. Thermal treatment of silver in air or under vacuum produced changes in the values of the most probable activation energy of the process. This phenomenon relates to the amount of oxygen on the surface and in the bulk of silver.

4.10.2.5 Metallic Silver Catalysts

The widely used silver (stacked screen or rolled screen) catalyst beds are typically made of 12 to 40 mesh/in. screen (wire mesh, gauze) and are either activated by etching with dilute nitric acid and/or by coating with calcined samarium oxide. These screens nominally have a pressure drop of 552 kPa (80 to 90 psid) across the bed, are relatively heavy, and are easily poisoned by typical stabilizers often found in HTP. The weave pattern of the silver wire mesh screens is sometimes described as a “herringbone weave”.

In Russia, catalysts based on silver and its alloys were prepared as wire grids, cocoons, and porous briquettes. In practice, pure silver catalysts did not find wide application, except for water and oxygen production in life support systems when cleanliness of decomposition products should be the highest [534]. Based on experience in Russia, pulse-mode operation of catalyst beds due to high thermal conductivity of silver an overheating of the injector head and valve area may occur, which in turn may result in explosive HP decomposition near the injector manifold. The catalyst activ-

ity of silver does not provide a start capability of catalyst beds at temperatures below 273 K (0 °C) with the characteristics required for thrusters.

There is always the concern about the poisoning effect of stabilizers on the activity of silver catalysts. It is important to compare stabilized and unstabilized HTP side-by-side [535]. Unfortunately, many catalyst tests reported in the mid-1990s did not identify the stabilizers in the HTP that was passed through the catalyst.

A method was developed for preparing silver surfaces that were reproducible in their reactivity toward both dilute and concentrated H_2O_2 , as evidenced by the rates of oxygen evolution measured in a static-type constant volume reaction chamber [536]. The pure metal was found to be more reactive to H_2O_2 than metal that had been either tarnished by exposure to the atmosphere or given a $\text{Sm}(\text{NO}_3)_3$ treatment. In the case of tarnishing, the initial reaction rate is believed to be controlled by the diffusion of H_2O_2 through a layer of combined oxygen on the silver surface.

The solubility of silver in 15 to 80% hydrogen peroxide was determined by direct means and by evaluating the $[\text{Ag}^+][\text{HO}^-]$ ionic product needed to start rapid catalysis [537]. Solubility was constant from 262 to 298 K (–11 to +25 °C). The rate of dissolution of silver metal in concentrated hydrogen peroxide solutions decreased progressively with time and approached zero when the solution became essentially saturated. Dissolution rates of silver in hydrogen peroxide at strengths over 50% were diffusion controlled. The addition of a little alkali to H_2O_2 solutions containing silver ion quickly initiates a more rapid decomposition with the simultaneous formation of a solid phase, which can be shown to be metallic silver. In solutions of H_2O_2 containing $\text{Ag}(\text{I})$ ion, rapid catalysis was initiated when the solubility product of silver(I) hydroperoxide (AgO_2H) was reached. The attainment of the solubility product of AgO_2H is postulated as the criterion for rapid catalysis in solutions of hydrogen peroxide containing silver ion. If NaCl was present, AgCl precipitated in the diffusion layer. Both the diffusion of $\text{Ag}(\text{I})$ ion from the silver surface and of chloride ion to the silver surface were considered in a study of concentration gradients.

Electronic conductivity measurements revealed that pH increased proportionally with the amount of silver dissolved, giving higher values at the two extremes of concentration than at intermediate concentrations [538]. The accelerating rate of decomposition that occurs when such solutions become saturated with these ions results from the continuous precipitation of particles of silver as decomposition proceeds. As further decomposition decreased the H_2O_2 concentration, Ag^+ and HO_2^- were removed from solution in accordance with the limiting ionic product.

The rate of decomposition of hydrogen peroxide on a smooth silver surface at 273 K (0 °C) rises linearly with concentration of peroxide up to about 50–60 mass-% and then becomes independent of the concentration up to about 70–80 mass-% H_2O_2 . At still higher concentrations the rate rises again [539]. It was tentatively concluded that decomposition occurs by a strictly heterogeneous mechanism at the metal/liquid interface in concentrations up to about 70–80 mass-%, but that a free-radical chain mechanism is superimposed above this concentration.

Measurements of the rate of the catalytic decomposition of H_2O_2 on the surface of single crystals of silver showed that the kinetics depended strongly upon the concentration and pH of the H_2O_2 solutions [540]. Even under the conditions causing the least change in the surface during reaction the rate constants were the same for all the orientations examined. During the reaction the surface became covered with a layer, possibly silver oxide, which masked the original orientation of the crystal; the formation of this inhibiting layer is the most likely reason for the absence of any orientation dependence. Silver(I) ions were found in the solution.

A hydrogen peroxide decomposition catalyst can be made by silver plating a stainless-steel screen with coarse, porous silver, coating the porous silver with potassium permanganate and baking it in place [541]. This catalyst can start the decomposition of HTP only once at temperatures below 273 K, but it can restart repeatedly if the catalyst and propellant temperature is above 294 K (21 °C).

The decomposition of hydrogen peroxide at silver surfaces showed that two distinct decomposition regions exist with an abrupt transition from one region to the other that occurs at about 291 K (18 °C). The low temperature reaction rates were measured in a static system with active stirring at constant temperature and constant pH. A small piece of silver wire was cleaned, weighed, and dropped into the stirred solution. The gas evolution was measured with a wet test meter. At low temperatures, the rate of HP decomposition was proportional to the product of wetted area times the HP concentration [542]. The rate of silver mass loss was proportional to product of wetted area times the square of the HP concentration. If the rate of silver mass loss (spanning four orders of magnitude) is plotted in a double-logarithmic graph versus the HP concentration, one obtains a nice straight line. The rate of silver loss was inhibited by the presence of silver and hydroxide ions in the HP solution and decreased when increasing the pH from 2 to 3. The data at low temperatures indicated that a chemical reaction at the silver surface controls the rate of HP decomposition. The activation energy determined from the slope of the Arrhenius plot was 43.5 kJ/mol (10.4 kcal/mol). A chain mechanism thought to be consistent with the experimental evidence was postulated. Expanding the range of temperatures tested to higher temperatures, the heterogeneous decomposition of 90% H_2O_2 on silver was investigated as a function of the bulk solution temperature, silver surface temperature, and pressure [543]. The apparatus used for study of the high-temperature decomposition differed from the one used for the study of the low-temperature decomposition. A dynamic rather than a static reactor had to be used. The dynamic reactor consisted of a 6-mm (0.25 in.) long piece of 0.12 mm (0.125 in.) diameter silver rod held at the tip of a hypodermic needle with an internal thermocouple. A supply of HTP flowed at a rate of 45 g/min through a pressurized hot water bath for pretest temperature conditioning, over the catalyst, and the reaction products were cooled, passed through a backpressure regulator, and the amount of gas evolved measured in a wet test meter. At high temperatures, the decomposition of 90% HP is rate-limited by heat transfer. At constant bulk solution temperature, the silver surface temperature, and the HP decomposition rate increased

with increasing pressure in the manner expected for a heat-transfer-limited process. At constant pressure with increasing bulk solution temperature, the silver surface temperature slowly increased, while the HP decomposition rate and the silver loss rate slowly decreased.

It has been claimed that coating the silver with oxides of elements from IUPAC Group 12 (former Group IIb) of Mendeleev's Periodic Table of the Elements in an amount such as to cover at least 10%, but not more than 90% of the silver surface, i.e., coating with zinc oxide or cadmium oxide, will form catalysts that are capable of decomposing much greater amounts of hydrogen peroxide per unit weight of silver lost than with prior art catalysts with an all-silver surface [544]. Zinc or cadmium are applied to roughened silver surface as a solution of their nitrate or formate salts, and dried and baked to form the oxides. It is not necessary to coat all silver screens in the catalyst bed. It suffices to insert the coated (e.g., 0.5–1.5 mg ZnO or CdO /cm² of silver surface) silver screens into the upstream section of the bed, where some of the zinc or cadmium is leached and reduces silver loss rates in the downstream sections of the bed.

The decomposition of liquid H₂O₂ on a silver catalyst is complicated by the existence of a vapor barrier at high peroxide concentrations. The barrier arises because localized decomposition at the catalyst surface raises the temperature of the silver far above the boiling point of the hydrogen peroxide, and any liquid approaching it is vaporized. Passing cooling water through a silver catalyst tubing can lower its temperature and suppress the vapor barrier [545]. Under these conditions the decomposition is changed and approaches the expected behavior. The vapor barrier is also diminished by increasing the pressure, which supports the thesis that the vapor barrier retards the chemical kinetics of the decomposition. As the pressure in the reaction chamber was increased, the silver loss was decreased.

The catalytic decomposition of hydrogen peroxide on silver follows a second-order reaction in 10–25M solutions [546]. In the range of lower concentrations, it follows first-order kinetics. During the decomposition the catalytic activity of silver diminished, depending on the solution concentration and various other experimental conditions. The gradual inhibition was caused by a partly irreversible sorption of the reaction product oxygen. Oxide layers were formed only in 2–5M H₂O₂ solutions. Decomposition and gradual inhibition were rarely influenced by the effects of metal dissolution by the reactants, by the surface changes, or by silver ions in solution.

The kinetics of silver-catalyzed decomposition of concentrated hydrogen peroxide solutions on a catalyst that was made in the form of a rotating disk was investigated as a function of bulk solution and silver surface temperatures and of different speeds of disk rotation [547]. An abrupt transition between regions of lower to higher decomposition rate occurred with an increase of temperature, similar to the transition from nucleate boiling to film boiling. Hydrogen peroxide decomposition in the region of a lower reaction rate was surface-reaction controlled. From experimental data in this

region, the rate was proportional to the square root of hydrogen peroxide activity. The activation energy was 55.6 kJ/mol (13.3 kcal/mol).

The decomposition of H_2O_2 on silver and gold follows basically different reaction mechanisms, which are not only different limiting cases of one mechanism. The decomposition of H_2O_2 on silver-gold alloys in the concentration range from 5 to 0.05 M H_2O_2 and in the temperature range from 283 to 333 K (10 to 60 °C) at pH 8 on oxide-free contacts transitioned continuously from second order with silver (above 0.3 M H_2O_2) to first order with gold [548]. The experimental activation energies and pre-exponential factors increased from silver to gold at first less strongly and later more so. The catalyst behavior was primarily determined by the oxygen affinity of the catalyst, in respect to which gold and silver differed substantially, although otherwise they have largely similar properties.

Both silver-plated nickel 200 screens and pure silver screens were used as the active metal catalyst for decomposition of 85% HTP during the development of a pressure-fed liquid fueled upper-stage bipropellant engine with an HTP predecomposition chamber [549]. The catalyst bed variables tested were screen material, screen loading configuration, screen plating and coating processes, screen mesh size, bed loading, and catalyst bed head loading uniformity. A modular, cartridge type, nominal 50-lb_f monopropellant rocket engine was used for performance evaluation of catalyst bed designs. The diameters of the catalyst bed and the engine throat were 2.4 cm (1 in.) and 0.79 cm (0.311 in.), respectively. The c^* efficiency of the predecomposition reactor performance was used for the evaluation of catalyst activity and decomposition efficiency. The data indicated that a high decomposition efficiency (>90%) of 85% HTP could be achieved at a bed loading of 7.1 kg cm⁻² s⁻¹ (0.51 lb_m in⁻² s⁻¹) with pure silver screens. This performance was duplicated with silver plated, nickel 200 screens. Samarium oxide coating on silver plated nickel 200 screens was also evaluated but retarded the decomposition process, and the catalyst was flooded at lower bed loading. The effects of catalyst bed aging were investigated to determine the degree of deterioration in the performance of the catalyst bed with cumulative runtime. A throughput of 90.6 kg (200 lb_m) of HTP was achieved during 1000 s runtime with performance degradation beginning only after approximately 400 s. The starting transients experienced were disappointingly long at ambient temperatures. Fourteen catalyst bed configurations were tested in an effort to provide design data. In addition to the nominal 50-lb_f monopropellant engine, a subscale engine with a 3.5-in. diameter catalyst bed was used to verify the scalability. Over 250 tests were performed before the final selection of the catalyst bed configuration. The decomposed gas had a sufficiently high temperature to ensure the auto-ignition of JP-8 fuel in the bipropellant engine to be tested next.

In addition to the silver screen catalysts described above, solid catalysts using precious metals (Pt, Ir on alumina) were also developed for the decomposition of HTP with 85 to 98 mass-% H_2O_2 [550]. Preliminary results showed that the catalyst had a strong reactivity even after 15 min of H_2O_2 decomposition. The development effort

also included some homogeneous catalyst testing. Various non-toxic catalysts were evaluated with 98% peroxide and hydrocarbon fuels. The results of open cup drop tests indicated ignition delays around 11 ms.

Silver Plated on a Nickel Screen

A catalyst bed made from silver-gold alloy plated on nickel screen and stacked screens inserted in a catalyst bed showed short startup times and long endurance operating times [551]. The nickel screen is electro-etched and rough nickel plated to roughen its surface (to give it a “rugose” surface) prior to plating with the silver-gold alloy. The silver-gold alloy contains about 99% Ag and 1% Au.

In order to make a catalyst, a 20 ×20 mesh nickel screen was first flame-sprayed with a coating from an alloy of 70% Ag/30% Pd, then roughened by etching with nitric acid and activated by immersion in a 10% aqueous solution of $\text{Sm}(\text{NO}_3)_3$, then baked to obtain a discontinuous coating of samarium oxide [552]. This catalyst was very active with 98% H_2O_2 , and 90% of steady-state chamber pressure was attained within 190 ms. Similar results were obtained when the nickel screen was flame-sprayed with an alloy of 70% Ag/25% Pd/5% Mn.

Silver plated on nickel screen was used in subscale 1-in. and 3.5-in. diameter reactors during the development of a catalyst bed for a large Upper Stage Flight Experiment H_2O_2 /JP-8 bipropellant engine [553]. The evaluation was performed with two different bed diameters. A 50-lb_f monopropellant engine with a 1.0-in. ID reactor was used to determine the optimal catalyst bed configuration, and a subscale engine with a 3.5 in. diameter reactor was used to verify the scalability. Silver-plated nickel 200 screens were used for the catalyst bed. Over 250 tests were performed before the final selection of the catalyst bed configuration. The catalyst bed design variables included bed loading, screen material, screen loading configuration, screen plating processes, screen mesh and wire size, catalyst bed head load uniformity, operational characteristics, and the cost of catalyst bed. It was previously reported that pure silver metal was found to be more reactive with hydrogen peroxide than silver metal which had been either tarnished or treated with $\text{Sm}(\text{NO}_3)_3$. In the tests at Kaiser Marquardt, the $\text{Sm}(\text{NO}_3)_3$ -treated silver-plated screens afforded a “catalyst” that was not reproducible in activity towards H_2O_2 . The results of the tests with 85% H_2O_2 agreed with previously reported findings. In order to maintain high decomposition efficiency, the silver screens were not coated with samarium oxide in the Upper Stage Flight Experiment H_2O_2 /JP-8 engine catalyst bed development program.

It was noted that pretreatment with hydrogen peroxide promotes the initial catalytic activity of the silver screen catalyst plated on nickel screen [554]. The results indicated that the initial activity and the startup performance of the catalyst were greatly improved by the pretreatment with 90% HTP. Scanning electron microscopy and X-ray photoelectron spectroscopy results showed that fissures and active species of Ag_2O appeared on the silver screen surface after the pretreatment. These are probably the main reasons for the improvement of the catalyst activity.

Silver Plated on a Copper Screen

A catalyst bed made from copper screen that was coated with silver by flame spraying and then anodized in an alkaline carbonate bath and then ammoniated in an ammonia bath in which silver oxide has been dissolved is described in [555–558]. Catalyst supports in which the catalyst is metallic silver are anodized in a bath of sodium carbonate solution until a full block anodized film is obtained on the silver, and then ammoniated by immersion in 25% ammonia solution for at least 2 h. The catalyst supports may be pellets consisting predominantly of sintered silver (e.g., 93% silver, 7% copper); or pure nickel or stainless steel provided with a nickel surface flash, overlaid with copper and finally coated with silver. The anodizing can be carried out in the range 20 A/sq. ft. for 3 min to 11 A/sq. ft. for 3 h. Instead of plating silver on a copper screen, one can also mix silver powder with copper powder and press and sinter them into pellets [559]. The pellets are then anodized and ammoniated, similarly to the method proposed for the treatment of screens.

Silver Plated on a Stainless Steel Screen

Silver cannot be electroplated on stainless steel without a primer flash of gold and/or copper.

Instead of electroplating or flame spraying silver onto stainless steel wire mesh, it was attempted to sinter a dip coat of silver powder, ceramic oxides, and various binders onto stainless steel wire mesh [560, 561]. This catalyst was intended for sustained decomposition of 90% HTP or even 98% HTP. A basic catalyst formulation consisted of a mixture of silver powder, manganese(IV) dioxide, and aluminum oxide. A suspension of the powders in oil and slow drying lacquers, the catalyst mixture was applied as a coating on stainless steel screen, dried, and calcined. It was found that adding gold to the basic catalyst improved the activity up to a maximum for a gold concentration of about 2.5%. Adding glass powder to the formulation improved the adherence of the coating. Catalyst activity declined with increasing sintering temperatures. However, even for a sintering temperature of 1339 K (1950 °F), the catalyst gave a decomposition rate 33% higher than that of conventional silver-plated stainless screen catalysts. Substituting samarium oxide for part of the aluminum oxide in the basic formulation eliminated the need for final activation. Using 40 to 60% of samarium oxide in place of aluminum oxide improved activity and the adherence of the coating.

Silver Plated on a Brass Screen

The steam generator used to drive a turbine that drove the propellants pumps on the X-15 supersonic research plane used silver-plated brass screens. There were problems with the silver plating delaminating from the brass base and propellant channeling through the bed [562, 563].

Silver Alloy Catalysts

This section deals only with all-metallic silver alloys as catalysts. Alloyed supported catalysts are discussed in a different section. Silver-gold and silver-platinum alloys were found to have a higher activity than silver metal, samarium nitrate-treated silver, or silver-silica cermets. The enhancement of silver catalytic activity by gold is offset by the ability of gold to alloy with silver. The use of smaller proportions of gold makes it possible to prepare a catalyst having a continuous phase of silver flocked with Ag-Au alloy. A mixture containing 10.7% Au was pressed into a pellet and examined under a microscope. Distinct areas of two different materials were observed. Heating to 1273 K (1000 °C) did not alter the structure. Catalytic activity toward 87% H_2O_2 was high and remained high. A higher concentration of gold tended to form continuous phase alloys with lower activity. A silver/platinum catalyst gave extremely high activity, which, however, dropped markedly after heating the catalyst to 1273 K (1000 °C).

A layered catalyst bed patented in [564] consists of an upstream section with pelletized sintered 95% silver/5% Cu 3-mm diameter pellets and a downstream section with stacked 20-mesh copper screens plated with silver.

Metallic Gold Catalysts

Radiolysis of heavy water in a pressurized water nuclear reactor will produce D_2O_2 , an unwanted contaminant. A study of the heterogeneous catalytic decomposition of both hydrogen peroxides in heavy water showed that the catalytic decomposition of H_2O_2 in H_2O or D_2O_2 dissolved in heavy water (both on the surface of glass in alkaline medium and on metallic gold) is different. The results, compared with those obtained under similar conditions for H_2O_2 in ordinary water, indicated that D_2O_2 was much more stable than ordinary H_2O_2 toward gold catalysts [565].

A study of the catalytic decomposition of acidic H_2O_2 solutions (10^{-4} to 10^{-1} M) in the presence of gold showed that in H_2SO_4 solution gold is not active [531]. Silver-gold alloys are among the most active catalysts for HTP decomposition that have been reported [566].

4.10.2.6 Platinum Group Metal Wire Mesh Screens and Foils

Defect sites in crystal lattices are better catalysts than perfectly ordered crystals. The decomposition of dilute solutions of hydrogen peroxide on platinum foils is dependent on the crystalline state of annealed or worked (wrinkled) platinum foils [567]. The first-order reaction rate constant was found to increase with the degree of cold work, and a direct relationship between the catalytic activity of the platinum and its degree of deformation was established. The increase in activity is apparently directly due to deformation since the possible effects of preferred orientation and increased surface area proved to be negligible.

The catalytic decomposition of dilute aqueous solutions of hydrogen peroxide has been studied on several IUPAC Group 8, 9, 10 metals and binary alloys, includ-

ing palladium-gold [568]. This was not done for rocket but for fuel cell applications. The kinetics were measured at 300 K (27°C) as a function of the catalyst composition and pH of the solution. In neutral solutions, the activity of the individual metals of the third period of Group 8, 9, 10 was generally greater than those of the second period, the order of specific activity (per unit surface area) decreasing in the sequence $\text{Pt} > \text{Os} > \text{Ir} > \text{Pd} > \text{Ru} > \text{Rh}$. Alloys of $\text{Pt}\bullet\text{Pd}$, $\text{Pt}\bullet\text{Ru}$, and $\text{Pt}\bullet\text{Rh}$ showed activities intermediate between those of the constituent metals. Alloys of $\text{Pt}\bullet\text{Ir}$ and $\text{Pd}\bullet\text{Au}$ exhibited maximum activities at intermediate alloy compositions. The kinetics depended strongly on the pH of the solutions, the rate rising to a sharp maximum at pH values of 10–11, in accordance with a postulated radical-chain mechanism for the decomposition.

A stacked screen wire mesh catalyst made from annealed nickel wire flame-sprayed with an alloy containing 20–35% Pd and 65–80% Ag and coated with a film of Sm_2O_3 (formed by five consecutive immersions in a 10% $\text{Sm}(\text{NO}_3)_3$ solution and calcination at 811 K (1000°F) for 5-min cycles) was tested in a rocket engine with 98% HTP [569]. The engine had a very short response time, and 90% of p_c was reached within 90 to 40 ms.

4.10.2.7 Nickel and Nickel Alloy Wire Mesh Screens and Porous Pellets

Because all-silver catalyst packs have poor startup capabilities, and the high thermal conductivity of silver allows more heat to soak back to the injector and valve area of thrusters during operation and in particular during heat soakback after shutoff in pulse-mode operation, Russia has placed emphasis on development of catalysts based on nickel and nickel alloys [534]. In order to eliminate the aforementioned drawbacks, a new technology of silver deposition on stainless steel grids with subsequent activation was developed. The catalyst designated as K-86 had good mechanical strength and high specific activity; however, due to its grid form the specific surface of the given catalyst inside bed was low. In contrast, the specific surface and the activity of catalysts based on porous metal materials impregnated with potassium permanganate (designated K-87) were much higher. Catalyst K-87 had high activity and a long operating life. It was made from porous nickel tablets impregnated with the potassium permanganate. The catalyst was available as 4–5-mm tablets, and the porosity of catalyst bed ranged from 40 to 50%. Catalyst K-87 enabled the start of catalyst beds at temperatures down to 233 K (–40°C).

4.10.2.8 Supported Metal Catalysts

In analogy to supported metal catalysts used for the decomposition of hydrazine as a monopropellant, supported metal catalysts are equally effective for the decomposition of hydrogen peroxide, but very sensitive to poisoning by stabilizers commonly added to HTP.

Supported Platinum Group Metal (PGM) Catalysts

Ruthenium in the form of ammonium ruthenium(III) chloride, as a coating on alumina pellets or on nickel wire mesh, as ruthenium(III) chloride solution, or as a metallic sponge was patented as a catalyst for H_2O_2 decomposition [570]. The same palladium catalyst that allows the direct synthesis of H_2O_2 from its elements will also cause decomposition of H_2O_2 [122].

The activity of various catalysts for the decomposition of hydrogen peroxide was studied with platinum supported on silica or silver, iridium, platinum/tin or manganese oxides supported on alumina [571]. The activity was measured using two different reactors: **(1)** a conventional constant pressure reactor for the determination of the gas evolution versus time using diluted H_2O_2 solutions and **(2)** a constant volume reactor to measure the pressure increase using more concentrated solutions. The first reactor allows the determination of the kinetic order of the reaction, a comparison of the activities of the different samples, and the characterization of the potentially poisoning influence of some stabilizers of H_2O_2 solutions on the catalytic activity. Two kinetic orders were found, depending on the catalyst: a zero order and a first order. The shape of the catalysts' samples is an important parameter, with powders always being more reactive than grains and pellets. The catalyst activities are listed here in the order of increasing activity: $(\text{Pt} + \text{Sn})/\text{Al}_2\text{O}_3 < \text{Ir}/\text{Al}_2\text{O}_3 < \text{Pt}/\text{SiO}_2 < \text{MnO}_x/\text{Al}_2\text{O}_3 < \text{Ag}/\text{Al}_2\text{O}_3$. The presence of a pyrophosphate stabilizer led to a loss of activity, mainly as a result of passivation in the case of MnO_x -supported samples, whereas the presence of stannate slightly increased the activity of silver/alumina and exerted no influence on the manganese oxide catalyst samples.

Two supported platinum on spherical γ -alumina catalysts were tested in a heavy-duty flanged reactor with 70 and 87.5% HTP [572, 573]. The reactor was intended as the prototype for a 5-N thruster with 8 mm ID and an L/D of 4.0. The SASOL 06/170 γ -alumina spheres had a diameter of 0.6 mm, a surface area of $170 \text{ m}^2/\text{g}$, and a pore volume of 0.53 mL/g . The two catalysts, LR-57 and LR-59, differed in the way the active metal was deposited. Based on SEM-EDAX measurements, the active metal loading on the surface was about 0.4 atom-% Pt. In the test with 70% HTP, the bed loading was $76.6 \text{ kg m}^{-2} \text{ s}^{-1}$, and the chamber pressure was 0.6 MPa. After only 80 s of runtime, the pressure drop with the LR-59 catalyst increased dramatically due to catalyst breakup. With the 87.5% HTP, the LR-59 pressure drop increased after only 15 s and the test had to be terminated. The performance of the LR-57 catalyst bed was a little better than that of the LR-59 catalyst but it only accumulated 20 s before the pressure drop became prohibitive due to catalyst breakup. These brief run times are several orders of magnitude shorter than what is required in the real world of space propulsion.

The activity of platinum deposited on silicon carbide refractory foam, vitreous carbon open-celled foam, or cordierite ceramic honeycombs with 400 cells per square inch was tested with 30% H_2O_2 solutions [529].

In the wake of premature breakup of γ -alumina catalyst spheres in the LR-57 and LR-59 catalysts, a structural model of the thermal transient and the associated ther-

mal stresses in rapidly heated catalyst pellets was supposed to help in the selection of alternate catalyst carriers resulting in a new Pt/Al₂O₃ catalyst (LR-III-127) [574]. In addition to α -alumina (corundum), cordierite, zirconia, and silicon carbide (carborundum) has been evaluated as catalyst carrier. The pellet breakup problem was solved by using smaller (100 μ m α -alumina granules instead of 600 μ m γ -alumina spheres) and higher stress resistance supports. The LR-III-127 catalyst lasted longer, but only at the expense of increased pressure drop through the catalyst bed as a result of the reduced size of the granules. Progressive occlusion of the catalyst bed due to fragmentation was effectively eliminated.

In South Korea a platinum deposited on alumina catalyst was developed and tested it in 1-N and 50-N thrusters for a microsatellite and upper stage RCS [575, 576]. The catalyst was prepared from γ -type bimodal alumina 1/16-in. pellets from Alfa Aesar that had a surface area of 255 m²/g, total pore volume of 1.14 cm³/g, and median pore sizes of 70 μ m and 5000 Å (bimodal type). The catalyst was impregnated with H₂PtCl₆ solution as a precursor, using the incipient wetness method. Each impregnation was followed by drying (363 K = 90 °C for 12 h), calcination (573 K = 300 °C for 4 h), and H₂/N₂ reduction (573 K = 300 °C for 4 h). The catalyst coating process was done twice to increase the total mass fraction of loaded platinum. After completion of the coating, 23 mass-% of active metal was deposited on the support. The maximum catalyst capacity, which was defined as allowable propellant mass flow rate divided by the volume of the catalyst bed, was 1.27 g s⁻¹ cm⁻³.

Similar 3% Pt/Al₂O₃ catalysts were tested in a small flanged reactor [577]. The best performance was shown for a 30–40 mesh catalyst when the H₂PtCl₆ precursor was dissolved in DI water instead of acetone. The best pH for impregnation was 2.6.

Platinum catalysts initially intended for decomposition of hydroxylammonium nitrate (HAN)-based monopropellants would be equally useful for decomposition of hydrogen peroxide: Spherical granule supports from silica-doped alumina with an average diameter of 1.5 mm were prepared using two procedures starting from the same sol-gel Si-doped boehmite by dripping it into an oil bath, calcining the solidified droplets at 1473 K (1200 °C) and impregnating them with platinum by an incipient wetness procedure, drying at 393 K (120 °C), and H₂-reduction at 673 K (400 °C) [578].

Platinum-based catalysts supported on γ -alumina (grains and pellets) were evaluated using two laboratory scale reactors [579]. The catalysts were characterized by XRD, SEM, and elemental analysis before and after exposure to hydrogen peroxide. Two main parameters were studied: internal (pellets and grains) and external (grains size) surface diffusion. The characterization results of all prepared catalysts showed a homogeneous distribution of platinum particles (average size 1.6 nm) on the support surface. The kinetic study of the catalytic decomposition reaction of dilute H₂O₂ (2 mass-%) showed that decomposition on all platinum-based catalysts followed a first-order kinetic decomposition reaction. Moreover, the granular shape catalysts showed much higher activity than the pellet catalysts leading to a rapid decomposition of H₂O₂. It was shown that the grain size of the catalysts has a strong

influence on the reaction rate of decomposition reaction. For an equivalent amount of catalyst, the external surface increases when the grain size of the catalysts decreases, which leads to a higher catalytic activity.

Comparing a 0.5% platinum on alumina pellets and silver gauze catalyst in a thruster operating with 87.5 mass-% HTP led to the conclusion that the 0.5% platinum pellets had a higher performance, achieving a steady-state decomposition efficiency of 95.4%, with neither catalyst showing signs of exhaustion after several minutes of operation [580]. A commercially available catalyst consisting of 5% platinum on alumina pellets was used for the development of a 20-N thruster [581]; see also [582]. All later tests used commercially procured 5% platinum on alumina pellets.

Nafion is a conductive polymer and has a low melting point. It is not suitable as a catalyst carrier for rockets but has been used for laboratory studies. Pt-Pd aggregated nanoparticles were immobilized on a Nafion-117 membrane to decompose hydrogen peroxide in 0.1-M solutions [583, 584]. The Pt or Pd particles by themselves decomposed hydrogen peroxide only at an insignificant rate, but a bimetallic Pt-Pd catalyst caused steady decomposition at an appreciable rate at room temperature. It remains to be seen if this works also with more concentrated hydrogen peroxide solutions.

Supported Silver Catalysts

After all the success with silver screens for decomposition of hydrogen peroxide in rocket engines, one wonders why not more work has been done with supported silver catalysts. Why should one carry around all the silver buried deep in the core of the silver wires that never gets to see any hydrogen peroxide? Of course, with the conventional silver screens, there is substantial silver loss, and a thin silver coating on the surface of a ceramic catalyst carrier would be lost in a hurry.

Supported silver catalysts were studied many decades ago but did not find any practical applications [585].

Two types of supported catalysts were prepared and compared to silver gauzes reacting with Propulse 89 mass-% H_2O_2 stabilized with 0.1 mg/L phosphate and 4.4 mg/L tin [586]. Discs of silver gauze with a wire diameter of 0.2 mm were stamped out from a sheet, and a known number of discs were compressed into a reactor chamber (12.5 mm D $\times$ 20 mm L), 60 to 100 gauzes weighing about 9 g with a specific surface area of about 40 cm²/g. Alumina-supported silver catalysts were prepared by impregnating alumina carrier with silver nitrate AgNO_3 solution by the incipient wetness method. The support was previously treated in air at 873 K (600 °C) for 5 h and reduced at 573 K (300 °C) for 1 h. Two supports were used: (1) alumina provided by Snecma, spheres 1.2–1.6 mm, BET surface area 250 m²/g; (2) Alcoa alumina, spheres 1.4–2.8 mm, BET surface area 170 m²/g. The active metal loading level in silver was in the range from 5 to 60 mass-%. The supported silver catalyst was compared to a silver screen and a manganese oxide supported on Snecma alumina catalyst containing 10 mass-% Mn. Testing in a rocket engine at sea level was done with

flow rates of 5 g/s. The silver screen catalyst had to be preheated to 373 to 473 K to achieve a startup. If the silver screen catalyst was not preheated, the 89% HTP would shoot right through undecomposed, and the temperature went up by only 100 °C. The 5 or 10% Ag supported catalyst could be started at 293 K and sustained HTP decomposition repeatedly. Increasing the Ag loading beyond 10% Ag did not improve the activity but resulted in less active catalysts. The 5% Ag catalyst was similar to the 10% Ag catalyst. Post-test catalysts removed from the reactor were examined by XRD and TEM. Additional comparative tests were done in a constant volume batch reactor with 30% H_2O_2 . Nanosilver can be deposited on a silica carrier to obtain active HTP decomposition catalysts [587].

4.10.2.9 Metal Oxide Catalysts for Hydrogen Peroxide Decomposition

Metal oxide catalysts can be either simple (binary) oxides of the M_xO_y type or ternary of the type $\text{A}_x\text{B}_y\text{O}_z$, or even multiple mixed oxides of the type $\text{A}_w\text{B}_x\text{C}_y\text{O}_z$. They can be used by themselves (if the powder form they usually start with can be shaped to form erosion-resistant granules for a packed-bed reactor) or deposited onto a catalyst carrier that has the required physical shape and mechanical strength. These metal oxide materials are typically obtained in the form of powders and ceramic processing methods must be used to obtain usable catalyst shapes. The powders can be shaped by fusion, pressing, extruding, sintering, mixing with a ceramic binder and extruding, or by deposition from a slurry onto granular, spherular, or monolithic catalyst carriers.

Many of the metal oxide catalysts described in this section were intended not so much as catalysts for a rocket engine than as catalysts in catalytic oxidation of organic compounds and waste products. Some of the experience gained with those applications will benefit the use of metal oxide catalysts in H_2O_2 monopropellant rocket engines. Unfortunately, several of the publications referenced here describe only work with relatively dilute solutions of hydrogen peroxide, and one will have to extrapolate to higher concentrations that are of interest to a rocket propellant chemist. Reactions in more dilute solutions are of interest for wastewater treatment of test facility rinse waters containing small amounts of H_2O_2 .

Binary Metal Oxides as Hydrogen Peroxide Decomposition Catalysts

Ceramic materials for HTP decomposition have advantages over traditional silver/stainless steel catalysts for their lower weight and better thermal and chemical resistance. Among them, manganese oxides deposited on different supports, such as titania, zirconia, alumina, silica, or cordierite monolith honeycombs, have been a popular choice.

Many transition metal oxides have catalytic activity in the decomposition of H_2O_2 . If they are deposited and supported on catalyst carriers, they can be applied in the form of aqueous solutions of their nitrates as precursors, which are then calcined to convert the soluble nitrates into their insoluble oxides [588]. Because of their high catalytic activity in the decomposition of hydrogen peroxide, oxides of variable multiva-

lence elements are used as promoters in oxygen electrodes of fuel cells and in the treatment of wastewater by oxidation with oxygen and peroxide and could, thus, also be useful as catalysts in monopropellant rockets and gas generators. It has been shown that when hydrogen peroxide acts on solid oxides forming redox systems, a change in the ratio of valence states of the element occurs, leading to changes of chemical composition on the surface and activity of the catalysts.

The vapor-phase decomposition of hydrogen peroxide was studied in a flow system on a wide range of metallic oxide surfaces in the range 311–457 K (38–184 °C) using nitrogen as the carrier gas and H_2O_2 partial pressures up to 1 mm [589]. Oxide surfaces were held on vacuum-flashed metal films, metal strips, or as compressed tablets of the bulk oxide. The activity series, in order of decreasing activity was $\text{Mn}_2\text{O}_3 > \text{PbO} > \text{Ag}_2\text{O} > \text{CoO/Co}_2\text{O}_3 > \text{Cu}_2\text{O} > \text{green NiO} > \text{CuO} > \text{Fe}_2\text{O}_3 > \text{CdO} > \text{ZnO} = \text{MgO} > \text{SnO}_2 > \text{glass (Pyrex}^\circledast\text{)}$. The activity of these oxides may be related to the defect site's density and type and promoting electron mobility.

A study of the decomposition of H_2O_2 on some metal oxide catalysts showed that any oxide of the element that may form a redox system involving two different oxidation states of the element and having a higher standard potential (reduction) E_0 than the corresponding value E'_0 of the system $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}_2$ is a good catalyst, and oxides having potential E_0 lower than E'_0 are poor catalysts [590].

The kinetics of 0.2-M H_2O_2 decomposition were investigated using ZrO_2 impregnated with transition metal ions (not oxides) by simple immersion in 10^{-3} M solutions of transition metal sulfates, including Ag(I), Cu(II), Hg(II), Co(II), Mn(II), Fe(III), Ni(II) [591]. The amount (mg) of metal ion per g of air-dried ZrO_2 catalyst for Ag(I), Cu(II), Hg(II), Co(II), Mn(II), Fe(III), Ni(II) was 0.53, 3.56, 0.32, 0.91, 2.51, 0.76, and 1.96, respectively. At pH = 6.8, the reaction rate exhibited a first-order dependence on the initial H_2O_2 concentration at low concentrations. The order of activity of the different catalysts was strongly dependent on the H_2O_2 concentration used. The rate increased with increasing pH and attained a limiting rate at higher pH. At lower H_2O_2 concentrations, before the formation of an inhibitory intermediate, the decreasing order of activity was: Ag(I) > Cu(II) > Hg(II) > Co(II) > Mn(II) > Ni(III) > Fe(III). This order can be correlated with both the amount of the metal ion loaded and its redox potential. Comparing Ag(I) with both Mn(II) and N(II) reveals that the redox potential has a pronounced effect. It would be difficult to extrapolate from this work with low H_2O_2 concentrations to actual catalysts useful for rocket applications.

Some metal oxides may not be catalysts in their own right but may be suitable as catalyst supports. The decomposition of hydrogen peroxide that had formed by radiolysis of water in nuclear reactors or spent fuel rod storage depositories and came in contact with corrosion products was studied to better understand corrosion phenomena due to the inadvertent but unavoidable formation and accumulation of hydrogen peroxide under those conditions. Suspended alumina or zirconia particles, corrosion products from deteriorating nuclear reactor fuel elements, will alter the rates of formation and decomposition of H_2O_2 in water-filled pools where spent fuel rods are in

temporary storage, awaiting reprocessing. The studies included Al_2O_3 nanoparticles [140] or ZrO_2 slurries [141]. The activation energy for the H_2O_2 decomposition reaction on ZrO_2 suspensions was $E_a = 33 \pm 1.0 \text{ kJ/mol}$.

In addition to alumina slurries, the adsorption and decomposition of H_2O_2 on nano- and micrometer-sized particles of other ceramic metal oxides, ZrO_2 , TiO_2 , and Y_2O_3 were characterized by measuring the reaction rate constants, the Arrhenius activation energies, and the activation enthalpies for the processes of adsorption and decomposition of H_2O_2 [142]. The experimentally obtained enthalpies of activation for the decomposition of H_2O_2 catalyzed by these materials were $30 \pm 1 \text{ kJ/mol}$ for ZrO_2 , $34 \pm 1 \text{ kJ/mol}$ for TiO_2 , and $44 \pm 5 \text{ kJ/mol}$ for Y_2O_3 . Other ceramic oxides studied included SiO_2 , Al_2O_3 , TiO_2 , CeO_2 , and ZrO_2 [143]. The activation energy was $42 \pm 5 \text{ kJ/mol}$ for the overall decomposition of H_2O_2 independent of the type of oxide. The oxide type had a strong effect on the preexponential rate term with increasing rate in the order of $\text{SiO}_2 < \text{Al}_2\text{O}_3 < \text{TiO}_2 < \text{CeO}_2 < \text{ZrO}_2$. The rate coefficient for H_2O_2 decomposition increased with increasing surface area of the oxide.

In the following, metals from which oxides were formed are arranged in the sequence of groups of the periodic table of elements (New IUPAC version).

Oxides of Group 3 Elements (Sc, Y, La, Rare Earth)

It is strange that for half a century people have been coating silver screens with samarium oxide, but very little work has been done on the catalytic qualities of Sm_2O_3 by itself without the underlying layer of silver. There is very little information on the mixed oxides formed in the $\text{Ag}_2\text{O}/\text{Sm}_2\text{O}_3$ or $\text{AgO}/\text{Sm}_2\text{O}_3$ system and their catalytic properties for H_2O_2 decomposition.

Oxides of Group 7 Elements (Mn, Re)

Next to silver, manganese oxides of various states of oxidation are the most extensively investigated hydrogen peroxide decomposition catalysts. Experimenters have attempted to shape manganese oxide powders into useful shapes (pellets, bricks, monoliths) or deposit them onto ceramic catalyst carriers of a suitable shape. Manganese-oxide based catalysts prepared by an impregnation procedure that involves the wet impregnation of the ceramic support with an aqueous solution of a suitable manganese precursor have certain disadvantages: The anchorage of the active phase onto the support occurs mainly by physical interactions between precursor and the support surface, or the manganese oxide particles are held within the support pores. This technique does not allow a good control of the chemical composition of the final materials as well as of their chemical homogeneity, especially for formulations with multi-component mixed oxides. Catalysts made this way suffer particle fragmentation, active material solubilization, and spalling off, due to the strong erosive power of the H_2O_2 solution impinging on the catalyst at the high temperature generated from its adiabatic decomposition.

Dissolved manganese(II) ions have no catalytic effect. It is quite likely that the catalytic effect of potassium permanganate is due to the reduction of permanganate ion to a finely divided, colloidal form of MnO_2 or its hydrate, which is the actual catalyst [592]. The composition of manganese(IV) dioxide is rarely truly stoichiometric. It is possible that other valences of Mn play a role in H_2O_2 decomposition. The activity of manganese oxide deposited on alumina was at a maximum when the state of oxidation was between 3 and 4. The catalysis by manganese(IV) dioxide may proceed via a redox cycle where manganese oscillates between the trivalent and tetravalent state. In addition to MnO_2 in its pure form, also naturally occurring pyrolusite mineral has been proposed as a catalyst [593, 594].

There are so many papers on evaluation of manganese oxide catalysts for decomposition of hydrogen peroxide that we could select only a few representative ones and we had to arrange them in chronological order.

The activity of supported manganese oxide catalysts as a function of the concentration of manganese on the support showed an increase with decreasing manganese concentration, followed by a sudden decrease for very low manganese concentrations [595]. It depended on oxidation state, pH, support phase modification, and temperature. The catalysts were made by impregnating γ -alumina with $\text{Mn}(\text{NO}_3)_2$ solution, drying, and calcining at 473 K.

A paste made from a mixture of potassium permanganate, potassium dichromate, lead oxide, a ceramic cement, and water was poured into a mold, cut into 8-mm cubes, and calcined at 1173 K (900 °C) to obtain a hydrogen peroxide decomposition catalyst [596, 597].

Manganese oxides precipitated and supported on $\text{Mg}(\text{OH})_2$ had better catalytic activity in the decomposition of 0.1-M H_2O_2 than coprecipitated mixtures of the hydroxides or catalysts supported on MgO. The use of MgO as a carrier for manganese oxides produced a catalyst with higher activity than that of either oxide by itself [598].

Removal of unwanted residual hydrogen peroxide in aqueous solutions is required in many food processing applications where the processing equipment has been sterilized with hydrogen peroxide to remove bacterial contamination. Sometimes, an enzyme, immobilized catalase, is used for this purpose to decompose hydrogen peroxide in the effluent stream. Manganese(IV) dioxide supported on alumina was a more durable catalyst for this application [599]. Kinetic and deactivation studies were conducted in a tubular flow reactor and indicated a first-order reaction.

Electrode potential measurements showed that the state of oxidation of Mn on the surface of manganese oxides (β - MnO_2 , β - Mn_2O_3 , β - Mn_3O_4 , and MnO) varied markedly in hydrogen peroxide solutions [600]. A rearrangement of the surface layer crystal structure takes place as the potential adjusts shortly after the first immersion. On prolonged treatment with hydrogen peroxide, an identical steady state of the surface is established for all the oxides, which is characterized by the very same electrode potential value. The decomposition of hydrogen peroxide includes stages of catalyst oxidation-reduction and electron transfer.

The kinetic parameters of the decomposition of hydrogen peroxide on manganese oxide(s) were determined in the concentration range 0.03 to 1 N and the temperature range 275 to 315 K (1.5 to 42°C) and pH from pH 2 to 10 [601]. The electrode potentials of the oxides and their catalytic activity change in parallel.

The oxidation state of oxide surfaces brought to the state of stationary catalytic activity by H_2O_2 pretreatment corresponds to the oxidation state of manganese in Mn_3O_4 [602]. The structure of this stationary surface layer differs, however, from that in Mn_3O_4 .

The decomposition of hydrogen peroxide on thin layers of platinum-supported manganese oxides was studied in the stationary and non-stationary regions [603]. The catalytic activities and the electrode potentials of the oxides were measured simultaneously. In the stationary region, the surface's oxidation state and structure were independent of the temperature, the hydrogen peroxide concentration, and of the presence of KCl and Mn^{2+} in the solution.

The catalytic activity of MnO_2 prepared by different methods was determined from the initial rate of decomposition of dilute solutions of H_2O_2 [604]. Experimental evidence showed that the presence of Mn^{3+} as MnOOH in the MnO_2 lattice is mainly responsible for the catalytic activity in non-stoichiometric manganese dioxide, where electron transfer between Mn^{4+} and Mn^{3+} ions can take place. The promoting effect of CuO in MnO_2 -CuO catalysts may be due the formation of surface CuMn_2O_4 through the exchange of Cu^{2+} on the hydrated manganese oxide surface.

Manganese sesquioxides with oxidation states between Mn^{+2} and Mn^{+4} have better catalytic activity than either pure MnO or MnO_2 . Sesquioxides can be prepared by partial reduction of MnO_2 with hydrazine [605].

The catalytic decomposition rates of hydrogen peroxide solutions in contact with 12 different MnO_2 samples followed a similar order to those of the reduction of MnO_2 , also dependent on the rate of proton diffusion in the crystal lattice [606].

The pyrolysis and calcination of ammonium permanganate NH_4MnO_4 gives finely distributed manganese oxide, which is a very active catalyst for the decomposition of H_2O_2 [607]. The catalytic decomposition of H_2O_2 was investigated on various calcination products of NH_4MnO_4 , prepared in the temperature range 423–1023 K (150–750°C). Correlating reaction rates with physicochemical characteristics of the catalysts, it was deduced that the most active sites for the heterogeneous reaction in aqueous solution were those involving a mobile-electron within the Mn^{4+} - Mn^{3+} coupling.

For several decades, manganese dioxide catalysts were prepared by decomposition of potassium permanganate or sodium permanganate or manganese salts of organic, combustible acids deposited on a porous carrier. The interference by sodium or potassium was usually ignored. Thus, it was a significant improvement when a new, much cleaner method for depositing high surface area manganese dioxide by decomposition of permanganic acid was developed [608]. Unsupported and ψ -alumina supported MnO_x catalysts (1–10 mass-% Mn) were prepared from aqueous solutions of HMnO_4 and compared with nitrate based samples. They were

characterized by XRD, X-ray photoelectron spectroscopy (XPS), BET surface area, oxygen storage capacity, and by their catalytic behavior. The unsupported oxide was amorphous at 573 K (300 °C) with a high surface area (45 m²/g) and transformed to α -Mn₂O₃ when heated to below 873 K (600 °C). The supported samples showed high dispersion that correlated well with high catalytic activity and the absence of detectable crystalline phases.

β -manganese dioxide doped with 0.1 M chromium(VI) trioxide was sintered at 523, 773, 1023, and 1273 K (250, 500, 750, and 1000 °C), and the products were characterized by XRD [609]. The catalytic activity of the catalysts for H₂O₂ decomposition was tested in aqueous and alkaline solutions. XRD revealed that the addition of 0.1 M CrO₃ stabilized the β -MnO₂ crystalline form at 773 K (500 °C). The transformation of β -MnO₂ into cubic Mn₂O₃ was detected after heating at 1023 K (750 °C). At 1273 K (1000 °C) a crystalline Mn₃O₄ was produced. The addition of 0.1 M CrO₃ to β -MnO₂ decreased the catalytic activity for H₂O₂ decomposition in aqueous solution. The activity of the mixed catalysts was higher than that of pure β -MnO₂.

Unsupported and alumina supported manganese oxide catalysts were evaluated by decomposition of H₂O₂ in dilute aqueous solutions at 303 K (30 °C) [610]. Three precursors were used to prepare the various series of unsupported and supported manganese oxide catalysts: **(1)** manganese(II) nitrate, **(2)** ammonium permanganate NH₄MnO₄, and **(3)** manganese(II) hydroxide obtained by slow addition of Mn(NO₃)₂ solution to aqueous ammonia followed by filtration and drying. In the case of manganese nitrate and ammonium permanganate, the supported catalysts were obtained by impregnation from aqueous solutions of various concentrations. The samples were subsequently dried and then calcined at 423, 573, or 873 K (150, 300, or 600 °C) in air. The catalysts were characterized by differential thermal analysis (DTA), XRD, XPS, BET, temperature-programmed reduction (TPR) under hydrogen, and by their oxygen storage capacity as indicated by their ability to oxidize repetitive pulses of carbon monoxide ("gas titration") at 573 K (300 °C) until the carbon monoxide passed through unchanged. There was a good correlation between H₂O₂ decomposition activity and oxygen storage capacity. The most active catalysts were those derived from decomposition of ammonium permanganate after calcination at 573 or 873 K (300 or 600 °C).

The activity of manganese oxide octahedral molecular sieve catalysts doped and undoped with transition metals (Fe, Ni, Cu, Co) were tested with dilute H₂O₂ solutions [611]. These materials were more active than plain MnO₂, but they do not have the temperature resistance required for operation with higher HTP concentrations in rocket engines.

The decomposition activities of a range of Mn₂O₃-based composite catalysts were measured in an attempt to define the surface attributes of the H₂O₂ decomposition activity of manganese oxides [612]. It was shown that the decomposition activity of Mn₂O₃ can be promoted by transition metal oxide additives that are capable of the formation of microcrystallites of mixed or composite oxide phases with the host oxide and exposing them on the surface of intimately coupled ionic species of different

oxidation states. Of particular interest are additives of NiO , BiO_x , and CuO_x , which generate $\text{Mn}^{3+}/\text{Mn}^{4+}$ couples at the surface, as well as $\text{Ni}^{2+}/\text{Ni}^{3+}$ couples in the case of the $\text{Ni}_x\text{Mn}_y\text{O}_3$ catalyst. A reaction mechanism including the hydroperoxide/superoxide anion was proposed. The decomposition of dilute hydrogen peroxide on manganese(III) oxide at pH 7 was represented by a pseudo first-order model. In addition, both H_2O_2 decomposition and the production of anion were accelerated in alkaline solution. Manganese ion dissolved into solution was negligible in neutral and alkaline conditions, but it greatly increased in acidic conditions. These bulk and surface compositions generate the optimal electron availability of the bulk and electron-mobile environment at the surface and facilitate the redox pathway of H_2O_2 decomposition. The activation energy of H_2O_2 decomposition on the nickel-promoted catalyst NiMnO_x was 11.6 kJ/mol, which was much lower than that of manganese oxide alone (77.1 kJ/mol).

One-inch diameter samples of catalyst-coated Celcor monoliths were immersed in hydrogen peroxide with a concentration of <10 mass-% H_2O_2 and allowed to react in a controlled environment to measure their activity [502]. The carrier was coated with KMnO_4 or NaMnO_4 with or without additional KOH or NaOH as promoters from an aqueous solution and calcined at 573 K (300 °C) in air for 8 h, and this cycle was repeated once or twice. The best performing samples were later tested in a 1-in. D $\times$ 5 in. L flanged reactor with HTP. Monolith samples with 11000 cells per square inch (cps) gave much better results than samples with coarse 400 cps. The paper fails to report the HTP concentration used for the reactor tests where a decomposition temperature of 1023 K (750 °C) was achieved, but one must assume that the same HTP as for the single drop tests with a pipet was used (95–98% H_2O_2). The work continued with characterization of additional substrates for the catalytic decomposition of hydrogen peroxide [613].

The application of manganese oxides as catalysts for the adiabatic decomposition of concentrated solutions of H_2O_2 suffers from particle fragmentation, solubilization, and active metal elution due to the strong solvating and erosion power of the H_2O_2 solutions under high-temperature conditions [614].

H_2O_2 decomposition over different manganese oxide-based perovskites ($\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$; Ln = La or Nd and A = K or Sr and $x = 0.0\text{--}0.4$) was measured [615]. XRD and XPS analyses showed the presence of the single crystalline perovskite phases with an enrichment of the surface with potassium for the $\text{Ln}_{1-x}\text{K}_x\text{MnO}_3$ samples. δ -oxygen non-stoichiometries of the perovskites were studied by chemical analyses, temperature programmed reduction (TPR), and oxygen desorption (TPD) experiments. The results suggested that the catalytic H_2O_2 decomposition over these perovskites is not determined by the surface K, Ln, and Mn concentration nor by the $\text{Mn}^{4+}/\text{Mn}^{3+}$ surface ratio. On the other hand, a good correlation between the catalytic H_2O_2 decomposition and the δ -oxygen non-stoichiometries was found, especially for La perovskites. A suprafacial mechanism was suggested, where the oxygen vacancies participate in the H_2O_2 decomposition.

A series of manganese oxides loaded on to an active alumina support was prepared by impregnation methods, and the kinetics of H_2O_2 decomposition in an aqueous medium were studied in the presence of these oxides [616]. The amount of manganese, expressed as Mn_2O_3 , varied between 3.7 and 55.3 mass-%. The catalytic activities increased initially as the amount of manganese present increased, attaining a maximum value at 13.4 mass-% Mn_2O_3 and then decreased again. The apparent activation energy for H_2O_2 decomposition conducted over these catalysts was unaffected by a change in the amount of manganese present. Doping with lithium did not improve the activity for decomposition of H_2O_2 but accelerated the sintering and loss of surface area [617]. The catalytic activities and the values of BET surface area of pure and doped mixed oxides were found to decrease by increasing the amount of Li_2O present. It is common practice to prepare supported manganese oxide catalysts by impregnating carriers with permanganates and then decompose them [618].

A doping with Zn ions was found to improve the activity of $\text{MnO}/\text{Al}_2\text{O}_3$ calcined at 873 K [619]. The catalytic activities of the pure and doped mixed solids increased with increasing the reaction temperature and calcination temperature up to 873 K (600 °C), whereas no measurable activity was observed for catalysts calcined at 1273 K.

The effect of ferric and manganese oxide dopants on thermal and physicochemical properties of Mn-oxides/ Al_2O_3 and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ systems was studied [620]. The pure and doped mixed solids were prepared by an impregnation method, then thermally treated at 673–1273 K (400–1000 °C). Pyrolysis of pure and doped mixed solids was investigated via TGA and differential thermogravimetry (DTG) techniques. The products were characterized by XRD. The catalytic behavior of the thermal products was tested using the decomposition of H_2O_2 reaction. The activity of manganese oxide catalysts can be increased by doping with aliovalent metals, essentially creating ternary oxides, perovskite-like compositions. Iron(III) ion additives were found to promote the H_2O_2 decomposition activity of $\text{Mn}_2\text{O}_3/\text{Al}_2\text{O}_3$ up to a certain loading level, whereas Mn^{3+} ion additives to $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ continued to progressively increase the activity with the loading level.

Doping with La^{3+} ions has been found to increase the activity of $\text{MnO}/\text{Al}_2\text{O}_3$ or $\text{NiO}/\text{Al}_2\text{O}_3$ in proportion to the amount of dopant [621]. The effects of doping of Al_2O_3 -supported nickel and manganese oxides with La_2O_3 on their surface and catalytic properties were investigated using the oxidation of CO by O_2 at 423–473 K (150–200 °C), and the decomposition of H_2O_2 at 303–353 K (30–50 °C). The dopant concentration was varied between 1.0 and 6.0 mol-%. La_2O_3 -doping of alumina-supported metal oxides increased their catalytic activities towards CO-oxidation by O_2 and H_2O_2 decomposition to an extent proportional to the amount of dopant added. The doping process did not modify the activation energy of the catalyzed reaction but increased the concentration of catalytically active constituents taking part in the catalytic processes without changing their energetic nature.

Catalysts containing 2, 5, 7, or 10 mass-% MnO_2 supported on TiO_2 were prepared by impregnation of a high surface area TiO_2 with $\text{Mn}(\text{CH}_3\text{COO})_2 \times 4\text{H}_2\text{O}$ solutions and

examined for H_2O_2 decomposition activity [622, 623]. Samples were calcined at 773 K (500 °C) in air. XRD, SEM micrographs, and BET surface area measurements gave evidence of a uniform distribution of the active phase on the support surface and of the absence of segregated manganese oxide phases. Temperature programmed reduction measurements showed the presence of different Mn oxides species formed by interaction between the active phase and the support surface, besides MnO_2 . Catalytic activity tests were performed in a batch reactor with 50 or 70 mass-% H_2O_2 solutions. Catalytic activity was very high at the beginning of the tests and decreased with time, reaching a final constant value that increased with manganese content. Kinetic constants, evaluated assuming a first-order reaction rate, were comparable or higher than those of similar unsupported manganese-based catalysts. An optimal MnO_2 content was found, corresponding to the quite complete surface monolayer coverage.

Additional catalysts were prepared by deposition of 5–10% MnO_2 on partially stabilized ZrO_2 and totally stabilized ZrO_2 , commercial cordierite monolithic samples and tested for activity with 60% H_2O_2 [624]. The zirconia was stabilized with a mixture of MgO , CaO , and Y_2O_3 . Off-the-shelf Mn_2O_3 powder (30 m^2/g) showed negligible activity, while MnO_2 powder (53 m^2/g) showed high activity, suggesting that the catalytic H_2O_2 decomposition mechanism depends on the availability of Mn^{4+} ions at the surface. The kinetic rate constant of MnO_2 powder was an order of magnitude higher than that of supported MnO_2 . Catalytic activity increased with increasing Mn content; see also [625].

A new preparation method has been developed to produce homogeneous coatings of manganese compounds on alumina-coated monoliths by redox deposition-precipitation using acetone as solvent [626]. The deposition is produced by reduction of manganese(II) permanganate with ethanol. The Lewis acid sites on the alumina catalyze this reaction. Thus, the precipitation preferentially takes place on the surface of the monolith and not in the bulk of the solution. Monoliths prepared by this method are very active for the decomposition of H_2O_2 and the complete oxidation of oxygenated volatile organic compounds (VOCs). The active material on these monoliths consists of a mixture of complex phases including aluminum oxide, sulfated alumina, potassium sulfate, and manganese oxide.

Up to now, the development of catalysts for H_2O_2 decomposition has been a strictly empirical effort [as is (was) the development of any catalyst, which until recently was considered a “black art”]. Based on the observations of the activity of manganese oxides in the decomposition of H_2O_2 , theories have been proposed trying to explain the mechanism that takes place on the surface of metal oxide catalysts. A good summary of such theoretical approaches is provided in [627].

Two different catalysts have been prepared, characterized, and evaluated for the catalytic decomposition of 70% H_2O_2 for ignition of a bipropellant rocket engine using ethanol as the fuel [628, 629]. The catalyst substrate was a commercial mullite ceramic in the shape of honeycomb monoliths. Three different washcoating procedures were compared with the aim to allow a good anchorage of the active phase precursors: sil-

ver nitrate or sodium permanganate. For the silver catalysts, XRD indicated the presence of mullite, corundum, and metallic silver phases. After firing, a loss of silver was evidenced as well as the formation of silver oxide, depending on the washcoating procedure. Manganese oxide-based samples exhibited a better activity than silver-based catalysts and could survive the endurance test of 100 min in a rocket engine.

The decomposition of hydrogen peroxide on manganese(IV) oxide at pH 7 can be represented by a pseudo first-order model [594]. The maximum value of the observed first-order rates constant (k_{obs}) was 0.741 min^{-1} at a $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$ ratio of 11.8. The average pseudo first-order rate constant ($k \text{ MnO}_2$) was $0.025 (\text{min mM})^{-1}$ when $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$ ranged from 39.2 to 11.8. When $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$ was 3.92, the rate constant ($k \text{ MnO}_2$) was $0.061 (\text{min mM})^{-1}$ at its maximum. Oxygen production showed that the initial rates increased with decreasing $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$, and the actual amount of oxygen was slightly less than the theoretical stoichiometric value (0.5) in most experiments. The mechanism most likely includes propagation reactions with intermediates such as hydroperoxide/superoxide anions in solution. Both H_2O_2 decomposition and the production of anions were accelerated in alkaline solution.

Highly ordered mesoporous $\alpha\text{-Mn}_2\text{O}_3$ with well-defined mesopores, high surface area, and high oxygen vacancy exhibited excellent catalytic activity toward H_2O_2 decomposition at low temperatures [630].

The effect of catalyst support on the performance of monopropellant thrusters was investigated using three different support materials (monolith honeycombs, 1/8-in. alumina pellets and 16–20 mesh alumina granules) [631]. A reference catalyst ($\text{Na}_{0.2}\text{MnO}_2$) was coated on both catalyst supports and reacted with 90 mass-% hydrogen peroxide. Alumina sol was prepared from commercial alumina (Disperal® P2 by Sasol Company). The washcoat layer was dried and calcined ($393 \text{ K} = 120^\circ\text{C}$, 1 h and $773 \text{ K} = 500^\circ\text{C}$, 2 h) after it was coated on the monolith support. The washcoat layer had $260 \text{ m}^2/\text{g}$ specific surface area, $0.47 \text{ cm}^3/\text{g}$ pore volume, and 6.9 nm average pore size after calcination. The washcoated monolith support was loaded with $\text{Na}_{0.2}\text{MnO}_2$ by wet impregnation using NaMnO_4 solution as the precursor. The support was then dried ($323 \text{ K} = 50^\circ\text{C}$, 24 h) and calcined ($773 \text{ K} = 500^\circ\text{C}$, 2 h). The sodium ions were washed out with water, and the catalyst-loaded monolith was finally calcined ($1023 \text{ K} = 750^\circ\text{C}$, 2 h). The procedure for activating the pellet catalyst carrier was identical to that used for the monolith bed in all steps, except that it did not involve the washcoating step. The performance of two thrusters of different sizes with each thruster using either monolith honeycomb or alumina pellets as the catalyst bed was evaluated by measuring the product-gas temperature at the downstream end of the catalyst bed and the pressure of the gas at the inlet and outlet of the catalyst bed with constant propellant feed pressure. Under the given test conditions, the performance of the thrusters was better when using alumina pellets as the catalyst support than when using monolith honeycombs. Since the monolith support was less reactive than the pellets, pressure buildup in the former case was relatively small. Consequently, the chamber pressure and temperature were

lower when using the monolith support than when using the pelletized support. The pressure drop across the catalyst bed was moderate in both cases (0.02–0.1 bar in the case of a monolith and 0.3–0.7 bar in the case of a pellet catalyst).

A lead-promoted $\text{MnO}_2/\text{Al}_2\text{O}_3$ catalyst was more active with 90% HTP and less prone to chugging than a lead-free $\text{MnO}_2/\text{Al}_2\text{O}_3$ catalyst when tested in three reactors with different aspect ratios [632]. Al_2O_3 pellets of 1/8 in. (Alfa Aesar) with a BET surface of $255 \text{ m}^2/\text{g}$ were crushed, sifted to 10–16 mesh (1.18–2.0 mm) and 16–20 mesh (0.85–1.18 mm), and soaked with NaMnO_4 and $\text{Pb}(\text{NO}_3)_2$ solutions as precursor for MnO_2 and PbO , respectively, so that the atomic ratio of $\text{Mn}:\text{Pb}$ was 1:1. The catalyst was dried (95°C for 12 h) and calcined ($773 \text{ K} = 500^\circ\text{C}$ for 4 h). After calcination, the catalyst was washed with water to remove Na ions and impurities and dried ($368 \text{ K} = 95^\circ\text{C}$ for 12 h) again.

Manganese oxide coated monolithic catalysts were tested first with H_2O_2 vapor in the laboratory in a plug-flow reactor and then in a bolt-up flanged reactor on the rocket test stand [633]. The catalyst active phase was deposited on yttria-stabilized zirconia supports by: (a) soaking the support in manganese acetate $(\text{CH}_3\text{COO})_2\text{Mn}\cdot 4\text{H}_2\text{O}$ solution with vacuum impregnation, (b) drying, and (c) calcination. These steps can be repeated, typically five times. Whatever the specific preparation procedure, no wash-coat layer, traditionally used to increase the catalyst surface area, was applied in this study. Two different support configurations were tested: **(1)** tubes with an ID of 6 mm, an OD of 14 mm, and two different lengths (30 or 60 mm); and **(2)** honeycombs, with an OD of 13 mm, a cell density of 400 cells per square inch, and two different lengths (30 or 60 mm). A plug-flow reactor that carried H_2O_2 vapor in a helium stream was used to evaluate different catalysts. For this test, hydrogen peroxide (Propulse™ 875, nominal concentration 87.5 mass-%) was diluted to 50 mass-% and fed to the evaporator/reactor through a pump. The Pyrex® glass reactor can be divided into three zones:

- The preheating zone (135 mm L $\times$ 6 mm D) allows full vaporization of the solution, which mixes with helium.
- The catalytic zone (80 mm L $\times$ 19 mm D) has a larger diameter to allow catalyst insertion.
- The reaction products zone (175 mm L $\times$ 6 mm D).

At the exit of the reactor there was a condenser, to capture water vapor and any undecomposed hydrogen peroxide. The stream of helium and oxygen was then fed to a thermoconductivity detector to measure the hydrogen peroxide conversion. The best performing catalysts were then tested in a flanged heavy-duty stainless-steel reactor. The injection plate was made by laser-drilling 270 cylindrical holes of 0.1-mm diameter each. The bed length could be varied by choosing different cylindrical sections, 30 or 60 mm long. The reactor operated at flow rates of 6 to 10 g/s, and the chamber pressure was 0.3–0.6 MPa (3–6 bar). c^* efficiency decreased rapidly as soon as flow rates approached 7 g/s, indicating beginning flooding. While flooding is very detrimental for monopropellant thrusters, it may be tolerable for a reactor that is intended as an

igniter for a hybrid motor (as long as the decomposition products are hot enough to ignite the fuel).

Manganese-yttrium-zirconium mixed oxide nanocomposites with three different Mn loadings (5, 15, and 30 mass-%) were prepared by sol-gel synthesis and tested as catalysts for H_2O_2 decomposition in the liquid phase [634]. Their catalytic activity was higher than that of previously studied Mn/Zr oxide systems prepared by impregnation with manganese salts. Mesoporous materials with high surface area values (70–100 m^2/g) were obtained by annealing in air at 823 K (550 °C). They were amorphous or contained nanocrystals of the tetragonal ZrO_2 phase (T- ZrO_2) depending on the Mn amount and exhibited Mn species with oxidation state higher than 2 as confirmed by temperature-programmed reduction under hydrogen. The decrease of catalytic activity with time was blamed on leaching of a limited fraction (up to 15%) of Mn into the $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ solution.

Hydrogen peroxide monopropellant thrusters with manganese dioxide catalyst require preheating the catalyst bed for efficient operation in a space environment. Preheating requirements of 90 mass-% hydrogen peroxide in a monopropellant thruster with manganese dioxide catalyst were tested in a 50-N vacuum thrust class monopropellant thruster [635]. The preheating temperature was increased from 323 to 523 K (50 °C to 250 °C) in increments of 50 °C, and a test in cold start was included as a control group. The results indicate that a significant improvement in pressure rise time and avoidance of pressure instability was observed until the preheating temperature reached 423 K (150 °C). However, there were no noteworthy improvements when further increasing the preheating temperature beyond 423 K (150 °C).

Oxides of Group 8 Elements (Fe, Ru, Os)

Rust is present everywhere, and it is an active catalyst for decomposition of hydrogen peroxide, often in unwanted situations where rust-catalyzed decomposition may lead to accidents.

Iron(III) oxide catalysts are used for many industrial processes, and it helps to better understand the mechanisms that determine Fe_2O_3 catalyst activity and selectivity for those reactions. The decomposition of hydrogen peroxide is a very simple reaction (compared to some of the industrial multi-component reacting mixtures), and it has been used as a model reaction to study Fe_2O_3 catalysts. Although various shapes of Fe_2O_3 (and Fe_3O_4) catalysts are commercially available, there is little information about their use as catalysts in H_2O_2 monopropellant rocket engines.

The Fenton-type Fe(II) ion catalyzed reaction of hydrogen peroxide that is used for wastewater treatment requires acidic pH and Fe in a soluble form. It is generally accepted that lower pH values (2–4) are favorable for classical Fenton-like reactions performed with soluble Fe(II) homogeneous catalysts, yet two disadvantages accompanying the reactions are the acidic environment itself and the necessary separation of the dissolved iron from the reactive solution after process completion. For environ-

mental cleanup applications it would be desirable to develop an Fe-catalyst that operates near neutral pH and is heterogeneous, so that it will settle in a settling pond and can be reused after the cleanup is complete, and all organics are destroyed. With heterogeneous iron catalysts, the acidic environment should be avoided because leaching of iron oxides can cause a loss in catalytic activity. The highest rate constants so far achieved for iron oxides were reported for poorly ordered ferrihydrite and porous goethite (α -FeOOH) [636].

A comparative study of the catalytic efficiency in the decomposition reaction of hydrogen peroxide using different iron(III) oxides showed that the highest activity was achieved with amorphous ferrihydrite possessing the largest surface area, followed by crystalline oxides needlelike goethite and platelike hematite with the lowest surface area [637]. The rate constant observed for ferrihydrite was two orders of magnitude higher than for the other two iron oxides. However, when normalized with the surface area, the differences in the rate constants measured became far less significant.

Various iron(III) oxide catalysts were prepared by controlled decomposition of iron(II) oxalate dihydrate, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in air at the minimum conversion temperature of 448 K (175 °C), yielding amorphous Fe_2O_3 nanoparticles. The catalytic efficiency of the synthesized nanoparticles was tested by measuring the rate of decomposition of hydrogen peroxide [638]. The kinetic data obtained gave an unconventional non-monotone dependence of the rate constant on the surface area of the samples. The amorphous nanopowder with the largest surface area of $401 \text{ m}^2/\text{g}$ revealed the lowest catalytic efficiency, while the highest rates were achieved with samples having a significantly lower surface area, $337 \text{ m}^2/\text{g}$, exhibiting a prevailing content of crystalline α - Fe_2O_3 phase. The rate constant obtained, $26.4 \times 10^{-3} \text{ min}^{-1} (\text{g/L})^{-1}$, is one of the highest values published. The observed rare catalytic phenomenon, where the particle crystallinity prevails over the surface area effects, was unexpected. The unique behavior of iron(III) oxide nanoparticles, the catalytic efficiency of which is strongly determined by the crystallinity of the particles rather than by their surface area, supports the theory of local increase in catalytic activity with particle crystallinity and the general effect of the “surface quality” prevailing over the commonly accepted key role of a large surface area.

If colloidal or nanosized iron(III) oxide could be permanently suspended in fuels for H_2O_2 bipropellant rocket engines, it might be possible to hypergolize fuels that otherwise would not ignite when they come in contact with H_2O_2 .

Iron(II) oxalate dihydrate can be used as a readily decomposable substance for the controlled synthesis of nanosized iron(III) oxides. The polymorphous composition, particle size and surface area of these iron oxide nanoparticles were controlled by varying the reaction temperature between 458 and 773 K (185 and 500 °C). As-prepared samples were characterized by XRD, Mössbauer spectroscopy, BET surface area, and TEM and tested as heterogeneous catalysts in hydrogen peroxide decomposition [639]. The catalytic data demonstrated that the crystal structure of iron(III) oxide (i.e., the relative contents of maghemite and hematite) does not influence the rate of hydrogen

peroxide decomposition. However, the rate constant increased monotonously with increasing sample surface area (and decreasing thermolysis temperature), reaching a maximum of $27 \times 10^{-3} \text{ min}^{-1}(\text{g/L})^{-1}$ for the sample with a surface area of $285 \text{ m}^2/\text{g}$.

Most environmental waters contain suspended iron hydroxides in one form or another. These small amounts of iron hydroxides are enough to affect the survival rate of hydrogen peroxide that has formed as the result of sunlight illumination or biological activity. The same catalysts enhance the ability of hydrogen peroxide to destroy organics in wastewater. The heterogeneous catalytic reaction of H_2O_2 with iron oxides or hydroxides is an important reaction for the environment since both H_2O_2 and iron oxides and hydroxides are common constituents of natural and atmospheric waters. Three ferrihydrites were prepared by different procedures. The heterogeneous catalytic reaction of H_2O_2 with three ferrihydrites in aqueous solution demonstrated that the apparent reaction rate was affected by the preparation procedure of ferrihydrite besides pH, temperature, and the dose of catalyst [640]. Depending on the method of preparing the iron(III) hydroxide, the activation energy of the decomposition reaction of H_2O_2 was between 59 and 76 kJ/mol.

Oxides of Group 9 Elements (Co, Rh, Ir)

Oxides of cobalt, nickel, and copper, alone and in mixtures, were tested as catalysts for decomposing hydrogen peroxide [641]. For the individual oxide, equimolar quantities of a cobalt oxide, CuO , and Ni_3O_4 gave decomposition rates in the respective ratios 0.013:1.20:0.029. Various ternary and binary mixtures were studied, but only those with the compositions 80 Co:20 Ni or 80 Co:15 Ni:5 Cu were more active than the cobalt oxide alone.

The rate of decomposition of hydrogen peroxide in the presence of cobalt(III) oxide was first order but tended toward second order at low concentrations [642]. The order also increased with temperature. The suggested mechanism, a reduction-oxidation cycle, is like that for the reaction on MnO_2 catalysts.

Catalysts for decomposition of hydrogen peroxide have been developed based on cobalt and molybdenum oxides and their binary compositions supported on aluminum oxide [643]. Pure and ZnO-doped cobalt(II,III) sesquioxide catalysts were prepared by thermal decomposition in air at 673–973 K (400–700 °C) of pure basic cobalt(II) carbonate that had been treated with different amounts of zinc nitrate (0.46–2.25 mass-% ZnO) [644]. XRD powder diffractometry and BET surface area analysis of nitrogen adsorption isotherms investigated the crystalline bulk structure and the surface area of pure and doped samples, respectively. The hydrogen peroxide decomposition activity was determined by oxygen gasometry of the reaction kinetics at 293–313 K (20–40 °C). The results showed that the treatment of Co_3O_4 with ZnO at 673–973 K (400–700 °C) brought about a significant increase in the specific surface area of cobalt(II,III) oxide. The catalytic activity of cobalt(II,III) oxide for H_2O_2 decomposition was considerably increased by doping with ZnO.

Oxides of Group 10 Elements (Ni, Pd, Pt)

Active H_2O_2 decomposition catalysts that were tested in an activity test apparatus and in a rocket engine with 91% HTP were prepared by impregnating high surface area alumina with a solution of AgNO_3 and $\text{Ni}(\text{NO}_3)_2$, drying, and calcining [645]. The maximum activity was achieved with catalysts that contained silver and nickel in an atomic ratio of 1:9. In a side-by-side test in a rocket engine with samarium oxide activated silver screen and the AgO/NiO catalyst, the AgO/NiO catalyst was able to start the engine at 277 K (40 °F), while the silver catalyst flooded. Of the steady-state chamber pressure 90% was attained within 200 to 300 ms.

Nickel oxide was prepared by decomposing and calcining $\text{Ni}(\text{NO}_3)_2$ and used as catalyst for the decomposition of hydrogen peroxide vapor generated from a 99.9% H_2O_2 supply [646]. The activation energy of H_2O_2 vapor decomposition on a nickel oxide catalyst was $54 \pm 2 \text{ kJ/mol}$ ($13.0 \pm 0.5 \text{ kcal/mol}$).

A study of the vapor phase decomposition catalyzed by nickel oxide single crystals was conducted in an isothermal flow reactor [647]. Catalyst pretreatment consisted of annealing the crystals at various temperatures and in several atmospheres. This produced crystals with defects and non-stoichiometric compositions. The catalytic activity was characterized by the amount of decomposition per unit surface area. The kinetic parameters were compared with the electrical characteristics of single crystals, and it was found that the maximum catalytic activity occurred with a pretreatment at 1000 °C. As the calculated nickel vacancy concentration increased, the catalytic activity first increased then began to decrease.

A similar effect was also observed with other oxide catalysts. Preirradiation created crystal defects in the crystal structure of metal oxides [648]; see also [649].

Preirradiation with γ -rays may allow the formation of more active (crystal defect) sites in nickel(II) oxide or mixed nickel/silver oxides when tested as catalysts for the decomposition of hydrogen peroxide [650–653]. The H_2O_2 decomposition activity of samples containing 0–91 mass-% NiO is determined by the catalytic efficiency of the silver component present in the catalyst, and this efficiency seems to be connected with the surface concentration of Ag^+ ions. The γ -irradiation (dose 10 kGy) of samples containing an excess of silver lead to a lower catalytic activity, but irradiation of samples with a higher content of nickel oxide increased their activity. Irradiation of catalysts with fast neutrons appreciably decreased their activity, irrespective of their composition, while irradiation with β -radiation (dose 5.6 MGy) had no effect on their activity.

Oxides of Group 14 Elements (Si, Ge, Sn, Pb)

In this group of metal oxides, tin oxide predominates as a stabilizer, not as a catalyst for H_2O_2 decomposition. Silicon dioxide in the form of quartz is one of the most inert and non-catalytic materials in which to store H_2O_2 or conduct experiments in quartz vessels. Lead oxides have low melting points and are rarely used as catalysts, but con-

tamination by lead solder has been blamed for some of the more dramatic accidents involving H_2O_2 explosions. Therefore, lead and lead oxide must be examined. Lead solder is avoided in all systems where it might come in contact with H_2O_2 .

Freshly precipitated lead hydroxide is a very active catalyst for hydrogen peroxide decomposition. Lead hydroxide was more active than any of the other metal hydroxides studied.

It has been shown that surface reactions involving H_2O_2 may lead to interconversion of PbO_2 and PbO . Considerable changes of the rate and mechanism of catalytic decomposition of H_2O_2 are the result of changes in the composition of lead oxides and of the solution pH [654]. It was informative to correlate catalytic activity and potential poisoning by organic substances with the composition of PbO_2 and PbO . Since lead(II) oxide exists in yellow and red forms, and yellow PbO may pass into bright-orange Pb_3O_4 in the presence of oxygen, decomposition of H_2O_2 on different forms of lead oxides was investigated.

Lead oxide was used as a catalyst with 70% stabilized H_2O_2 for torpedo propulsion in the US for a few years after WW-II but was later replaced by silver-plated screens ("argent") or cobalt-plated brass screens ("irium").

If a mixture of lead powder with sulfur, selenium or tellurium powder, powdered lead oxide (litharge) and potassium permanganate is pressed together with a small amount (up to 1%) of asbestos or other refractory fibers as a binder, and the resulting pellets are ignited by means of a flame, a self-sustaining solid-state reaction gets started. This reaction leaves behind a hard pellet of very high catalytic activity for the decomposition of hydrogen peroxide, which can be used in combination with catalysts made from metallic silver, cobalt oxide, chromates, or a mixture of potassium permanganate and lead monoxide [655].

Mixed Metal Oxide Catalysts for Hydrogen Peroxide Decomposition

The catalytic activity of mixed metal oxides in the decomposition of H_2O_2 is not simply an additive effect of the two (or more) oxides from which they are synthesized, but there is a potentiating effect where the mixed oxides at very narrow mixture ratios are sometimes more than an order of magnitude more active than the oxides from which they are made. The mixed metal oxides are made from an ideal combination of a transition metal with multiple states of oxidation (preferably Mn, Fe, Co, Cr) and a ceramic metal oxide with a high melting point (such as Al_2O_3 , ZrO_2 , Y_2O_3 , La_2O_3). Depending on the ratio of transition metal oxide to ceramic oxide, these mixed oxides assume a variety of crystal structures that are often named after naturally occurring minerals. The mixed oxides do not necessarily have to be in stoichiometric proportions to each other to make good catalysts. On the contrary, non-stoichiometric proportions create a number of crystal defects that enhance catalytic activity by oxygen mobility. Sometimes traces of aliovalent metals are added to create specific types of crystal defects. Some of the mixed metal oxides have unique electric properties (normal electric conductivity, superconductivity, magnetism) that go hand-in-hand with catalytic ac-

tivity. Another group of mixed metal oxides has been developed for solid oxide fuel cells for the direct conversion of hydrocarbons and air to electricity. The same oxides are also being tested as potential hydrogen peroxide (and HAN or nitrous oxide) decomposition catalysts.

Traditionally, mixed metal oxides have been prepared by dry sintering (“shake and bake”, ceramic method) physical mixtures of the oxides in the proper proportions at very high temperatures until chemical bonding takes place. Sometimes, sintering aids are added to allow the forming of ceramic shapes at lower temperatures. The disadvantage of that method is that the resultant materials have very low active surface areas and may need to be activated with wash coats to obtain useful catalysts.

Another method of preparation of mixed metal oxides is coprecipitation from a mixture of the metal nitrates by slow addition of alkali and raising the pH. However, metal oxides of different metals precipitate at different pH, and the resulting precipitate may not be homogeneous. The preferred methods of precipitation are the so-called sol-gel methods, which result in coprecipitation of nanometer-sized crystals that can then be dried and sintered. Chemical bonding of the dried material is complete at much lower temperatures than with the “shake and bake” method, and, consequently, the resulting materials have a higher surface area. Compared with the conventional ceramic routes, such as coprecipitation, grafting, or impregnation, the sol-gel method exhibits many advantages, among them the low process temperature and a strict control of purity, composition, microstructure, and textural properties of the final material. Particularly for mixed-oxides this synthesis procedure allows one to obtain materials with a high dispersion of the active phase in the matrix on both molecular and nanometer scale.

A detailed study of the flow decomposition of hydrogen peroxide vapor on a wide range of XO/Y_2O_3 mixed metal oxides showed that mixed metal oxides are more active than the binary oxides they are derived from [656].

In Russia, mixed metal oxide catalysts were produced in quantity and flight-qualified for thrusters with hydrogen peroxide concentrations up to 95.5 mass-% H_2O_2 [534]. Catalysts with the designation K-83, K-85, K-86, or K-87 have been commercially produced by RSC Applied Chemistry since 1966 and are intended for decomposition of HTP of concentrations up to 95.5%. As of 2001, catalysts K-88, K-90, and K-95 were in an advanced development status and were intended for decomposition of HTP concentrations up to 100% H_2O_2 . The catalysts were characterized by liquid phase and vapor phase H_2O_2 decomposition activity and activation energies. Although catalyst K-85 provided initiation of HTP decomposition at temperatures down to 233 K (−40 °C), it was quickly destroyed during extended operation that resulted in increase of pressure drop of a catalyst bed and in decrease of the HTP flow rate. Therefore, catalyst K-85 was applied in a mixture with catalyst K-83, which is less active, but was more durable. Catalysts K-86, K-83, and K-85 were used in 75-, 100-, and 150-N thrusters. A cross section of one of these thrusters is shown in a figure in *Encyclopedia of Monopropellants*, chapter “Hydrogen Peroxide Monopropellants”. In catalyst beds for 12-

and 16-N thrusters, the catalysts K-86 and K-87 were used instead, which had smaller granule sizes. The catalyst K-86 assured completeness of HP decomposition. The catalyst K-87 was in the shape of tablets and, therefore, allowed packing of the catalyst by hand in a controlled manner. The catalyst K-86 was in the shape of disks with a diameter equal to the diameter of the catalyst bed. It was capable of complete decomposition of HP and was very durable. Design examples of thrusters using these catalysts are shown in *Encyclopedia of Monopropellants*, chapter "Hydrogen Peroxide Monopropellants".

The thermal decomposition under hydrogen of binary complex compounds (BCCs) consisting of complex cations and complex anions is a method for preparation of catalysts that also find use in Fischer-Tropsch synthesis, CO oxidation in automobile exhaust, and oxidative destruction of pollutants. The catalytic activity of binary metal catalyst samples that were obtained via the thermolysis of binary complex compounds (BCCs) in a hydrogen atmosphere for hydrogen peroxide decomposition was determined by measuring the rate constants and activation energies for the catalytic reaction [657]. The establishment of a correlation between catalytic activity, composition, specific surface area (S_{sp}), and particle size of the samples was attempted. Several conclusions were drawn about the decomposition of H_2O_2 on semiconducting oxides:

- (1) The rate-determining step is the emission of electrons from the surface of the catalyst.
- (2) The dependence of the reaction rate on specific surface area is negligible.

The rate constants and BET surface areas of 28 binary Cr, Co, Fe, Cu mixed metal oxide catalysts reduced under hydrogen at different temperatures between 573 and 1173 K (300 and 900 °C) for the decomposition of H_2O_2 were measured and their crystal structures determined by XRD.

Spinels

Two types of cobalt-iron spinel oxides $Co_xFe_{3-x}O_4$, ($0 \leq x \leq 3$) prepared by hydroxide or oxalate coprecipitation routes were studied in order to define the intrinsic and microstructural factors influencing the catalytic activity for heterogeneous H_2O_2 decomposition in alkaline solution [658]. The activity sequence in order of decreasing activity was found to be $x = 1.0 > 1.5 > 2.0 > 2.4 > 3.0 > 0.6 > 0.0$ based on diffusion-free activation energies for the decomposition reaction. This order agreed with results obtained by measuring the initial rates of H_2O_2 decomposition, provided that the rates were normalized for the area of reaction available at the catalyst surface. The activity order could be interpreted in terms of the electronic structure of cobalt-iron oxides, and a key factor was the presence of Co^{2+} ions on the octahedral lattice sites, which can initiate a cyclic electron transfer process (redox reaction) on the catalyst surface. The maximum activity and the lowest activation energy for the reaction occurred at $x = 1$ since the greatest availability of octahedral Co^{2+} occurred at this composition.

Cobalt-ferrite spinel oxides of the type $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$, ($0 \leq x \leq 3$) were synthesized by coprecipitation [659]. Kinetic studies revealed pronounced activity of these oxides in the catalytic decomposition of hydrogen peroxide. The optimum activity of this decomposition reaction is at lattice composition of $x = 1.5$ in the spinel system. XRD and SEM results indicated that at $x = 1.5$, the Co^{++} ions are at the octahedral lattice sites of the ferrite support.

Some ferros spinels of the $\text{M}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$ type act as catalysts for the decomposition of H_2O_2 . Their effectiveness is dependent on the composition of the catalyst. A set of ferrites of different composition ($\text{M}^{\text{II}} = \text{Mn, Co, Ni, Cu, Zn, Cd}$) was synthesized by coprecipitation and characterized by chemical analysis, XRD, and BET surface area measurements [660]. The catalytic activity decreased in the order $\text{MnFe}_2\text{O}_4 > \text{CoFe}_2\text{O}_4 > \text{CuFe}_2\text{O}_4 > \text{NiFe}_2\text{O}_4 > \text{CdFe}_2\text{O}_4 > \text{ZnFe}_2\text{O}_4$. The first in the list, MnFe_2O_4 , was much more effective than any of the others by a factor of 50–100 [661].

The effects of doping and thermal treatment on catalytic properties of pure iron(III) oxide solid were studied by means of thermal analyses (TG-DTG-DTA), XRD, BET analysis of nitrogen isotherms, and hydrogen peroxide decomposition activity measurements at 293–323 K (20–50 °C) [662]. A series of Co_3O_4 - Fe_2O_3 and Mn_2O_3 - Fe_2O_3 mixed oxides were prepared from cobalt nitrate, basic iron(II) carbonate, and manganese nitrate salts by an impregnation method. Both Co_3O_4 and Mn_2O_3 were used as dopants (0.25–4.00 mol-%) for pure Fe_2O_3 . The pure and doped solids were baked at 623, 823, 1023 or 1273 K (350, 550, 750, or 1000 °C). The solids baked at low temperature led to formation of free oxides in physical admixture. The doped solids calcined at high temperature resulted in the formation of ferrites (CoFe_2O_4 or MnFe_2O_4). The catalytic activity of pure Fe_2O_3 significantly increased with increasing the amount of cobalt or manganese oxides dopants. The observed increase in activity was attributed to increasing the concentration of catalytically active constituents and/or formation of new active sites. The measurement of activation energy of the catalytic reaction for pure and doped solids revealed that the doping process did not modify the energetic nature of the active sites involved in the catalyzed H_2O_2 decomposition reaction. While the catalytic activities of doped solids increased by increasing the calcination temperature from 623 to 823 K (350 to 550 °C), above that it significantly decreased with further increase of baking temperature up to 1023 K (750 °C). The progressive decrease in the activity was due to formation of inactive ferrite compounds and/or sintering processes.

Perovskites

The heterogeneous decomposition of hydrogen peroxide was studied in alkaline electrolytes on $\text{LaFe}_x\text{Ni}_{1-x}\text{O}_3$ perovskite-type oxides intended to be used as electrodes in fuel cells [663]. The reaction was found to be of first order in HO_2^- concentration. Maximum catalytic activity was found for $x = 0.25$. The optimum temperature of synthesis by the “shake and bake” method was between 873 and 973 K (600 °C and 700 °C), this being a compromise between a sufficiently high temperature to synthesize the per-

ovskite structure and a sufficiently low temperature to produce a high surface area catalyst with a low number of oxygen vacancies.

Lanthanide perovskite oxides can catalytically decompose hydrogen peroxide not only in rocket engines, but also in electrochemical sensors for analytical applications. The catalytic properties of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ perovskites are due to their oxygen vacancies and are influenced by the oxide non-stoichiometry δ and increase with increasing non-stoichiometry, x [664].

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0 < x < 0.8$) perovskite-type oxides were synthesized by the combined EDTA-citrate complexing method, characterized by XRD, and their catalytic activity for the decomposition of caustic 1.2-M hydrogen peroxide solution was investigated at 303, 308, and 313 K (30, 35, and 40 °C) [665]. Hydrogen peroxide decomposition was a first-order reaction on these catalysts. With the increase of Sr substitution, the catalytic activity increased accordingly, and $\text{La}_{0.2}\text{Sr}_{0.8}\text{MnO}_3$ was the most active catalyst tested. It was suggested that the active sites for hydrogen peroxide decomposition on $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ catalysts can be attributed to Mn^{4+} ions.

Supported perovskite catalysts were prepared by impregnating the $\gamma\text{-Al}_2\text{O}_3$ carrier (with a BET surface area of $176 \text{ m}^2/\text{g}$) with an aqueous solution containing appropriate amounts of $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Mn}(\text{NO}_3)_2$, followed by drying at 393 K (120 °C) for 8 h and then calcined at 1023 K (750 °C) for 3 h in air [666]. A catalyst made by coating 25% $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ on alumina was tested with 85% HTP in a 10-N thruster at a flow rate of 5 g/s. The first 10-s pulse looked good, but by the time the pulsing was repeated 19 times, the chamber pressure roughness had increased to a point that the reactor had to be shut off; see also [667].

A ceramic monolith was coated with 13% $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (Lanthanum Strontium Cobaltate = LSC) and performed well in the lower bed of a gas generator with 80% HTP [668, 669].

Perovskites were synthesized by thermal decomposition of metal citrate mixtures and tested as catalysts for decomposing hydrogen peroxide [670]. The ignition delaying times (IDT) of H_2O_2 were measured with 90 or 30% H_2O_2 on different wetted catalysts. The IDT depended more on the wetted level of the catalysts than on the chemical composition. The activity of catalysts depended on the chemical composition. The activity order (in order of increasing activity) was $\text{LaNiO}_3 < \text{LaCoO}_3 < \text{LaMnO}_3 < \text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3 < \text{LaMn}_{0.8}\text{Co}_{0.2}\text{O}_3 < \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.8}\text{Co}_{0.2}\text{O}_3$. To prepare a commercial catalyst, 30% $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.8}\text{Co}_{0.2}\text{O}_3$ were supported on $\gamma\text{-Al}_2\text{O}_3$ microspheres. At high bed-loading (higher than $5 \text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$) in a simulated rocket engine, the longevity of the supported catalyst was better than 4000 s.

The isomorphic substitution of Mn in the LaMnO_3 structure by different amounts of Fe and Mo to produce $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ and $\text{LaMn}_{0.1-x}\text{Fe}_{0.90}\text{Mo}_x\text{O}_3$ created active catalysts [671]. The Fe and Mo can vary their oxidation states, and this property can improve the catalytic activity in oxidation processes. These perovskites were characterized, and the catalytic activity was investigated using 7 mL of 2.9-M H_2O_2 (2.9 mol/L)

and 60 mg of catalyst. Fe addition decreased, and Mo improved the rate of H_2O_2 decomposition.

Perovskites of the type $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ are active catalysts for decomposition of hydrogen peroxide not only in rocket engines, but also in fuel cells [672]. Perovskite-type series of compounds $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with different x were synthesized by a sol-gel method using chitosan as the gelling agent. The catalytic activity for hydrogen peroxide electroreduction in 3-*M* KOH at room temperature was evaluated by means of cyclic voltammetry and chronoamperometry. The effects of the annealing temperature and the ratio of La to Sr on catalytic performance was investigated. In this series of compounds, $\text{La}_{0.4}\text{Sr}_{0.6}\text{MnO}_3$ calcined at 650 °C exhibited the highest activity, which was comparable with Co_3O_4 .

$\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.0, 0.2, 0.4$, and 0.6) perovskites were synthesized using the citrate gel method, characterized by TGA, DTA, XRD, SEM, and BET surface area, and their catalytic activities were examined for the hydrogen peroxide decomposition reaction [673]. The catalytic activity was improved with increasing calcium content in the catalyst, and it was suggested that factors such as δ -oxygen non-stoichiometry and shifting manganese average valence states were responsible for the catalytic activity of these materials.

Other Mixed Oxide Catalysts

Dry-mixed oxides were pressed into pellets at 33000 psi and sintered at up to 810 K (1000 °F) and tested by immersing a pellet in 10 mL of 98% H_2O_2 in a graduated cylinder and measuring the time required for complete consumption of the liquid [674, 675]. Mixed oxides $\text{BaO}/\text{Mn}_2\text{O}_3/\text{PbO}$ and $\text{BaO}/\text{Mn}_3\text{O}_4/\text{PbO}$ with low lead content showed good activity. Most of these pellets showed a rapid decline in activity with repeated testing.

Catalytic activities of two non-conducting cuprates ($\text{Ba}_2\text{Cu}_3\text{O}_5$, Y_2BaCuO_5) and a superconducting cuprate $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, prepared by two different methods, were compared using H_2O_2 solutions [676]. The two non-conducting barium cuprates were found to be about two orders of magnitude more active than the superconducting perovskite-like $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. First-order kinetics were observed for the catalyzed decomposition of H_2O_2 solution over the non-perovskite Y_2BaCuO_5 at the initial stages of the reaction, similarly to that of the superconducting perovskite catalyst. A tentative scheme of the possible catalytic reactions for the decomposition of H_2O_2 solution over the insulator Y_2BaCuO_5 indicated that electron transfer from the lone electron pairs in HOOH to the d-orbitals of copper is not a rate determining step of H_2O_2 decomposition on this catalyst.

A catalyst consisting of mixed manganese oxide-lead oxide supported on 18–30 mesh high surface area alumina granules has been developed in China [677]. In this catalyst, the lead oxide greatly promoted the activity of manganese oxide in the decomposition of hydrogen peroxide. Manganese and lead nitrates were dissolved in deionized water to obtain the impregnating solution. The catalysts with various mo-

lar ratios of $\text{MnO}_2:\text{PbO}$ were prepared by impregnating the alumina support with the solution, and the impregnated catalysts were dried, and then calcinated in air at 673–693 K (400–420 °C) for 5h. The total loading of the metal oxides was 10 mass-%. The catalyst activity was measured by a traditional gasometric method using 0.03 g catalyst mixed with 10 mL H_2O_2 ($d = 1.3336 \text{ g/cm}^3$). The other evaluation was done in a monopropellant rocket thruster. A catalyst with a $\text{MnO}_2:\text{PbO}$ mass ratio of 1:1 had the highest activity. The activity of the catalyst for hydrogen peroxide decomposition was attributed to the formation of a new phase, and this new phase was characterized by XRD, XPS, and TPR.

New catalysts for H_2O_2 decomposition based on manganese-yttrium-zirconium mixed oxide nanocomposites have been prepared by a sol-gel method [678]. Materials with different active metal loadings of the active phase were prepared in order to optimize the chemical composition of the material for maximum catalytic activity. A mixture of $\text{Zr}(\text{OC}_3\text{H}_7)_4$, $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ dissolved in isopropanol was slowly hydrolyzed by addition of water to form the sol and then the gel. Three compositions were made with different percentages of Mn (5, 15, and 30% Mn) with respect to 100 g of matrix, whose molar composition was $95\text{ZrO}_2 \cdot 5\text{Y}_2\text{O}_3$. Three annealing temperatures were chosen for the dried gels: 773, 973, and 1273 K (500, 700, and 1000 °C). The lower temperature is the minimum temperature at which it is possible to obtain complete decomposition of nitrate ions and elimination of the solvent and residual organics (stabilized gels). The higher temperature values were selected to force the crystallization of the samples. The activity of the finished catalysts was tested by measuring the rate of oxygen evolution in contact with 30–40% H_2O_2 in a stirred reactor. The 30% Mn catalyst with a BET surface area of $100 \text{ m}^2/\text{g}$ was the most active catalyst tested in this series.

Molecular sieves do not have the high-temperature capability required for H_2O_2 in rocket engines, but they can also decompose H_2O_2 in a fixed-bed reactor [679]. Tetrahedrally coordinated Ti in a titanasilicate molecular sieve was more active in H_2O_2 decomposition than octahedrally coordinated Ti.

4.10.2.10 Metal/Metal Oxide (Cermets) Catalysts for Hydrogen Peroxide Decomposition

Many metals are good catalysts for the decomposition of hydrogen peroxide, but their melting point is too low. Many metal oxides are good catalysts for the decomposition of hydrogen peroxide, but it is difficult to bond metal oxide powders together. If one melts them, they lose all surface area and most of their catalytic activity. Some sort of glue is needed to hold them together. Finely divided malleable metals like silver, copper, and their alloys can be pressed together with metal oxide powders and will provide cold-pressed bodies with some mechanical strength, which can be improved by further sintering. Such composites made from **ceramics** and **metals** are called “cermets”. Similar cermet materials have been used for other parts in rocket engines, such as nozzles or reentry heat shields.

Cosolidified silver/metal oxide mixed catalysts also called “cermet catalysts” showed significantly higher activity in the decomposition of concentrated H_2O_2 than that of silver metal alone [680]. The effect of discrete particles of catalytically inactive material, uniformly dispersed in a continuous phase of silver metal, upon the phenomenon of vapor binding at silver surfaces in contact with concentrated H_2O_2 was investigated. A method for producing the desired surface was developed to yield a cermet in which inactive material is uniformly distributed throughout the body of the “catalyst.” The behavior of such cermets toward concentrated H_2O_2 was followed by measuring oxygen evolution rates of semiadiabatic, atmospheric pressure reactions in a constant volume reactor. The cermets, prepared in pellet form, contained silica, silicon carbide, or copper oxide as the inert material. The startup activity of all cermets with concentrated H_2O_2 was better than that of pure silver and markedly higher than that shown by $\text{Sm}(\text{NO}_3)_3$ -treated silver surfaces. Reactivity with concentrated H_2O_2 per unit apparent silver surface area was as much as 20 times higher than that of consolidated silver.

Sintered pelletized compositions containing powdered silver and copper oxide are useful for decomposing hydrogen peroxide. The preferred catalyst contained 87 mass-% silver and 13% CuO [681].

A pelletized catalyst can be made by sintering 80 to 95% silver with 5 to 20% copper oxide [682]. No low-melting eutectic forms in the sintering step, in contrast to the pellets described in other patents where metallic copper is used. The pellets can be heat treated nearly to the melting point of silver. The preferred composition contained 91.3% Ag and 8.7% CuO . Copper(II) oxide is a relatively good catalyst even without being sintered with silver. Even inert ceramic oxides (other than copper(II) oxide) can be sintered with silver and still obtain a cermet catalyst with decent activity [683, 684]. Active silver powder can be mixed with inert ingredients, such as Al_2O_3 , SiO_2 , or SiC (all of which are stable up to the melting point of silver), and then pelletized. A typical catalyst contained 75% silver and 25% of inert material.

The sintering of metallic silver catalysts often causes incomplete decomposition at cold start and chamber pressure oscillations towards the end of their useful life. Chugging will induce flow instabilities in the feed system. It was shown that the addition of ceramic materials to silver increased the thermal resistance of catalyst beds [685]. These cermets are also called “composite silver catalysts”. By proper catalyst bed packing, it was possible to obtain excellent catalyst test results. The I_{sp} from a cold start was 104.9s, and I_{sp} during hot steady-state firings was 114.9s. The start transient was about 100 ms and 50 ms from cold and hot fire, respectively, which included the operating time of the solenoid valve. In continuation of this catalyst characterization, a 1-N thruster prototype using a combination of silver and ceramic cermet material as catalyst bed for hydrogen peroxide monopropellant decomposition was tested [686]. With a chamber pressure of 150 psi, the thrust was 0.7 N at atmospheric pressure, and the specific impulse was about 102s. The catalyst bed has been modi-

fied and tested over 4000 s using 90% H_2O_2 propellant. Repeatability demonstration, blow-down tests, and environmental tests were planned.

4.10.2.11 Other Catalysts for Hydrogen Peroxide Decomposition

The catalysts discussed here may not be suitable for rocket engines, but they illustrate the wide variety of compounds that will catalyze hydrogen peroxide decomposition, even in living systems. Hemoglobin-bound iron in blood platelets and other metals inserted into porphyrin complexes are active catalysts for the decomposition of hydrogen peroxide. The decomposition of hydrogen peroxide by four kinds of silica-supported Cu- and Co-porphyrins was measured by kinetic studies, and the reaction rates were expressed based on the kinetic data [687]. The rate differences with various metallo-porphyrins were explained by the different processes for the formation of intermediates.

Saliva contains peroxidase and catalase. Just spitting into a dilute solution of hydrogen peroxide will cause it to decompose, similar to peroxide processes happening during digestion, metabolism, and assimilation. One can notice this reaction when using dilute (<1%) H_2O_2 solutions as mouthwash and for gurgling. The enthalpy of decomposition of hydrogen peroxide by catalase has been determined calorimetrically in isotonic saline solutions at 25 °C [293].

It has been attempted to improve startup properties of HTP with marginal quality catalysts by dissolving “promoters” in the HTP. These promoters were usually organic peroxides which are known to be compatible with HTP. The data in the literature about purported benefits of dissolving promoters in HTP are not convincing and safety property testing is lacking. It was claimed that HTP made by an electrolytic process, which is free of organic residues, would decompose more slowly than HTP from an IPA or AO process. When organics were added to electrolytic grade HTP, it decomposed faster when in contact with silver wire catalyst and showed an increased rate of oxygen evolution, a faster rise in temperature, and improved starting at low temperatures as compared with hydrogen peroxide not containing the residue [688].

Colloidal and nano-size catalyst particles suspended in an emulsion have shown superior activity for the decomposition of hydrogen peroxide. In one example, Ag nanoparticles were prepared in tetraethylene glycol monododecyl ether/cyclohexane/ AgNO_3 microemulsions by reducing with excess NaBH_4 solution [689]. Then colloidal silica was added as a catalyst carrier and acetone was used to destabilize the microemulsions to allow the silver particles to stick onto the colloidal silica. The prepared silica-supported Ag catalysts are in a well-dispersed powder state with a color of light yellow. The activity of Ag/ SiO_2 catalysts for the decomposition of H_2O_2 was evaluated in a glass volumetric apparatus and was higher than any catalyst previously tested.

Promoters and Activators for Catalytic Decomposition of Hydrogen Peroxide

It has been claimed that certain organic additives that are compatible with hydrogen peroxide can enhance the startup and the rate of hydrogen peroxide decomposition on silver screen catalysts. Some of the additives said to be active in this regard are organic, unidentified (most likely organic peroxide) contaminants often (unintentionally) remaining in hydrogen peroxide that was made by autoxidation of 2-propanol (i.e., the Shell process). A patent [690] describes a method for decomposing hydrogen peroxide of about 30 to 100 mass-% H_2O_2 , which comprises contacting the hydrogen peroxide with a solid silver-containing decomposition catalyst in the presence of between ~50 and ~10000 mg/L of organic peroxide-containing residue from hydrogen peroxide production by oxidizing an organic compound selected from the group consisting of alkyl anthraquinones, alcohols, hydrocarbons, or hydrazobenzenes.

Along the same line of claims, it has been claimed that addition of 0.7–1.4 mg/L of ions of zinc or cadmium in the form of salts where the anions do not form insoluble salts with silver, for instance, in the form of $\text{Zn}(\text{NO}_3)_2$ or $\text{Cd}(\text{NO}_3)_2$, will improve decomposition of H_2O_2 on fixed bed catalysts and reduce loss of silver catalyst in repeated operation at ambient or lower startup temperatures [691]. It would have generally been predicted that additives for increasing the specific decomposition rate of hydrogen peroxide on solid silver catalysts would be undesirable since they would be expected to make the hydrogen peroxide more unstable during storage prior to use. The additives claimed do not have this disadvantage but are selective in their action. They promote the catalytic decomposition of the hydrogen peroxide by solid silver catalysts but do not increase the rate of hydrogen peroxide decomposition in the absence of such silver catalysts. Similar improvements were said to be achieved by dissolving silver or cadmium salts in the form of their acetate or benzoate salts in amounts that introduce into the hydrogen peroxide about 0.1 to about 10 mg of total zinc and/or cadmium ion per liter of the hydrogen peroxide, most advantageously amounts that provide from about 0.3 to about 3 mg of these metals per liter [692].

4.11 Decomposition of Hydrogen Peroxide by Energetic Radiation

4.11.1 Decomposition of Hydrogen Peroxide by Microwaves

Analysis of the emission spectra from hydrogen peroxide vapor flowing through a low-pressure microwave cavity discharge plasma showed that both $\cdot\text{H}$ and $\cdot\text{OH}$ were produced in proportions that varied with the power applied [693]. When the dissociated vapor was condensed at 195 K, only water was obtained, but at 77 K, H_2O_2 and H_2O_4 were also obtained. Their formation could not be increased by increasing the $\cdot\text{H}$ atom or $\cdot\text{OH}$ radical concentration in the plasma. When the reaction time of the dissociated vapor between the plasma exit, and the cold surface was increased, the rate of H_2O_2 formation increased at the expense of water formation. It appears that, as in the case of the reaction of $\cdot\text{H}$ with O_2 , the rate of H_2O_2 formation is dependent on the concen-

tration of O_2 produced in the spatial afterglow by the gas-phase reactions of the $\cdot OH$ radicals.

In 2003, an SBIR/STTR Phase I contract was awarded to a team from Materials Modification Inc. and Vanderbilt University for the study of microwave-induced thermal decomposition of hydrogen peroxide [694], but there was no follow-on Phase II contract, and there were no publications on the results of this work.

Methods were sought that will heat a small hydrogen peroxide decomposition chamber in a pilot reactor rapidly to a point where catalytic decomposition of hydrogen peroxide can be safely and spontaneously initiated. External heat would have to be applied in the form of an electrically heated heating jacket or a microwave heater to drive off the condensate and facilitate multiple restarts [695]. The heat output from the pilot reactor will then bring the main reactor up to operating temperature. Complex permittivity measurements on hydrogen peroxide with different concentrations were carried out to identify the frequency region for maximum microwave absorption for a given H_2O_2 concentration. Microwave dielectric heating experiments in the frequency region of maximum absorption were then performed to establish a relationship between microwave power requirements and the reactor volume for repeated rapidly heated decomposition of hydrogen peroxide.

4.11.2 Radiolysis of Hydrogen Peroxide

Hydrogen peroxide not only forms in the radiolysis of water, but once formed, it is also decomposed by ionizing radiation. In the end effect, radiolysis of water reaches only a stationary concentration where equal amounts of H_2O_2 are formed and decomposed in a given time period. Hydrogen peroxide that is used as a propellant in satellites is exposed to cosmic radiation that is energetic enough to penetrate the propellant tanks (which is usually made from aluminum, which is a poor radiation shield). The decomposition of H_2O_2 is accelerated by ionizing radiation such as electrons, protons, neutrons, or γ -radiation, most of which are found in cosmic radiation [696, 697]; see also [698].

In an initially oxygen-free neutral H_2O_2 solution, H atoms as well as electrons are formed on irradiation. As the decomposition proceeds, enough oxygen is formed to react with the precursors of the H atoms such that all the reducing species produced are in the form of H_2O^- . It was assumed that the precursors of the H atoms are excited H_2O^* molecules, but such hypotheses were later disputed [699]. Computer calculations of the radiolytic decomposition of dilute hydrogen peroxide solutions have shown that earlier results support the value $ge_{aq} = 2.3$ if the rate constant ratio

$$k(e_{aq^-} + O_2)/k(e_{aq^-} + H_2O_2) = 1.53.$$

Accepting this value of ge_{aq^-} makes the assumption of a small yield of a second oxidizing species unnecessary [700].

Radiolysis of Hydrogen Peroxide by Fast Electrons or Ions

Fast electrons will knock additional electrons out of neutral H_2O_2 molecules and ionize them so that they can be analyzed in a mass spectrometer. The lifetime of H_2O_2^+ is very short, and it will decompose to other species as it travels through the electrostatic and magnetic field of the mass spectrometer or a time-of-flight mass spectrometer.

Mass spectrometric measurements on hydrogen peroxide were carried out with a modulated molecular beam sampling system to eliminate interferences from decomposition products [701]. The mass spectrum of pure hydrogen peroxide differs considerably from previously reported spectra, which did not include an estimate of the H_2O^+ and O_2^+ ion intensities because of decomposition problems. Appearance potentials of the ions were measured with the following results: $I(\text{H}_2\text{O}_2) = 10.92 \pm 0.05 \text{ eV}$, $A(\text{HO}_2^+) = 15.36 \pm 0.05 \text{ eV}$, $A(\text{O}_2^+) = 15.8 \pm 0.5 \text{ eV}$, $A(\text{H}_2\text{O}^+) = 14.09 \pm 0.10 \text{ eV}$, $A(\text{OH}^+) = 15.35 \pm 0.10 \text{ eV}$, and $A(\text{O}^+) = 17.0 \pm 1.0 \text{ eV}$. It was found that the H_2O^+ and OH^+ ions are evolved without excess energy, while the dissociative processes producing O_2^+ and O^+ require excess energy.

Radiolysis of Hydrogen Peroxide by β - or γ -Radiation

Instead of irradiating H_2O_2 externally (and dealing with radiation being absorbed in the glass holding the sample and causing secondary radiation) one can use an internal source of radiation in the form of tritium water T_2O . For irradiation by $\text{T}\beta$ -particles, 6-M H_2O_2 solution was tritiated with T_2O to an activity of 0.3 curie/mL and frozen in glass sample tubes in liquid nitrogen [702]. Tritium was chosen as an internal source of radiation since it allows one to avoid the background of irradiated glass in the EPR spectrum. The resulting EPR spectrum was very similar to the spectra reported for H_2O_2 irradiated by ultraviolet light and has been ascribed to the $\text{HOO}^\bullet$ free radical. It was hoped that one would find H_2O_4 in the condensate.

Radiolysis of H_2O_2 forms $^\bullet\text{HO}_2$ and $^\bullet\text{O}_2^-$ free radicals, which can either recombine or react with more H_2O_2 to sustain a chain reaction. The rates of reaction of $^\bullet\text{HO}_2$ and $^\bullet\text{O}_2^-$ with hydrogen peroxide were studied by ^{60}Co γ -radiolysis as a function of pH at 296.6 K (23.5 °C) [703]. The numerical values for the two rate constants,

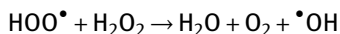
$$k(^\bullet\text{HO}_2 + \text{H}_2\text{O}_2) = (0.50 \pm 0.09) \text{ M}^{-1} \text{ s}^{-1}$$

and

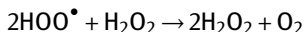
$$k(^\bullet\text{O}_2^- + \text{H}_2\text{O}_2) = (0.13 \pm 0.07) \text{ M}^{-1} \text{ s}^{-1}$$

were computed from molecular oxygen yields, which resulted from the radiation-induced chain decomposition of aqueous hydrogen peroxide solutions. The experimental results were consistent with a chain mechanism that takes into account the dissociation of $^\bullet\text{HO}_2$ in equilibrium $^\bullet\text{O}_2^- + \text{H}^+$ ($\text{pK} = 4.7$) and the competition between the reactions ($^\bullet\text{HO}_2 + \text{H}_2\text{O}_2$ and $^\bullet\text{O}_2^- + \text{H}_2\text{O}_2$) and the recombination reactions of the superoxide and perhydroxyl radicals ($^\bullet\text{HO}_2 + ^\bullet\text{HO}_2$ and $^\bullet\text{HO}_2 + ^\bullet\text{O}_2^-$).

A mechanism for the γ -ray initiated decomposition of 0.1-M aqueous solutions of hydrogen peroxide was deduced from data showing a dependence of the decomposition product yield on the square root of hydrogen peroxide concentration and the inverse square root of the dosage rate in intermittent radiation experiments [704]. Termination was shown to occur through a termolecular reaction involving two hydroperoxyl radicals and a hydrogen peroxide molecule. It was shown that



is the rate determining propagation, and



is the chain termination step.

The radiolysis of pure (97%) solid H_2O_2 films by 50 keV H^+ at 17 K was characterized using UV-visible and infrared reflectance spectroscopies, a quartz-crystal microbalance, and a mass spectrometer in order to measure the absolute concentrations of H_2O , O_2 , H_2O_2 , and O_3 products as a function of irradiation fluence [705]. Ozone was identified by both UV and infrared spectroscopies and O_2 from its forbidden transition in the infrared at 1550 cm^{-1} . The radiation yields (G-factors) for the decomposition of hydrogen peroxide were particularly high, which was explained by the participation of chemical chain reactions.

Decomposition of Hydrogen Peroxide by Neutron Radiation

Hydrogen peroxide, or more accurately, deuterium peroxide, forms inadvertently and unavoidably in the heavy water that is used as the moderator and heat transfer fluid in pressurized water reactors of the CANDU type. Deuterium peroxide that has formed in this way will be decomposed just as fast by neutron radiation, thus a stationary concentration will be achieved in a closed-loop system. Sampling the coolant loop water will show low D_2O_2 concentrations because thermal decomposition continues even after the coolant leaves the hot zone of the reactor.

As a model for D_2O_2 reactions in heavy-water moderated nuclear reactors, the thermal decomposition rate of H_2O_2 was measured in the aqueous phase at elevated temperature [706]. It was shown that the reaction follows first-order kinetics, and the rate constant was determined as a function of temperature. A mechanism was derived for the aqueous phase decomposition in relation to the activation energy of the reaction. Calculations were carried out for the reactions of O_2 , H_2 , and H_2O_2 in the boiling water reactor sampling line. It was shown that some H_2O_2 (and D_2O_2) disappears before the analysis can be completed.

Radiolysis of Hydrogen Peroxide by X-Rays

X-ray irradiation not only initiates the formation of hydrogen peroxide from water but also causes the decomposition of hydrogen peroxide once it is formed [707]. In an ap-

paratus with continuous X-ray irradiation of water, only a small stationary concentration of H_2O_2 is attained (at the best).

4.11.3 Photolysis of Hydrogen Peroxide

Photolysis of hydrogen peroxide is discussed here in quite some detail because photolysis affects the use of hydrogen peroxide as a rocket propellant and many other applications. Photochemical processes lead to the formation and decomposition of hydrogen peroxide in many locations, not only on Earth but also on other celestial bodies, and possibly even in interstellar space.

It is certain that large quantities of hydrogen peroxide are formed on the icy moons of the large planets Jupiter and Saturn under the influence of UV radiation from the sun. At the same time, hydrogen peroxide that has collected in the ice will be destroyed by the same radiation that helped its formation in the first place. There are tons of hydrogen peroxide floating around in the atmosphere and stratosphere on Earth, and it is subject to photolysis just as fast as it forms under the influence of UV radiation. If one conducts H_2O_2 photolysis studies with gradually shorter and shorter wavelength light, the wavelength of light where H_2O_2 is first observed to decompose is an indication of the bond energies and the level of excitation (vibration and rotation) that ultimately leads to dissociation of the molecule. This level can be measured experimentally and predicted by quantum mechanical calculations. This section deals with both methods.

Photolysis interferes with analytical spectroscopic methods, where the initial intent was to measure the absorption of light, but the light caused the premature decomposition of the analyte at the same time.

Photolysis, often in combination with catalysts, would be the preferred and environmentally friendly method for destruction of hydrogen peroxide in wastewater, rinse waters from propellant spills, and disposal of surplus hydrogen peroxide (after sufficient dilution with water).

Laser photolysis has been considered as a method to initiate decomposition of hydrogen peroxide (and other monopropellants) in thrusters, thus becoming independent of the limited lifetime of catalysts often used for the initiation of hydrogen peroxide decomposition in thrusters. Photolysis of H_2O_2 by intense laser light would be a reliable method to initiate the decomposition of HTP in a rocket engine, even with multiple starts and pulse-mode operation.

Hydrogen peroxide is a reactant in chemical lasers, and its premature photolysis would interfere with the operation of the laser.

Photolysis mechanisms of the decomposition of hydrogen peroxide are very similar to the mechanisms during radiolysis by other types of energetic radiation. The two chapters are closely related and complement each other. Radiolysis of rocket propellants stored in space and subjected to cosmic radiation is inevitable.

Photolysis of hydrogen peroxide with quenching of the reacting mixture may be a method to synthesize superoxides of hydrogen, such as $\text{H}-\text{O}-\text{O}-\text{O}-\text{O}-\text{H}$, which should make good rocket propellants (if they are stable at room temperature).

Photolysis of hydrogen peroxide is a convenient and clean method for generating a stream of hydroxyl-free radicals, which are often used to study reactions with other materials, including living cells, where they can cause mutations. The photolysis of 1-M hydrogen peroxide can effectively kill oral pathogenic microorganisms.

Photolysis experiments with H_2O_2 can be conducted with the chemical in the vapor, solid, or liquid state. Most of the experiments were conducted with H_2O_2 vapor, which is the state it is encountered in the Earth atmosphere. However, additional photolysis experiments were conducted with frozen H_2O_2 or H_2O_2 in a matrix of water ice, simulating the condition in which it may occur in other parts of the solar system. Photolysis of frozen H_2O_2 in a matrix of frozen noble gases allows one to trap some of the short-lived free radicals that play a key role in H_2O_2 formation and photolysis.

Photolysis of Hydrogen Peroxide Solutions

The quantum yield of the photochemical decomposition of hydrogen peroxide at relatively high light intensity is independent of the concentration of hydrogen peroxide, of acidity, and of the presence in the solution of Br^- , Cl^- , NH_4^+ , or Mn^{2+} [708]. At 298 K (25 °C) the limiting quantum yield at 2537 Å is 0.98 ± 0.05 and at 273 K (0 °C) it is 0.76 ± 0.05 . The primary efficiencies were taken as 1/2 of the limiting quantum yields. Tracer experiments showed that the oxygen formed in the photodecomposition originated entirely from the hydrogen peroxide. The exchange between O_2 and H_2O_2 during the photodecomposition is at most very slight.

In aqueous hydrogen peroxide-formic acid solutions, a chain reaction is initiated by ionizing radiation or by 2537 Å light absorbed by the hydrogen peroxide. The principal gaseous product is carbon dioxide. The reaction is inhibited by oxygen, and from the quantum yield of oxygen consumption the primary quantum yield of hydrogen peroxide dissociation at 2537 Å was deduced to be 0.49 ± 0.065 [709]. From this yield and a comparison of the photochemical experiments with those in which the reaction is induced by γ -rays, one can calculate a G value of 3.06 water molecules decomposed to radicals per 100 eV of absorbed energy. These results suggested that the higher primary quantum yield reported earlier was in error. An alternate mechanism was proposed that fits the experimental data better.

Photolysis of Hydrogen Peroxide Vapor

The dynamics of photodissociation of H_2O_2 from low-lying excited electronic states was studied by classical trajectory calculations [710]. Potential energy functions were constructed for both the ground state and two excited states of H_2O_2 . Parameters in the ground-state function were chosen to fit measured vibrational frequencies, potential barriers, and the equilibrium structure. Parameters in the excited state functions were chosen to fit the observed $\bullet\text{OH}$ rotational state distribution and to be consistent

with the electronic spectrum. The moderate rotational excitation of the $\bullet\text{OH}$ radicals is mostly explained by the fact that the repulsive O—O force exerts a small torque around the center of mass of the $\bullet\text{OH}$ radicals as they leave the molecule.

A complete characterization of the scalar and vectorial properties of the $\bullet\text{OH}$ fragment formed by photodissociation of jet cooled H_2O_2 using Doppler and polarization spectroscopy showed that when hydrogen peroxide is optically excited at 193 nm, the hydroxyl radicals are formed exclusively in the $X^2\Pi_{3/2,1/2}$ ground state with 84% of the available energy ($E_{\text{av}} = 417 \text{ kJ/mol}$) being released as OH recoil translation [711, 712]. The remaining energy is transferred in product rotation. Vibrationally mediated photodissociation of hydrogen peroxide and variable curvature coordinates for molecular vibrations were described in [713].

In order to elucidate the mechanism of H_2O_2 photodissociation, especially the origin of the Λ -type preference of product $\bullet\text{OH}$, the potential energy surfaces containing the singlet and triplet states were calculated and the spin-orbit coupling was examined [714]. The relation of the Λ -component ratio with the product rotation J was consistent with the experimental findings of vector correlation.

A reinvestigation of the vibrationally mediated photodissociation spectrum of the third OH stretching overtone ($4\nu\text{OH}$) of jet-cooled H_2O_2 revealed anomalous double resonance spectral intensities compared with those observed via high-resolution absorption spectroscopy [715]. The origin of these intensity perturbations is traced to $J'\text{KaKc}$ level-dependent variations in the photodissociation cross section, δ_{00} , out of the intermediate overtone state. The photofragment $\bullet\text{OH}$ ($X, v = 0$) rotational state distribution generated by photodissociation of H_2O_2 ($4\nu\text{OH}$, $J'\text{KaKc} = 202$) was then determined. Combined with the relative cross-section data, these results implied that delocalization of the overtone state wavefunction into wide amplitude O—O stretching regions of the ground state is profoundly influenced by parent molecular rotation, primarily about the a and b axes. The intermediate state with $J' = 0$ was shown to be much more highly localized, and hence more likely to display mode selective behavior, than its $J' > 0$ counterparts.

The near-threshold dissociation of overtone-induced H_2O_2 corresponds to the dissociation through combination modes that contain five quanta in the OH local-mode stretching vibration, and various amounts of energy in other modes, such as O—O stretching, OOH bending, torsion, and molecular rotation [716]. The lifetime depends on whether or not the O—O stretching mode contains any excitation. The lifetimes of the bending combination modes are strongly affected by torsion and/or rotation, whereas the O—O combination lifetimes are less influenced by such additional excitations.

The primary quantum yields of $\bullet\text{OH}(X^2\Pi)$, $\text{H}(^2\text{S})$, and O atoms [$\text{O}(^1\text{D}) + \text{O}(^3\text{P})$] produced in the photodissociation of H_2O_2 at 193 and 222 nm were measured at 298 K [717]. At 193 nm, the primary quantum yields were 1.51 ± 0.18 , 0.16 ± 0.04 , and <0.02 , for $\Phi(\text{OH})$, $\Phi(\text{H})$, and the sum of $\Phi(\text{O})$ and $\Phi(\text{O}(^1\text{S}))$, respectively. At 222 nm, the OH yield was $\Phi(\text{OH}) = 2.02 \pm 0.35$, the H atom yield was $\Phi(\text{H}) = 0.024 \pm 0.012$, and $\Phi(\text{O})$ was

<0.002 . The OH product was directly monitored by pulsed laser-induced fluorescence, and the atomic species were detected via continuous wave (CW) resonance fluorescence. The OH quantum yields reported were measured relative to known product quantum yields in the dissociation of H_2O_2 at 248 nm. Up to 15% of the OH produced in the 193 nm photolysis may be vibrationally excited, but no evidence of vibrationally excited OH was observed at 222 nm.

Quantum mechanical calculations were carried out for UV photodissociation of H_2O_2 at photon energies of 248 nm [718]. The photodissociation process of H_2O_2 was simulated by the standard two-surface energy surface model using an *ab-initio* ground potential energy surface and a simple empirical excited surface. A time-dependent approach was employed in quantum dynamics calculations due to the short lifetime transient nature of the dissociation process. The computed rotational state distribution of the OH fragments was in qualitative agreement with results published by earlier investigators, with most of the excess energy being carried away by the relative translational motion of the $\bullet\text{OH}$ fragments. The effect of torsional mode on the rotational state distribution was investigated by calculating the Franck-Condon factors of photodissociation using torsionally excited bound state wavefunctions.

A quantum mechanical study on UV photodissociation of H_2O_2 at 248 and 266 nm looked at the rotational distributions of the product $\bullet\text{OH}$ on both the A and B energy surfaces [719]. The $\bullet\text{OH}$ radicals were found to be considerably hotter than those obtained in a previous quantum mechanical calculation. The dissociation preferentially produces $\bullet\text{OH}$ rotations with a high $J_1 \sim J_2$ correlation. These conclusions were in good agreement with earlier calculations.

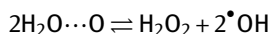
Hydrogen peroxide was photodissociated at 355 nm using both linearly and circularly polarized light, and $\text{OH}(^2\Pi)$ rotational distributions, spin-orbit branching ratios, doublet populations, and angular momentum J polarization were measured by polarized laser probing of the products using laser induced fluorescence [720]. There was evidence supporting preferential dissociation of ground-state molecules far from the equilibrium configuration, indicating possible mechanisms for the orientation of the product's angular momentum in the molecule frame.

The photolysis of hydrogen peroxide is a free radical reaction. The rate of decomposition of hydrogen peroxide vapor by photolysis at very low pressures, simulating processes in the upper atmosphere, will be affected by addition of free radical scavengers or reducing agents like hydrazine or hydroxylamine [721, 722]. The quantum yield of H_2O_2 photolysis decreased by 50% in the presence of hydrazine. It is known that the combination of hydrogen peroxide and hydrazine in the liquid state or at higher vapor concentrations is hypergolic, so one is curious why anyone would want to study the reaction of the two rocket propellants at very low pressures with illumination by actinic light. At higher concentrations, ultraviolet light illumination would trigger ignition of the two chemicals; see also [379].

4.11.3.1 Photolysis of Frozen Hydrogen Peroxide

Hydroxyl radicals formed by UV photolysis of hydrogen peroxide-water solutions can be trapped in a matrix of frozen ice at 90 K and identified by analysis with an electron spin resonance spectrometer [723, 724].

Fourier transform IR and luminescence spectroscopy diagnostics applied to UV-induced (from 193 to 380 nm) photolysis of H_2O_2 in solid argon at 18 K showed that the major photolysis products were: **(1)** a complex of monomeric water with atomic oxygen and **(2)** free $\cdot\text{OH}$ radicals [725]. A three-component photokinetic scheme



described all the features observed quite well. The wavelength dependence of the kinetics was measured, which gave the rate constants as a function of excitation wavelength. It was proposed that a photoinduced charge transfer between H_2O and O takes place with concomitant recombination into H_2O_2 .

Similar photorecovery of H_2O_2 from the tight $\text{H}_2\text{O}\cdots\text{O}$ complex was observed in Kr and Xe matrices instead of an Ar matrix [726]. The similarity of spectral position and efficiency of the photorecovery reaction in various rare gas solids indicated its fundamental character, supporting the theory of charge-transfer excitation of $\text{H}_2\text{O}\cdots\text{O}$ as its origin. In UV photolysis of H_2O_2 , a relatively small concentration of isolated $\cdot\text{OH}$ radicals was found in a Kr matrix, and no $\cdot\text{OH}$ radicals appeared in a Xe matrix. Among the photolysis products, the loose $\text{H}_2\text{O}\cdots\text{O}$ complex may be stabilized in Kr and Xe matrices. This loosely bound complex is quasistable and decomposes at relatively low temperatures (<20 K), quantitatively forming the known tight $\text{H}_2\text{O}\cdots\text{O}$ structure.

4.11.4 Decomposition of Hydrogen Peroxide in Intense Ultrasound Fields

It has been proposed to achieve instant decomposition of HTP by first aerating it with many small bubbles of an inert gas with a high adiabatic coefficient (e.g., helium with $\gamma = 1.66$) and then passing it through an intense ultrasonic (20 kHz) field [727]. Ultrasonic agitation and cavitation cause a dissipation of kinetic energy per unit mass of the fluid. This dissipation of turbulent energy will provide enough heat to instantly initiate decomposition of hydrogen peroxide, e.g., in a rocket engine.

4.12 Decomposition of Hydrogen Peroxide in the Vapor Phase

Hydrogen peroxide vapor decomposes much faster than H_2O_2 in the liquid phase, in particular at temperatures near or even above its sea-level pressure boiling point. The rate of hydrogen peroxide vapor decomposition depends on the vapor concentrations, temperature, pressure, vessel size, and mode and level of initiation stimulus. Both homogeneous and heterogeneous decomposition take place in a competing fashion.

The heterogeneous rate is very dependent on the wall material that the vapor is in contact with.

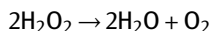
The slow vapor phase decomposition of hydrogen peroxide can be investigated in closed vessel static reactors (with manometric or spectrometric tracking of the progress of the reaction) or in dynamic flow reactors with on-line analyzers (such as mass spectrometers or spectrophotometers), or grab samples taken at specific times. The fast decomposition can be analyzed in shock tubes (usually with fast-registering spectroscopic diagnostics of the reacting species).

Satterfield and coworkers [728, 729] conducted a thorough study of hydrogen peroxide vapor decomposition and concluded that in the end all surfaces, also extremely clean ones, accelerate the decomposition of H_2O_2 vapors. Parts of the studies were conducted in a tubular reactor [730], while the rest of the experiments used a packed bed reactor with a larger exposed surface area [731]. Quartz and borosilicate (Pyrex[®]) glass are not as active as soft glass or even metal surfaces. Homogeneous decomposition was insignificant under all conditions studied there; it does not become appreciable at these concentrations until temperatures of about 723 K (450 °C) are reached. The experimental apparatus consisted of a vaporization section and a decomposition section. In the vaporization section, a hydrogen peroxide-water solution was fed continuously to an electrically heated borosilicate glass boiler through a leveling device that maintained a constant liquid level in the boiler. The boiler pressure was regulated by an external helium system. This system was capable of producing a steady flow of hydrogen peroxide vapor at a constant concentration. The hydrogen peroxide-water vapor mixture from the boiler first passed through an entrainment separator (aerosol trap) and then through an electrically heated borosilicate glass preheater. A portion of the vapor at this point was withdrawn for analysis by condensing it in a cold trap and determining the hydrogen peroxide content by potassium permanganate titration. The remainder of the vapor flowed through the reaction tube, and the effluent from the reactor was similarly condensed and analyzed. In passing the $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ vapor over a non-porous catalyst in a tubular reactor, the H_2O_2 concentration was varied from 3 to 32 mass-%, the catalyst temperature was varied from 478 to 755 K (400 to 1000 °F), and the Reynolds number in a 6.3 mm diameter and 46 or 61 cm long bed was varied from 3200 to 10000. In tests with a packed bed of 5-mm diameter silver beads in a 4.8-cm or 7.5-cm diameter reactor, with a catalyst bed length of 2.4 cm, the H_2O_2 concentration was varied from 5 to 24 mass-%, the catalyst temperature was varied from 478 to 811 K (400 to 900 °F), and the Reynolds number in a 4.8 cm diameter reactor was varied from 22 to 161.

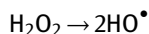
4.12.1 Kinetics of Slow H_2O_2 Decomposition in the Vapor Phase

A thorough understanding of the kinetics of H_2O_2 decomposition in the vapor phase will help the rocket engineer avoid hazardous conditions in the vapor space above liquid H_2O_2 in missile and satellite tanks, and in the coolant jacket and injector of rocket

engines, where H_2O_2 may evaporate after engine shutdown. The kinetics of H_2O_2 vapor decomposition also influence the efficiency of heterogeneous catalysts in H_2O_2 -powered gas (steam) generators and rocket engines. Decomposition of H_2O_2 vapor can proceed by several pathways, but the main end products are always water (steam) and oxygen.

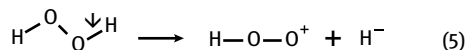
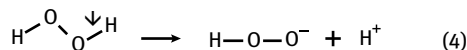
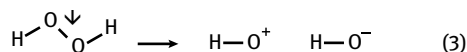
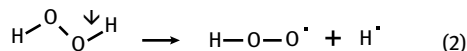
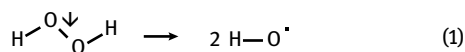


The O—O bond is the weakest bond in the molecule and as such the most likely one to rupture first. Intermediate reactions in the thermal decomposition of hydrogen peroxide are likely those involving dissociation into two hydroxyl-free radicals as the first step:



Subsequent disproportionation of hydroxyl radicals or hydrogen abstraction leads to the ultimate decomposition products.

Decomposition of energetic chemicals starts with breaking a chemical bond. Before starting to summarize the H_2O_2 decomposition kinetics literature, one can categorize the various reactions by the type of initial valence bond breaking process. Five types of initiation can readily be recognized. The vertical arrow indicates the place of bond scission:



The top two reactions do not involve electrically charged (ionic) fragments. The first two methods of bond breaking are examples of homolytic valence bond fission. Each fragment carries a free electron, which is characteristic of a free radical. The radicals formed are hydroxyl radicals $\text{HO}^\bullet$ in the first case (a hydroxyl radical mechanism), and hydroperoxyl (“perhydroxyl”) $\text{HOO}^\bullet$ and atomic hydrogen $\text{H}^\bullet$ in the second case.

The dot indicates the free electron. The lifetime of hydroxyl radicals in the presence of water vapor or in aqueous solutions can be extended by a rapidly occurring proton exchange.

The last three heterolytic scission mechanisms in which the electron from the shared bond remains with one of the fragments result in electrically charged ions. Therefore, these types of mechanisms are called ionic mechanisms. Mechanism (3) is called a hydroxyl ion mechanism. The last mechanism, mechanism (5) leading to a hydride ion H^- is very unlikely to occur and can be neglected in the following discussion.

The remaining four mechanisms can occur side-by-side as competing mechanisms. In most cases it is possible to identify the prevailing mechanism or the rate-determining mechanism. In the vapor phase with thermal, photolytic, glow discharge, or radiolytic stimulation, a free radical mechanism is most likely, not only for plain decomposition of pure H_2O_2 , but also for its reaction with other species. In the liquid phase, in aqueous solutions, it is more likely to encounter ionic species as intermediates, depending on the pH of the solution.

The reaction mechanisms of H_2O_2 decomposition have been elucidated by isotope labeling of either the hydrogen (deuterium or even tritium) or the oxygen (^{18}O) positions.

When the first shipments of impounded German HTP reached the shores of the US after WW-II, very little was known about the decomposition kinetics of this chemical. Consequently, largely with US Government funding and in support of on-going efforts to use HTP as an energy source and rocket propellant, H_2O_2 decomposition kinetics under various conditions (liquid and vapor) and with and without the presence of catalytic surfaces was actively investigated, resulting in a flood of reports and publications during the years 1945 through 1959.

The kinetics of the decomposition of hydrogen peroxide in the vapor state were studied by a static manometric method at pressures ranging from 10 to 20 mm Hg and temperatures from 343 to 473 K (70 to 200 °C), starting with pure hydrogen peroxide at a concentration of about 99.5 mass-% H_2O_2 and using Pyrex[®] or soda-glass vessels [732]. Under these conditions, the reaction was purely heterogeneous, of the first order up to 413 K (140 °C) but more complicated at higher temperatures. The rates were not affected by air, carbon dioxide, or water vapor, but they varied greatly with the size and shape of the vessel. The reaction was very slow on fused Pyrex[®] but very rapid on soda-glass. No explosions were encountered up to 608 K (335 °C) at a pressure of 180 mm Hg. The apparent activation energies in various vessels ranged from 56.4 to 77.4 kJ/mol (13.5 to 18.5 kcal/mol), which is much lower than that of a true vapor decomposition reaction.

The decomposition of hydrogen peroxide vapor at pressures of less than 1 mm Hg in silica vessels has been investigated over the temperature range 288–413 K (15–140 °C) with most data taken at 353 K (80 °C) [733]. Oxygen at low pressures was

found to have no appreciable influence on the rate of decomposition, but water vapor retarded the rate slightly. The reaction was predominantly a surface catalyzed reaction. In one vessel, the decomposition was bimolecular with respect to the peroxide pressure, the rate being given by

$$k[\text{H}_2\text{O}_2]^2/(1 + b[\text{H}_2\text{O}])^2.$$

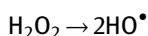
In another case, the bimolecular reaction of the final stages at low peroxide pressures was preceded by one of order approximately 0.7 at the higher pressures. Higher pressures of oxygen and nitrogen retarded the decomposition appreciably. At higher pressures of water vapor, a pronounced periodicity in rate was evident. The apparent activation energy over the temperature range investigated was not constant. It was 4.2 kcal/mol from rates at 288–413 K (15–70 °C) and 8.4 kcal/mol from rates at 353 and 413 K (80 and 140 °C). On the assumption that the lower value more closely represents a surface reaction, the velocity of decomposition, calculated for 1 mm Hg pressure of peroxide at 323 K (50 °C) by the theory of absolute reaction rates, was $0.70 \times 10^{13} \text{ mol cm}^{-2} \text{ s}^{-1}$, in agreement with the experimental value of $0.76 \times 10^{13} \text{ mol cm}^{-2} \text{ s}^{-1}$.

Decomposition of H_2O_2 vapor can proceed by several pathways; the main products are always water (steam) and oxygen. The following reactions are possible in H_2O_2 decomposition, but not all participate to the same extent. The reaction energies at 298 K of several of these reactions are summarized in Table 47.

Table 47: Reaction energy of hydrogen peroxide decomposition reactions.

Reaction	Enthalpy, kcal/mol	Enthalpy, kJ/mol
$\text{O}_2 \rightarrow 2\text{O}$	118.3	495
$\text{H}_2\text{O} \rightarrow 2\text{H} + \text{O}$	221.1	925
$\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$	119.9	502
$\text{OH} \rightarrow \text{O} + \text{H}$	101.2	423
$\text{H}_2\text{O}_2 \rightarrow 2\text{H} + 2\text{O}$	254.9	1067
$\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$	52.6	220
$\text{H}_2\text{O}_2 \rightarrow 2\text{H} + \text{O}_2$	136.6	572
$\text{H}_2\text{O}_2 \rightarrow \text{H} + \text{O}_2\text{H}$	90	377
$\text{O}_2\text{H} \rightarrow \text{H} + \text{O}_2$	46 (uncertain)	192 (uncertain)

In this table, the dissociation of H_2O_2 into two hydroxyl-free radicals has one of the lowest energy levels and is most likely the easiest one to achieve with only modest levels of energy input as a stimulus. Intermediate reactions in the thermal decomposition of hydrogen peroxide are likely those involving the first step of dissociation into two hydroxyl-free radicals:



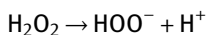
The O—O bond is the weakest bond in the molecule, and as such the most likely one to rupture first. Subsequent disproportionation of hydroxyl radicals or hydrogen abstraction leads to the ultimate decomposition products.

The decomposition of hydrogen peroxide at partial pressures of 1–2 mm Hg was studied in the presence of one atmosphere of oxygen or nitrogen or hydrogen using a flow system [734, 735]. The concentration of H_2O_2 was measured photometrically, using continuous ultraviolet absorption. Measurement by this means was more rapid and allowed less chance of errors of manipulation than wet chemical analysis. A first-order reaction with an activation energy of 40 kcal/mol was found for the homogeneous reaction in boric acid treated vessels at temperatures in the 470 to 540 °C range. Data in the presence of hydrogen indicated that the reaction proceeds by a chain mechanism involving no direct reaction between hydrogen and hydrogen peroxide molecules, at least not at low hydrogen concentrations. It was found that hydrogen+oxygen mixtures undergo appreciable reaction at temperatures where the rate of reaction is normally very small if small amounts of hydrogen peroxide are added first.

Another possible pathway involves the dissociation into hydroperoxyl free radicals and atomic hydrogen [736]:



Other decomposition pathways involve ionic species. One mode of dissociation is

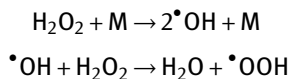


This reaction also occurs in the liquid phase and is responsible for the weakly acidic reaction of H_2O_2 solutions. At 298 K, the equilibrium constant for this reaction is 2.24×10^{-12} .

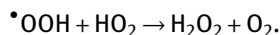
The thermal decomposition of hydrogen peroxide vapor was investigated by a static method as a function of initial pressure at pressures up to 22 mm Hg, and in the presence of inert gas (helium, oxygen, and water) up to 100 mm Hg [737]. In each case, the apparent first-order rate constant increased linearly with pressure. It was demonstrated that under those experimental conditions, the pyrolysis of hydrogen peroxide showed behavior typical of an elementary unimolecular reaction in its low-pressure, second-order region. The reaction was accompanied by a heterogeneous decomposition, which in the presence of foreign gas became inhibited. Helium was used as inhibitor over the temperature range 703–743 K (430–470 °C), which permitted calculating the activation energy for activation with peroxide and with helium. The kinetic rate expression is $10^{15.7} \exp(-48000/RT) \text{ L mol}^{-1} \text{ s}^{-1}$. It was noted that the preexponential term is much higher than the normal collision rate, which is why others postulated a chain reaction.

A flow system was used to investigate the decomposition of hydrogen peroxide vapor between 514 and 932 K (241 and 659 °C) [738]. It was shown that above 693 K

(420 °C), a homogeneous decomposition predominates, which is second order and occurs by the reactions:



followed by



The first reaction, which is rate-determining, occurs at a velocity depending upon the efficiency of M; the experimental order of third-body efficiencies being $\text{H}_2\text{O}_2 > \text{H}_2\text{O} > \text{CO}_2 > \text{N}_2 > \text{O}_2 > \text{He}$. When hydrogen peroxide was taken as M (the absence of diluent gases), the rate constant of the first reaction was calculated to be $10^{15.4} \exp(-48000/RT) \text{ L mol}^{-1} \text{ s}^{-1}$. It was shown that the results of earlier research were consistent with the above reaction scheme and rate constant. Although there have been several investigations into the kinetics of the decomposition of hydrogen peroxide vapor, there was no general agreement with respect to the order of the reaction or the magnitude of the activation energy of the vapor phase decomposition in the absence of catalytic surfaces [739]. In order to determine this, one of the main experimental difficulties was the elimination of heterogeneous decomposition. Some investigators used reaction vessels coated with boric acid, while others found that this coating was unsatisfactory and recommended the use of clean Vycor glass. Others used phosphoric acid coated vessels. Eventually, it was decided to use clean Pyrex[®] and silica vessels, which had been cleaned by rinsing with 40% hydrofluoric acid. It was shown that Pyrex[®] and silica surfaces thus cleaned are effective in the preservation of liquid and gaseous hydrogen peroxide. One series of experiments employed a flow reactor from Pyrex[®] (38 mm I.D. and 20 cm L) and an inert gas at 1 atm pressure as carrier, the hydrogen peroxide being decomposed at 241 to 478 °C. The source of vapor was from 85% hydrogen peroxide (containing a non-volatile stabilizer) kept in two or three bubblers whose temperatures could be adjusted.

Earlier investigators found the order of the homogeneous gas-phase decomposition of hydrogen peroxide to be unity with respect to peroxide. They also found the rate to be independent of total pressure. Forst [737] and Hoare, Protheroe, and Walsh [738] established both the first-order nature of the decomposition and the dependence of the rate on total pressure. This was confirmed and the range of experimental investigations was extended, and the decomposition of H_2O_2 in the presence of H_2 was examined [740]. For this study, the carrier gas (normally N_2) was saturated at 293 K (20 °C) by passage through two bubblers in series containing 90 or 99% H_2O_2 . A second diluent stream of N_2 could be added after the saturators. A large bulb ensured complete mixing, and in experiments with H_2 a third stream containing H_2 could also be added. The gas was then split into two almost equal parts by two capillary tubes in parallel. One stream passed directly through two cold traps in series, which condensed the perox-

ide vapor at 193 K (−80 °C). The second stream passed through the hot reaction vessel and then through cooled traps. The system could be operated at pressures down to 25 mm Hg. Reaction vessels were 20 cm in length, of diameters 6, 12, and 24 mm, with inlet and exit tubes of 6 mm bore. Plotting the data of homogeneous decomposition of H_2O_2 in aged boric-acid-coated vessels for three different diameters (23, 12, and 6 mm) and two different temperatures (762 K = 489 °C and 732 K = 459 °C) showed that the homogeneous process for the three vessel diameters was independent of diameter. The previously assumed activation energy $E = 190.3 \pm 2.1 \text{ kJ/mol}$ ($45.5 \pm 0.5 \text{ kcal/mol}$) agreed well with the value of $k_7 = 8.5 \times 10^{13} \exp(-45500/RT) \text{ mol L}^{-1} \text{ s}^{-1}$ obtained from the slope of that curve. With pure H_2 as carrier gas, the half-life relation suggested an order of approximately 1.5. Plotting the variation of the initial decomposition rate with the mol fraction x of H_2 for two initial concentrations of H_2O_2 showed that the initial rate increased linearly with x initially, then a maximum was reached, and the rate then decreased as x was further increased.

Hydrogen peroxide is an intermediate in the oxygen/hydrogen combustion reaction, but it decomposes just as fast as it forms [117]. The role of hydrogen peroxide in the formation of singlet atomic oxygen in the COIL chemical laser has been extensively investigated. The question has arisen why atomic singlet Δ oxygen cannot be generated from hydrogen peroxide directly without the involvement of chlorine or hypochlorite. A study of hydrogen peroxide decomposition kinetics with regard to hydroxyl-free radical formation and singlet oxygen formation was done in the hope of explaining the interaction of reacting hydrogen peroxide on the surface of hybrid fuels [741]. It was tried to demonstrate, from thermodynamic and kinetic point of views, the effect of introducing singlet oxygen and hydroxyl radicals into the gaseous mixture that can oxidize the solid fuel in a hybrid engine. From a literature survey, it has been shown that both reactants can be formed by the decomposition of hydrogen peroxide on selective catalysts, but under conditions quite different from the real-world operating conditions in a rocket engine. This paper contains a set of kinetic rate data that are also useful for kinetic evaluation of other reactions involving H_2O_2 .

4.12.2 Slow Vapor Phase Decomposition of Hydrogen Peroxide

It is difficult to study the vapor phase decomposition of pure hydrogen peroxide without interference from the wall materials. Most wall materials, even if they have previously been passivated, exert a catalytic effect on the decomposition reaction, which makes it difficult to determine kinetic rates of the homogeneous vapor reaction. Often, tests are conducted with different volume : surface ratios in order to single out surface effects. All these vapor phase decomposition tests were conducted at very low pressures. There are hardly any vapor phase decomposition tests that were conducted at rocket engine operating pressures, which is what we really need to know. Everything else is just an academic exercise that may be of interest to atmospheric pollution meteorologists but not to rocket propellant chemists.

4.12.2.1 Closed Vessel Static Reactor Experiments

The decomposition of H_2O_2 vapor was studied at low pressures in the temperature range from 323 to 693 K (50 to 420 °C) to determine the effect of the type and the pretreatment of the surface of the reaction vessel [742]. One-liter round bottom flasks made of Pyrex[®], soft glass, quartz, or metalized glass were used as reaction vessels. In most cases, the decomposition was found to be of the first order, but the rates varied from one vessel to another, even those made of the same type of glass. In a quartz vessel, the reaction at low temperatures was preceded by an induction period. The marked surface effects pointed strongly to a heterogeneous reaction, which was further shown by a wide spread of values for the energy of activation from 8 to 20 kcal/mol. The catalytic nature of the decomposition due to wall effects is difficult to characterize.

The kinetics of the vapor-phase decomposition of H_2O_2 were studied by a static method at 0.2–20 mm Hg between 573 and 873 K (300 and 600 °C) [743]. The rates were first order with respect to time, and the reaction products were H_2O and O_2 . Below 673 K (400 °C) the surface-catalyzed reaction predominated, whereas above 673 K the gas phase reaction was faster. After correction for the residual surface decomposition, the vapor rate equation becomes

$$k = 10^{13} \exp(-48000/RT) \text{ s}^{-1}$$

With initial pressures around 1.3 kPa (10 mm Hg), the apparent activation energy was 180 kJ/mol = 43 kcal/mol. On subtracting the extrapolated rate of surface decomposition from the overall rate, the activation energy for the homogeneous reaction was estimated to be 201 kJ/mol (48 kcal/mol), or about the magnitude of the O—O bond dissociation energy. The rate increased with increasing partial pressure. The presence of inert gases or glass packing had only a slight effect. D_2O_2 vapor showed the same rate as H_2O_2 vapor. The following mechanism was suggested:



This is rate determining and is followed by:



4.12.2.2 Dynamic Flow Reactor Experiments

It is very difficult to eliminate wall effects if one wants to measure homogeneous vapor decomposition of hydrogen peroxide. A study of the thermal decomposition of hydrogen peroxide vapor under flow conditions in a relatively inert glass reactor showed a transition from heterogeneous to homogeneous reaction in the temperature range of 673 to 723 K (400 to 450 °C), at a partial pressure of 2 kPa (0.02 atm) [744]. The homogeneous reaction was at 3/2 order and had an activation energy of 230 kJ/mol

(55 kcal/mol). The decomposition mechanism appears to involve a very long straight chain reaction.

A series of US Government contracts in the late 1940s and throughout the 1950s sustained a very active research group at Massachusetts Institute of Technology in Cambridge, MA, which resulted in many progress reports, several Master's and PhD theses, and a book on the decomposition of hydrogen peroxide [745–748].

The heterogeneous decomposition of H_2O_2 vapor on platinum or CRES-304 was studied in a 6-mm (0.25 in.) ID tubular reactor at temperatures of 403 to 733 K (130 to 460 °C), Reynolds numbers of 370 to 4100, and vapor concentrations up to 2.1 mol-% H_2O_2 at atmospheric pressure [729, 749]. Nitrogen carrier gas was passed through HTP in a bubbler flask in a constant temperature bath and saturated with H_2O_2 according to its vapor pressure at that preselected temperature. The reactor(s) had an ID of 6 mm and were 91 cm (36 in.) long and carried an array of thermocouples. The platinum reactor was a copper tube with a 0.47 mm (0.0185 in.) thick platinum coating on its inside. All data showed first-order overall kinetics with respect to H_2O_2 , which were not affected by the presence of O_2 , H_2O or N_2 . A surprising result was that the first-order overall rate constant for H_2O_2 decomposition on platinum or stainless steel went through a maximum at about 573 K (300 °C). For a fixed Reynolds number in either the laminar or turbulent flow region, the overall rate constant went through a maximum. The slope of the Arrhenius plot of the log of the rate versus the reciprocal absolute temperature on CRES 304 indicated an activation energy of 60 kJ/mol (14.3 kcal/mol). Another Arrhenius plot provided a comparison of the silver and stainless steel data from this study to data reported for the homogeneous decomposition and decomposition on Pyrex[®] glass cleaned with either phosphoric acid or hydrofluoric acid.

A special type of flow reactor consisting of a tube whose walls are made of a porous material through which an inert gas can be passed to reduce diffusion of the reacting species back to the potentially catalytic vessel surface was used for the study of homogeneous H_2O_2 vapor decomposition [750]. This method allows one to separate the relative contributions of homogeneous and surface-catalyzed effects in a gaseous reaction involving both mechanisms, or at least to minimize the surface effects. Porous-walled tubes of Pyrex[®] (fritted glass) or CRES-316 were jacketed, respectively, with impervious Pyrex[®] or CRES tubes, wrapped with a heating jacket and mounted vertically. Flow rates through the core tube were 0.04 to 0.4 mol H_2O_2 /min, and reactor temperatures were from 358 to 451 K (85 to 178 °C). The inert carrier gas was bubbled through thermostatted HTP solutions and picked up ~4 mol-% H_2O_2 , along with some water. Diluent gas flowing through the porous wall prevented H_2O_2 from contacting the hot wall.

4.12.2.3 Wall Effects During Vapor Phase Decomposition of Hydrogen Peroxide

Various reactor wall materials have been tested in an effort to find a material that does not interfere with measuring vapor decomposition rates. Typical materials tested are Pyrex[®] glass or quartz (silica).

A study of the heterogeneous radical decomposition of hydrogen peroxide vapor discovered the accumulation of HO_2 radicals in the gas phase during the decomposition of H_2O_2 on surfaces of Pyrex[®] glass or silica [751]. It was found that for short contact times (10^{-2} s) and low pressures (of the order of several hundred Pa), the decomposition of H_2O_2 occurred mainly on the external surface. An activation energy of 4.6 kJ/mol was obtained for the heterogeneous decay of HO_2 radicals on these surfaces at 473–623 K.

By measuring the decomposition of hydrogen peroxide vapor on Pyrex[®] glass, SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, MgO , or CuO over temperatures ranging from 373 to 623 K for dwell times for the flow to pass through the reactor of 10^{-3} to 10^{-2} s, at a partial pressure of H_2O_2 of 0.072 kPa and a total pressure of the mixture of 0.53 kPa in a carbon dioxide atmosphere, it was shown that the decomposition of H_2O_2 on oxides is autoaccelerated [752]. The effective activation energy of the process in the autoacceleration region was greater than at the fastest rates. The decomposition of H_2O_2 under these conditions was accompanied by the liberation of HO_2 radicals from the surface to the gas phase. The rate of H_2O_2 decomposition and generation of HO_2 radicals increased in the order: glass < SiO_2 < $\gamma\text{-Al}_2\text{O}_3$ < MgO < CuO .

From experimental data on the influence of water on the state of the surface, it was tentatively concluded that clusters are formed on the surface with the participation of adsorbed water molecules, and that the decomposition of H_2O_2 on these clusters proceeds more efficiently than on other surface centers, thus auto-accelerating the process [753]. After the test, holding the system under vacuum resulted in removal of the weakly bound water, breakdown of the clusters, and reversion of the surface to its initial state; see also [754].

4.12.3 Rapid Vapor Phase Decomposition of Hydrogen Peroxide

In order to obtain accurate kinetic rates at high temperatures, one must bring the sample to the test temperature very quickly, otherwise the decomposition that is already taking place while bringing the sample up to test temperature will mess up the results. The fastest and most reproducible method to bring a sample to high temperature is in a shock tube.

One of the most reactive and short-lived intermediates in H_2O_2 decomposition is the hydroxyl-free radical $\bullet\text{OH}$, which has a telltale signature in both emission and absorption spectra or can even cause chemiluminescence in the shocked vapor as it cools off after the shockwave has passed through [755].

Hydrogen peroxide and hydrazine are both energetic monopropellants, and studies of the rapid decomposition of these compounds in the vapor state typically used shock tubes. Some studies deal with both compounds and studied them side-by-side (but not premixed in the same tube).

The thermal dissociation of H_2O_2 , highly diluted with argon, was investigated in a shock tube [756]. The unimolecular dissociation of H_2O_2 near the low-pressure limit was investigated by an ultraviolet absorption technique, which gave

$$k_4 = 10^{16.5} \exp(-43000/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

between 950 and 1450 K. Experiments at 2.02 MPa (20 atm) indicated the beginning of the fall-off region. In addition to H_2O_2 spectra, light absorption corresponding to an unknown species that forms and is consumed again during the reaction, possibly due to HO_2 , was observed around 2300 Å.

A study of the mechanism and the reaction rates of the hydrogen peroxide decomposition for temperatures in the range of 1000–1400 K reported the activation energy for hydrogen peroxide decomposition [757, 758]. The high gas temperatures required for the experiments were obtained by means of a shock tube apparatus, which was a pressure-driven type having a driver section of 3.95 m (13 ft.) and a driven section of 7 m (23 ft.) Helium-air mixtures were used as the driver gas, while 3 vol-% hydrogen peroxide-argon and 3 vol-% hydrogen peroxide-nitrogen mixtures were the two test gas mixtures used at 5.3 kPa (40 mm Hg). The shock tube, made of 316 stainless steel, was found to catalyze the heterogeneous decomposition of H_2O_2 and had to be passivated by passing H_2O_2 vapor through for several hours prior to each test. The activation energy of H_2O_2 decomposition was 208 kJ/mol (49.8 kcal/mol) in argon and 223 kJ/mol (53.3 kcal/mol) in nitrogen. This is in good agreement with literature data reporting this number as 48 kcal/mol. This is close to the energy required for breaking an O—O bond in the HO—OH molecule (217 kJ/mol = 52 kcal/mol).

High concentrations of short-lived $\text{HOO}^\bullet$ free radicals are formed as intermediates during the thermal decomposition of H_2O_2 . With sensitive instrumentation, an electronic spectrum of the free radical could be detected [759]. The thermal decomposition of H_2O_2 in argon as carrier gas has been studied in reflected shockwaves at $950 < T < 1450$ K. In addition to the H_2O_2 absorption continuum, a second continuum was found at $2200 < \lambda < 2800$ Å, which has been attributed to $\text{HOO}^\bullet$. The time dependence of this second absorption continuum agrees well with predictions for the $\text{HOO}^\bullet$ decay time under a wide variety of conditions. The absorption coefficient of $\text{HOO}^\bullet$ can be estimated from measurements taken during the decomposition of H_2O_2 .

A study of the mechanism of the reactions of hydrogen peroxide in the gas phase gave agreement with the experimental data within a broad range of conditions [760]. The reactions of hydrogen peroxide may slow down the rate of combustion of hydrogen but may be neglected at temperatures greater than 1000 °C.

Because of the large amount of experimental data and theoretical analysis available, the dissociation of hydrogen peroxide has become a textbook model case for simple unimolecular bond fission processes. Detailed and simplified statistical adiabatic channel calculations of specific rate constants $k(E, J)$ and product quantum state distributions for the simple bond fission reaction $\text{HOOH} \rightarrow 2^\bullet\text{OH}$ were compared with measurements of state-resolved dissociation rates, product state distributions, $^\bullet\text{OH}$

recombination rates, and thermally averaged rate coefficients [761]. A simple modification of phase space theory based on a statistical adiabatic channel model successfully predicted product state distributions and rate constants.

Hydroxyl-free radical $\text{HO}^\bullet$ concentration-time profiles were recorded during the thermal decomposition of H_2O_2 in shockwaves between 930 and 1680 K by monitoring resonance absorption near 308.4 nm [762]. The results were analyzed with respect to the reactions



and



Above 800 K, reaction (1) showed a strong increase of the rate constant with temperature. Over the range $240 \leq T \leq 1700$ K, the apparent rate constant was represented as

$$k_2 = 1.7 \times 10^{18} \times \exp(-14800 \text{ K}/T) + 2.0 \times 10^{12} \exp(-215 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The rate constant k_3 decreased from a value of 2.0×10^{13} at 1100 K to a minimum value of 1.1×10^{13} at 1250 K, and rose again to a value of $4.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 1600 K. The anomalous temperature dependences of k_2 and k_3 suggested mechanisms involving intermediate intermolecular complex formation.

The thermal decomposition of H_2O_2 was studied behind reflected shockwaves using absorption spectroscopy at 215 nm with light from a laser source and at 215, 230, and 290 nm with light from a UV lamp [763]. Due to the improved detection sensitivity for H_2O_2 and $\text{HOO}^\bullet$, rate constants for the reactions



and



could be derived with much better precision than was possible in earlier work. Rate constant minima for reactions (3) and (4) near 800 and 1100 K, respectively, agreed with previous measurements. Falloff curves of reaction (1) near the low-pressure limit were measured in experiments at about 1, 4, and 15 bar. Limiting low-pressure rate constants for reaction (1) of about

$$k_{1,0} = [\text{Ar}] 10^{16.36 \pm 0.23} \exp[-(21962 \pm 608) \text{ K}/T] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

were obtained over the temperature range 950–1250 K. The deviations from the low-pressure limit at relatively low pressures may provide experimental evidence for non-exponential lifetime distributions of dissociative H_2O_2 such as observed in classical trajectory calculations on the *ab-initio* potential of H_2O_2 .

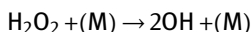
Statistical adiabatic channel model/classical trajectory calculations of the dissociation/recombination dynamics of hydrogen peroxide, $\text{H}_2\text{O}_2 \rightleftharpoons 2\text{HO}^\bullet$, have been performed on an *ab-initio* potential energy surface, providing specific rate constants $k(E,J)$, thermal rate constants $k_\infty(T)$ and lifetime distributions [764]. The thermal high-pressure rate constants for $\text{HO}^\bullet$ recombination agreed with experimental data.

The thermal decomposition of hydrogen peroxide was measured behind reflected shockwaves in H_2O_2 /inert gas mixtures using a sensitive laser diagnostic method for water vapor concentration measurement [765]. In these mixtures, the rate of water formation was predominantly controlled by the decomposition rate of H_2O_2 . Rate determinations were made over a temperature range of 1000–1200 K and a pressure range of 0.9–3.2 atm using either argon or nitrogen as the carrier gases. Good detection sensitivity for water was achieved using the tunable diode laser absorption of water at 2550.96 nm within its ν_3 fundamental band. Hydrogen peroxide decomposition rates were found to be independent of pressure at 0.9 and 1.7 atm and showed only a slight influence of pressure at 3.2 atm. The best fit of the data to the low-pressure-limit rate for H_2O_2 dissociation in the range 1000–1200 K in argon gas was

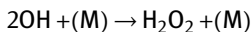
$$k_1 = 10^{15.97 \pm 0.10} \exp(-21220 \pm 250 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Experiments conducted in nitrogen carrier gas showed a relative collision efficiency of argon to nitrogen of 0.67.

Experimental rate coefficients for the thermal dissociation



and the reverse recombination



were combined with modeling results based on an *ab-initio* potential energy surface calculation [766]. The rate coefficients derived from the complementary experimental and modeling results were represented over wide ranges of temperature and pressure, including ranges of interest for practical applications, including limiting low- and high-pressure rate coefficients as well as detailed and simplified expressions for rate coefficients in the falloff range.

The rate of hydrogen peroxide decomposition behind reflected shockwaves in diluted H_2O_2 /Ar mixtures between 930 and 1235 K and at three different pressures (1, 2, and 10 atm) was measured using mid-IR absorption of H_2O_2 near $7.7 \mu\text{m}$ [767]. Under these conditions, the decay of hydrogen peroxide was sensitive only to the decomposition reaction rate, $\text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{OH} + \text{M}$ (k_1). The second-order rate coefficient at low pressures (1 and 2 atm) did not exhibit any pressure dependence, suggesting that the reaction was in the low-pressure limit. The rate data measured at 10 atm exhibited falloff behavior. The decomposition rates measured can be expressed in Arrhenius forms as follows:

At 1 atm and at 2 atm:

$$k_1 = 10^{(16.29 \pm 0.12)} \exp(-21993 \pm 301/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

and for 10 atm:

$$k_1 = 10^{(15.24 \pm 0.10)} \exp(-19955 \pm 247/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

See also [768, 769].

4.12.4 Ignition Limits of Vapor Phase Decomposition of Hydrogen Peroxide

Explosive characteristics of hydrogen peroxide vapor at atmospheric and subatmospheric pressures, including values for the ignition limit over this pressure range and the effect of the nature of diluent gases and method of initiation on the limit have been reported [770, 771]. In continuation of these studies, ignition limits were determined over the pressure range of 101 to 655 kPa (14.7 to 95 psia) [772]. The term “ignition limit” was defined as the minimum concentration of hydrogen peroxide in a vapor mixture,

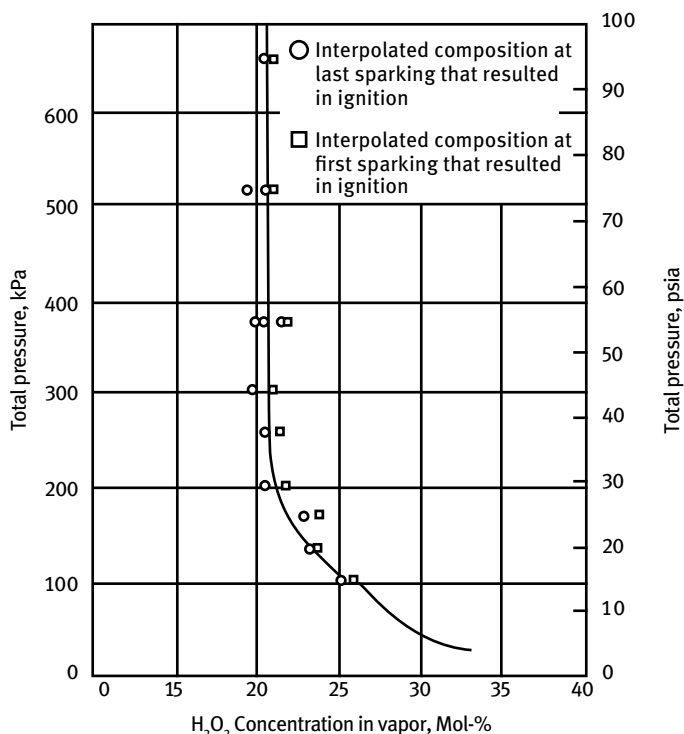


Figure 51: Ignition limit of hydrogen peroxide/water vapor at pressures above atmospheric pressure. (Reprinted and modified from [772], with permission from © 1959 American Chemical Society; permission conveyed through RightsLink.)

under specified conditions, below which powerful external ignition cannot initiate a self-propagating reaction. The concentration of H_2O_2 in the vapor phase of a high-pressure boiler pressurized with nitrogen was allowed to gradually increase until ignition by a high-voltage spark caused ignition in a 5-cm (2-in.) diameter bulb. Upon ignition, the temperature in the ignition bulb jumped sharply and extensively. Between 2- and 6-atm pressure, the ignition limit was found to be constant at 20.7 mol-% H_2O_2 in the vapor. At atmospheric pressure, the limit was found to be 25.6 mol %, slightly lower than the previously established value of 26.0 mol-% (Figure 51).

4.13 Strand Burning, Droplet Burning, and Explosion Limits of Hydrogen Peroxide

4.13.1 Flame Speed of Stabilized Hydrogen Peroxide Vapor Flames

Hydrogen peroxide vapor decomposition flames can be stabilized on a burner even in the absence of a combustible fuel. The energy of the decomposition flame is derived solely from the monopropellant-mode exothermic decomposition of the energetic chemical. The hydrogen peroxide decomposition flames are not very luminous since the temperatures are relatively low, and there are no species in the flame that emit radiation in the visible range.

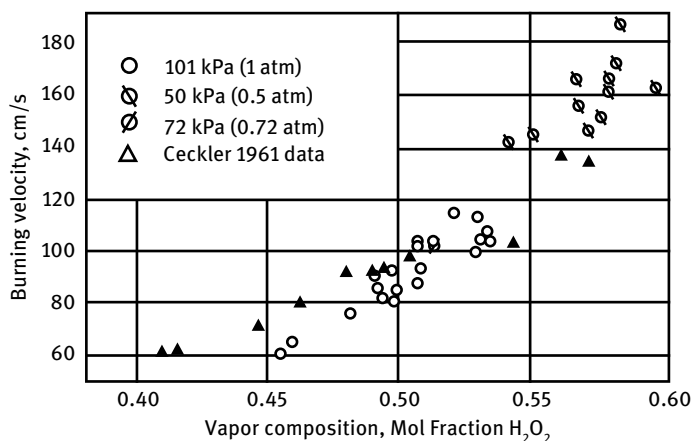
For the decomposition above the liquid, flames were obtainable over the liquid of lower concentrations only at temperatures close to the boiling point of the liquid. At the higher concentrations, flames could be obtained and sustained over a considerable range of liquid temperatures. Hence, only at these higher concentrations was it possible to map the effect of liquid temperature on the flame velocity. Flames were sustained in the range of 71.2 to 100 mol-% of H_2O_2 . Flames may be obtained at boiling liquid concentrations as low as 69.8 mol-%. If the tube diameter was increased, no apparent influence was observed on the flame velocity except when working at high concentrations [773].

The flame speed of H_2O_2 decomposition flames at reduced pressures from 50, 72, and 101 kPa (0.5, 0.72, and 1 atm) was measured using a Bunsen burner method [774, 775]. A plot of the logarithm of the product of the square of the burning velocity and the pressure versus the reciprocal flame temperature gave a good correlation between the data obtained here at all pressures. Another graph, plotting the product of the square of the burning velocity and the pressure versus the strand burning velocities above liquid solutions of H_2O_2 , gave also an almost linear relationship. This covered a 200-fold range of burning velocities. In another graph, the burning velocity was also correlated with the quenching distance and some approximate blowoff and flashback limits of the vapor flame. The flame speed dependence on vapor temperature followed the kinetics expected for a first-order reaction with an activation energy of 146 kJ/mol (35 kcal/mol). Table 48 and Figure 52 give the flame speed as a function of the H_2O_2 concentration. The vapor temperature was always kept 9 °C above the prevailing boiling point in order to prevent condensation; see also [776, 777].

Table 48: Flame speed of H_2O_2 vapor at 101 kPa.

H_2O_2 Concentration, mass-%	Flame speed, m/s
51.5	0.30
55.0	0.41
57.0	0.52
60.0	0.61
62.5	0.89

Data source: [774, 775]

**Figure 52:** Burning velocity of hydrogen peroxide vapor as a function of vapor concentration. (Reproduced and modified from [774].)

4.13.2 Strand Burning Rates of Liquid Hydrogen Peroxide

The strand burning regression rate of liquid H_2O_2 was measured in quartz tubes [778]. The liquid regression rate agreed with the vapor flame speeds. The mass consumption rate (normalized by the cross-sectional area of the burning strand) as summarized in Table 49 agreed with the calculated vapor flame speed summarized in Table 50.

The ignition temperature of H_2O_2 vapors on a hot surface was measured for different materials [778]. This information is useful for the safe design of hydrogen peroxide distillation systems where hot spots must be avoided by all means; see also [779].

The strand burning velocity of 90% H_2O_2 at 0 and 30 psig was measured in 8-mm ID tubes by Rocketdyne [780]. Such tubes were selected because the literature appeared to indicate that wall effects were negligible in a container of that size. Ignition was accomplished with a nichrome resistance wire heated to a bright red hot 1144 to 1255 K (1600 to 1800 °F). Ignition could not be obtained in either the vapor or liquid phase when the bulk liquid temperature was below 383 K (230 °F) at 0 kPa gauge

Table 49: Mass consumption rates during strand burning of H₂O₂ solutions at sea-level atmospheric pressure.

H ₂ O ₂ concentration in liquid	Vapor temperature		Density	Theoretical adiabatic flame temperature		Mass consumption rate
	°C	K		°C	K	
Mol-%			g/cm ³			mg s ⁻¹ cm ⁻²
95.0	119	392	1.32	1044	1317	26
96.0	118	391	1.33	1045	1318	25
87.0	115	388	1.30	920	1193	16
85.5	115	388	1.30	907	1180	16
83.0	117	390	1.28	854	1127	14
74.0	132	405	1.25	824	1097	10
96.8	126	399	1.32	1054	1327	33

Data source: [778]

Table 50: Calculated flame speed of decomposition flames above H₂O₂ solutions.

H ₂ O ₂ concentration in vapor	Vapor temperature		Theoretical adiabatic decomposition temperature		Flame speed
	°C	K	°C	K	
Mol-%					m/s
40.3	142	415	1062	1335	0.545
39.4	143	416	1048	1321	0.436
36.3	171	444	1017	1290	0.375
41.4	152	425	1090	1363	0.506
38.5	176	449	1056	1329	0.570
39.9	146	419	1058	1331	0.452
45.0	150	423	1148	1421	0.870
47.9	154	427	1198	1471	0.927

Data source: [778]

(0 psig) or below 390 K (242 °F) at 206 kPa gauge (30 psig). Ignition could not be accomplished at 688 kPa gauge (100 psig) even at a bulk liquid temperature of 439 K (330 °F). The burning rates obtained are summarized in Table 51 and illustrated in Figure 53.

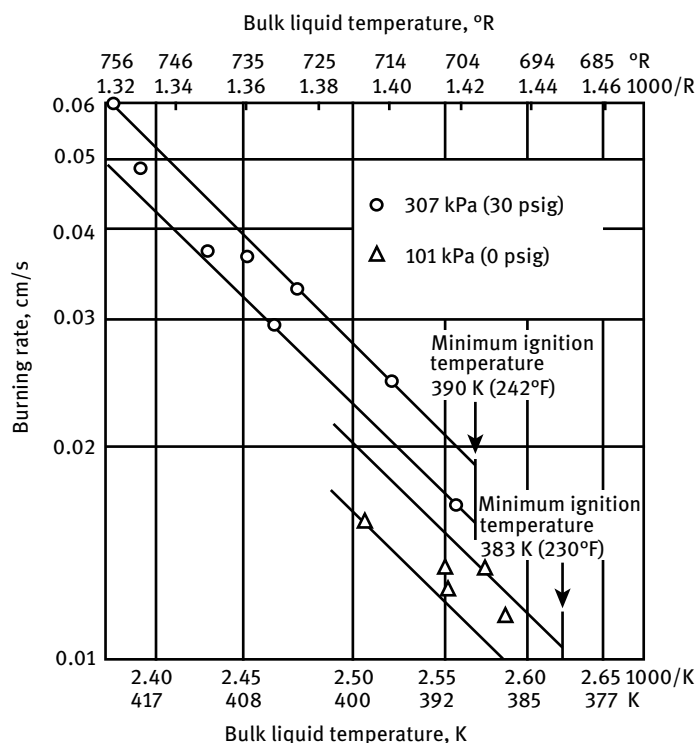
4.13.3 Strand Burning Rates of Liquid Hydrogen Peroxide Mixtures

A ternary PERSOL-1 blend consisting of 46% AN, 38% H₂O₂, and 16% H₂O had a very low freezing point of 248 K (−25 °C) and a density of 1.415 g/mL and was evaluated as an oxidizer for a non-hypergolic non-toxic fuel. Attempts to measure strand burning rates of PERSOL-1 at ambient temperature, 313 and 333 K, in a windowed constant pressure bomb failed because the oxidizer failed to propagate and reaction was quenched as soon as the electric power to the heated nichrome igniter wire was turned off [781].

Table 51: Strand burning rates of 90% hydrogen peroxide in 8-mm ID tubes.

Pressure, kPa gauge	Pressure, psig	Average tempera- ture, K	Average tempera- ture, °F	Burning rate, cm/s
0	0	387.4	237.7	0.0115
0	0	392.0	245.9	0.0126
0	0	388.9	240.4	0.0134
0	0	391.9	245.8	0.0136
0	0	398.6	257.8	0.0156
206	30	391.2	244.5	0.0167
206	30	396.5	254.0	0.0246
206	30	405.9	271.0	0.0294
206	30	404.3	268.0	0.0330
206	30	408.4	275.5	0.0368
206	30	411.8	281.5	0.0373
206	30	417.6	292.0	0.0488
206	30	420.1	296.5	0.0596

Data source: [183]

**Figure 53:** Strand burning rate of 90% H_2O_2 versus reciprocal absolute temperature. (Reproduced and modified from [183].)

4.14 Droplet Burning Rates of Liquid Hydrogen Peroxide

Hydrogen peroxide droplets injected into and suspended in a flow of hot gas will evaporate and decompose rapidly. This happens in the zone close to the injector of bipropellant rocket engines and in the second stage of catalyst-free monopropellant rocket engines with a pilot reactor. The hot gas the droplets are injected into could be created by a pilot reactor (with catalyst), which would be started and brought up to steady-state temperature before the H_2O_2 is injected into a downstream hollow secondary reaction chamber.

A liquid spray of high concentration hydrogen peroxide was injected into a hollow chamber holding a stream of peroxide decomposition products at pressures ranging from 2.07 to over 5.5 MPa (300 to over 800 psia) [782]. A decomposition efficiency was calculated based on the ratio between measured chamber pressure and chamber pressure predicted by equilibrium chemistry calculations. Experimental parameters included concentration of the liquid H_2O_2 , residence time, mass, and momentum ratio between the decomposition stream and the injected liquid, and injection area. Decomposition efficiencies ranging between 10 and 90% were achieved. A limited number of highly accurate differential pressure measurements were made to determine local axial pressure gradients. The results indicated that liquid mass fraction was inversely proportional to decomposition efficiency, while the residence time and hydrogen peroxide concentration were directly proportional. Aqueous hydrogen peroxide solutions with two different weight concentrations, 90 and 98%, were used as secondary flows. The first 22 tests, called preliminary tests, were performed simply to determine an efficiency map and the flooding limits. One of the main goals of the preliminary tests was to map the decomposition efficiency of injected liquid with different ratio between mass-weighted decomposed gas and injected liquid.

In continuation of these studies, a well-instrumented subscale combustor was used to measure axial pressure profiles [783]. The results were compared to 1-D numerical modeling to determine the axial energy release profile in the combustor. Again, a liquid spray of high concentration hydrogen peroxide (HTP) was injected into a gas stream of decomposed hot products of HTP from a catalyst bed at chamber pressures ranging from 1.38 to 6.2 MPa (200 to 900 psia). The effects of area variation, mass and enthalpy addition, heat transfer, and frictional effects were evaluated. A study of design parameters (injector design, contraction ratio, and chamber length) and operating parameters (mass flow rate fraction, gas-to-liquid ratio, HTP concentration, gas-to-liquid momentum ratio, and residence time) helped to evaluate the combined effects on the thermal decomposition of the injected HTP. These measurements later helped to develop a model of HTP droplet evaporation in hot gas flows in a rocket engine [784, 785] (*Encyclopedia of Monopropellants*, chapter “Hydrogen Peroxide Monopropellants”).

A one-dimensional model was developed to investigate the thermal decomposition of rocket-grade HTP injected as a fine droplet spray into a stream of previously

decomposed HTP products [786–789]. The model assumed steady, one-dimensional adiabatic flow and included basic mass balances, droplet evaporation, gas-phase decomposition kinetics, droplet dynamics, and control volume conservation laws. The code was adjustable for HP percent concentration for both main and secondary flows, mass flow rates for both flows, and the initial temperature of each. Results were shown to be consistent with prior experimental measurements. Additional parameters are initial droplet size, secondary injectant flow, mass velocity in the primary stream, HTP concentration, and initial liquid temperature on the decomposition process. In general, results indicated unacceptably-long decomposition distances assuming 90% HP decomposition products in the primary stream. Using 98% HTP showed some improvement due to the enhanced decomposition temperature of this fluid as compared to 90% HTP.

An alternate approach to the catalytic decomposition for HTP decomposition is thermal decomposition, where no catalyst is required (at least not in the downstream part of the reactor). If the rate of thermal decomposition can be controlled, the ensuing technology will prove to be a viable and inexpensive alternative to using catalysts. A kinetic and CFD detailed model of the steps for HTP decomposition over a wide range of temperatures and pressures combined with CFD simulations of a dual-chamber (catalytic-non-catalytic) was applied to a HTP decomposer described in a patent by Pratt & Whitney [790] and was based on the fundamental kinetic rates for 27 reactions involving O and H [791]. Computation results were shown for injecting different concentrations of H_2O_2 (10, 30, 40, 50% H_2O_2) into the hot gas delivered by the primary reactor. A similar model can be applied to model decomposers for generating a stream of atomic oxygen in a COIL laser.

It was planned to conduct the fundamental research necessary to understand the purely thermal decomposition kinetics of HTP and its interactions with common stabilizers, in order to design a practical non-catalytic thermal decomposer [792, 793]. The utilization of HTP as rocket propellant could be greatly simplified by using a thermal decomposer rather than a catalyst bed for decomposition. This would require a thermodynamic analysis of self-reactivity and a reaction kinetics model for thermally decomposing HTP, and stability and inhibitor modifications thereof, that could serve as the basis of a conceptual design of a practical thermal decomposer.

4.15 Analysis of Hydrogen Peroxide

In using hydrogen peroxide and other rocket propellants, the analyst will face different tasks. The most important one is the assurance that hydrogen peroxide that has been stored for a while still meets the specification requirements for assay. The incessant decomposition of hydrogen peroxide, as slow as it may be, is a continuing concern for rocket engineers. Other analytical tasks relate to the detection of traces of H_2O_2 vapors in the atmosphere at workplaces and in the wastewater leaving the test

sites. For many H_2O_2 applications, such as in catalytic monopropellant reactors, the stabilizer content is troublesome because too much stabilizer may foul the catalyst. The types of stabilizer and the amount used may need to be analyzed from time to time, in particular each time after switching H_2O_2 suppliers. Organic contaminants in H_2O_2 may be residuals from the manufacturing process (if not using an electrolytic method), or they may have been added as stabilizer (oxine, citric acid). Other organic contaminants may have been introduced inadvertently and leached from gaskets or transfer hoses. In either case, we need methods to analyze organics in hydrogen peroxide.

Military procurement specifications specify not only the required assay and purity levels, but also contain recommended or required methods on how to perform the analysis.

The previously quoted books and monographs on hydrogen peroxide contain chapters on analytical methods [2, 18]. Manufacturers' product information bulletins may also provide additional information on analytical methods [794]; see also [23, 795].

4.16 Assay of Hydrogen Peroxide

Although MIL-P-16005D recommended determination of H_2O_2 assay by ceric sulfate titration, a survey of the industry indicated that as of the 1960s, most laboratories preferred H_2O_2 assay determination by a permanganate titration because of the ease in identification of the end point by color change. However, all laboratories can perform the ceric sulfate titration with equivalent accuracies.

The fastest non-chemical method to determine the H_2O_2 content in aqueous solutions up to very high H_2O_2 concentrations is the measurement of the refractive index [796]. Density and refractive index methods for determining hydrogen peroxide in cleaning baths were compared to the potassium permanganate titration method. The refractive index method was shown to be rapid and simple and required only a few drops of sample. This method exhibited a $\pm 0.14\%$ H_2O_2 standard deviation for a single measurement and an average bias of -0.002% H_2O_2 compared to the titration method. The refractive index method has been implemented at a process line for fast results at a substantial cost savings. Refractive index data for 293 and 298 K were already summarized in Tables 20 and 21.

Attempts to determine the assay of H_2O_2 by measuring the density with a spindle or a pycnometer are often thwarted by the small bubbles forming on the glass surface.

Another method to determine the assay of H_2O_2 solutions between 70 and 95% is to measure the adiabatic decomposition temperature in a catalytic reactor and compare the temperature to the theoretically predicted or empirically derived temperature [795, 797]. This apparatus does not need much electricity and can be operated under

field conditions. It may take up to 16 min before stationary reactor temperature conditions are achieved. The concentration can be calculated from the following equation:

$$t_{\text{ad.}} = 2540c - 1545 + 2.00(t_0 - 20)$$

where $t_{\text{ad.}}$ = adiabatic decomposition temperature, °C, c = mass-% H_2O_2 , and t_0 = initial temperature of liquid H_2O_2 , °C. One may have to carry out a calibration series and apply a corrective factor, depending on the apparatus used. The standard deviation can be as low as 0.05% H_2O_2 absolute.

A comparison fluid density measurement, refractive index measurement, and the potassium permanganate volumetric methods of analysis ranked the methods by accuracy in the sequence Manual KMnO_4 Titration > Refractive Index > Density, with the refractive index method having the best precision (± 0.02 mass-% H_2O_2) [437, 798]. The recommended technique of HTP assay is the permanganate titration method, which yields credible results over time of HTP storage and is consistent with supplier certification data and the historical analysis database. Results of an assay by refractive index tend to be approximately 0.8 mass-% lower than for KMnO_4 titrations with 98% HTP but is judged as equivalent when 90% HTP is analyzed and compared to the permanganate method. The refractive index method for HTP concentration offers superior precision and ease and convenience of analysis. Results from densitometry data were unreliable, with variability likely due to the less mature measurement techniques used at that time. Densitometry is not as convenient a technique as the other two methods but can be shown to provide equivalent results to either alternate tests if using accurately calibrated pycnometers and stable temperature control. The use of modern state-of-the-art density meters, such as the Mettler DE45, may afford acceptable results but may require additional method development effort.

The NMR transverse relaxation time T_2 of aqueous H_2O_2 solutions depends on the rate of exchange of the spin-bearing protons between H_2O_2 and H_2O molecules. For pulse separations exceeding the inverse exchange rate, this value becomes a constant, depending only on the proton exchange time and the magnetic field strength. This exchange time depends in a non-analytical way on the concentration of H_2O_2 and on the pH value. Thus, a measurement of T_2 and pH allows the inversion of the data for the non-invasive quantitative determination of the H_2O_2 concentration [298, 449]. The method was applied to measure the time profile of a heterogeneously catalyzed H_2O_2 decomposition using commercial catalyst pellets by monitoring the reactant concentration and the effective diffusion coefficient of the liquid in the vicinity of the pellet or in a defined closed volume. The decrease of the concentration during the course of the reaction was monitored, and the long-time deactivation of the pellet can be demonstrated using this technique. This is a new method for contact-free and non-invasive on-line monitoring of H_2O_2 concentrations.

The mass fraction of hydrogen peroxide can be determined by a titration method in accordance with the Chinese National Standard GB 1616-2003 [799]. The uncertainty

caused by the potassium permanganate standard solution is the worst contributor to inaccuracies.

4.16.1 Analysis of Traces of Hydrogen Peroxide Vapors in the Atmosphere

There are numerous contact and non-contact, remote sensing methods to analyze H_2O_2 in the atmosphere on Earth and other planets. This is done to identify the role that H_2O_2 plays in natural processes (in particular as the result of increasing UV radiation passing through a damaged ozone layer) in the atmosphere, as well as H_2O_2 formed in the wake of industrial pollution. These methods are also useful in monitoring the air in workplaces, such as rocket test sites and launch sites where personnel may be exposed to H_2O_2 vapors, and occupational hygiene threshold limit values must not be exceeded.

The following method arose from the need to analyze for more than traces of H_2O_2 in the air of surgical equipment manufacturing and packaging facilities. The widespread use of hydrogen peroxide as a clean, non-residue disinfectant is based on its ability to kill harmful bacteria and not leave any residues. Hydrogen peroxide vapor is used in a method like ethylene oxide or ultraviolet light to prevent bacterial contamination during the packaging and sealing of sterile surgical supplies and dispensing of IV solutions. Like ethylene oxide, hydrogen peroxide vapor in these industrial settings is an explosion hazard and needs to be closely monitored. A calorimetric gas sensor for the detection of vaporized H_2O_2 in aseptic filling processes was built up on a polyimide foil as substrate material in order to optimize the sensor response behavior [800, 801]. These sensors are built up in the form of a differential setup of a catalytically active and a passive temperature-sensitive structure. The sensor was catalytically activated with a dispersion of manganese(IV) oxide. The calorimetric gas sensor possessed a linear response behavior with a sensitivity of $7.15\text{ }^\circ\text{C}/(\text{vol.}\% \text{H}_2\text{O}_2)$ in a H_2O_2 concentration range from 0 to 8 vol.-%.

Tunable diode laser absorption spectroscopy is one of the most sensitive methods to determine hydrogen peroxide vapor in ambient air with sub-ppb_v (parts per billion by volume) detection limits for fast measurement times of the order of minutes [802]. Calibrating the instrument with constant vapor concentrations of a labile substance is not easy. In atmospheric chemistry, the mixing ratio usually refers to the mol ratio, which is defined as the amount of a constituent n_i divided by the total amount of all other constituents in a mixture. Ambient air monitoring with the tunable diode laser system indicated that the hydrogen peroxide mixing ratio was often smaller than 0.3 ppb_v. Five-minute average mixing ratios of up to 2.9 ppb_v were measured at sites in southwestern Ontario, Canada, during the summer months of 1984 and 1985, while the highest 1-h average value observed was 2.1 ppb_v.

Much higher concentrations of H_2O_2 are encountered where H_2O_2 is vaporized to sterilize hospital rooms, air ventilation ducts, or surgical equipment. On-line and essentially continuous measurements of hydrogen peroxide vapor in the presence of water vapor can be made using near infrared (NIR) spectroscopy using fiber optic cables

to transmit infrared radiation between the remote location where measurements must be made, e.g., a sterilization chamber and the NIR instrument located behind barriers [803]. Hydrogen peroxide absorbs selectively at about 1420 nm, where water vapor also absorbs, but the absorbance at 1420 nm can be corrected for water by taking separate vapor measurements at remote wavelengths (1350–1400, 1830–1900, or 915–950 nm) where H_2O_2 is transparent.

The Draeger short-term detector tubes have proven to be a very cost-effective and reliable way to measure toxic gases and vapors in the workplace. The Draeger Hydrogen Peroxide tube, Catalogue Part No. 81 01 041, measures 0.1–3 ppm H_2O_2 .

The Draeger CHIP is a self-contained unit that has a pump and a digital readout. Each disposable chip contains ten measurement capillaries filled with a substance-specific reagent system. The reactive preparations necessary for detection are kept in hermetically-sealed glass capillaries until needed. When the chip is inserted into the analyzer, all information required for detection is transferred to the analyzer by means of a bar code:

- type of gas
- measuring range
- measuring time
- parameters for the calibration function
- required flow rate

The analyzer records the measurement effect optoelectronically, thereby eliminating human error in reading a color scale. In the CHIP Measuring System, miniaturization has resulted in a reduction in the sample volume necessary for a measurement (compared to the manual bellows pump with ten strokes). For a typical measurement, only 30 mL of air is needed for a measuring time of approximately 2 min and a flow of 15 mL/min. The power needed for operation of the analyzer is provided by four AA batteries. After inserting the chip, an optical system calculates the number of remaining measurements still available on the chip being used and displays this together with the gas type and the measuring range. Up to 50 measurement results can be stored in the machine with the name of the measured substance, the concentration, date and time of the measurement, and a code letter to help identify the measurement location.

For a more accurate, continuous monitoring of hydrogen peroxide vapors in air, the H_2O_2 (XS) electrochemical sensor with a Draeger Pac III apparatus has a range of 0–20 ppm H_2O_2 , a resolution of 0.1 ppm, and the Draeger Part Number is 68 09 170.

The Dräger X-am 5100 was specifically developed for the detection of hydrogen peroxide or hydrazine reactive gases in air. The X-am 5100 with the sensor XS is particularly suited to applications such as monitoring H_2O_2 during the bleaching process in pulp and paper production, monitoring sterilization units used in the medical field, and monitoring hydrogen peroxide at the workplace.

Hydrogen peroxide vapor concentrations in sterilization chambers for surgical equipment or beverage cartons can be monitored by a calorimetric gas sensor using

manganese(IV) oxide as the catalyst [804]. XPS was used to unravel the surface chemistry prior to and after exposure of the catalyst to hydrogen peroxide vapor at elevated temperature. The surface characterization revealed a change in oxidation states of the metal oxide catalyst after exposure to hydrogen peroxide.

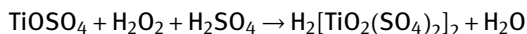
4.16.2 Analysis of Small Concentrations of Hydrogen Peroxide in Aqueous Solutions

The need to analyze for small concentrations of hydrogen peroxide in water may arise when analyzing rinse waters from HTP propellant tanks before discharging them into surface waters or sewers or sending them to holding ponds for neutralization. Some passivation procedures require the rinsing to continue until all H_2O_2 is removed from the tank. In this case, it would be good to have an instant readout from a probe dipped into the outgoing rinse water to decide when the rinse is complete. The turnaround time for the analysis of grab samples would just be too long. Similar, but rare occasions arise where HTP has been spilled accidentally and washed down with copious amounts of water. Then the next question is how much H_2O_2 remains in the impounded deluge water, and how it should be treated before it can be released.

Hydrogen peroxide can be an oxidizing agent or a reducing agent. Potentiometric and amperometric electrical analysis methods have been developed to analyze small concentrations of H_2O_2 in aqueous solutions in the absence of interfering agents.

4.16.3 Analysis of Hydrogen Peroxide in Wastewater

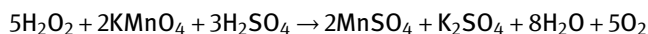
The easiest-to-perform qualitative test for traces of hydrogen peroxide in aqueous solutions uses a solution of titanyl sulfate in dilute sulfuric acid. Titanyl ions form an intensely yellow complex with hydrogen peroxide:



The test can be sensitive to H_2O_2 concentrations in water as low as 1 to 2 ppm. It is best performed by acidifying the sample with 6-N sulfuric acid and adding several drops of a 10% solution of titanyl sulfate in 6-N sulfuric acid. The test is specific for H_2O_2 , and there are few interferences. Peroxydisulfate or ozone do not interfere, and the color does not fade as quickly as that produced by organic reagents for H_2O_2 .

A simple and rapid method for the spectrophotometric determination of hydrogen peroxide used potassium titanium(IV) oxalate [805]. The method can be used to measure peroxide concentrations down to about $10\text{ }\mu\text{M}$ (0.3 mg/kg) under the most favorable conditions. A variety of complexing and reducing agents, and catalysts of peroxide decomposition, known to interfere with the alternative iodide method for peroxide determination, had no effect. Fluoride was found to interfere.

For quantitative determination of hydrogen peroxide in dilute aqueous solutions and in the absence of other reducing materials one will best use the manganometric volumetric titration.

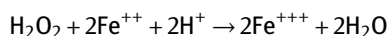


The source of the dioxygen formed in this reaction was unclear initially in the early years of H_2O_2 chemistry. It has now been shown that the dioxygen comes from the H_2O_2 , and that the oxygen from the KMnO_4 ends up as water.

In order to carry out a manganometric titration, the sample containing approximately 350 mg H_2O_2 is diluted with 50 to 100 mL of 3-N (25%) sulfuric acid and titrated with 0.5-N KMnO_4 solution to a persistent purple color. Another redox titrant that can be used for this analysis is cerium(IV) sulfate, which is more stable for storage as a solution. KMnO_4 solutions often change their titer during storage and need to be recalibrated by titration with sodium oxalate. Another volumetric method adds an excess of potassium iodide to the acidified sample, allows it to stand for 5 min, and titrates the liberated free iodine with standardized sodium thiosulfate solution, adding starch indicator only toward the end of the titration.

The volumetric methods are not sufficiently accurate to determine assays of highly concentrated H_2O_2 . Small amounts of H_2O in H_2O_2 are better analyzed using physical methods instead of wet chemistry methods.

The oxidation of iron(II) by hydrogen peroxide is a convenient source of free hydroxyl radicals (Fenton's reagent). The end products are iron(III) and water



In looking for a method for continuous analysis of flowing H_2O_2 solutions in a flow-through cell, polarography was evaluated as one of the candidate methods [806] using a dropping-Hg electrode and a stationary Pt electrode. The diffusion current increased linearly with peroxide concentrations up to 0.15% with 0.1-N KCl as supporting electrolyte. At higher concentrations the electrode became erratic. When a fixed Pt electrode was used, the diffusion current increased linearly with concentrations up to 0.9%. Rotating Pt electrodes gave unsatisfactory results. Since the limiting current in solid microelectrodes is dependent both on dissolved O_2 and peroxide content, they are of little value in continuous analysis of flowing H_2O_2 solutions.

4.16.3.1 Volumetric Methods

The assay of hydrogen peroxide can be determined by titration with cerium(IV) sulfate solution with ferroin indicator as described on pages 9–13 of a US Army analytical procedure [807].

4.16.3.2 Electrical Potentiometric and Polarographic Methods

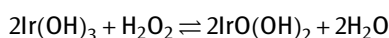
Many of the electrodes used for electrochemical analytical methods will also serve as electrodes for fuel cells. In fuel cells, one wants to keep the output voltage constant, thus one must maintain a constant H_2O_2 concentration in the cell. In analytical applications, the concentration of H_2O_2 is unknown, and one must wait for the voltage potential to stabilize before one can take a reading. In either case, the electrodes must not be such good catalysts that they decompose the H_2O_2 prematurely even while no

current is flowing. In other applications, one can deliberately coat the electrode with a catalytic layer and then measure the potential of the oxygen gas evolved.

Hydrogen peroxide can be polarographically assayed by anodic oxidation. This method is very sensitive but lacks specificity for peroxide in the presence of other redox-active substances that undergo anodic oxidation, such as ascorbic acid. However, if H_2O_2 is first catalytically decomposed to O_2 and H_2O , then the O_2 can be assayed polarographically using an oxygen electrode. Furthermore, specificity for just oxygen can be obtained by placing a hydrophobic membrane over the O_2 electrode. Polarographic measurement of O_2 or H_2O_2 is the basis for several enzyme-coupled electrodes. An inorganic catalyst electrode was made by covering an oxygen electrode with a membrane that catalyzed the breakdown of hydrogen peroxide to oxygen [808]. This electrode is similar in principle to an enzyme electrode, but has better stability gained by using an inorganic catalyst instead of catalase. Of the many different metal compounds that were tested, only the compounds of manganese, cobalt, or ruthenium showed high catalytic activity.

Hydrogen peroxide sensors can use carbon-based electrodes loaded with perovskite-type oxides [809] or Prussian Blue-based artificial peroxidase [810]. Other electrodes are made from carbon nanotubes [811].

Some of the electrodes for analysis of H_2O_2 in air or in water can be miniaturized and mounted on a semiconductor chip. A hydrogen peroxide sensor was developed based on an electrolyte MOSFET (E-MOSFET), and different types of redox materials were tested as gate materials with respect to sensitivity and detection limit [812]. E-MOSFETs with electro-active gate materials such as iridium oxide, potassium ferric ferrocyanide, and osmium polyvinylpyridine containing a peroxidase enzyme were tested with respect to their sensitivity, detection limit, and stability. The determination of hydrogen peroxide is based on the oxidation of the iridium(III) oxide by hydrogen peroxide



Another sensor was based on osmium-polyvinylpyridine (Os-PVP) doped with horseradish peroxidase. An enzyme catalyst can be used as the gate material, or it can be immobilized into a gate membrane material. Horseradish peroxidase is known as an enzyme that can selectively catalyze the reduction of hydrogen peroxide, and it can be immobilized in the cross-linked redox polymer OsPolyvinylpyridine (Os-PVP), which is a non-diffusional mediator. The operating range of three different electrode materials for H_2O_2 detection was:

Ir oxide	$10^{-4} - 10^{-1} \text{ M}$
Prussian Blue	$10^{-5} - 10^{-3} \text{ M}$
Os-PVP horseradish peroxidase	$10^{-7} - 10^{-5} \text{ M}$

A fiber-optic sensor sensitive to hydrogen peroxide was based on the electrostatic layer-by-layer self-assembly method using Meldola's blue and a catalyst hemin de-

posited in a polymeric structure formed by polycyclic aromatic hydrocarbon PAH^+ and PAA^- [813]. The concentrations that could be detected ranged between 10^{-7} and 10^{-1} M, and recovery of the sensor after immersion in a reducing agent was quick.

4.16.3.3 Electrical Amperometric Methods

Hydrogen peroxide could be analyzed using electrodes of ruthenium/rhodium deposited as thin layers on gold foils when the cathodic reduction at potentials was lower than +170 mV, or the anodic oxidation was at higher potentials [814]. Under flow injection conditions H_2O_2 was detected between 1 and 1000 μM H_2O_2 at a potential of -100 mV and between 2 and 500 μM H_2O_2 at a potential of +250 mV vs. $\text{Ag}/\text{AgCl}/0.4\text{-M}$ KCl .

4.16.3.4 Electrical Coulometric Methods

A direct coulometric determination of hydrogen peroxide with electrogenerated hypobromite is both sensitive and precise [815]. The end point is determined amperometrically with two polarizable electrodes. As little as 1 μeq of peroxide was determined with a 0.2% error.

A procedure was developed for the determination of hydrogen peroxide by controlled-potential coulometry [816]. The method involved the oxidation of hydrogen peroxide at a platinum electrode at +0.93 volt versus SCE (saturated calomel electrode) in a supporting electrolyte of 1-M sulfuric acid, a complete electrolysis required 3 to 2 min. Moderate amounts of cations, common organic stabilizing agents, peroxydisulfate ion, and chloride ion did not interfere. The heterogeneous, catalytic decomposition of hydrogen peroxide at the platinum electrode at open circuit was nearly as rapid as the electrolytic oxidation. In the range of 0.1 to 2 mg of hydrogen peroxide in a solution volume of less than 5 mL the relative standard deviation of the determination was $\pm 0.1\%$.

4.16.3.5 Spectrophotometric Methods

Infrared Spectrophotometric Methods

Near infrared spectroscopy has been used for the determination of hydrogen peroxide in antiseptic pharmaceutical preparations where it is found in concentrations of about 3.0% [817]. Standard solutions containing hydrogen peroxide in the range 0–10% were prepared and analyzed. Absorbance spectra in the wavelength range from 850 to 1800 nm were obtained using a transreflectance probe with an optical path length of 1 mm. The region from 1400 to 1550 nm is dominated by a strong absorption band from water, the first overtone of O—H. A decrease in the absorption in this region is observed in the presence of H_2O_2 , while an increase in the absorption is noted in the region from 1550 to 1750 nm. The method was evaluated by using prepared and commercial samples of pharmaceuticals containing H_2O_2 in the range from 1 to 20%, resulting in a mean square root standard error of 0.05%.

Midinfrared attenuated total reflection (ATR) spectroscopy was used to measure the concentration of hydrogen peroxide in aqueous matrices [818]. The performance of different ATR crystals mounted in flow cells was investigated in the presence of aqueous hydrogen peroxide solutions. Quantitative determination was achieved by evaluation of specific OH stretching and deformation vibrations with linear correlation between peak areas or peak heights and hydrogen peroxide concentration in the range of 1–10% H₂O₂.

Raman Spectrophotometric Methods

A handheld Raman spectrometer can be used to determine hydrogen peroxide concentration in aqueous solutions in a very short time using relative peak heights of the strongest peroxide (876 cm⁻¹) and perchlorate (932 cm⁻¹) bands with sodium perchlorate as an internal standard [819]. This method provides a very rapid technique to allow the determination of hydrogen peroxide concentrations in the field, for example, at suspected improvised explosives manufacturing sites.

Chemiluminescence Methods

Luminol (5-amino-2,3-dihydro-1,4-phthalazinedione, 3-aminophthalic hydrazide) reacts with oxidants like hydrogen peroxide in the presence of catalysts [hemoglobin, iron(II)hexacyanide] under the emission of light. The light intensity is proportional to the amount of hydrogen peroxide, even if it is present in only very low concentrations. The chemiluminescence method can be combined with chromatographic methods and used as a means of detecting hydrogen peroxide peaks in the effluent.

The optimum conditions of high-performance liquid chromatography combined with luminol chemiluminescence detection were established for the determination of hydrogen peroxide at picomol levels using a cation exchange gel column [820]. A gel column with distilled water as the mobile phase allowed a good separation of H₂O₂ without causing any irreversible binding of H₂O₂ to the column surface. The detection limit and the quantification limit of H₂O₂ were 4 and 6–600 pmol, respectively.

A chemiluminescence method with a subnanomolar detection limit for the determination of H₂O₂ is based on the catalytic [cobalt(II)] oxidation of luminol by hydrogen peroxide in an alkaline solution [821]. The mixed reagent is optimized for pH and concentration of luminol and Co²⁺. The method has been used to determine the concentrations of H₂O₂ in seawater samples in the open ocean as well as on the continental shelf.

A flow injection type hydrogen peroxide detection system based on chemical photoluminescence spectroscopy had the lowest detectable limit of 0.3 ppb H₂O₂. The relationships between the hydrogen peroxide concentration and luminous intensity were expressed as a linear function and a quadratic function of the H₂O₂ concentration [822]. The dependencies of the chemiluminescent intensity on luminol concentration and pH of the mixed reagent were mainly determined by a balance between OH radical concentration and luminol concentration.

4.16.3.6 Analysis of Stabilizer Type and Content in Stabilized Hydrogen Peroxide

The Constantine and Cain *Hydrogen Peroxide Handbook* [246] gives a useful summary and comparison of various analytical methods for determination of contaminants in HTP, based on interviews with chemists of the analytical laboratories of several HTP producers at that time.

Phosphate

The DuPont procedure for the determination of the phosphate ion is essentially identical to MIL-P-16005D, except that the ether extraction is omitted. The Shell procedure also omits the ether extraction and uses hydrazine instead of stannous chloride to develop the molybdenum blue color [823]. The FMC procedure is somewhat different. FMC reported that attempts to use this procedure (MIL-P-16005D) failed to give valid or reproducible results.

The phosphate content of hydrogen peroxide can be determined by a phosphomolybdate yellow spectrophotometric method measuring absorbance at 460 nm [824]. The minimum detectable content is 0.5 µg/mL.

Tin and Stannate

Both DuPont and FMC suggested the use of a polarographic method for determining tin in contrast to the spectrophotometric technique recommended in MIL-P-16005D. Shell used a spectrophotometric technique, which was different from that in MIL-P-16005D; the stannic tin is extracted into an 8-hydroxyquinoline-chloroform solution at a pH of 0.85, and the tin was determined spectrophotometrically in the chloroform extract. Tin in hydrogen peroxide can be determined by atomic absorption spectrophotometry [825].

Nitrate

Nitrate can be added to HTP as a stabilizer. FMC analytical methods recommended that the heating step with the phenoldisulfonic acid reagent, employed in the determination of the nitrate ion, be increased to 15 min (up from 5 min) to ensure complete contact and nitration of the sample residue. The Shell procedure utilizes a larger sample size and increases the heating time to 10 min.

4.16.3.7 Analysis of Inorganic Contaminants in Hydrogen Peroxide Chloride

At a time when Shell Chemical was still producing HTP, their chemists suggested determination of the chloride ion by the measurement of turbidity with a colorimeter instead of the spectrophotometer specified in MIL-P-16005D [823].

The FMC procedure is a colorimetric method using mercuric thiocyanate and ferric ammonium sulfate [826].

Sulfate

For the determination of sulfate, DuPont recommended the use of a preliminary perchloric acid oxidation to measure total sulfur, instead of only sulfate sulfur. Shell recommended precipitation with barium chloride, stabilization of the suspension by the addition of alcohol and glycerin, and turbidity measurements with a photoelectric colorimeter-nephelometer. FMC also suggested the use of a turbidimeter (rather than the spectrophotometer) and a method that converts SO_4^{2-} to H_2S instead of a caustic addition with BaSO_4 precipitation.

Aluminum

In the spectrophotometric procedure specified in MIL-P-16005D for the determination of the aluminum ion, an aluminum-gelatin buffer solution is used for color formation. The DuPont and Shell procedures suggest the use of 8-hydroxyquinoline and extraction with chloroform for color formation.

Ammonium

In determination of the ammonium ion by spectrophotometry, the DuPont method separates the ammonia from the other contaminants by Kjeldahl-type distillation before color formation. The FMC and Shell procedures essentially agreed with MIL-P-16005D, except FMC suggested that greater accuracy may be achieved by increasing the sample size from 10 to 50 mL.

4.16.3.8 Analysis of Organic Contaminants in Hydrogen Peroxide

Volatile organic contaminants in hydrogen peroxide can be analyzed by combustion gas chromatography [827].

Typical contaminants found in Propulse™ rocket-grade HTP are illustrated in Figure 54 from [100].

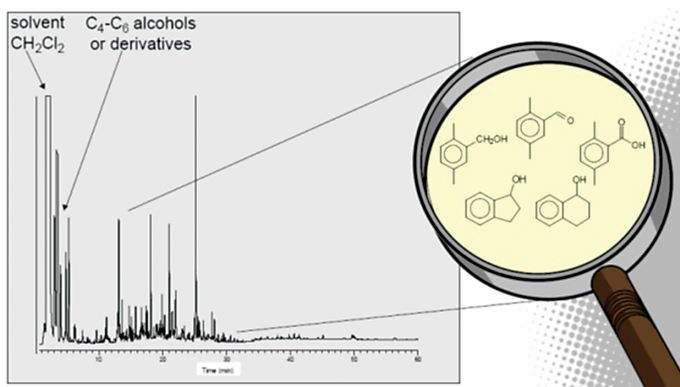


Figure 54: Typical contaminants found in Propulse™. (From [100], with permission granted by Evonik Operations GmbH.)

The total carbon content in hydrogen peroxide can be analyzed by using a Multi N/C 2100 total C/N analyzer [828]. This method exhibited good linearity, the relative standard deviation was less than 5%, the standard recovery was from 99 to 107%, and the detection limit was as low as 194.2 µg/L.

4.17 Procurement Specifications for Hydrogen Peroxide

Procurement specifications for hydrogen peroxide for military and space propulsion applications have evolved over the years. The most commonly used specifications are the military specifications.

The first military specifications issued covered 70 and 90% HTP intended for use in torpedoes [829]. It required much higher stabilizer levels than the later issued MIL-P-16005. It required the simultaneous use of all three stabilizers for 90% HTP: tin, 4 mg/L, added as sodium stannate $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, 4 mg/L phosphate added as disodium hydrogen phosphate dodecahydrate $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 20 mg/L nitrate added as sodium nitrate NaNO_3 and supplemented by nitric acid for pH adjustment. This stabilized HTP was called *E-stabilized hydrogen peroxide*. The impurity limits established for torpedo-grade hydrogen peroxide were based on the stabilization requirements for maximum storability with respect to torpedo use; thus, very high concentrations of the phosphates, tin, and nitrate ions were required. In the establishment of limits for propellant-grade hydrogen peroxide, minimum stabilization requirements had to be met, but concentrations of stabilizers that cause catalyst poisoning were strictly controlled and kept as low as necessary. Phosphate, which acts as a stabilizer by complexing the heavy metal ions that promote H_2O_2 decomposition, is a severe catalyst poison; thus, its content in propellant-grade H_2O_2 is limited. Tin (as stannous chloride) is added to the peroxide as a stabilizer to offset the effects of residual phosphate; therefore, a minimum limit was established for tin. The tin content in H_2O_2 will gradually decline during storage due to colloid agglomeration and suspended particle settling from the solution. The chloride and sulfate ion concentrations are limited because they cause container corrosion (through solution of aluminum). Nitrate has been found to inhibit the effects of chloride and sulfate, and a lower level has been established for this ion to inhibit container corrosion.

MIL-P-16005 Rev. E was released in 1968 and canceled in 1988. MIL-P-16005 Rev. E was intended to control 90 and 98% H_2O_2 rocket oxidizer and monopropellant and was used in programs such as Redstone, X-15, and Scout. The cancellation coincided with termination of the Scout satellite launch vehicle in the US (the Scout derivative rocket was used in Italy a few years longer than in the US). At that time, hydrogen peroxide covered by the MIL-SPEC was made by three different methods: electrolytic, anthraquinone, and isopropyl alcohol methods. As of 2000, only the anthraquinone process is still in use in the US. That affected the types of contaminants one had to look for. MIL-P-16005 Rev. F was issued in 2003 [830, 831].

Table 52 gives a summary of the purity and assay requirements established by military specifications for several types and grades of HTP. There are two different grades for HTP: Grade ES – **extra** stabilizers, which contains higher concentrations of stabilizers, and Grade HP – **high** purity which conforms with stricter limits on types and concentrations of stabilizers and metals.

Table 52: Military Specification MIL-PRF-16005E requirements for hydrogen peroxide assay and purity.

Properties	Limits				
	Type 70	Type 85	Type 90	Type 98	
	Grade ES	Grade ES	Grade ES	Grade HP	Grade HP
Hydrogen peroxide assay (percent by weight)	71.0–73.0	85.0–87.0	90.0–91.5	90.0–91.5	98.0–99.0
Anions					
Chloride (Cl ⁻) mg/kg	0.8 max	0.2 max	2 max	0.5 max	0.5 max
Nitrate (NO ₃ ⁻) mg/kg*	3.9 max	5.0 max	7.5 max	5.0 max	5.0 max
Phosphate (PO ₄ ³⁻) mg/kg	0.2 max	0.2 max	0.5 max	0.2 max	0.2 max
Sulfate (SO ₄ ²⁻) mg/kg	2.3 max	0.5 max	5 max	0.5 max	0.5 max
Ammonium (NH ₄ ⁺) mg/kg	2.3 max	3.0 max	3.0 max	3.0 max	3.0 max
Stability (24 h/100 °C) % loss of active oxygen	2 max	2 max	2 max	2 max	2 max
Evaporation residue mg/kg	15 max	10 max	—	20 max	20 max
Total carbon, mg/L	200 max	40 max	105 max	40 max	40 max
Metals					
Aluminum (Al) mg/L	0.2 max	0.2 max	1.0 max	0.35 max	0.35 max
Tin (Sn) mg/L	0.8–3.1	1.0–4.0	0.7–7.0	1.0–4.0	1.0–4.0
Chromium (Cr) mg/L	0.11 max	0.03 max	—	0.03 max	0.03 max
Lead (Pb) mg/L	0.04 max	0.03 max	—	0.03 max	0.03 max
Manganese (Mn) mg/L	0.04 max	0.03 max	—	0.03 max	0.03 max
Iron (Fe) mg/L	0.11 max	0.03 max	—	0.03 max	0.03 max
Copper (Cu) mg/L	0.04 max	0.03 max	—	0.03 max	0.03 max
Nickel (Ni) mg/L	0.04 max	0.03 max	—	0.03 max	0.03 max
Antimony (Sb) mg/L	—	—	—	0.03 max	0.03 max
Arsenic (As) mg/L	—	—	—	0.03 max	0.03 max
Gold (Au) mg/L	—	—	—	0.03 max	0.03 max
Zinc (Zn) mg/L	—	—	—	0.03 max	0.03 max
Titanium (Ti) mg/L	—	—	—	0.03 max	0.03 max

*A high-purity grade shall be available with a minimum level of 2.0 mg/kg nitrates when requested

MIL-PRF-16005D in its 1965 issue specified only two grades of HTP, and the purity requirements for the Type II (98–99% H₂O₂) were essentially the same as for the Type I (90–91% H₂O₂). Total carbon is the same as **total organic carbon**, often abbreviated as TOC. Evaporation residue is the same as non-volatile residue (NVR).

As of 2002, there were insufficient data to support the establishment of tolerable contaminant levels for 98% HTP. In an effort to establish tolerable levels of contaminants, pure 98% HTP was doped with known amounts of contaminants (one at a time) and tested in two small thrusters with two different catalysts for run times up to cumulative 3000 s [832]. The results of the thruster tests with pure and adulterated HTP propellants are shown in *Encyclopedia of Monopropellants*, chapter “Hydrogen Peroxide Monopropellants”. The recommended 98% HTP specification is shown in Table 53 in comparison to the standard MIL-SPEC.

Table 53: Recommended 98% HTP specification in comparison to MIL-SPEC.

	Recommended 98% HTP specification	MIL-P-16005E
Assay, mass-%	98–99%	98–99%
Aluminum (Al^{3+})	0.35 mg/L max	0.5 mg/L max
Chloride (Cl^-)	0.5 mg/L max	1.0 mg/L max
Ammonium (NH_4^+)	3.0 mg/L max	3.0 mg/L max
Nitrate (NO_3^-)	3–5 mg/L	3–5 mg/L
Phosphate (PO_4^{3-})	0.2 mg/L max	0.2 mg/L max
Sulfate (SO_4^{2-})	0.5 mg/L max	3.0 mg/L max
Tin (Sn)	1–4 mg/L	1–4 mg/L
Total organic carbon	40 mg/L max	200 mg/L max
Non-volatile residue	20 mg/L max	20 mg/L max
Stability	2.0% max AO	2.0% max of AO
Ni	0.03 mg/L max	N/A
Cr	0.03 mg/L max	N/A
Fe	0.05 mg/L max	N/A
Cu	0.03 mg/L max	N/A
Mn	0.03 mg/L max	N/A

Table 54 is a comparison of supplier’s certificates with the expired MIL-SPEC requirements.

As of 2001, none of the MIL-SPECs were still in effect, and it was recommended that the HTP industry and HTP should form a working group and agree on a new specification. In addition, a new specification would be needed for 98% H_2O_2 , which was not yet covered by any of the expired specifications. The expired MIL-P-16005E could be used as “model” for the new specification [833].

If the hydrogen peroxide renaissance had survived, eventually the USAF Directorate of Aerospace Fuels in San Antonio, TX would have had to stock up on HTP to supply government and contractor users with this propellant [834]. They offered a draft of a new procurement specification that covered 70, 85, and 90% HTP (but not yet the 98% grade).

Table 54: Comparison of supplier's certificates with the expired MIL-SPEC requirements.

Hydrogen peroxide, mass-%	Type I MIL-P-16005E	FMC	Degussa "Propulse"
Property, ppm max	90.0–91.0	90.0–91.0	90.0±0.5
Aluminum	0.35	0.2	1.0
Chloride	0.7	0.2	2.0
Ammonium	2.2	0.2	1.4
Sulfate	2.2	0.2	5.0
Nitrate	3.6 max, 2.2 min	3.5 max, 2.2 min	7.2
Phosphate	0.15	0.15	0.5
Tin	2.9 max, 0.7 min	3.0 max, 1.0 min	5.0 max, 2.0 min
Carbon	144	50	72

In Russia, organic impurities contents in the 35–40% product that goes into concentrators are limited by Russian specifications to 0.55–0.7 mass-%, containing 0.2–0.3 g/dm³ of isopropanol, 6–8 g/dm³ of acetone and 6–8 g/dm³ acetic acid [107–109].

5 Materials of Construction for Hydrogen Peroxide

The literature on materials of construction for hydrogen peroxide can be chronologically subdivided in two major groups: one before 1960 and one after 1995, with a wide gap of inactivity in between. The older materials compatibility data have the disadvantage that they were obtained using obsolete test methods, or that many of the commercial materials (in particular polymeric materials and lubricants) tested are no longer available or have been reformulated. The other problem is that many recently developed materials (metallic and polymeric) have not yet been tested for compatibility with HTP.

In discussing materials of construction and declaring them compatible or incompatible with hydrogen peroxide (or any other rocket propellant), one must differentiate between the effect of leached materials on the stability of the propellant or the corrosive effect of the propellant on the material, eventually causing it to lose its structural integrity. In the worst case, both can occur at the same time. Both phenomena are generally lumped together under the term "compatibility", and either one can cause a material to be branded as "incompatible" and rejected for further use with H₂O₂.

A good collection of compatibility data is in an old, historical Becco company bulletin that is no longer available [835], but its contents have been absorbed and reprinted later in other hydrogen peroxide handbooks [836]. Third-hand sources are usually less reliable and often depend on undocumented information, some of it copied several times. Each time such information gets copied, it loses some of its

authenticity and accuracy. The current book at hand is only a third-hand source but tries to evaluate the reliability of the information provided. Some of the information is now obsolete and has been superseded by more recent data.

Another good and very comprehensive source of physical properties and materials compatibility data is the *Hydrogen Peroxide Handbook* compiled by Rocketdyne under contract to the AFRL [246]. It contains reprinted (and untested – no warranty implied for accuracy) materials compatibility data taken from HTP manufacturers' product bulletins that are no longer available directly from the producers.

The first edition of our book on rocket propellants in 1968 contained a lengthy list of materials recommended by Becco, which was a major manufacturer of HTP at that time. The materials were categorized into four classifications of suitability, and this categorization is still used nowadays:

1. Suitable for service under all conditions, also temperatures up to 373 K (100 °C) and long storage times.
2. Suitable for repeated exposure and short-term use, such as in valves, plumbing, pumps, and run tanks in stationary rocket test sites. These materials should not be allowed into contact with HTP for longer than 4 h at 343 K (70 °C) or 1 week at 294 K (21 °C).
3. Only suitable for very short contact times with liquid or vapor H_2O_2 , such as in combustion chambers or propellant ducts in expendable launch vehicles.
4. Not suitable for use under any circumstances. These materials either catalyze the decomposition of H_2O_2 or lose their structural integrity once contacted by H_2O_2 . Other modes of incompatibility lead to the formation of explosive mixtures, such as those formed by H_2O_2 and hydrocarbon oils used as lubricants.

5.1 Other Summaries of Information on Compatibility of Materials of Construction with Hydrogen Peroxide

Hydrogen peroxide was evaluated as an oxidizer for an advanced propellant staged combustion feasibility program, and its physical, chemical, and handling properties were compiled in a handy summary report, although most of the data were taken from the book by Schumb and various manufacturers' bulletins [183]. It is just that these product bulletins are no longer available because some of the HTP manufacturers are no longer in business. However, the Anderson summary is still available on the Internet, and it is a valuable resource, although the quality of reproduction is poor, and some of the text is hard to read; see also [24, 837].

5.2 Test Methods for Evaluation of Materials of Construction for Hydrogen Peroxide

There are several test methods that are specifically suitable for the testing of various materials of construction in contact with hydrogen peroxide, simulating conditions under which the materials might be used in a rocket. This list is essentially a replica of methods already described in Section 4.7 for the evaluation of the thermal and storage stability of hydrogen peroxide by itself in containers known to be compatible.

Material test methods from the good old 1960s were used as a starting point in evaluating materials compatible with HTP for use in a new generation of space launch vehicles at the beginning of the twenty-first century. These established test methods were modified to incorporate modern analytical laboratory equipment and to test a wide range of materials incorporating the new polymer and composite materials that have become available since the 1960s [838]. Testing was accomplished in three stages, from quick screening to detailed analytical tests. A long-term storage test of a subscale tank lasted only 7 months before being stopped due to a polar boss material breakdown. Chemical examination of the hydrogen peroxide and residue left on the polar boss surface quite clearly identified a material corrosion problem.

The test procedure used at Angeles Crest Engineering consisted of immersing material specimens having a surface area of 30 to 60 cm² in about 90 mL of concentrated hydrogen peroxide contained in a Pyrex[®] glass vessel of about 125 mL capacity [839]. Several such vessels were placed in air convection chambers with precise temperature control for 200 h. Typically, nine to twelve vessels were placed in each convection chamber. Three convection chambers were available so that tests could be performed simultaneously at three different temperatures of 316.4, 325.3, or 335.3 K (43.3, 52.2, or 62.2°C). The gas evolved was collected in water-filled inverted graduated cylinders, one for each test sample. The published results are useless because the concentration of hydrogen peroxide and the identity of the materials tested were not revealed.

A crude method of testing crucible-shaped metal samples for compatibility with HTP was described in [840] (although 140 day is **not** a “**long-term** storage test demonstration”!). Crucibles of Al-3003, zirconium, and tantalum were filled with HTP, placed in a glass beaker at room temperature, and the gas evolved was collected by inflating (and periodically venting) the attached rubber balloons. Zirconium had good compatibility, Al-3003 was the worst, with tantalum in-between.

5.3 Metallic Materials of Construction for Hydrogen Peroxide

A summary of materials of construction and their classification into the above four-class categories is given in Table 55, along with some observations on changes of the material as the result of H₂O₂ exposure.

Table 55: Materials compatibility with 90% H₂O₂, Part I Metals.

Material	Compatibil- ity group	Rate of loss of active oxygen in H ₂ O ₂ , %/week at 66°C	Remarks, observations, effects on Material under test
Wrought and rolled Al alloys			
Al-1060	1	1.5	None
Al-1100	1	3.0	None
Al-1160	1	1.5	None
Al-1260	1	1.5	None
Al-2014	4	100	None
Al-2017	4	100	None
Al-2024	3	16.4	None
Al-3003	2	13.8	None
Al-4043	2	52	None
Al-5052	2	8.3	None
Al-5054	2	—	None
Al-5056	2	13.1	None
Al-5652-0	2	5.0	None
Al-5254-0	2	7.8	None
Al-6061	2	4.8	Corrodes
Al-6063	2	16.0	None
Al-6363	2	7.6	None
Al-7072	1	2.1	None
Al-7075	4	100	None
Cast Al alloys			
Al-40 E	4	100	Corrodes
Al-150	2	28.7	None
Al-214 B	2	50.0	Spotty appearance
Al-214 F	2	35.9	None
Al-B 214 F	3	96.4	None
Al-218	4	100	Corrodes
Al-355 F	4	100	None
Al-356F	2	50	None
Al-B 356	1	2.8	None
Al-A 360	3	96.8	None
Al-750	4	100	None
Al-A 750	4	100	Complete decomposition in 3 days
Al-B 750	4	100	Complete decomposition in 3 days
Stainless steels			
CRES-202	2	19.0	Discoloration
CRES-302	2	21.0	Assumes a bronze color
CRES-304	2	40	Assumes a bronze color
CRES-304 ELC	2	58.6	Assumes a bronze color

Table 55: (continued)

Material	Compatibil- ity group	Rate of loss of active oxygen in H ₂ O ₂ , %/week at 66 °C	Remarks, observations, effects on Material under test
CRES-309	2	54.2	Assumes a bronze color
CRES-310	2	37.1	Assumes a bronze color
CRES-316	2	19.8	Assumes a bronze color
CRES-316 ELC	2	10.5	Assumes a bronze color
CRES-317	2	36.0	Assumes a bronze color
CRES-318	2	69.4	discolors
CRES-321	2	37.0	Assumes a bronze color
CRES-322	2	30.0	Assumes a bronze color
CRES-329	3	100	Assumes a bronze color
CRES-347	2	57	Assumes a bronze color
CRES-410	4	91.4	Rusting
CRES-416	4	100	Rusting
CRES-420	4	100/18 h	Complete decomposition in 18 h
17-7PH passivated	2	20	Assumes a bronze color
Other Metals			
Beryllium	4	100	Corrodes
Cadmium	4	100	Corrodes
Chromium	4	100	None
Cobalt	4	100	None
Copper	4	100	None
Iron	4	100	Rusting
Lead	4	100	Dissolves
Magnesium	4	100	None
Manganese	4	100	None
Molybdenum	4	100	dissolves
Nickel	4	100	None
Tantalum	1	none	
Tin	2	28.7	None
Zirconium	1	3.2	None
Zinc	4	100	Corrodes
Chemalloy H 3	4	100	Pitting corrosion
Hastelloy-B	4	100/16 h complete decompo- sition in 16 h	None visible
Haynes Stellite-3	4	100/48 h complete decompo- sition in 48 h	None visible
Inconel	4	100	None visible
Monel	4	100	None visible

Data source: Becco FMC

Although aluminum by itself and many stainless steels by themselves are compatible with H_2O_2 , a combination of these two metals will cause galvanic corrosion, and the aluminum becomes coated with a gel of aluminum hydroxide.

The most common metals for hydrogen peroxide tankage and storage installations are aluminum alloys. The following sections provide detailed information on individual materials intended to supplement the overly simplified summary given in Table 55.

In selecting aluminum alloys for H_2O_2 service, it is important to select alloys with low copper content. Copper is often added to aluminum alloys to increase tensile strength. One can find a direct correlation between the amount of allowed copper in the alloys and the rate of gas formation when H_2O_2 is in contact with these alloys.

Metal coupons were immersed in HTP at room temperature and elevated temperature, and the weight change of the coupons and the loss of H_2O_2 content of the liquid was measured for varying lengths of time [365]. The few satisfactory materials in which concentrated peroxide may be handled or stored are (in the decreasing order of preference) Pyrex[®] glass, aluminum (99.6% pure or better), aluminum-magnesium alloys, pure tin, pure tantalum, pure cadmium, and stainless steel. All of these surfaces must be conditioned (passivated) before use with HTP.

Several hundred metals and other materials of construction were evaluated in contact with 90% HTP in a multi-year effort at Shell Development Company [166]. The surface activities of fresh and passivated metals were compared to find the most effective passivation methods. The aluminum alloys tested were Al-1260, Al-1100, Al-2219, Al-5052, Al-6061, Al-7039, and Al-7072. One of the test methods was to measure the rate of oxygen evolution of the metal coupons kept in 90% HTP (with different stannate stabilizer levels) at 373 K (100 °C). The activity of CRES-304 and CRES-347 decreased with the duration of HTP immersion but was still several orders of magnitude worse than what can be achieved with aluminum alloys. In addition to passivated metal samples, some tin-electroplated metal samples were also tested. It would be desirable to revisit some of these reports and put the data in a user-friendly graphical format, also in comparison to other materials compatibility studies conducted at other organizations during the same time or in the interim.

While compatibility with HTP has been worked on for 80 years, newer materials were not yet considered in the early years. To fill this gap, various metals, polymers, and composites were examined by microcalorimetry [841]. At first, methods were developed for the production of HTP on site [842], and then compatibility test methods selected included accelerated aging by heating, coupled with assay of concentration and stabilizer loss, observation of reactivity by means of isothermal microcalorimetry, and evaluation of changes to the materials by short-beam shear testing and by photoacoustic-Fourier transform infrared spectroscopy. Material coupons (Al-6061, CRES-304, 17-4PH, CRES-330C) were immersed in 4 mL of 90% H_2O_2 and heated to 338 K (65 °C) for 6 h. The mass loss and concentration of the surviving H_2O_2 gave a measure of compatibility. The reactivity decreased in the order Al-6061, CRES-304, 17-4PH, and CRES-330C. The HTP in contact with CRES-330C decomposed totally.

Welding of stainless-steel leaves behind an oxide and slag layer that may be less compatible with H_2O_2 than the clean, passivated parent metal. Many metal oxides such as those found in weld slag are perfect catalysts for decomposition of H_2O_2 , and the presence of metal oxides in weldments is a problem for the manufacturing of HTP equipment. The HTP compatibility of welded versus unwelded stainless steel was studied using microcalorimetry [843, 844]. An isothermal microcalorimeter (Model 4400, Water Bath Model 7238, Calorimetry Sciences Corp, Provo, UT) was used to obtain heat flow measurements at 333 K (60 °C). Welded specimens of CRES-304L and CRES-316 were significantly less compatible than their unwelded counterparts, with the CRES-304L falling beyond the upper limit of Class 2 materials. In the heat-affected zone of the weld, the ratio of chromium to iron increased from 0.28 to 0.44 in CRES-304L and from 0.26 to 0.79 in CRES-316. Chromium oxide is a bad actor for H_2O_2 compatibility.

Using the same microcalorimetry method, various candidate metals to be used in the injectors of HTP rocket engines were tested [845, 846]. Inconel-625 and Ni-200 had very poor compatibility and were immediately excluded from further evaluation. A-286 had marginal compatibility. CRES-347 had acceptable compatibility considering the short duration it would be in the wetted state.

5.3.1 Contaminant Effects on Corrosivity of Hydrogen Peroxide

5.3.1.1 Corrosion Inhibitors

Chlorine impurities introduced into the hydrogen peroxide during the manufacturing process from water or are introduced by water used in less carefully controlled handling operations, can make hydrogen peroxide significantly more corrosive. To counteract this corrosive nature, nitrates were sometimes added to act as a corrosion inhibitor. Advances in the manufacturing technology of hydrogen peroxide may have reduced the chlorine level, thereby reducing the corrosive behavior of hydrogen peroxide. It is possible that modern propellant-grade hydrogen peroxide may no longer have the corrosive effects on 6061 aluminum that it had in the past.

The chloride content of H_2O_2 has a pronounced effect on the rate of corrosion of all alloys in H_2O_2 . It has been suggested that addition of ammonium nitrate as a corrosion inhibitor can retard the rate of corrosion caused by chloride contamination. The maximum amount of chloride in HP grade HTP allowed by MIL-PRF-16005E is 0.5 ppm.

5.3.2 Aluminum and Aluminum Alloys

One of the most frequently used aluminum alloys for H_2O_2 service is Al-1060. It is essentially soft, pure, unalloyed aluminum with 99.6% Al. It has a negligible rate of corrosion, and the loss of H_2O_2 concentration during storage is minimal. In those few cases where corrosion (pitting corrosion) was observed with this alloy, it was usually traced contaminants introduced during machining or welding.

In long-term storage tests, 90.5% H_2O_2 was stored in 114-L Al-1060 drums for over 3 years. The average rate of loss of H_2O_2 concentration was only 1% absolute. In large, spherical storage tanks holding 95000L, the loss of H_2O_2 concentration during 12 months storage could not be detected. If HTP has been shipped in drums and is not intended to be used immediately, it may be advantageous to transfer it into a single, large on-site tank. The transport drums are not intended for long-term storage of the material. Different Al alloys (Al-1060, Al-5052, Al-5652, and Al-5254) were tested as material of construction for 55-gallon drums. Based on storage tests at customer installations extended to 3 years, none of the samples lost more than 2% H_2O_2 per year when the drums were returned to the manufacturer (Becco) for examination.

Al-1060 causes the least amount of H_2O_2 decomposition, but it is a very soft alloy and does not have the mechanical strength required for some applications. If the system is designed for high-pressure operation, the wall thickness of tubing and tanks must be increased accordingly. Materials like Al-5254 or Al-5652 have better strength and may be used for tank cars that have to withstand higher mechanical loads (road vibrations) than stationary tanks. Although HTP is normally not stored in these tank cars, storage times of up to 3.5 months have been monitored without complications.

The mechanical strength of aluminum alloys also depends on the annealing (tempering) cycle the material has undergone since it was extruded, rolled, or welded.

Aluminum 6061-T6 is the most frequently used aluminum alloy for many structural elements. Although it has good mechanical properties, it does not hold up well when the service requires alternating exposure to H_2O_2 liquid, H_2O_2 vapor, and water. It has been recommended to render it more compatible by anodizing it in sulfuric acid.

Al-2014, Al-2017, and Al-2024 are stronger alloys than Al-6061 but have been downgraded to a Class 3 compatibility category because they accelerate H_2O_2 decomposition during storage. Their compatibility could not be improved by anodizing.

For many years, pump and valve casings have been made from Al-43 and Al-356, although these are categorized in Group 3 and are not very compatible with H_2O_2 . It is possible to manufacture Al-356 with a controlled and reduced copper content, earning it the designation Al-356B and classification in Group 1.

Comparing the rate of unstabilized HTP (87.2% H_2O_2) decomposition in contact with aluminum of five different grades of purity (increasing purity from 99.39, 99.49, 99.61, 99.70 to 99.80%) but decreasing iron content (0.51, 0.43, 0.26, 0.23, 0.14% Fe) showed a direct inverse correlation of the rate of HTP decomposition with the iron content in the aluminum [365].

The mechanism of corrosion of Al alloys in H_2O_2 (in the absence of chloride) can be studied by measuring electrochemical potentials of aluminum coupons against reference electrodes. There are two different rates of corrosion, one related to the rate of forming a protective film of aluminum oxide and the other related to the rate of aluminum oxide film dissolution or spalling [847]. A distinction can be made between the electrochemical corrosion of metallic aluminum, in which aluminum oxide is formed, and the chemical solution of the aluminum oxide, eventually leading to the interac-

tion of aluminum ions with the stannic acid stabilizer. The electrochemical reaction is facilitated by chloride ions and retarded by nitrate ions, whilst the chemical solution is enhanced by hydrogen ions and the presence of stannic acid sol. Only the chemical reaction affects the stability of the stannic acid stabilizer.

Nine wrought and three cast aluminum alloys were exposed to commercial 90% H_2O_2 as manufactured and 90% H_2O_2 with 3 g/L chloride ion and 4 g/L nitrate ion added [848]. Testing included wrought alloys 1100-H14, 5254-H14, 1260-H14, 6363-T5, 3003-T14, 6061-T6, 5652-H34, 5086-H34, and 1060-H14, and three cast alloys Al-356, Al-43, and Al-B-214. Most of the exposures were of 6 month's duration. Some of the specimens had to be removed prematurely due to severe corrosion or rapid deterioration of the hydrogen peroxide. Samples were characterized by tensile strength, stress corrosion, metallographic examination, and chemical analyses of the hydrogen peroxide in order to determine its loss of active oxygen. The presence of chloride ion was found to accelerate corrosion greatly in all of the alloys. Wrought alloys 5254 and 3003 were found to be the most compatible, and B-214 was the best cast alloy.

Currently, aluminum alloy 5254 is the state-of-the-art material for HP storage, but its yield strength is very low (420 ksi), and it may not be suitable for the development of light-weight propellant tanks for Hyper-X vehicles. A new high strength and HTP propellant compatible aluminum alloy has been developed for NASA Hyper-X vehicle propellant tanks and structures [849]. The tensile strength of the new alloy is more than three times better than that of the conventional Al-5254-H112 alloy, while it still maintains an HTP compatibility similar to that of Al-5254 (i.e., Class 1 category). The alloy development strategy is to add scandium, zirconium, and other transition metals with unique electrochemical properties, which will not act as catalysts and will not decompose liquid HP. Test coupons were machined from sheet metals for HTP compatibility testing in a microcalorimeter, long-term immersion testing and mechanical properties testing [850]. The Appendix to this report contains a description of the standard test methods to determine materials compatibility (expressed as AOL) and HTP stability.

It was attempted to reduce the deactivation of stannate stabilizer by aluminum uptake into HTP from aluminum storage tanks by plating the aluminum with tin [166, 174]. Unfortunately, aluminum is difficult to electroplate with any metal, and the only metals tin can be easily electroplated onto are those that are very active in H_2O_2 decomposition. Those more active metals would have to be completely coated with tin without any pinholes.

The electrochemical behavior of aluminum in concentrated hydrogen peroxide has been studied by measuring the electrode potentials and the "corrodance", i.e., the inverse of polarization resistance [851]. Electrode potentials depended on the presence of chloride and nitrate ions. "Corrodance" determination is a convenient method for the rapid measurement of the very low corrosion rate of aluminum in hydrogen peroxide.

Al-6061-T6 has the desirable strength but is incompatible with HTP. In storage tests with 85% HTP for 10–20 weeks in tanks made from sections of 7.5-cm (3-in.) diameter pipe, increased decomposition was observed not only while the HTP was in contact with the metal but also homogeneous decomposition due to leached metal ions after the propellant was unloaded [852]. The compatibility could be improved somewhat by anodizing the aluminum. The off-loaded propellant was analyzed for leached metals and fewer metals were leached from the anodized aluminum Al-6061-T6.

Cleaning and Passivation of Aluminum Tanks

The Hydrogen Peroxide Handbook by Constantine and Cain contains a good summary of the cleaning and passivation methods used for metal tanks prior to their first use with HTP [853]. Several of the following sections on recommended passivating methods have been excerpted from that source:

Non-anodized aluminum and aluminum alloy parts may be descaled by immersion in a 1% HF-10% HNO₃ solution for 30 s to 5 min at 319 K (115°) maximum. Immediately following the cleaning (or descaling) operation, the metal parts should be subjected to the “basic passivation” step.

Aluminum and aluminum alloy materials are usually passivated with a solution of 45% HNO₃ at room temperature for a period of 1 h; however, FMC recommends the use of 35% HNO₃ as the passivation acid. The materials should be rinsed and flushed with water to remove all traces of nitric acid, and unless immediately conditioned with the propellant, the materials should be drained and dried by purging with dry, filtered, hydrocarbon-free nitrogen or air, or dried in a clean oven at 333 to 339 K (140 to 150 °F). Machined aluminum bar stock parts do not normally require descaling or passivating processes and can be prepared for service by degreasing and thoroughly rinsing. Welded, cast, or corroded parts will require descaling, cleaning, and passivating. Anodized aluminum parts will not be descaled or passivated and should be prepared for service by degreasing and thorough rinsing.

5.3.3 Stainless Steel Alloys

Stainless steels of the 300-series are suitable only for short term use (Group 2). Cast-iron steels are not recommended (Group 3). CRES-303 has caused problems in the past and is generally avoided.

The compatibility of 98% H₂O₂ with four nickel alloys (Ni-200, INCO-625, CRES-347, and A-286) was tested and found to be much better than that of 90% H₂O₂ under the same test conditions [402]. This observation was explained by the hypothesis that an inert protective metal oxide layer formed on the surface of nickel alloys in the presence of 98% H₂O₂. No such oxide layer formed when similar coupons were immersed in 90% H₂O₂ solution. For compatibility tests, material coupons were immersed in H₂O₂ solution at 339 K (66 °C) for 1 week. The ratio of coupon surface to H₂O₂ volume

was about 0.33 in.^{-1} . The off-loaded HTP was analyzed for leached metals by inductively coupled plasma (ICP) emission spectrometry. For stability tests, 50 mL of H_2O_2 solution was maintained at 373 K (100 °C) for 24 h. The reserve stability of stabilized H_2O_2 solutions towards decomposition was challenged by adding controlled amounts of five metal cations in the form of their nitrates that might be leached from container metals. With 98% H_2O_2 , the order of decreasing catalytic activity of these cations is $\text{Mn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Cr}^{3+} > \text{Ni}^{2+}$ (Figure 55).

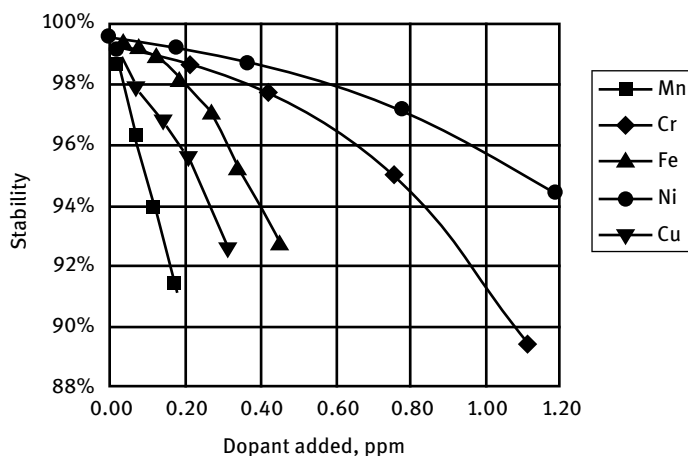


Figure 55: Stability of 98% HTP as a function of contaminant dopant concentration. (Reproduced and modified from [402].)

Trends in stability for doped and undoped H_2O_2 solutions were quantified for the concentration range of 10–98% H_2O_2 . A study of the role of pH on stability showed that a broad maximum in stability existed over a pH range of 0 to -2.5 (Figure 44). Stannate at 2.7 ppm Sn provided a reserve stability (with no change in measured stability) up to 190 ppb of added Fe.

The thermal decomposition rate of 98% HTP in contact with candidate materials of construction was tested by measuring gas evolution by volumetry and heat evolution by isothermal microcalorimetry (IMC). Materials were analyzed for compatibility with HTP, including a study of the effect welding on stainless steel elemental composition and its relation to HTP decomposition [854]. Using an isothermal microcalorimeter it was found that two of the metal samples were not compatible with 98% HTP and, therefore, they are not recommended for use as structural materials. Composition changes in stainless steel CRES 304L and CRES 316L due to welding were apparent from an X-ray fluorescence (XRF) analysis. A correlation between an enhancement in Cr and Cu in the weld bead and an increase in the HTP decomposition rate in the IMC

was supported by the data obtained by XRF. This report is useless because the metals M1, M2, M3, and M4 were not identified.

Gas evolution rates of stainless steel (15–5 PH, CRES 304L, AISI 430) cylinders immersed in 87.7% H_2O_2 in 25-mL Pyrex[®] flasks were measured at four different temperatures (278, 293, 305, 323 K = 5, 20, 35, 50 °C) in four parallel tests along with a control flask that contained only HTP and no metal sample [855]. The surface: volume ratio was 1.1 cm^{-1} . The gas evolution rates plotted on a semilogarithmic scale versus temperature showed a linear relationship.

Water and hydrogen peroxide are very poor lubricants for metal pieces in sliding contact with each other as in the bearings of pumps and flowmeters. Pin-on-disc tests to investigate the tribological behavior of an AlCoCrFeNiCu alloy under rotating friction conditions with 90% H_2O_2 solution in comparison to lubricant oil demonstrated that the AlCoCrFeNiCu alloy was well lubricated with 90% H_2O_2 or lubricant oil, both significantly improving friction and wear-resistance properties [856].

The rate of friction wear of an AlCoCrFeNiTi0.5 alloy in high-concentration hydrogen peroxide solution depends on the crystalline microstructure formed during the annealing process, which leads to an increase of the hardness of this alloy [857]. Friction curves of 1Cr18Ni9Ti and AlCoCrFeNiTi0.5 stainless steels in contact with SiC or ZrO_2 ceramics were measured.

Stainless steel is widely used in strongly oxidizing hydrogen peroxide environments. It is important to study its wear behavior and failure mode under conditions of high friction. The tribological properties and oxidation of 304 stainless steel were investigated using an MMW-1 tribo-tester with a three-electrode setup in H_2O_2 solutions with different concentrations [858]. Corrosion current densities (CCDs), coefficients of frictions (COFs), wear mass losses, wear surface topographies, and metal oxide films were analyzed and compared. The results showed that the wear process and oxidation processes interacted with each other. Increasing the H_2O_2 concentration or the oxidation time was useful to form a layer of integrated, homogeneous, compact, and thick metal oxide film. The dense metal oxide films with higher mechanical strengths improved the wear process and also reduced the oxidation reaction. The wear process removed the protective metal oxide films to increase the oxidation reaction.

Cleaning and Passivation of Stainless Steel Tanks

In preparation for passivation, stainless-steel parts should be etched for a minimum period, and not longer than 60 min, at room temperature, 289 to 300 K (60 to 80 °F), with a mixture of 3% technical-grade hydrofluoric acid and 10% technical-grade nitric acid in water. Immediately following the cleaning (or descaling) operation, the metal parts should be subjected to the “basic passivation” step, which consists of immersing stainless-steel parts in a solution of 45% HNO_3 at 289 to 300 K (60 to 80 °F) for a minimum period of 30 min. FMC recommended the use of 70% HNO_3 for a period of 4 to 5 h as the stainless-steel passivation step [859]. The parts should then be rinsed and flushed thoroughly with deionized or distilled water to remove all traces of the

passivating solution. Unless the part is immediately placed in the propellant-conditioning solution, it should be drained and dried by purging with dry, filtered, hydrocarbon-free nitrogen or air, or dried in a dust-free oven at 333 to 339 K (140 to 150 °F). The part should then be protected from recontamination by sealing in a sealed clean plastic bag.

The nitric acid passivation solution should be used for AISI 300 and 400 series stainless steels. The protective film resulting from this passivation process will not normally be visible, but the surfaces will be uniform in appearance, free from scaling, corrosion, pitting, and contaminants. Normal discoloration from welding will be permitted, provided that no scale or rust is associated with the discoloration. Some organizations recommend electropolishing of stainless-steel parts (except for AN 355) by the best available commercial practice as an alternate method for stainless-steel passivation. Following electropolishing, the material should be cleaned with detergent, rinsed thoroughly with deionized or distilled water, and dried in an oven.

When stainless steel is immersed in HTP, an oxide film is formed on the surface of the metal. The rate of formation, composition, and stability of this film were investigated by chemical analysis and electrometric methods. The film consisted mainly of oxides of iron, and at 30 °C it grew to a fairly constant thickness of 3×10^{-6} cm in 3–4 weeks [860]; see also [861].

5.3.4 Cleaning and Passivation Methods for Metal Tanks

The Hydrogen Peroxide Handbook by Constantine and Cain [246] contains a good summary of cleaning and passivation methods used for metal tanks prior to their first use with HTP. The following was excerpted from that source:

All material surfaces that come in contact with propellant-grade hydrogen peroxide must be specially cleaned and treated prior to their use to minimize hydrogen peroxide decomposition and material corrosion. The material surfaces should be subjected to passivation after part fabrication and before component or system assembly.

Basically, items such as valves, pumps, actuators, system piping, etc., cannot be cleaned properly in the assembled state, because the solvent, cleaning solution, residual contamination, etc., may be trapped in inaccessible areas. The cleaning should be conducted immediately before component or system assembly, unless provisions are made for packaging of the passivated part to protect them against recontamination until ready for assembly. After assembly, components, such as valves, should be packaged until they are utilized in the final system assembly. It is also common practice to check all passivated items for gas evolution with propulsion-grade hydrogen peroxide prior to assembly in the system.

The general terminology applied to this process, which is designed to provide an inactive surface and eliminate potential contamination active sites, is *passivation*. The passivation procedure essentially consists of **three primary steps** prior to the material contact with propellant-grade hydrogen peroxide. The initial step is a chemical

and physical cleaning procedure designed to remove oxides, scale, dirt, weld (and heat treat) slag, oil, grease, and other foreign material from the base material. The second step is usually the treatment (“basic passivation”) of the material with an alkaline or acidic solution to form a surface film (probably a complex oxide) on the surface to minimize chemical or catalytic activity between the surface and the propellant. Finally, the material is subjected to propellant conditioning to check the completeness of the chemical treatment and to eliminate, through further oxidation and chemical complexing, all remaining active sites. Normally, propellant conditioning is conducted in 35% H_2O_2 , although many organizations prefer additional propellant conditioning of materials under the same conditions (H_2O_2 concentration and temperature) that will be experienced in actual application of the material.

A comparative evaluation of several passivation or surface preparation techniques was conducted to: (1) determine the effectiveness of selected passivation methods on 321 stainless steel, 6061-T6 aluminum (bare and anodized), and Silastic 9711, (2) determine the influence of cyclic exposure of passivated surfaces to hydrogen peroxide, and (3) investigate the effects of various storage conditions upon passivity of materials used in hydrogen peroxide service [862]. The passivation methods under study were:

- LTV Astronautics Division CVA-10-62a
- North American Aviation, Inc., El Segundo, California, LA 0110-003
- Walter Kidde 520007
- FMC Becco Bulletin 104
- McDonnell A/C 13002
- LTV Astronautics Division 308 – 20-3
- LTV Astronautics Division CVA-10-64a

The company-internal documents where these passivation methods are described in detail are unfortunately no longer available. LTV Astronautics Division developed several passivation methods during the development of the Scout satellite launcher. The preferred passivation method for 321 stainless steel was found to be CVA 10-62a with post-treatment with 35% commercial hydrogen peroxide. For 6061-T6 aluminum (bare and anodized), the best passivation technique was according to North American Aviation Specification LA-0110-003. The ease in passivation of all materials was found to improve with each subsequent exposure to concentrated hydrogen peroxide. Environmental exposure tests revealed that 321 stainless steel can be stored best in clean air with relative humidities up to 1.00%. Anodized 6061-T6 aluminum remains more passive in a dry nitrogen atmosphere.

5.3.5 Effect of the Surface Finish of Metal Tanks

The effect of the surface finish on materials compatibility with H_2O_2 was studied by comparing five different surface finishes applied to 304 stainless steel and aluminum

alloy 6061-T6 (both bare and anodized) in contact with 90% H_2O_2 to determine the influence of the surface finish on the stability of H_2O_2 [863]. The stainless-steel specimens were passivated according to CVA Specification 10-62a with post-treatment in 35% inhibited (0.03% H_3PO_4) hydrogen peroxide. The aluminum specimens were passivated according to North American Specification LA 0110-003. Although inconsistent correlations were obtained between the surface finish and AOL with the 304 stainless steel and the bare Al-6061-T6 specimens, the active oxygen loss resulting from the anodized aluminum in contact with the hydrogen peroxide indicated an increase in AOL values with surface roughness.

5.3.6 Effect of Dissimilar Metals in Contact (Galvanic Corrosion)

Hydrogen peroxide is a good electrolyte, and many metals that occupy different potentials in the order of electronegativity will corrode more rapidly if the metals are in electrically conductive contact with each other as in a galvanic element. The same happens in any rocket propellant that is electrically conductive.

The decomposition rate of 90% H_2O_2 and metals compatibility was measured with the following dissimilar metal couples: 1060 Al + 6061-T6 Al; 6061-T6 Al + 321 stainless steel; 6061-T6 Al + 316L stainless steel; and 321 stainless steel + 316L stainless steel [864]. The active oxygen loss (AOL) and H_2O_2 stability were determined during an exposure of 10 days at 316.5 K (110 °F) and 7 days at 339 K (151 °F). The tests at 316.5 K (110 °F) revealed no significant influence of the dissimilar metals upon the H_2O_2 . However, the 339 K (151 °F) test revealed that the catalytic decomposition of H_2O_2 was greater for the dissimilar metal couples than for either of the single-metal alloys.

5.4 Non-metallic Materials of Construction for Hydrogen Peroxide

Non-metallic materials include organic polymers and inorganic ceramic materials.

5.4.1 Organic Polymeric Materials of Construction for Hydrogen Peroxide

The selection of non-metallic materials for H_2O_2 service is mostly about the selection of organic elastomers to be used as gaskets, valve seats, and flex hoses. More recently, the search has been expanded to include oxidizer-resistant polymers as liners for tanks and composite-overwrapped tanks that would be much lighter than metal tanks for satellites. The selection of elastomers for protective clothing for propellant servicing personnel will be discussed in a separate chapter. The concern here is about the reactivity of H_2O_2 with elastomers, keeping in mind that the combination H_2O_2 /polyethylene is a popular hybrid rocket propellant. One wants this reaction to take place only in the rocket engine, not prematurely in the tank or in the feed system or on the glove of a propellant fueling technician that the propellant has been spilled on!

Many elastomers contain plasticizers. Whereas the parent material may be compatible with H_2O_2 , the plasticizer may not be. It may either be leached into the propellant or it may become oxidized, or both. One can call oneself lucky if it does not spontaneously burst into flames the first time peroxide comes in contact with plasticized polymers.

In ranking four candidate materials for H_2O_2 service, the ranking would be in the sequence Teflon[®], Kel-F[®], polyethylene, and PVC [865].

Teflon TFE fluorocarbon film was inert to 90% hydrogen peroxide for 900 h at 293 K (70 °C) [866]. There was no evidence of chemical attack on the film, nor any change in its physical properties. The mechanism of chemical attack of 90% hydrogen peroxide on polyethylene films between 323 and 343 K (50 and 70 °C) was identified, and found to vary, depending upon the structure of the polyethylene.

Packing for the glands in dynamic seals around valve stems and pump shafts are best made of Teflon[®] or similar perfluorinated elastomers. If the use of Teflon hoses becomes prohibitive for cost reasons, polyethylene-lined hoses can be used for short-term service just as well, but one must keep the flammability hazard in mind.

Table 56 is essentially a continuation of Table 55; it uses the same four-class compatibility rating scale.

PVC elastomers such as those manufactured under the brand names Vinylit or Koroseal are not suitable for H_2O_2 service because chloride may leach from the elastomer into the H_2O_2 liquid, which subsequently becomes quite corrosive toward all aluminum alloys [867, 868].

Silicone rubber is usually considered compatible with HTP, but there are reports where a silicone rubber bladder ignited accidentally [869].

During the development of the X-15 rocket plane RCS system, it was difficult to find materials that were compatible with the propellant because of the corrosive nature of the 90% concentrated hydrogen peroxide [870]. The selection of a suitable material for the expulsion bladder was especially difficult, inasmuch as it had to be compatible with the hydrogen peroxide propellant under long-time exposures at low temperatures and had to withstand repeated flexing without fatigue in order not to rupture under high load conditions. The first expulsion bladders were constructed of Teflon, but later bladders were made of Vicone, a fluorosilicone rubber. Both bladders functioned satisfactorily except for a tendency to rupture along the creases formed after the propellant is fully expelled, and the bladder is compressed around the standpipe. This structural deficiency has resulted in a short and inconsistent bladder life.

O-rings need to have the elasticity to make a good seal and should not cold-flow under pressure. Eight types of O-rings were evaluated by immersion in 90% HTP at 339 K (66 °C) for 1 week [871]. Only one of the eight O-ring materials was acceptable for use with HTP.

O-ring seals of selected elastomeric and compliant materials were evaluated for resistance to 90% HTP in a simulated end-use test at 296 K (23 °C = 73 °F) [872, 873]. The candidate elastomers were placed under compression in closed cells and exposed to

Table 56: Non-metallic materials compatibility with 90% H₂O₂.

Material	Compat- ibility Group	Rate of loss of ac- tive oxygen in H ₂ O ₂ , %/week at 66 °C	Remarks, observations, effects on material under test
Fluoroflex T-TP 1001	1	3.6	None
Fluran B-4100	3	48.3	Bleaching
Hypalon S-2	4	100	Completely destroyed within 1 h
Hypalon V-56-A	4	100	Swelling
Kel-F	1	3.5	None
Kel-F 800	1	4.5	Slight hardening
Kel-F 820	2	9.0	Hardening
Polyethylene	2	1.0	No visible change but may combust
Teflon (white)	1	2.8	None
Carbon-filled Viton A (black)	3	80.6	Bleaching, blistering, swelling
Koroseal-116	3	23	Bleached and hardened
Tygon B-20	3	2.2	Bleached and hardened
Tygon B-63	3	1.7	Bleached and hardened
Vynlite VG 1914	2	1.5	Bleached and hardened
Vynlite VS1310	3	2.3	Turns opaque, blistering
PVC	3		Turns opaque, blistering
Silicone GE 12650	2	48.5	Slight swelling
Silastic 161	3	43.4	Hardened
Silastic 240	2	24.9	None
Silastic 9711	2	7.4	Slight bleaching
BunaN	4		May combust
Butyl rubber	4	100	Coalesced to a shapeless mass
Mylar A	1	5.0	None
Mylar B	1	1.7	None
Neopren	4	100	Autoignites and burns
Nylon	4		Dissolves
Plexiglas	4	100	Softens and dissolves partially, may combust
Polystyrol	2	9.1	No visible changes but not recommended
Thiokol Polysulfide EC-801-LP-2	4	100	Ignites spontaneously and burns

Data source: Becco FMC

the liquid and vapor of liquid rocket fuels and oxidizers for extended periods of time. The rate of propellant loss through the seal and the change in physical properties of the seal materials were determined. In addition, the effect of temperature on elastomer endurance was determined by exposing the O-rings to H₂O₂ at 344 K (160 °F).

Proper materials for hardware components such as check valves, metering valves, and flow lines, were also difficult to select. The original X-15 reaction control system

was constructed entirely of aluminum. It was discovered, however, that the chemical reaction between the aluminum and the hydrogen-peroxide propellant formed hydroxides. Deposits of these substances resulted in “sticky” valves, clogged orifices, a short catalyst-bed life, and other component failures. During the interim, certain components that came into direct contact with the peroxide propellant were then constructed of stainless steel. However, use of the two different metals caused electrolytic galvanic corrosion wherever the metals were joined and came into contact with hydrogen peroxide and, thus, resulted in various component failures and contaminated propellant. The entire system was finally constructed of stainless steel, which eliminated the problems and increased component reliability.

Lubricants for H_2O_2 service cannot be of the conventional hydrocarbon type used for automobile and other lubrication jobs. Even silicone grease is not suitable. Instead, one must use perfluorinated greases such as Fluorolube[®], Kel-F[®], and PerFluoroLube[®]. Hydrocarbon greases form potentially detonable mixtures with HTP, which may even be shock- and friction-sensitive (like what is observed with LOX). A drop weight apparatus was developed to test the shock sensitivity of H_2O_2 /oil mixtures [874, 875]. One particular lubricant was made from perfluorinated C_4 - C_6 trialkylamines mixed with PTFE powder [876].

The selection of materials for service with 98% H_2O_2 requires increased awareness of potential adverse reactions. Generally, the same materials that previously qualified for the less concentrated 90% H_2O_2 can be used. Only in the case of organic elastomers is the destructive power of 98% H_2O_2 stronger than that of 90% H_2O_2 .

Table 57 gives a comparison of the materials compatibility (both metallic and non-metallic materials) and of their behavior toward 90 and 98% H_2O_2 at 303 and 339 K (30 and 66 °C).

A lot of work has been devoted to identifying the best materials of construction for H_2O_2 systems to minimize the rate of pressure buildup during storage and to eliminate the need for having to vent the tanks periodically to release overpressure. A study of the influence of materials of construction on the rate of the decomposition of very pure H_2O_2 showed that it is essentially impossible to eliminate the effect of the container wall. The decomposition of 90 and 98% H_2O_2 proceeded with measurable speed even in Teflon containers. It can be slowed down by passivating the surface before usage and by adding stabilizers, but it never goes down to zero. Unlike other chemical equilibria, the decomposition cannot be retarded or even reversed by increasing the storage pressure. It has only been attempted to minimize the adverse effect of oxygen overpressure buildup by adding an oxygen scavenger to the vapor space.

Teflon TFE fluorocarbon film was inert to 90% hydrogen peroxide for 900 h at 343 K (70 °C) [877]. There was no evidence of chemical attack on the film, nor of any change in its physical properties. The chemical attack of 90% hydrogen peroxide on polyethylene films between 323 and 343 K (50 and 70 °C) was found to vary depending upon the polymer structure of the polyethylene.

Table 57: Effect of materials of construction on storage stability of 90 and 98% H₂O₂ at slightly elevated temperatures.

Loss of active oxygen, %/week				
Material	90% H ₂ O ₂		98–100% H ₂ O ₂	
	Temperature, °C		Temperature, °C	
	30	66	30	66
	Temperature, K		Temperature, K	
	303	339	303	339
Al-1060 (99.6% Al)	<0.2	3.1	0.4	1.5
Al-5052	<0.2	8.3	1.1	2.6
Al-6061	3.4	12.0	1.2	5.2
Al-2024	—	100	0.5	100
Al-355 cast	3.3	100	0.2	100
Al-356 cast	0.7	50.0	0.2	3.9
CRES-304	1.1	50.0	1.5	12.0
CRES-316	4.4	47.0	3.2	53.0
CRES-347	2.8	57.0	6.4	30.0
Polyethylene	0.4	2.0	0.5	2.3
Kel-F	—	3.2	0.2	8.3
Teflon	0.4	2.5	1.1	2.6
Vynlite Vu 1930	0.5	2.4	0.9	2.7

Data source: [239]

Attenuated total reflectance measurements were made on a perfluorosulfonic acid ion exchange membrane exposed to 90% hydrogen peroxide at 343 K (70 °C). A definite attack on the membrane was shown in a 2-h period, indicating that not all perfluoro organic compounds are inert to 90% hydrogen peroxide [299].

Degussa investigated the long-term compatibility of high-strength hydrogen peroxide with various thermopolymers often used in plastic drum fabrication [97]. In the study, 2-mm thick coupons made from high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride/urethane (PVC-U), and a fluorinated polymer (PVDF) were directly immersed in 87% HTP for time periods of up to 3 months, at temperatures of 313 and 343 K (40 and 70 °C). Interim sampling was carried out after 14 days, 1 month, and 2 months, in addition to the ultimate 3-month objective. The coupons were then subjected to physical endurance tests including tensile strength, weight loss/gain, elongation, and mechanical hardness. In addition, the HTP was analyzed to detect any loss of activity. The results of these immersion tests are shown in Table 58.

The study concluded that the high-density polyethylene and PVDF thermopolymers did not exhibit any significant changes in mechanical strength or weight and were considered as having a better long-term stability profile than either polypropylene or PVC. There was, however, a slight loss of HTP activity (from 87.1 to 84.2%), but this might not be entirely attributable to the exposure to the thermopolymer. Under the

Table 58: HTP Thermoplastic polymers immersion test data.

Material	Temperature K	Weeks	Weight change %	Tensile strength N/mm ²	Elongation %	Hardness N/mm ²	H ₂ O ₂ concentration Mass-%
HDPE		0	—	21.8	>600	42	87.2
	313	12	-0.24	22.3	>600	41	84.2
PP		0	—	35.4	>600	77	87.2
	313	12	+0.43	28.7	16	77	84.0
PVC-U		0	—	54.0	40	122	87.2
	313	12	+0.07	57.2	30	120	74.2
PVDF		0	—	56.6	80	130	87.2
	313	12	0.01	58.6	30	127	85.7
HDPE		0	—	21.8	>600	42	87.2
	343	8	-3.5	18.7	24	41	59.8
PP		0	—	35.4	>600	77	87.2
	343	4	+3.7	N/A	N/A	N/A	60.0
PVC-U		0	—	54.0	40	122	87.2
	343	2	-0.11	61.0	20	122	13.3
PVDF		0	—	56.6	80	130	87.2
	343	12	-0.18	57.6	25	126	80.2

Data source: [97]

high-temperature conditions (343K), only the fluorinated PVDF material maintained its durability characteristics. It was concluded that PVDF would be the best all-around choice for the transportation of HTP.

Thermotropic liquid crystal polymer (LCP) resins have been shown to be compatible with rocket grade hydrogen peroxide (RGHP) [878]. It was a challenge to effectively form them into useful net shape articles for the containment and transport of RGHP. Due to the high degree of anisotropy and high melt temperature, controlled tests were set up to explore processing parameters and characteristics of thermoplastic processing as applied to these high-strength polymers [879]. Tanks made from four new Ticona Vectra[®] LCP resins, all sharing aromatic copolyester chemistry, were blown including: Vectra[®] A115, LKX1098, LKX1099, and LKX1100. Results with LKX1099 and LKX1098 were favorable from a processing perspective, but these fumed silica filled resins are the most difficult to manufacture.

Since the 1960s high-performance new fluoropolymers have been developed, which had not yet been extensively tested with HTP. PFA and FEP are two polymers showing the chemically resistant characteristics of PTFE but with thermoplastic properties making them easy to manufacture into propellant tanks (composite-overwrapped tanks or soft liners for metal tanks).

Perfluoroalkoxy or PFA is a type of fluoropolymer with properties similar to polytetrafluoroethylene (PTFE). It differs from the PTFE resins in that it is melt-processable using conventional injection molding and screw extrusion techniques. PFA is very

similar in composition to PTFE and FEP. PFA is softer than PTFE and melts at 578 K (305 °C).

Fluorinated ethylene propylene or FEP is a copolymer of hexafluoropropylene and tetrafluoroethylene. It differs from the PTFE resins in that it is melt-processable using conventional injection molding and screw extrusion techniques. FEP is very similar in composition to PTFE and PFA. FEP and PFA both have low friction and non-reactivity but are more easily formable. FEP is softer than PTFE and melts at 533 K (260 °C).

The thermoplastic nature of the two resins reduces the troublesome porosity sometimes associated with PTFE, however, it retains its inert characteristics. Testing of the decomposition rate of HTP on the two polymers was done by measuring the pressure rise in a sealed borosilicate glass system of a coupon of the polymer immersed in HTP at a constant 305 K (32 °C) [880]. The surface of the samples was examined using X-ray photoelectron spectroscopy (XPS) to determine any changes in the surface chemistry of the polymer and to assess the degree of oxidation (if any) that might have occurred on exposure to HTP. XPS spectra showed that there was no discernable change after the exposure to the HTP, and that no or very little oxidation had taken place. The maximum tensile stress, the offset yield stress, and the tensile modulus were measured for the initial samples with no exposure, after 2 months' exposure and, finally, 4 months' exposure. There was no evidence to suggest that the polymers might lose their mechanical properties with long-term exposure (although 4 months is too short a test to make such a statement). Permeability is a difficult parameter to measure, and the numbers shown in Table 59 are just estimates from a 35-day test.

Table 59: H₂O₂ permeation rate of fluoropolymers.

	Gas volume collected cm ³	Permeation rate g cm ⁻² year ⁻¹ mm ⁻¹
FEP	2.14	0.01005
PFA	2.61	0.01225

Note: Sample thickness 0.5 mm

Data source: [880]

Stored HTP was passed through a silver catalyst to see if any catalyst poisons had leached from the polymers. Silver gauze discs were exposed to the stored hydrogen peroxide and the resulting discs examined using XPS to pick up any poisoning elements. As the result of these tests, FEP and PFA polymers were classified as Class I materials, with decomposition rates comparable to the best materials available. However, they are not significantly better than the 5254-0 or 5254-H34 aluminum alloys; in fact, based on these tests, the aluminum alloys should actually perform better. How-

ever, for spacecraft in orbit for long periods, the PFA and FEP liners complicate the storage problem due to the high rate of permeation. Even with a decomposition rate of 0.3% AOL, some form of tank venting will still have to be implemented, and this either requires a spin-stabilized spacecraft or a propellant management device, to separate the gas from the liquid.

Three small vessels were machined from fluoropolymers including unsealed lids of the same material to study hydrogen peroxide permeation [852]. They were filled partly with 85% HTP (stabilized at the time) and left undisturbed on a bench top at $294 \pm 1\text{ K}$ ($21 \pm 1\text{ }^\circ\text{C}$). A thin-walled PVDF vessel containing 125 g of HTP gained 8 g in 1.5 years and an additional gram over the following year. A 40-g sample in a thicker container gained 0.2 g over 4 months and then lost 0.9 g over 2 years. An identical thick-walled vessel made of PCTFE contained 42 g of HTP and gained 2 g over 2 years at a roughly constant rate. Of all the materials tested, PVDF clearly offered the most potential for 1-year sealed HTP storage. In this study, PVDF was studied as a liner material and was thought to be a good candidate until it started to peel. It was thought that the HTP permeated the plastic and decomposed between the metal and its coating.

Five polymers based on the polymerization of dicyclopentadiene were tested for compatibility with HTP [881]. Telene[®] 1650X was the most compatible polymer of five polymers immersed in high concentrations of HTP for 200 days. Telene[®] 1650BRR was the second best compatible, having similar effects on the HTP and less compatibility when being acted upon by HTP. Paramount 1 was the least compatible of the five polymers because it was greatly affected by HTP. The concentration of 90% HTP exposed to the polymers dropped from 90 to 70–80% during the 7-month test. Some of the polymer samples gained 10–20% weight during the immersion.

Much of the initial work with HTP was performed in the 1950–1960 time period. Since this time, new polymers have been introduced, some of which may avoid the storage problems of the past and may be more resistant to attack by HTP. More recent compatibility work performed with non-metals immersed in HTP has shown that it is often difficult to bring the results from different laboratories to a common denominator.

The most common polymer used for storage hydrogen peroxide is polyethylene (PE). Various sources specify that PE is a Class 1 or a Class 2 material, depending on the temperature of exposure. Most sources suggest that long-term storage in polyethylene is acceptable, as long as the peroxide concentration is no greater than 52% H_2O_2 . Kel-F (polychlorotrifluoroethene), or Neoflon[®], is also a common polymer for use with HTP. Most sources indicate that it is favorable for use as a diaphragm material in contact with HTP. Unplasticized Kel-F was tested as a tank material for a 275-gallon HTP tank for the US Navy, so there is some precedent in using Kel-F as a storage tank material [882].

Polyvinylchloride (PVC) is recommended only for short-term storage of HTP and is typically classified as Class 2 or Class 3 material, depending on the temperature.

PVC may also leach chloride ions into the HTP. Koroseal[®] is a PVC material that is generally not recommended for long-term HTP exposure. Koroseal 700, however, was developed especially for H₂O₂ service as a gasketing material, but it may no longer be manufactured.

Teflon[®] in its various forms (PTFE, PFA, and FEP) is the best choice of polymeric material in regard to HTP compatibility and can be used for storage of HTP, and it has often been cited as a Class 1 material. Many of the fluorinated polymers have been recommended as the best polymeric storage medium for HTP. They are recommended as a valving or sealing material as well. One of the problems with the fluorinated polymers is their lack of structural strength. For this reason, Teflon is more often recommended as a liner material than as an actual storage container material. The rationale for this justification is that if the container is somehow damaged, whether during transit or by general mistreatment, the fluorocarbon container would not provide adequate protection from damage.

Viton[®] A and B, fluoroelastomers, are typically used as O-ring materials for HTP storage tanks. They are not typically considered as a viable candidate as a tank wall material.

PVDF (polyvinylidene fluoride), or Kynar[®], was recommended as a possible alternative to PTFE compounds. In the study cited, which examined various polymers as tank materials, the concentration of an 87% solution of H₂O₂ decreased to 80% over 3 months (at 343 K = 70 °C). PVDF was the only polymer that maintained its durability characteristics [97].

PFA (Perfluoroalkoxy) and FEP have been examined in several studies and are both very promising candidates that may merit consideration. In two studies by the University of Surrey, PFA and FEP were examined in detail. They were good at containing peroxide, but their intrinsic compatibility was not as good as pure aluminum. However, such polymers do permit oxygen to permeate.

Compatibility tests indicated that many polymers decompose 90% hydrogen peroxide appreciably, while the effects of others were negligible. The appearance of some polymers remained unchanged after immersion in this oxidizer. The steady-state diffusion rate through several polymers was measured in a test apparatus constructed of Teflon [883]. The hydrogen peroxide, which permeated any film, was determined quantitatively by means of a spectrophotometric method. Experimental curves of the amount permeated as a function of time agreed with those predicted theoretically. A correlation was found between water vapor and hydrogen peroxide permeabilities for several polymers at room temperature. The hydrogen peroxide permeabilities of many polymers measured at 347 K (74 °C) over 96 h varied over four orders of magnitude. Teflon, Teflon 100-X, and polyethylene exhibited the lowest permeability of all the polymers tested. The temperature dependence of hydrogen peroxide permeabilities was found to conform to an Arrhenius type relationship. Activation energies for hydrogen peroxide permeation through plasticized polyvinyl chloride and polyvinylidene chloride were 66.9 and 75 kJ/mol (16 and 18 kcal/mol), respectively.

Short-term (240-h) immersion tests of polyformaldehyde (POM) and ultra-high molecular weight polyethylene (UHMWPE) in rocket-grade hydrogen peroxide solution were carried out in combination with tribological experiments [884]. The objective was to provide the knowledge for selecting or developing polymeric materials for tribological friction-wear applications in rocket-grade hydrogen peroxide. The micrographs of polymer specimens with various aging times indicated that POM had poorer aging resistance in hydrogen peroxide solution than UHMWPE. A new absorption peak assigned to the hydroxyl group appeared in the FTIR spectra of POM after aging tests due to the oxidation by hydrogen peroxide. The wear rates of POM and UHMWPE presented different trends with the increase of aging time; the wear rate of POM decreased, whereas the wear rate of UHMWPE increased.

5.4.2 Inorganic Ceramic Materials for Hydrogen Peroxide Service

Ceramic materials have been used for roller bearings and as coatings for metallic components in contact with hydrogen peroxide. Of course, ceramics are also used as catalyst carriers, but for that application, the contact time with liquid H_2O_2 is only very short because the liquid decomposes as soon as it contacts the catalyst.

Protective coatings of zirconium nitride deposited by plasma vapor deposition prevent corrosion of the metal parts, decomposition of HTP, and leaching of metal ions into the propellant [885].

Water and hydrogen peroxide are very poor lubricants for ceramic/metal pairs in sliding contact with each other as in the bearings of pumps and flowmeters. The wear patterns of ceramic/metal contact rubbing pairs in several hydrogen peroxide/water mixtures with increasing hydrogen peroxide content were evaluated by examining the wear surfaces and the abraded metal particles under the microscope [886]. The wear resistances of three types of ceramics (ZrO_2 , Al_2O_3 , Si_3N_4) rubbing against 1Cr18Ni9Ti stainless steel were analyzed under 0 (pure water), 10, 30, 50, 70, and 90% hydrogen peroxide solution. The results showed that, under different concentrations of H_2O_2 solution, the worn surface roughness of the 1Cr18Ni9Ti stainless steel was bigger than that under pure water when the counterpart was a ZrO_2 ceramic ball, while the worn surface roughness of the 1Cr18Ni9Ti stainless steel was smaller than that under pure water when the counterpart was a Al_2O_3 ceramic ball. For the ZrO_2 , Al_2O_3 , and Si_3N_4 ceramics balls, the average worn surface roughness of the Al_2O_3 ceramic ball was the smallest, and the average worn surface roughness of the Si_3N_4 ceramic ball was the worst when the concentration of H_2O_2 solution was only 10%. The metal particles from the ZrO_2 /1Cr18Ni9Ti and Al_2O_3 /1Cr18Ni9Ti stainless steel rubbing pairs showed wear features with large size and bright surfaces. The surfaces of the metal particles were visibly oxidized when the concentrations of H_2O_2 solutions were 70 and 90%.

Similar tribological friction pairs of Al_2O_3 ceramics in contact with 1Cr18Ni9Ti stainless steel were examined in hydrogen peroxide solutions of several different concentrations [887]. The wear mass loss of a 1Cr18Ni9Ti stainless steel ring sample in all

H_2O_2 solutions was worse than that in pure water. The wear mass loss was the worst in 70% H_2O_2 solution. Additional tests were performed with ZrO_2 , Al_2O_3 , Si_3N_4 ceramics and 1Cr18Ni9Ti stainless steel rubbing pairs in a tribo-tester under different concentrations of H_2O_2 solutions [888]. The rubbing pairs of Si_3N_4 ceramics/1Cr18Ni9Ti stainless steel had the best tribological properties in H_2O_2 solutions.

6 Components for Hydrogen Peroxide Service

This section describes components for ground handling and flight use of HTP. The design of test facilities for HTP rocket testing (monopropellant, bipropellant or hybrid rocket testing) has evolved over the years. Often, obsolete test facilities get torn down to be replaced with more modern test facilities with improved data acquisition and expanded capabilities.

Test facilities for HTP testing as a monopropellant are described in *Encyclopedia of Monopropellants*, chapter “Hydrogen Peroxide Monopropellants”; see also [867, 889, 890].

6.1 Storage Tanks for Hydrogen Peroxide Service

Hydrogen peroxide as it sits and slowly decomposes releases heat all the time. It has been argued that storage tanks for HTP should not be thermally insulated from the environment because if they were to have an unexpected exothermic reaction due to internal contamination, it would result in a runaway thermal reaction much faster. On the other hand, if storage tanks or tank cars or large transport tanks on ships became involved in an external fire, the fire department response time to a catastrophic tank rupture event would be extended if the tank had a fireproof thermal insulation. If a 4000-gallon tank containing 70 mass-% H_2O_2 became involved in an intense, enveloping fire, what happens during the first 30 min? In answer to this question, the response time for large 4000-gallon tanks on a ship containing 70% H_2O_2 was calculated from laboratory measurements of decomposition rates for a bare tank and an insulated tank [396].

Hydrogen peroxide storage tanks are normally fabricated with Class 1 materials. Most tanks used for bulk storage of H_2O_2 are made from aluminum 1060, which is 99.6% aluminum and very soft. When greater strength is required, aluminum alloys 5254 and 5652 can be used for bulk storage tanks. In consideration of the requirements for high-pressure lightweight tankage, AM 350 stainless steel has been used successfully, but only for short storage durations. The 17-7 precipitation hardening stainless steel has been used successfully in closely monitored 76 and 90% H_2O_2 systems. However, this material is generally more difficult to passivate than the AM 350 material, particularly when used in 90 and 98% H_2O_2 systems. Both steels offer yield strengths

of 160000 psi. The hydrogen peroxide tankage used in rocket test facilities and various other feed and ready storage applications (which required only short periods of hydrogen peroxide storage) is usually fabricated from 347 stainless steel. Other materials successfully utilized in tankage for these types of applications are the low-carbon 304, 316, and 321 stainless steels. The cryogenic prestrained 301 stainless steel has demonstrated excellent compatibility with 90 and 98% H_2O_2 , and the high yield strength of this material (260 ksi) favors its use for hydrogen peroxide tankage in flight vehicles and for high-pressure applications.

The material specifications of the containers for storage and delivery of high-purity aqueous hydrogen peroxide solutions for the electronic industry, container washing, and contaminant inspection methods are important to preserve the purity of the material. The containers of Mitsubishi Gas Chemical Co., Sumitomo Chemical Co., and Aisero Chemical Co. used for storage and delivery of high-purity aqueous hydrogen peroxide solution were compared [891].

In short-term storage tests evaluating four different materials for a breadboard test system tank with 98% H_2O_2 , pressure buildup due to gas evolution in contact with Al-6061, anodized Al-6061 or polycarbonate exceeded 15 bar in only 15, 33, or 52 days [892]. A tank made from polyvinylidene fluoride had the lowest rate of gas evolution, reaching 8 bar in 170 days, which is still too high for any type of space mission.

6.1.1 Flightweight Tanks for Hydrogen Peroxide Service

A composite tank using an epoxy resin and graphite fibers shell was fabricated for use in the space program. If HTP is to be used as the oxidizer, FEP (fluorinated ethylene/propylene) is recommended as the liner material [893].

The US Air Force has done work with a composite fuel tank for storage of HTP as well in connection with their Space Maneuver Vehicle (SMV) Program, with a “Teflon-like” liner [894].

For the Upper Stage Flight Experiment using a 90% HTP/JP8 engine, an integral composite carbon fiber overwrapped tank was designed, built, and hydraulically pressure tested to destruction [895]. The Upper Stage Flight Experiment was a technology demonstrator for the US Air Force’s operational Modular Insertion Stage (MIS). MIS was to be a low-cost expendable upper stage for the reusable space operations vehicle. The tank had the following dimensions and design parameters:

overall length	45.0 in.
skirt ID	24.0 in.
oxidizer chamber volume	5.5 cubic feet
fuel chamber volume	2.3 cubic feet
MEOP	800 psi
proof	$\text{MEOP} \times 1.25$
burst (minimum)	$\text{MEOP} \times 1.8$

The liners for both oxidizer and fuel were initially intended to be Tefzel but were later changed to PVDF. The bosses were from 316L stainless steel. During the hydraulic pressure burst test, the fuel liner failed at 2500 psi, allowing water to flow through the composite overwrap. Failure at 2500 psi showed a realized safety factor of 3.1 (the design was 1.8); see also [896, 897].

6.1.2 Expulsion Diaphragms and Bladders for Hydrogen Peroxide Service in Zero-g

It is difficult to find a polymer for expulsion bladders for hydrogen peroxide that is compatible with the aggressive oxidizer and does not embrittle with time or contaminate the propellant with leached organics [898, 899]. These tanks were to be used in the four-stage solid propellant Scout satellite launch vehicle.

A commercial off-the-shelf bladder propellant tank was tested with hydrogen peroxide and found to be acceptable for “long-term” storage of the hydrogen peroxide with only minimal pressure rise during storage [900]. “Long-term” needs to be identified more accurately and may only be a matter of a few months.

The first six satellites of the FORMOSAT-7/ COSMIC-2 satellite constellation developed by the National Space Organization (NSPO) program of Taiwan used a hydrazine monopropellant system, but a future constellation was planned to have a 2-liter diaphragm type propellant tank with a loading capacity of 1-liter HTP [901]. Two engineering qualification models were designed, manufactured, and tested to make sure that they will meet the satellite mission requirements.

6.1.3 Tank Pressurization and Feed Systems for Hydrogen Peroxide Service

A self-pressurizing hydrogen peroxide rocket system using a differential area piston tank boot-strap propellant feed system was demonstrated using 87% hydrogen peroxide feeding a ~50 lb_f monopropellant thruster or a hybrid rocket [902]. It used a differential area piston tank and a gas generator to enable self-pressurization. A small amount of HTP was tapped off the propellant tank, flowed through a gas generator, and pressurized the propellant tank in a bootstrap mode using the decomposed HTP. The steam and hot O₂ pressurized the top of the differential area tank, moving the piston down, expelling HTP into the larger, main rocket engine, and maintaining feed pressure in the tank although propellant is withdrawn from it. Multiple system tests indicated that a closed-loop peroxide system can bring a system up to operating pressures of 1.37–3.44 MPa (200–500 psi) from an initial supply pressure of as low as 0.34 MPa (50 psi). Preliminary analysis indicated that a boot-strap system could be 2 to 12 times lighter than a traditional inert gas pressurization system. The system described is equally applicable to hydrazine propellants.

6.2 Pumps for Hydrogen Peroxide Service

Differential piston area propellant feed systems (“bootstrap systems”) have been developed and demonstrated for hydrazine as well as for hydrogen peroxide. In the case of hydrogen peroxide, the hot gas pressurized the piston tank. One design used a cylindrical tank assembly having two different diameters and a compound internal piston [903]. The pressurant gas acted over an area larger than the liquid piston to amplify pressure. In effect, such a pump is a refillable differential piston tank. The pump must shuttle back and forth, and hence it has valves for receiving and discharging both liquid and gas. A self-pressurizing feed system with reciprocating 85% HTP pumps was designed, built, and integrated in a complete maneuvering system that could be used in a kinetic kill vehicle or a microsatellite mockup since it can translate and rotate in all three directions of space with its complement of thrusters [903]. It was then tested on a linear track where the vehicle was suspended on a frictionless air cushion. Some of the hot gas from the gas generator was diverted to small hot gas thrusters providing four-degree-of-freedom attitude control.

The friction and wear behavior of 1Cr18Ni9Ti stainless steel, which may sometimes be used for pumps or other components, depends on the concentration of hydrogen peroxide [904]. The tribological properties of 1Cr18Ni9Ti stainless steel and the chemical composition of the passive film in different concentrations of hydrogen peroxide were studied by measuring surface potentials by electrochemical measurements and X-ray photoelectron spectroscopy [905]. The wear behavior of 1Cr18Ni9Ti/GCr15 steel rubbing pairs was investigated using a pin-on-disc tribometer. The results indicated that the corrosion resistance of nitric-acid-passivated 1Cr18Ni9Ti increased significantly due to the existence of passivation film, which was mainly composed of chromic oxide. Moreover, 1Cr18Ni9Ti passivated with diluted nitric acid exhibited lower friction coefficient and higher wear resistance than unpassivated steel in hydrogen peroxide. It was suggested that the main wear mechanism was a combination of adhesive wear, abrasive wear, and corrosive wear for the passivated and unpassivated 1Cr18Ni9Ti in different concentrations of hydrogen peroxide.

The wear and tear at the interface between ceramic bearings and moving metal parts depends on the type of materials and the strength of hydrogen peroxide that they are immersed in. The wear of three types of ceramics (ZrO_2 , Al_2O_3 , Si_3N_4) rubbing against 1Cr18Ni9Ti stainless steel was measured while immersed under 0% (pure water), 10, 30, 50, 70, and 90% H_2O_2 solutions [906]. The results showed that, under different concentrations of H_2O_2 , the worn surface roughness of the 1Cr18Ni9Ti stainless steel was worse than that under pure water when the counterpart was a ZrO_2 ceramic ball, while the worn surface roughness of the 1Cr18Ni9Ti stainless steel was better than that under pure water when the counterpart was a Al_2O_3 ceramic ball. For ZrO_2 , Al_2O_3 or Si_3N_4 ceramic balls, the average worn surface roughness of Al_2O_3 ceramic ball was the smallest, and the average worn surface roughness of Si_3N_4 ceramic ball was the worst.

A study of the wear of rubbing pairs of 2Cr13 stainless steel against 1045 metal in HTP, the decomposition and damage mechanism of materials, friction coefficients, wear mass loss, worn surface topographies, and electric current densities was conducted under different concentrations of H_2O_2 solutions [907]. There were significant differences in the tribological behavior and electrochemistry properties of the rubbing pairs in different H_2O_2 solutions.

The corrosive and tribological behaviors and the wear mechanisms and alloy grain structure effects of AlCoCrFeNi alloys under 90 mass-% H_2O_2 solution in contact with Si_3N_4 ceramics were examined [908]. Alloys with poorer corrosion resistance and higher strength could more easily achieve effective lubrication. The component inhomogeneity of different grain structures may promote the corrosion behavior.

The selection of sealing rotary seals in HTP pumps and valves is a difficult task [909]. Many HTP accidents have been caused by leaking seals and gaskets.

6.3 Pressure Relief Devices for Hydrogen Peroxide Service

The preferred emergency pressure relief device for hydrogen peroxide systems is a rupture disk because it does not involve any moving parts. The relief device should be rated at not more than 100% of the vessel or system operating pressure when used as a primary relief device or 105% when used as a secondary relief device. The sizing of the device should be large enough to prevent the pressure from rising 10% above the maximum allowable working pressure of the system under any projected condition. Burst relief devices on hydrogen peroxide tank cars are designed to relieve at 310 kPa gauge (45 psig) pressure.

Ball valves intended to be used for hydrogen peroxide service must have a provision to relieve the pressure likely to build up in the passage through the ball while it is closed on both sides, and liquid is trapped inside.

6.4 Flow Meters for Hydrogen Peroxide Service

The performance of any bipropellant rocket depends on accurate metering of the oxidizer and the fuel flow into the engine. For an HTP/kerosene engine, a differential pressure orifice flowmeter has been used to measure the propellant flows [910].

6.5 Filters for Hydrogen Peroxide Service

Filters are extremely important with HTP systems [911]. The function of a filter is to trap particulate contaminants, and most contaminants are catalytic with HTP; therefore a filter with accumulated particulate contaminants will slowly turn into a catalyst bed

and become a hotspot which is very dangerous. For complex test systems, especially those using cavitating venturi, small injector orifices or other contamination-sensitive components, filtering the HTP may be a necessity to keep out foreign material. HTP storage vessels and transfer equipment can contain particulate contamination, such as aluminum oxides, phosphates, Teflon tape shreds, metal burrs, wire, or weld slag metal oxides. If a filter is used it should be considered a high-risk component and not a passive part of the transfer system. Additional precautions should be used to monitor the behavior of the filter through periodic inspections, temperature (hotspot) measurements, pressure drop measurements, and occasional backflushing.

The inlets to propellant valves are usually protected by filters to retain particles that might get lodged on the valve seat and cause the valve to leak when it is commanded shut. The screen material on the filters must be compatible with the propellant, which in the case of HTP is not as difficult a task as with other oxidizers. The corrosion product (phosphate, oxide) film growing on the thin metal wires might cause a narrowing of the passages and increase the pressure drop or embrittle the wires. Similar wire mesh is used in surface tension propellant management devices in propellant tanks for zero-g operation. The long-term effects of propellant immersion on fine micronic stainless steel wire cloth were studied for HTP and eight other propellants [912]. Immersion time histories reported in the literature ranged from 3 months to 7 years.

7 Handling of Highly Concentrated Hydrogen Peroxide

With sufficient experience and well-trained personnel, HTP can be handled safely. Nevertheless, like most other rocket propellants, the handling of HTP is not without its specific set of hazards. The attempt by some rocket enthusiasts to classify HTP as a “non-toxic” “green” propellant does not adequately reflect the true potential hazards in handling this material. Hydrogen peroxide was one of the first rocket propellants tested, and its handling experience for rocket applications spans a range of over 75 years.

After green propellant and improved propulsion systems performance initiatives identified hydrogen peroxide (HTP) as a candidate propellant for propulsion and power systems, NASA Johnson Space Center (JSC), White Sands Test Facility (WSTF), began to develop a hydrogen peroxide reference document to be used by academia, the industry, and government installations. The purpose of this document was to provide a central source of information to enable the user to assess HTP hazards. While there were several mostly historical sources of HTP hazards assessment documents, they were all dated to before 1969, and therefore may not utilize data and other information necessary for modern materials selection processes or adequately address recent concerns and current regulatory requirement. Recognizing these issues, an effort was initiated to produce a more up-to-date HTP hazards manual.

Various presentations discussed the interim status of this program [913] until it was completed in 2005 [914]. The most complete and very detailed summary of the fire, explosion, compatibility, and safety hazards of hydrogen peroxide was compiled by NASA WSTF in 2005 [10]. This 300-page document exceeds all previous hydrogen peroxide manuals and handbooks in its thorough approach to document potential handling hazards, critical analysis of historical data reported in the literature, and reporting of additional new safety data obtained at NASA WSTF during the past decade. The *Fire, Explosion, Compatibility and Safety Hazards of Hydrogen Peroxide* NASA technical manual covers various topics concerning HTP, including fire and explosion hazards, material and fluid reactivity, materials selection information, personnel and environmental hazards, physical and chemical properties, analytical spectroscopy, specifications, analytical methods, and material compatibility data. A summary of HTP-caused accidents, incidents, close calls, mishaps, and lessons learned is included in the hope that this information will prevent future incidents of this type. Hydrogen peroxide users are cautioned when extrapolating from short-term compatibility test results to long-term compatibility predictions.

For additional historical information on the handling of hydrogen peroxide see the following now mostly antiquated references: [915–920].

A series of papers published by General Kinetics LLC during the period 1998 through 2007 set out to dispel some of the misconceptions and myths about hydrogen peroxide [840, 911]. General Kinetics Inc. ceased operations as of the end of the first quarter in 2012; see also [921].

7.1 Transport and Storage of High-Test Peroxide

7.1.1 Transportation of High-Test Peroxide

The transportation of solutions with >52 mass-% H_2O_2 within the US was regulated by 49 CFR § 173.266 [922, 923]. This rule has been updated periodically. Specification 42D describes Al drums with a vented closure in top head, not over 208 L (55 gallons), capacity. The drums must be marked “KEEP PLUG UP TO PREVENT SPILLAGE”.

7.1.1.1 US Transportation Regulations for Hydrogen Peroxide

Hydrogen peroxide solutions above 8% H_2O_2 are classified as “oxidizers” by the US Department of Transportation, and all containers must bear the yellow oxidizer DOT label.

Hydrogen peroxide, stabilized or hydrogen peroxide aqueous solutions, stabilized with more than 60% hydrogen peroxide are covered under UN2015, Hazard Class 5.1, but it does not state the maximum concentration allowed under this code. Special permits have been issued for transportation of hydrogen peroxide with more than 62% but less than 92% H_2O_2 [924].

As of 1999, Degussa-Hüls Corp. (a predecessor to Evonik) had safely shipped 90% HTP in the US in a variety of containers [925].

The US Department of Homeland Security (DHS) has classified H_2O_2 as a Chemical of Interest (COI) due to being a candidate for “theft and diversion”. Special regulations apply in that a H_2O_2 bulk transport vehicle may not be left unattended. Theft and diversion calculations for screening threshold quantities (STQ) of H_2O_2 have been published in 6 CFR 27.203(c), typically starting at 35%/400 lbs; which further states that chemicals in “transportation packages” are to be used for the STQ calculation.

7.1.1.2 Tanker Trucks and Railcars

The requirements for bulk packaging of high-hazard liquids are given in 49 CFR Part 173.243. The definition of bulk packaging includes railcars, cargo tanks (tanker trucks), and intermediate bulk containers (tote bins). Larger quantities of HTP are transported in tank cars in compliance with regulation ICC-103A-AI-W made of aluminum alloys. Such tank cars hold 15000 to 30000 L. In both Europe and the United States, all hydrogen peroxide shipped at concentrations exceeding 72% is subject to strict regulation in terms of the permissible means of commercial transportation. The International Maritime Dangerous Goods (IMDG) Code (which regulates international sea transportation) and the United States Department of Transportation regulations for bulk shipments of hydrogen peroxide over 72% concentration are not consistent in terms of bulk transport of HTP. The Degussa Corporation has petitioned the US Department of Transportation (DOT) for an exemption to the current regulations covering bulk shipments of high-strength hydrogen peroxide. If granted, this would allow transport of HTP within the continental United States in full truckload quantities using especially designed bulk containers. Table 60 summarizes some of the 1998 packaging and transportation options for HTP permitted under the applicable body of law.

High-strength hydrogen peroxide falls under the shipping classification 5.1, UN 2015, and PG 1, and must be transported and labeled in conformity with the specifications and standards provided in 49 CFR § 171–190 (various subsections) and the

Table 60: Transportation regulations for hydrogen peroxide.

Packaging	UN code	Volume	Land (Europe)	Sea (ex Europe)	Land (USA)
Combi-drum (PE lined steel)	6HA1	125 L	Not allowed	Partially Allowed	Allowed
		250 L	Not allowed	Not allowed	Allowed
Steel drum	1A1	125 L	Allowed	Allowed	Allowed
		250 L	Not allowed	Not allowed	Allowed
Aluminum drum	1B1	125 L	Allowed	Allowed	Allowed
		250 L	Not allowed	Not allowed	Allowed
Combi IBC	31HA1	1000 L	Not allowed	Not allowed	Not allowed
Steel bulk tank		varies	Allowed	Allowed	Not allowed
Combi bulk tank		varies	Allowed	Allowed	Not allowed

IMDG Codes. The 5.1 classification indicates a primary hazard as an oxidizer, with a subsidiary hazard (8) as a corrosive material. The product cannot be shipped by air under the controlling authority of IATA (for civilian carriers) and AFMAN 24-204 (for military air transport).

7.1.1.3 Storage of High-Test Peroxide

Four grades of Becco hydrogen peroxide were evaluated during an extended storage test: commercial 90 mass-% H_2O_2 , propulsion Grade 90 mass-% H_2O_2 , commercial 98 mass-% H_2O_2 , and propulsion Grade 98 mass-% H_2O_2 in 3.78-L (1-gallon) capacity TFE Teflon bladders were contained in mild steel test tanks at 294–295 K (70–72 °F) for 5 months, 322 K (120 °F) for seven days, and 347 K (165 °F) for 72 h [926]. The bladders were not as compatible as desired due to the bleaching and crack development experienced with this dispersion-type Teflon. These tests showed that the oxygen loss from the H_2O_2 during the storage period can be decreased by utilizing improved passivation techniques, surface pretreatment techniques, and improved stabilizers for the H_2O_2 . The use of an oxygen absorbent bag in the tank proved non-rewarding due to breakdown of the absorbent solution. The most promising test results were obtained with the 98% propulsion grade H_2O_2 containing stabilizer “P”. Brief screening tests showed other bladder materials such as NAA Vicone 185, 3M Fluorel #2141, and Dupont Viton B cure 805 to give comparable or superior compatibility in contact with the H_2O_2 when compared to the dispersion-type Teflon material.

Drums

Non-bulk packaging (i.e., drums) available from the former Degussa-Hüls Corporation complies with 49CFR Part 178 (DOT). These drums are 125-L type UN 6HA1, constructed of stainless steel with a high-density polyethylene molded inner liner. While these may suffice for 90% HTP, an incident at NASA Stennis when the same drums were used for storage (not shipment outside the facility boundary) of 98% HTP and started an exothermic reaction after the HTP had permeated the PE liner and came into contact with stainless steel, **cautions us not** to use these drums for higher (>90%) concentration HTP. The IMDG (International Maritime Dangerous Goods) Code only approves 1A1 (inert, steel) and 1B1 (inert, aluminum) drums for the transport of hydrogen peroxide of 60% or higher. However, at one time, Degussa-Hüls has had a special approval to use 6HA1 drums for shipping HTP containing up to 90.5% H_2O_2 .

A nicely illustrated summary of various HTP transportation and storage vessels is shown in [911], which is based on experience at General Kinetics LLC and FMC.

HTP is normally shipped in 110-L barrels made of aluminum and complying with ICC regulation 420, UN 2015, typically containing 115 kg of product. Numerous storage tests have shown that HTP loses no more than 1% H_2O_2 (absolute) per year in properly built, cleaned, and passivated drums that also have a pressure relief valve to vent any pressure buildup [927, 928]. The 144-L barrels were of the Type 42 D and made of 99.6%

Al, Al-525, or Al-XF-52S. The gasket and valve seat material on the pressure relief valves was a silicone rubber.

It is prohibited to place wooden pallets under hydrogen peroxide drums with $>27.5\%$ H_2O_2 .

ISOtainers

ISO's IM tanks, also called ISO containers or ISOs, are used by Degussa-Hüls to transport bulk quantities of Propulse™ H_2O_2 . ISOs are classified as IMO tank type 1 and DoT type IM 101. While it is approved to ship H_2O_2 concentrations greater than 72-mass-% internationally, domestic US transportation in IM 101 tanks is restricted to 72% or less by 49 CFR Part 172. The Degussa-Hüls Corporation has obtained exemption DOT-E 12003 to allow the transport of up to 92 mass-% H_2O_2 in IM 101 tanks and has delivered Propulse™ HTP in bulk domestically over the road.

ISO containers are ASME-coded vessels enclosed in a steel-tube framework that makes them safe and easy to handle as ocean and over-the-road freight [97]. ISOs have the following physical parameters:

- dimensions: 20 ft. long $\times$ 8 ft. wide $\times$ 8 ft. high
- capacity: 24000 kg (52800 lb) gross weight
- 20000 kg (44000 lb) payload weight
- 14280 liters (3780 US gallons) max. payload

Storage tanks (not tank car tanks) should be made of 99.6% Al or XF-52-S-Al, Al-1060, Al-5652 or Al-5254, with pipes of 99.6% Al or Al-2S. Valves and pumps can be made of 99.6% Al, Al-2S, or Al-43S. CRES-316 is not suitable for this purpose.

Due to the lack of other materials during WWII in Germany, plastic-lined steel containers were used for storage of H_2O_2 and were in use for several years [929].

If the pressure in storage drums (regardless of what the drums are made of) is not monitored regularly, and the pressure relief valves become stuck closed, excessive pressure buildup can rupture the drums [930, 931]. Figure 56 shows the consequences of premature hydrogen peroxide decomposition in a storage drum that was not properly vented. One can see how the sides of the drum bulged before it ruptured on the lid.

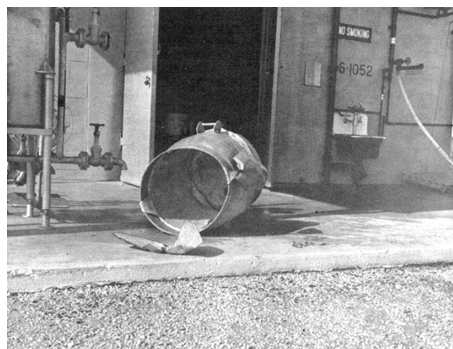


Figure 56: Ruptured HTP storage drum. (From [931].)

For this reason, H_2O_2 storage tanks should carry a pressure gauge and a pressure relief valve. Descriptions of the design of complete HTP storage and transfer facilities can be found in the literature [867]. HTP manufacturers will often assist their customers in the design of storage and transfer facilities and provide training for propellant handling personnel.

Only few climates will have outside storage temperatures below the freezing point of HTP. It has been observed that due to the high purity of HTP, the liquid tends to supercool, and it is often remaining in the liquid state at temperatures where theoretically it should be frozen. The unpleasant side effect of freeze-thaw cycles might be stratification and segregation, which cause a layer of the contents to approach higher H_2O_2 concentrations than what is printed on the label. The contents of drums retrieved from subfreezing storage would have to be thoroughly mixed before taking a sample for analysis or before withdrawing material for use. If all of the contents are transferred from one tank into another, enough turbulence will usually occur to result in a thoroughly mixed contents with uniform concentration throughout in the receiving vessel.

Contrary to water, H_2O_2 does not expand on freezing. So, at least, there is no drum rupturing hazard if the contents are inadvertently frozen. However, transporting drums with slugs of solid H_2O_2 over rough roads may subject the bottoms of drums to excessive impact loads from the slug of H_2O_2 ice for which they were not designed.

If it is mission critical to keep an HTP supply from freezing in arctic regions away from electric power supplies, a method of drum heating has been designed that sacrifices part of the drum contents, using its controlled decomposition as a heat source [932].

Small amounts of contaminants can cause a self-accelerating runaway situation where the heat evolved by decomposition of the contents exceeds the heat that can be conducted away through the walls of the containers. Thermal explosions have been studied, and methods for prevention of unwanted explosions have been developed [930, 933]. Figure 57 shows the predicted temperature history of a large storage container with contaminated HTP. For this calculation, a decomposition rate of 50%/year, outside and at the initial liquid temperature $298\text{ K} = 25^\circ\text{C}$, and a surface : volume ratio of 1 m^{-1} was assumed. The ambient air condition was stagnant air. A decomposition rate of 50%/year is rarely encountered and can only be the result of gross negligence [934]. But what can one do if a tank shows a temperature increase? One can try to add more stabilizer, cool the tank, dilute with water (if space is available in the tank), or drain the tank into a large holding pond with enough water to dilute the tank contents to below 5% H_2O_2 . Some storage and rocket test installations have H_2O_2 disposal reactors where surplus HTP can be decomposed and disposed of (see *Encyclopedia of Monopropellants*, chapter “Hydrogen Peroxide Monopropellants”).

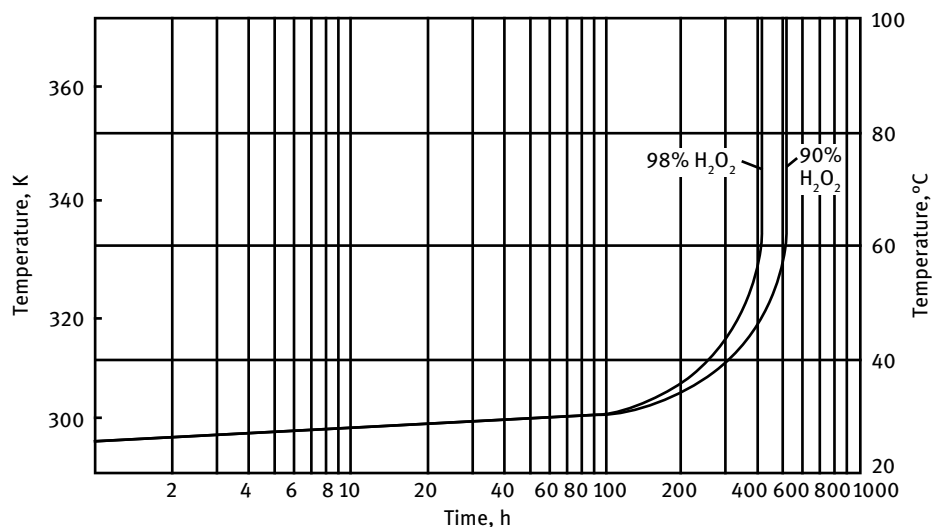


Figure 57: Predicted temperature increase in an HTP storage container due to an incipient uncontrolled decomposition/runaway situation. (Reproduced and modified from [930].)

HTP Storage

In Russia, where HTP is still actively used in the reaction control system (RCS) of Soyuz space capsules and steam generators in the Soyuz launch vehicle, HTP storage tanks are loaded to only 90% of their capacity during winter and 85% of their capacity during summertime [935]. HTP in quantities up to 100 m³ is stored in aluminum tanks. The tanks are thoroughly passivated before their first loading. During the whole storage period the internal HTP temperature must not exceed the ambient temperature (a warning sign of incipient decomposition), and it must not exceed 298 K (25 °C). In any case, if the HTP temperature reaches 303 K (30 °C), cold water must be sprayed over the storage tank to cool it from the outside. If the idle period of unused tanks, lines, and pumps exceeds 6 months, the equipment is washed out periodically with 30% H₂O₂ aqueous solution. During long-term (10–15 years) storage in very large (>2 m³) aluminum tanks, HTP (96–98 mass-%) decomposed approximately only 0.05% per year at 283–298 K (10–25 °C). Based on the operational experience in Russia since the early Vostok and Soyuz flights, 10-year storage on the ground is considered quite acceptable; see also [936].

A decrease of HTP self-decomposition during its storage can be achieved by saturating it with highly soluble gases. A significant decrease in HTP self-decomposition rates was observed when it was saturated with carbon dioxide.

NFPA Hazard Ratings

A rating system has been devised by the National Fire Protection Association (NFPA) to assist emergency responders – NFPA 704-1990. The system has also been incorporated into the Uniform Fire Code, Standard 79-3. This program utilizes a color-coded tank/site placarding system that visually alerts first responders to the types of hazards associated with the material (e.g., health, flammability, and reactivity). The appropriate labeling for various H₂O₂ concentrations is shown in Table 61.

Table 61: NFPA hazard diamond classifications for hydrogen peroxide.

H ₂ O ₂ Concentration, mass-%	Health	Flammability	Reactivity
<8	0	0	0
8–20	1	0	1
20–52	3	0	1
52–91	3	0	2
>91	3	0	3

The NFPA Diamond hazard label for hydrogen peroxide above 52 mass-% contains:

- health: 3 (blue section)
- fire: 0 (red section)
- reactivity: 2 (yellow section)
- specific hazard: OXY (white section)

7.1.1.4 Transfer of High-Test Peroxide

HTP can be transferred from one container to the other using pumps or vacuum suction transfer [937].

Very rarely will one be in a situation where one can use gravity flow from a higher positioned supply tank into another tank. The supply tank at grade (normal situation) or below grade (more severe situation due to hydrostatic head) must be rated to withstand the transfer pressure. Some transportation drums are not intended to be pressurized. Suitable pressurant gases are air, nitrogen, oxygen, argon, or helium.

The former Degussa-Hüls specified that product must be pumped out of the drums; the drums are not to be pressurized under any circumstances. Self-priming centrifugal or positive displacement (e.g., diaphragm or peristaltic) pumps are the best choices. Drum pumps are acceptable but normally employ an impeller at the bottom of the dip tube, thus preventing complete discharge of the product from the dip tube and downstream system. Where a vacuum system is used to convey product from the drum, the vacuum source must be an air-driven venturi, not a mechanical, oil-lubricated vacuum pump. Accidental conveyance of HTP into a vacuum reservoir or pump could result in an explosion.

7.2 Personnel Protective Equipment for Handling of High-Test Peroxide

Protective clothing worn by propellant handlers must be made of non-combustible splash-proof material. It has been shown that some of the not-so-suitable glove and apron materials will catch fire when HTP is sprayed onto them [938, 939]. The suitability of personnel protective equipment (PPE) for HTP service was determined by observations made when HTP was dripped onto swatches of protective clothing material. Samples of ten different chemical protective materials were cut into 4 in. by 4 in. swatches and tested as-received, in soiled condition and in grossly soiled condition. Materials were soiled by pretreating the material with potassium permanganate (KMnO_4) solution and then drying it to make the fabric a worst-case situation. Grossly soiled material samples had solid KMnO_4 sprinkled over their surface. Observations included visual changes to the hydrogen peroxide and materials, times to ignition, and self-extinguishing characteristics of the materials. All of the grossly soiled specimens ignited within 2 to 100 s when 98% HTP was dripped on them. In tests with clean materials, only leather ignited.

A complete HTP propellant handler's ensemble consists of a face shield and head cover, coverall, apron, gloves, and boots. Gas masks or respirators are normally not required.

A comprehensive summary of protective clothing for all types of corrosive chemicals, and the hazards of permeation of aggressive chemicals through the protective clothing during use is provided in [940] and [941].

7.3 Fire Fighting of High-Test Peroxide-Sustained Fires

Fires sustained by HTP and spilled fuels or combustible materials of storage buildings are best extinguished with copious amounts of water. Water will not only cool the flames but also dilute HTP to below the point where it can sustain combustion. Spilled HTP prior to ignition should also be diluted with water to below 30% before a cleanup is attempted. During the spill cleanup there may be an acute and a delayed ignition hazard.

7.4 Treatment of High-Test Peroxide Spills and Rinse Waters

Hydrogen peroxide is used in the dairy industry for the pasteurization of milk and equipment prior to cheese making. Excess hydrogen peroxide must be removed before the milk can be passed on to the next step of cheese making. The most benign and environmentally compatible way to remove small concentrations of H_2O_2 in dilute solutions would be with the enzyme catalase. However, the enzyme either in the soluble form or immobilized on a support degrades quickly. It has been attempted to

employ longer lasting catalysts made from manganese oxide on alumina that do not leave residues in the milk [942, 943]. The activity of the manganese oxide/alumina catalyst degraded quickly initially but leveled off after some time; see also [944].

7.5 Disposal of Surplus Hydrogen Peroxide

Surplus hydrogen peroxide that is no longer needed or is of a questionable pedigree or has become accidentally contaminated, or hydrogen peroxide that has been used to passivate a new tank can be disposed of in dedicated stationary hydrogen peroxide disposal reactors. Several of these disposal reactors have been installed at rocket test facilities in the US.

One such reactor was built by General Kinetics for NASA. It used MnO_2 pellets, which are much more economical than silver or stainless steel screen but would not qualify for use in flight thrusters. As of 2001, in one of these installations about 4500 kg (10000 lb) of surplus H_2O_2 with concentrations ranging from 50 to 98% was disposed of [945].

Our primary interest here is in the disposal of HTP, but there is a more widespread need for the disposal of hydrogen peroxide in dilute solutions that are widely used in industry and in the sterilization of medical equipment and contact lenses. There are many patented catalysts and methods for the disposal of hydrogen peroxide in dilute solutions. These catalysts are only capable of operating at low temperature and are useless for rocket applications.

7.6 Gelled Hydrogen Peroxide

Hydrogen peroxide, like other liquid rocket propellants, can be gelled to suppress sloshing of liquids in propellant tanks during the ascent phase of a rocket or to prevent leakage. This would be done only in cases where hydrogen peroxide is used as an oxidizer in bipropellant or hybrid rockets.

The rheological behavior of gelled hydrogen peroxide at different ambient temperatures (283, 293, and 303 K) in the shear rate ranges of 1 to 20 s^{-1} and 1 to 1000 s^{-1} was characterized using a rheometer [946, 947]. Six mass-percent of fumed silica (SiO_2 , 0.2–0.3 μm aggregate, Sigma Aldrich Corp.) was used for the gelation of hydrogen peroxide. As with all thixotropic fluids, the apparent viscosity with some yield stress (in the case of shear rate 1 to 20 s^{-1}) fell drastically with the shear rate. In the case of the shear rate range of 1 to 20 s^{-1} , the apparent viscosity and yield stress of the gel were significantly reduced at higher ambient temperatures. In the case of the shear rate range of 1 to 1000 s^{-1} , no significant effect of varying the ambient temperature on the gel apparent viscosity was observed. The up and down shear rate curves for hydrogen

peroxide gel formed a hysteresis loop that showed no significant change with variation in temperature for both the 1 to 20 s^{-1} and the 1 to 1000 s^{-1} shear rate ranges.

The gelling agent in gelled hydrogen peroxide may interfere with catalysts if hydrogen peroxide is predecomposed in a catalytic reactor to ignite a hybrid rocket [948].

7.7 Histories and Anecdotal Accounts of Incidents Involving Hydrogen Peroxide and Hydrogen Peroxide Mixtures

In this summary of accidents, we have listed explosions and accidental overpressurization of tanks containing hydrogen peroxide or hydrogen peroxide mixtures with insufficient venting capacity. Not all these events were true detonations, and some can be categorized as “overpressurization” rather than an explosion [949].

On July 16, 1934, in Kummersdorf, Germany, a rocket engine using hydrogen peroxide exploded, killing three people. As a result of this incident, Wernher von Braun decided not to use hydrogen peroxide as an oxidizer in the rockets he then developed after the development group moved to Peenemünde.

After WW-II, a German rocket scientist captured and involuntarily transferred to the UK after WW-II, Dr. Johannes Schmidt, was killed in an accident at the D Site at Westcott, UK on 14 November 1947. It is sadly ironic that this occurred while he was testing one of the few pieces of impounded German WW-II hardware (a Walter 509-510 engine) that were ever fired at Westcott [950].

During the development of the LR-40 HTP/JP-5 bipropellant engine at RMD/Chance-Vought, the HTP decomposition product steam-driven turbine was on the same single shaft as the two propellant pumps. The two pump seals shared a leakage collection cavity that should have had the drain opened during operation. An accident was caused by not removing a pump shaft leakage collector cavity drain plug prior to testing. A mixture of 90% HTP and kerosene that had leaked accumulated in the cavity and exploded when the drain plug was removed after the test, killing one technician and injuring several bystanders [951].

An accident occurred during the treatment of a surfactant with a peroxide/water solution that was usually highly diluted [952]. Due to several circumstances, a more concentrated solution was inadvertently applied at startup of the unit. This caused a sudden pressure increase, which burst a pipe, releasing large quantities of heating fluid, which caught fire. The fire destroyed the unit. In trying to explain what happened, the sudden pressure increase was simulated in the lab and the heat release measured by thermochemical methods. It was demonstrated that even concentrations of hydrogen peroxide as low as 10 mass-% in a homogeneous solution with organic material can cause sudden pressure increases in excess of the regular rating of most apparatus used in the chemical industry and high rates of pressure increase.

The author of a Russian book on fast reactions in energetic materials and high-temperature decomposition of rocket propellants and explosives [432] states

on page 173: “Based on his personal experience of working in committees that have investigated many accidents, the author of this book came to the conclusion that h/c H_2O_2 can be considered the most dangerous (with respect to explosions and fire hazards) liquid propellant component, especially in monopropellants. This conclusion is backed up by the following relatively recent serious accidents” and continues to list several accidents which he personally investigated.

An accident in the Russian submarine *Kursk*, which sank in the Barents Sea, involved a highly concentrated H_2O_2 -fueled torpedo explosion. Before this accident, on 18 March 1980, an A-7 rocket exploded during fueling, killing 48 people at the Plesetsk spaceport. As was discovered by Shteinberg, the accident was caused by the thermal explosion of HTP H_2O_2 that came into contact with catalytically active Pb-containing solder. The soldering alloy was mistakenly used by a manufacturer to solder a stainless-steel screen filter in the HTP H_2O_2 supply line.

Hydrogen peroxide is used during the reprocessing of nuclear reactor fuel elements to precipitate the separated plutonium in the form of plutonium peroxide. Two accidents happened at the EG&G-operated Rocky Flats Plant in 1957 and 1980, where 35–50% H_2O_2 became contaminated, and rapid decomposition overpressurized the reaction vessels and spilled plutonium outside the glove boxes [420].

Prior to 1963, a chemist was killed when he inadvertently poured highly concentrated hydrogen peroxide into a laboratory sink. The hydrogen peroxide reacted violently with some U-DETA (MAF-4, a mixed amine fuel consisting of unsymmetrical dimethylhydrazine (UDMH) and diethylene triamine (DETA)) remaining in the trap underneath the sink, and the trap exploded. At the time, U-DETA fuel was used in small storable missiles like the Bullpup.

At 0825 hours on 16 June 1955, the submarine *HMS Sidon*, a submarine of the S class, was lying alongside the depot ship *HMS Maidstone* at Portland, UK, when one of her torpedoes exploded [953]. The torpedoes had no warheads but contained hydrogen peroxide propellant. A peroxide line ruptured due to a system overpressure, and this allowed the peroxide to contact incompatible materials like copper and mild steel (a similar failure is thought to be the cause of the more recent, tragic loss of the Russian submarine, *Kursk*). The crew had just embarked the torpedoes before going to sea for trial firings. A sudden uprush of air and smoke poured through the conning tower hatch. The captain, other people on the bridge, and crew from *HMS Maidstone*, entered the boat to assist with the rescue operations. At 0845 hours, the submarine sank without warning. There were 56 men onboard at the time. Three officers and ten ratings lost their lives, but the remainder were saved. The wreck was raised on 23 June 1955 and beached the next day. The 13 bodies were recovered 2 days later. Another explosion of the hydrogen-peroxide torpedo at Arrochar torpedo range caused the development of the Mk12 torpedo to be canceled.

In Japan in 1999, a tanker truck loaded with 500 L of hydrogen peroxide waste blew up on the Tokyo Expressway [426]. The explosion was so strong that it blew off a 10-m section of a 2-m high soundproof barrier, scattering chunks of the wall onto cars

and passersby on the street 8.5 m below. Shockwaves from the blast shattered several windows of 28 buildings in the area. Fragments of the tank were scattered over a 100 m radius.

Table 62 is a summary of hydrogen peroxide transportation accidents, covering only a short period of several years.

Table 62: Accidents caused by H_2O_2 in USA and New Zealand – 2-year sample.

Date	Location	Fatalities	Injuries	Remarks
01/27/2005	San Bernardino, California	N/A	0	Tank container
01/13/2005	Vacaville, California	N/A	0	Road tanker
01/08/2005	Seabrook, Texas,	N/A	0	Rail tanker
12/23/2004	South Dunedin, New Zealand	N/A	N/A	Tank container
04/24/2004	Dallas, Texas	N/A	N/A	Tank container
04/05/2004	Mobile, Alabama	N/A	N/A	Waste storage
02/17/2004	Nr. Natchez, Mississippi	N/A	N/A	Transport

Data source: [954]

In 2000, an explosion injured 16 people in Stratford, CT, USA; this accident cost US \$700000.

Butadiene-free radical polymerization with hydrogen peroxide in the presence of an organic solvent occurs in the liquid phase at about 393 K (120 °C). Because of the reactive compounds involved and the relatively high temperature, this is an intrinsically dangerous reaction [955]. The presence of carboxylic acids and/or ionic iron contamination must be avoided.

The company named Peroxide Propulsion in Gunnilse, Sweden, was a producer of rocket grade hydrogen peroxide (also called HTP, high test peroxide) from 2004 to 2010. Lower grade hydrogen peroxide was concentrated to 80–90% concentration in a plant and treated in special processes to produce a very pure product well suited for gas generation and rocket propulsion. Some rocket projects in the US purchased peroxide supplies from the Swedish firm. On July 22, 2010 Peroxide Propulsion suffered a terrible accident at the production facilities in Gunnilse, Sweden. Founder and coowner, Erik Bengtsson, was working at the plant when hot hydrogen peroxide steam exploded in his face, blinding him temporarily. The plant subsequently burned to the ground. All stored supply of propellant-grade hydrogen peroxide was destroyed in the fire, and the company ceased operations [956].

On September 15, 2010, a powerful explosion occurred on the 307 National Highway in Jinzhou, Hebei, China [457]. The explosion was caused by a truck loaded with 5 tons of hydrogen peroxide. Shockwaves from the blast shattered most windows in a 150-m radius. Fortunately, there were no fatalities, but 19 people had injuries from flying debris.

Factory Mutual Insurance Co. has publications that summarize loss histories of hydrogen peroxide accidents in the industry [957, 958]. It does not include accidents at government installations.

One accident was caused by sudden decomposition of hydrogen peroxide in a caustic solution used in a chemical oxygen-iodine laser (COIL) test facility. An outdoor metal tank containing up to 300 gallons of high-concentration hydrogen peroxide exploded at a laser-testing facility at TRW in California, and the event was reported in 1999 [400, 401]. No one was hurt. The hydrogen peroxide in the tank had begun to decompose rapidly, generating enough pressure to blow the tank into three pieces of shrapnel. The tank had a pressure-relief system, but it was not adequately sized to handle the high gas release rates that occurred. It was believed that the tank had accumulated basic hydrogen peroxide (BHP) over a period of 3 months of laser testing during which the BHP was returned to the tank after testing and recycled for additional testing. The BHP was a hydrogen peroxide solution containing potassium hydroxide, lithium hydroxide, and sodium hydroxide. The preliminary finding was that overpressure in the tank was caused by the rapid decomposition of the hydrogen peroxide due to long-term storage, reuse, and consequent contamination of the hydrogen peroxide in the tank.

At NASA Stennis, a rapid decomposition event accident happened during a test of a catalyst bed assembly using H_2O_2 , at approximately 1 s into the test [439, 959, 960]. The test article and facility were damaged, but there were no injuries sustained by personnel. The event occurred approximately 1 s into the test following the completion of a successful test. Damage to the facility included rupturing a 1-in. (2.54 cm) diameter stainless steel supply line rated for 29 MPa (4200 psi) and the destruction of a pre valve rated for 20.7 MPa (3000 psi) service. For the test article, 14 1.27-cm (0.5-in.) diameter stainless steel bolts failed in tension, and a portion of the test article (7.3 kg = 16 lb_m) was ejected 30 m from the test stand. Subsequently, an investigation was conducted, and the causes of the incident were determined. There were several tests run on the night of the incident. Between the second to last test and the test in which the incident occurred, a leaking shutoff valve allowed liquid H_2O_2 to accumulate in a hot supply line just upstream of the catalyst bed. The temperature in this supply line region was approximately 394 K (250 °F). Liquid in the 373 to 422 K (212 to 300 °F) temperature range will create an ignitable vapor for 98% H_2O_2 . When the accumulated vapor was compressed by the opening of the valve for the last test, a rapid decomposition occurred.

A summary of accidents caused by HTP was compiled by staff at NASA WSTF [401]. It was hoped that understanding the causes and effects of these accident and incident examples would aid personnel currently working with HTP to mitigate and avoid similar situations. Lessons learned, best practices, and regulatory compliance information related to the cited accidents and incidents were also discussed.

Putting colloidal silica and sodium silicate into a tank with hydrogen peroxide resulted in an explosion, and it was fortunate that nobody got wounded or killed [961].

Within a period of 15 years, at least 3 bleach plants in North America experienced catastrophic equipment failures associated with the use of 50 mass-% hydrogen peroxide as a bleaching agent for paper and pulp, and people were badly injured in two instances [962].

7.8 Accident Histories of Hydrogen Peroxide Spills

When a semitrailer truck overturned near Romulus, MI on 14 July 2010, 300 gallons of hydrogen peroxide spilled onto the I-275 freeway [963]. The accident happened during the morning commute, and the freeway remained closed at I-94. The big concern was that a chemical reaction could happen and that there would be a sudden explosion. Nearly two miles of I-275 North just south of I-94 were shut down.

About two-thirds (about 22000 gallons) of the contents of a rail tank car loaded with 70% H_2O_2 spilled and leaked into a nearby ditch over 2 h when a slowly moving rail tank car was punctured by a log stacker forklift in a sawmill log yard next to a paper mill in Longview, WA [964]. Fire department crews sprayed water on the spill to dilute the hydrogen peroxide and fortunately nothing ignited when it came into contact with the oxidizer.

The following three transportation (one rail and two air transportation) incidents were quoted by [401]:

An aircraft transportation incident involving hydrogen peroxide occurred in 1988, and a passenger aircraft had to make an emergency landing after smoke, odor, and a softening of the cabin floor was detected. 120 passengers, 4 flight attendants, and 2 flight crew members followed emergency evacuation procedures. Nine passengers, two firefighters and three airline employees suffered minor injuries. The total repair costs for the airplane were \$228823. In this incident, 5 gal of undeclared and improperly packaged 50% H_2O_2 was transported in a fiberboard drum that also contained a 35% H_2O_2 container and a sodium orthosilicate-based material (laundry detergent). The drum was not affixed with directional arrows and had been stowed on its side. The 50% H_2O_2 was packaged in a 5-gallon, non-vented DOT-34 polyethylene drum. The investigation concluded that the 50% H_2O_2 leaked, coming into contact with the fiberboard, resulting in a fire.

Another aircraft transportation incident involving hydrogen peroxide occurred on 28 October, 1998 (National Transportation Safety Board No. DCA-99-MZ-001). Two gallons of a 35% H_2O_2 solution spilled in the cargo compartment of a passenger airplane flying from Orlando, FL to Memphis, TN. The solution leaked from two undeclared 1-gallon plastic bottles. The bottles were in an ice chest that belonged to a passenger on the flight and had not been properly checked as baggage. The leaking hydrogen peroxide contaminated three mail sacks and an undetermined number of passenger baggage pieces. The leak was not discovered until cargo handlers in Memphis began to unload the baggage. Thinking that the spilled liquid was water, the cargo handlers

ignored it and transferred some of the baggage to another passenger-carrying flight departing for Seattle, WA. When the flight arrived in Seattle, two bags in a cargo compartment were smoldering. One handler said the smoke was “like someone blowing on a good cigar.” As a result of the spill, several people required treatment. In Memphis, 11 employees were treated at the airport’s first aid station because their hands (which were tingling and turning white) had been exposed to the hydrogen peroxide. In Seattle, the employee who removed the smoldering bags from the cargo compartment was exposed to fumes and went to hospital for treatment.

A runaway train in Helena, Montana, collided with a helper train and derailed in 1989. Approximately 26250 gallons of 70% H_2O_2 in two tank cars, and approximately 12136 gallons of isopropyl alcohol from another tank car were released. A fire and explosions resulted. About 3500 residents of Helena, Montana had to be evacuated. Two crewmembers were slightly injured. The NTSB believed the H_2O_2 in contact with contaminants on the ground caused a chemical reaction that resulted in a fire. Seven individuals were treated for minor injuries associated with smoke inhalation, headaches, dizziness, sore throats, lacerations, anxiety, and fainting. The estimated damage (including cleanup and lading) exceeded 6 M\$. In this report, the NTSB briefly discussed a previous hydrogen peroxide release in which spilled hydrogen peroxide ignited several wooden rail crossties.

A richly illustrated personal account of H_2O_2 incidents at NASA Langley, based on stories provided by a former NASA employee and either oral history or personal knowledge, was posted on the internet [965]. It described that in the early 1960s, many of the supersonic fighter models tested in the supersonic wind tunnel at NASA Langley had hydrogen peroxide-powered thrusters to simulate the exhaust from an air-breathing jet engine. The exhaust from a turbojet engine could be closely simulated (temperature, gamma, initial plume angle, etc.). Although the exhaust simulation was not as good, a gradual change to cold high-pressure air exhaust simulation was made in the late 1960s because of increasing cost of H_2O_2 , which was used at a prodigious rate. The historic illustrations show how HTP was brought into the facility in railroad tank cars, stored in two above-ground storage tanks, and transferred to truck-mounted fueling carts. Also shown are the catastrophic results of a fire that erupted in a wind tunnel model of a F-11F-1 fighter model after a H_2O_2 leak. Also shown are the remains of the pants of a worker that caught on fire after he accidentally stepped into or knocked over a bucket with HTP. Many of the silver catalyst packs in the models had deteriorated and lost their activity before the test was completed and were spewing undecomposed wet H_2O_2 out in the vicinity of the test cell. Another incident occurred when an HTP monopropellant rocket that was to simulate the Apollo Command Module escape rocket separating from the command module was tested prior to installation in the wind tunnel and burst open, spilling the entire load of the run tank into a trench, and the overflow from the trench ignited the ground surrounding the building.

A table in a fire and explosion hazards of liquid propellants and related materials report lists the number of reported incidents with liquid rocket propellants. Hydrogen peroxide had the highest number of reported incidents of all propellants on that table.

Appendix E of the *HTP Manual* prepared by NASA WSTF contains a 22-page account of numerous hydrogen peroxide accidents, close calls, and lessons learned [966].

8 Toxic Properties of Hydrogen Peroxide

Dilute solutions of hydrogen peroxide are non-toxic since it is an intermediate in many metabolic processes, such as the conversion of sugars and proteins into carbon dioxide and water, allowing many living organisms to function and allowing us to move muscles and perform work. In short, if we did not have H_2O_2 in our bodies, we could not live. H_2O_2 is produced during normal aerobic cell metabolism. Using a radio-isotope technique, an average plasma level of $34\text{ }\mu\text{mol/L}$ (range $13\text{--}57\text{ }\mu\text{mol/L}$) H_2O_2 was found in human volunteers. The average blood level was $288\text{ }\mu\text{mol/L}$ (range $114\text{--}577\text{ }\mu\text{mol/L}$), suggesting that red or white blood cells are rich in H_2O_2 . It involves several enzymatic reactions, especially superoxide dismutase. H_2O_2 is decomposed to oxygen and water by enzymes such as catalase, peroxidase, and selenium-dependent glutathione peroxidase. Nevertheless, there is concern about the role that free radicals, such as the hydroxyl radical, which is formed as an intermediate during hydrogen peroxide decomposition, play in the aging of living cells and triggering of cancer. Many health stores advertise “radical scavenger” food supplements. The most readily available food supplement in this category and a good reducing agent is ascorbic acid (Vitamin C). At the same time, we must remember that hydrogen peroxide in higher concentrations is used as a disinfectant and as a mouthwash and will kill many small microbes.

Several good summaries of HTP toxicity, also in comparison with other propellants, have been published [967], but they need to be updated from time to time. The most comprehensive evaluation of hydrogen peroxide toxicity was compiled by the European Centre for Ecotoxicology and Toxicology of Chemicals as part of their Joint Assessment of Commodity Chemicals in 1993 [968]. The paper by Jacobi has a very good list of references on toxicity of hydrogen peroxide [969].

8.1 Inhalation Toxicity of Hydrogen Peroxide

The vapor pressure of hydrogen peroxide at room temperature is so low that the vapors evolving from hydrogen peroxide during open transfer do not constitute an acute inhalation toxicity hazard if adequate ventilation is provided (i.e., you stay upwind of it).

Figure 68 in the *Encyclopedia of Liquid Fuels*, chapter “Hydrazine”, gives a comparison of the hazard indices of various storable propellants. The hazard index is the quotient of vapor pressure divided by the LC_{50} or the Threshold Limit Value (TLV) concentration. The lower the threshold toxicity concentration, the higher the hazard index.

Aerosols can form if hydrogen peroxide sprays from a leak under high pressure. Hydrogen peroxide aerosols can be quite irritating to the mucous membranes and respiratory tract. Decomposition products of hydrogen peroxide that is actively decomposing in an open container will carry with them a certain amount of undecomposed H_2O_2 , which constitutes an irritant and respiratory hazard. Inhaling H_2O_2 aerosols at the scene of a leak causes significant immediate irritation of the respiratory tract and gasping, like that encountered when accidentally walking into a cloud of ammonia gas. A sharp, burning sensation in the nasal passages should warn workers to seek fresh air as fast as possible. Respiratory irritation in humans for repeated 4-h exposures starts at 10 mg/m^3 , and irritation of the skin starts at 20 mg/m^3 .

In the 1950s, it was the general attitude that the inhalation of vapors resulting from the spillage of 90% H_2O_2 do not constitute a major respiratory hazard [970, 971].

Acute exposure of mice to H_2O_2 vapor concentrations of 9400 mg/m^3 was rapidly fatal for most of the animals in the cage. Repeated exposure of mice to 80 mg/m^3 was still fatal to some of the animals.

In examining the categorization of HTP as a “non-toxic propellant” more closely, the reader will soon realize that in the more critical workplace toxicity hazard evaluation of the 1990s this statement can no longer be accepted, and more restrictive protective measures are now being taken.

8.2 Inhalation Toxicity Test Results

The following is a summary of animal tests that were conducted to determine the safe threshold for human exposure to HTP vapors. Some of the early investigators failed to report if the chemical was administered in the form of vapors or aerosols.

8.3 Chronic Inhalation Toxicity – Animal Tests

Because H_2O_2 decomposes so quickly on surfaces, it is difficult to maintain constant H_2O_2 vapor concentrations in the animal exposure cages for long periods of time.

Groups of rats were exposed to nominal “saturated” 4000 mg/m^3 (2840 ppm by volume) H_2O_2 vapors for 1 to 8 h but all animals survived with only minor clinical signs. Three groups of 10 male Wistar rats were exposed to 338 to 427 mg/m^3 (243 to 307 ppm by volume) H_2O_2 vapors for 4 h/day for up to 2 weeks [972]. Initially, they did not show any signs of poisoning, and all survived the experiments, but after 4 to 14 days of expo-

sure, some were sacrificed and necropsied, and it was noted that several had suffered lung edema and showed areas of alveolar emphysema. Other groups of rats were exposed to subacute concentrations ($79 \text{ mg/m}^3 = 57 \text{ ppm}$ by volume) for 6 h daily, 5 days/week for 6 months. All animals suffered irritation of the respiratory tract, and the hair of their fur was bleached. Brief exposure to aerosols at $9400 \text{ mg/m}^3 \text{ H}_2\text{O}_2$ was lethal to mice with effects limited to the respiratory tract and the eyes. After repeated exposure, mortality in mice was observed starting at 80 mg/m^3 . In rats and dogs, respiratory irritation and transient skin thickening have been observed at $1\text{--}10 \text{ mg/m}^3$ after prolonged exposure.

Dogs were exposed to $10 \text{ mg/m}^3 = 7 \text{ ppm H}_2\text{O}_2$ for 6 h/days, 5 days/week for 6 months. All animals suffered chronic irritation of mucous membranes, leading to sneezing and weeping. Again, their fur was bleached. After completion of the test, selected tissue samples were examined, and most lung tissues showed pathologic changes. Based on these tests, it was suggested that 4 ppm would be a safe concentration for workers, but that would not include any margin for safety. The ACGIH-recommended TLV for H_2O_2 as an 8-h time weighted average (TWA) is 0.14 mg/m^3 or 0.1 ppm [973].

A study of the short-term toxic effects in mice exposed to aerosols formed from 90% H_2O_2 in air showed that beginning mortality occurs at 13 mg/L for 10 min [974]. At concentrations from 3.6 to 5.2 mg/L no fatalities were observed for 5-min exposures. At 9 mg/L the threshold of fatality was reached, where some delayed fatalities occurred only 6 days after the end of the exposure. A 15-minute exposure to 12 to 19 mg/L can be fatal within 1 h (Table 63). Exposure to concentrations of up to 5 mg/L (3535 ppm) for 5 min produced evidence of mild nasal irritation, blinking, and slight gasping. There were no deaths from 5 mg/L exposures, but there was evidence of lung congestion at necropsy. Four out of twenty mice exposed to 5.2 mg/L (3676 ppm) showed necrosis of the bronchial epithelium. Animals exposed to concentrations of 9.4 mg/L

Table 63: Toxicity of 90% H_2O_2 aerosol in mice.

Inhalation duration Min	H_2O_2 concentration mg/L in air	Mortality	Survival time Min
5	3.6	0/10	
5	4.2	0/10	
5	5.2	0/10	
5	5.2	0/10	
5	9.4	0/10	
10	13.2	5/10	12 min to 6 days
10	13.4	1/10	6
10	19.0	1/10	11
15	11.8	5/10	5–50
15	16.7	9/10	11–50

Data source: [974]

(6645 ppm) or more for 5–15 min showed similar but more severe signs, and 10–50% of animals died within 1 h following a short convulsing period. Most of the animals that died showed pulmonary congestion. Animals that survived for several days to 8 weeks showed necrosis of the bronchial epithelium. In addition, animals surviving 9.4 mg/L (6645 ppm) or more suffered slowly developing corneal damage, which appeared about 5 weeks after exposure.

Whole-body exposure of white rats for 4 h to various concentrations of H_2O_2 , vaporized from a solution, resulted in an LC_{50} of 2000 mg/m^3 . The LOEC for the respiratory mucosa was 60 mg/m^3 , and exposure at 110 mg/m^3 produced hyperanaemia and transient thickening of the skin [975].

Inhalation Toxicity – Human Volunteer Tests

Hydrogen peroxide aerosol or vapor causes irritation and in severe cases damage to the upper respiratory tract and lungs [976]. The human response to the irritating effect of hydrogen peroxide on the mucous membrane and skin is far more sensitive than that of the rat. The threshold concentration for acute irritative effects of gaseous hydrogen peroxide on the respiratory tract is 60 mg/m^3 in rats, but only 10 mg/m^3 in humans; the corresponding values for skin are 110 mg/m^3 for rats and 20 mg/m^3 for humans.

In a study conducted in 1976, human volunteers were exposed to hydrogen peroxide vapors for different periods of time [975]. Respiratory irritation was assessed by nasal inhalation of H_2O_2 vapor. It was noted that irritation depended upon exposure concentration and to a lesser extent on exposure duration (between 5 min and 4 h). The threshold for respiratory irritations was found to be 10 mg/m^3 (7 ppm) in all cases. A statement by certain HTP-promoting marketing-type speakers [977] like: “There is growing evidence that HP does not lead to **any** systematic toxic effects” is irresponsible and totally wrong.

Eleven healthy volunteers were exposed to 0 (clean air), 0.5 and 2.2 ppm H_2O_2 for 2 h at rest to investigate subtle acute effects of inhaled hydrogen peroxide vapors [978]. Symptoms related to irritation and central nervous system effects were rated with visual analog scales. The ratings varied considerably but were generally low and with no significant differences between exposure conditions, although the ratings of smell ($p = 0.09$, Friedman’s test), nasal irritation ($p = 0.06$), and throat irritation ($p = 0.06$) showed borderline tendencies to increase at 2.2 but not at 0 and 0.5 ppm. Nasal airway resistance increased after exposure to 2.2 ppm hydrogen peroxide ($p = 0.04$, paired t-test) but not after 0.5 ppm. No exposure-related effects on pulmonary function, nasal swelling, breathing frequency, and blinking frequency were detected. No clear effects were seen on markers of inflammation and coagulation (interleukin-6, C-reactive protein, serum amyloid A, fibrinogen, factor VIII, von Willebrand factor, and Clara cell protein in plasma). In conclusion, the study suggested that hydrogen peroxide is slightly irritating at 2.2 ppm but not at 0.5 ppm.

It was claimed that “Humans are regularly exposed to greater than 1 ppm in some common foods and human breath can exceed 1 ppm from the natural hydrogen peroxide produced inside humans” [840], but we have been unable to verify this assertion. It was argued that if exhaled human air can contain more than 1 ppm H_2O_2 , then the 8-h TLV-TWA at the workplace established by ACGIH should be higher than 1 ppm.

8.4 Skin Effects of Hydrogen Peroxide

The hydrogen peroxide that permeates into skin quickly reacts with body fluids containing blood, glutathione, and enzymes and decomposes into water and oxygen. The decomposed hydrogen peroxide forms tiny gas bubbles on the skin surface capillaries creating microembolisms, which locally block blood flow in the skin causing a lack of blood flow and a change in the skin color from its natural flesh tone to white (Figure 58). Once the oxygen bubbles are absorbed into the body, blood flow returns to the skin, and the color returns to normal.



Figure 58: Effect of skin exposure to 35% hydrogen peroxide. (From https://en.wikipedia.org/wiki/Hydrogen_peroxide. Posted by Olli Niemitalo into the public domain on 13 April 2010)

Application of 90% H_2O_2 to the shaved skin of rabbits caused H_2O_2 absorption through the skin and caused death by gas embolism [979]. The dermal LD50 is 690 mg/kg for 90% HTP in the rabbit [980]. Additional fatality data were obtained on cohorts of pigs, dogs, and white and dark rats with doses from 2700 to 8200 mg/kg but insufficient data points to bracket an LD50.

The dermal toxicity of solutions of 35–75% H_2O_2 in rabbits was low (LD50, dermal, rabbit: >2000 mg/kg). LD50 values of 90% H_2O_2 ranged from ca. 690 mg/kg in rabbits to >2000 mg/kg in rats, pigs, and cats.

Skin contact with solutions containing more than 25% H_2O_2 is dangerous and damaging. On the thick skin on the inside of the hands, one quickly develops white and bleached spots and an itching sensation that abates after a few hours. The bleached spots persist for several days. It is believed that the white appearance and

opacity is formed by thousands of tiny gas bubbles formed in the thicker sections of skin by local decomposition of H_2O_2 as it permeates the skin. They do not last as long as the persistent yellow stains on the hands of negligent rocket test site or laboratory workers who have accidentally contacted nitric acid. HTP that has wicked under the fingernails is extremely painful. Higher concentrations of H_2O_2 can cause severe blistering if the liquid is not immediately washed away with large amounts of water. HTP causes immediate irritation in skin sections other than the hands where the keratin is thinner. The recommended first aid treatment for inadvertent H_2O_2 skin exposure is flushing with large amounts of water. For additional information, consult the Material Safety Data Sheets (MSDS) available from HTP suppliers.

Contact of hydrogen peroxide with the skin can cause severe skin damage. An accident report describes a case of skin injury induced by 35% hydrogen peroxide [981]. The patient was a 34-year-old man working in a dry-cleaning shop. While he was pouring 35% hydrogen peroxide, some of it accidentally splashed over his left shoulder and back. Soon after the exposure, an erythema, purpura, and vacuolar eruption, similar to bubble wrap, appeared on his left shoulder and down the left side of his back. Histologically, numerous vacuolar structured “oxygen bubbles” were observed in the epidermis, dermis, and subcutaneous tissue. Subcutaneous emphysema was detected by chest X-ray examination. All skin eruptions healed without scarring, and the healing was helped by the use of a steroid ointment.

Acute dermal toxicity depends on hydrogen peroxide concentration. With 90 mass-% hydrogen peroxide, the dermal LD50 in rabbit is 650 mg/kg, and in rat it is 4800 mg/kg [982].

8.5 Eye (Ocular) Effects of Hydrogen Peroxide

Besides pulmonary damage with frequently deadly consequences, high concentrations of H_2O_2 vapors may also cause opacification of the cornea. Splashes of liquid H_2O_2 into the eye cause turbidness of the cornea and can cause permanent blindness. Even H_2O_2 vapors can cause eye irritation, but usually without permanent damage, if the person is removed from the source of the vapors quickly, and the eyes are flushed with water at the eye wash fountain.

H_2O_2 solutions of 10% or more cause irreversible damage to the eye, including blindness. Solutions of less than 5% are not classified as irritant to the rabbit eye. The first effects on the rabbit cornea were observed with a 1% solution. In human beings, 1–3% solutions have been used for eye treatment without significant injury.

In animal tests, the ocular irritancy of 5–70% H_2O_2 solutions has been evaluated in rabbits: 0.1 mL was instilled into the conjunctival sac, and in certain cases, the eyes were washed with 100 mL tap water after 20–30 s [983]. A 5% solution caused minimal irritation to unwashed eyes. An 8% solution was moderately irritating to unwashed eyes (exhibiting severe conjunctivitis, slight corneal opacities, and iritis). A 10% so-

lution was extremely irritating to both washed and unwashed eyes: severe corneal opacity, iritis, and conjunctivitis were the result. A 35% solution was extremely irritating, producing corneal opacities, iritis, and moderate conjunctivitis, blanching of the conjunctiva, haemorrhagic iris, bubbles under the cornea, blanching of the cornea, or corneal ulcerations. A 70% solution was extremely irritating and corrosive to the eyes of rabbits.

8.6 Oral Toxicity of Hydrogen Peroxide (Animal Tests)

8.6.1 Animal Tests

Accidental oral (PO) ingestion of hydrogen peroxide is said to include the danger of rupturing of internal organs due to excessive gas evolution and overpressurization. Predominant clinical signs in rats administered 35% H_2O_2 included tremors, decreased mobility, prostration and oral, ocular, and nasal discharge. Most animals that died had reddened lungs, hemorrhagic and white stomachs, and blood-filled intestines. Some had white tongues. Table 64 is a summary of oral toxicity tests with different concentrations of hydrogen peroxide in rats.

Table 64: Oral toxicity of hydrogen peroxide solutions in rats.

Concentration of solution Mass-%	Strain	Sex	LD50 mg/kg	Observation period d	References
9.6	Wistar-JCL	Male	1517	7	[984]
9.6	Wistar-JCL	Female	1617	7	[984]
10	Sprague-Dawley		>5000	14	[985] ^a
35	Sprague-Dawley	Male	1193	14	[985] ^a
35	Sprague-Dawley	Female	1270	14	[985] ^a
50	Sprague-Dawley		>225, <1200	4	[985] ^a
60	Wistar	Male	872	14	[985] ^a
60	Wistar	Female	801	14	[985] ^a
70	Unknown		75	Unknown	[986] ^a

^a See original [985] for details on the source of data.

Repeated oral exposure in drinking water caused a decrease in body weight gain in most studies and resulted in deaths of rats and mice at concentration percents of H_2O_2 greater than 1%. Repeated dosing studies involving oral gavage (injection by stomach tube directly into the stomach) showed progressively more changes of blood parameters at lower concentrations (30–168 mg/kg), decrease of body weight starting at 60 mg/kg, and organ weight changes without histopathology, except for erosion and

scars of mucosa of the stomach, and that only at the highest dose of 506 mg/kg [984, 987].

Although detailed studies that would be needed to fully evaluate the chronic toxicity or carcinogenic potential of H_2O_2 are lacking, several studies showed that long-term oral administration of 0.1–0.15% H_2O_2 caused an inflammatory response in the gastro-duodenal tissue of mice. The response was limited to the glandular stomach and, to a lesser extent, to the peri-pyloric and proximal portion of the duodenum. Some of these lesions may convert into cancerous growths. No inflammatory response was observed in the oral cavity, forestomach, or distal intestinal tract.

The tumorigenicity of hydrogen peroxide (HP) was examined by administering 0.4% hydrogen peroxide solution in drinking water to various strains of mice [988]. In C57BL mice, gastric lesions in the forestomach occurred in over 67% of the mice treated with HP for 120 days, and duodenal lesions were noted in over 80% of the mice that received HP for 60 days. Gastric lesions were found only in the glandular stomach, and duodenal lesions were restricted to the peri-pyloric and proximal part of the duodenum. In mice given 0.4 and 0.1% HP for 420 to 740 days, 5 and 1%, respectively, had duodenal cancer by histological criteria, although they did not show any distant metastasis. In DBA and BALB mice given 0.4% HP for 90 to 210 days, the incidences of gastric lesions reached 30 and 10% at maximum, respectively, and the incidences of duodenal lesions were 60 to 100% and 40 to 69%, respectively.

8.7 Toxicity by Other Means of Hydrogen Peroxide Administration (Animal Tests)

Hydrogen peroxide injection into the bloodstream is an unlikely mode of accidental poisoning, but animal tests were conducted with this mode of administration because much of the H_2O_2 administered by inhalation is decomposed before it reaches the blood stream. Unlikely as it may seem, the literature actually reports one accidental death by accidental injection of dilute hydrogen peroxide into a patient in a hospital. The LD_{50} in rabbits injected intravenously (IV) with 90% H_2O_2 was 0.015 mL/kg body weight. Injections with more dilute H_2O_2 solutions down to 4% H_2O_2 resulted in a smaller LD_{50} , only 0.003 mL/kg body weight. It is assumed that at the higher concentration further distribution of the poison is blocked by immediate gas embolism at the site of injection.

8.7.1 Blood Effects

Erythrocytes separated from blood can degrade gram quantities of H_2O_2 in several minutes. Hemoglobin and similar transition metal porphyrin complexes are good catalysts for H_2O_2 decomposition [989]. During and after IV infusion of 1.0-M H_2O_2 in a 0.9% saline solution for 60 min at a rate of 3×10^{-3} mol H_2O_2 /min, H_2O_2 could not be

detected in dog plasma [990]. Hydrogen peroxide and luminol are used for detection of blood stains in forensic examinations at crime scenes.

8.8 Poisoning Accident Case Histories (Ingestion, Inhalation, and Skin Exposure)

The American Association of Poison Control Centers has tabulated reports of accidental exposure since 1985. Each year, there are several thousands of cases of accidental exposure in the US (including accidental or intentional ingestion) due to consumer use of H_2O_2 as a household topical disinfectant [991]. Fortunately, most of these exposures resulted in no or only minor toxicity symptoms, but fatalities have occurred.

Hydrogen peroxide causes toxicity and symptoms via three main mechanisms: corrosive damage, oxygen gas formation, and lipid peroxidation [992]. Concentrated hydrogen peroxide is an aggressive chemical, and exposure will result in local tissue damage. Ingestion of concentrated (>35%) hydrogen peroxide can result in the generation of substantial volumes of oxygen. Where the amount of oxygen evolved exceeds its maximum solubility in blood, venous or arterial gas embolism may occur, where bubbles prevent the proper flow of blood. The mechanism of central nervous system (CNS) damage is thought to be arterial gas embolism with subsequent brain infarction. Rapid generation of oxygen in closed body cavities can also cause mechanical distension, and there is potential for the rupture of the hollow viscus secondary to oxygen liberation. Intravascular foaming following absorption can seriously impede right ventricular output and produce complete loss of cardiac output. Hydrogen peroxide can also exert a direct cytotoxic effect via lipid peroxidation.

Ingestion of hydrogen peroxide may cause irritation of the gastrointestinal tract with nausea, vomiting, hematemesis, and foaming at the mouth; the foam may obstruct the respiratory tract or result in pulmonary aspiration. Painful gastric distension and belching may be caused by the liberation of large volumes of oxygen in the stomach. Blistering of the mucosae and oropharyngeal burns are common following ingestion of concentrated solutions, and laryngospasm and hemorrhagic gastritis have been reported. Sinus tachycardia, lethargy, confusion, coma, convulsions, stridor, subepiglottic narrowing, apnea, cyanosis, and cardiorespiratory arrest may ensue within minutes of ingestion.

Although most inhalational exposures cause little more than coughing and transient dyspnea, inhalation of highly concentrated solutions of hydrogen peroxide can cause severe irritation and inflammation of mucous membranes, with coughing and dyspnea. Shock, coma, and convulsions may ensue, and pulmonary edema may occur up to 24–72 h post exposure.

A 3-year old girl died following ingestion of an unknown quantity of 40% H_2O_2 solution [993]. Pathological findings at autopsy included edema of the lungs and small erosions of the stomach mucosa, probably due to the lavage tube used to wash out the stomach. The report indicates that the probable cause of death was asphyxia due to

obstruction of the distal respiratory tract by the foam liberated by the peroxide (oxygen gas).

A 6-year old girl died, and her 4-year old friend was in a critical condition with oropharyngeal burns after accidentally ingesting a solution of 35% H_2O_2 [994].

A near-fatality occurred when a 33-year-old woman unintentionally ingested the contents of a 1-pint bottle (<500 mL) of 35% H_2O_2 [995]. The patient was cyanotic and experienced seizures and foaming at the mouth. The abdomen was slightly distended. Neurological signs included the lack of spontaneous eye movement, no verbal response, and withdrawal from noxious stimuli. Laparotomy revealed gas bubbles in the stomach but no perforations. Recovery was complete following treatment.

A child died as a result of oxygen embolism after ingestion of hydrogen peroxide [996]. A total of five similar cases had previously been described. Gastric catabolism of hydrogen peroxide produces oxygen and water. When the amount of oxygen evolved exceeds its maximal blood solubility, venous embolization occurs.

Four unusual cases of caustic injury of the gastrointestinal tract due to hydrogen peroxide occurred in Spain, two cases due to oral ingestion, and another two due to the accidental administration of enemas containing hydrogen peroxide [997].

Then there is the case of a 39-year-old man who inadvertently ingested 250 mL of unlabeled 35% hydrogen peroxide [998]. The hydrogen peroxide was in an unlabeled container in a friend's refrigerator and was mistaken for water. Immediately after ingesting the hydrogen peroxide, he realized it was a caustic substance and drank 500 mL of water to induce vomiting. He experienced mild epigastric pain without shortness of breath or oropharyngitis. On arrival at the emergency department, he was hemodynamically stable and in no respiratory distress. The oral cavity and oropharynx were slightly erythematous, and the abdominal examination revealed mild epigastric tenderness but no distension, and normal bowel sounds. Esophagogastroduodenoscopy revealed a normal oral cavity and normal esophagus, but the stomach had suffered grade 2 diffuse caustic mucosal injury of the entire stomach, including the cardia, characterized by superficial erosions with exudates and edema.

Accidental ingestion of industrial-strength H_2O_2 is very rare. Fatal outcomes have been reported with 35% H_2O_2 solutions. There is the case of a 6-year-old boy who unintentionally ingested an unknown quantity of 60% hydrogen peroxide [999]. Upon admission to a pediatric intensive care unit he was intubated and received ventilatory assistance for 48 h. Upper gastrointestinal endoscopy was performed soon after admission, and laparoscopy was performed 24 h later. Recovery was satisfactory, and the patient was discharged on day 18 with no evidence of lasting pathological damage.

Hydrogen peroxide is used as a disinfectant during pasteurization of milk prior to cheese making where it is sometimes improperly stored in commercial drink containers without adequate labeling. Three cases of accidental ingestion of 60% H_2O_2 were reported in the milk industry in Spain [1000]. The patients were male stockbreeders aged 30, 45, and 62 years, respectively. After accidental ingestion, one of them was

admitted comatose and required assisted ventilation. After recovering consciousness, migratory paresis of the right limbs and of the cranial nerve were observed, which were reversed after 10 days, but a left hemiparesis persisted for 2 months. Upper gastrointestinal tract lesions, particularly in the stomach, were detected in all cases. The outcome was satisfactory in the three patients, with complete remission of the lesions within a few months.

Ingestion of a small amount of concentrated hydrogen peroxide can cause cerebral air gas embolism (CAGE). A 48-year-old male took two sips of 33% H_2O_2 [1001]. A short time later, he developed hematemesis, left-sided hemiplegia, confusion, and left homonymous hemianopsia. Diagnostics indicated ischemia due to CAGE. Hyperbaric oxygen therapy (HBOT) is the standard of care in the treatment of CAGE. The patient underwent HBOT at 3 atm absolute (ATA) for 30 min and 2.5 ATA for 60 min, 18 h after arrival, resulting in reversal of both the clinical and radiologic abnormalities.

Arterial gas embolization in the central nervous system is a relatively rare complication. There are three possible mechanisms of gas embolization: persisting patent foramen ovale, pulmonary gas emboli caused by aspiration of H_2O_2 to the lower respiratory tract, and formation of gas embolism after it reaches the brain. There is the case of a 54-year-old woman with brain gas embolism after accidental ingestion of concentrated H_2O_2 [1002].

A rocket test stand worker who inadvertently inhaled vapors from 90% H_2O_2 suffered increased salivation and a scratchy throat and developed a non-purulent inflammation of the upper respiratory tract.

8.9 Therapy of Hydrogen Peroxide Poisonings

Gut decontamination is not indicated following ingestion, due to the rapid decomposition of hydrogen peroxide by catalase to oxygen and water. If gastric distension is painful, a gastric tube should be passed to release gas. Early aggressive airway management is critical in patients who have ingested concentrated hydrogen peroxide, as respiratory failure and arrest appear to be the proximate cause of death. Endotracheal intubation, or rarely, tracheostomy may be required for life-threatening laryngeal edema. Contaminated skin should be washed with copious amounts of water. Skin lesions should be treated as thermal burns; surgery may be required for deep burns. In the case of eye exposure, the affected eye(s) should be irrigated immediately and thoroughly with water or 0.9% saline for at least 10–15 min. Instillation of a local anesthetic may reduce discomfort and assist more thorough decontamination.

Ingestion of concentrated H_2O_2 has been associated with venous and arterial gas embolic events, hemorrhagic gastritis, gastrointestinal bleeding, shock, and death. Although H_2O_2 is generally considered a benign ingestion poison in low concentrations, case reports have described serious toxicity following high-concentration ex-

posures. Hyperbaric oxygen (HBO) has been used with success in managing patients suffering from gas embolism with and without manifestations of ischemia. A case history identified 11 cases of portal gas embolism with victims' ages ranging from 4 to 89 years [1003]. In ten cases, 35% H_2O_2 was ingested, and in one case, 12% H_2O_2 was ingested. All abdominal computed tomography (CT) scans demonstrated portal venous gas embolism. Hyperbaric treatment was successful in completely resolving all portal venous gas bubbles in nine patients and nearly resolving them in two others. Ten patients were able to be discharged home within 1 day, and one patient had a 3.5-day length of stay.

Intragastric administration of 6% H_2O_2 induced gastric mucosal hemorrhagic lesions in rats. Intraperitoneal administration of rebamipide, an amino acid derivative of 2-(1H)-quinolinone, an anti-ulcer medication, at 10 to 100 mg/kg dose-dependently prevented the H_2O_2 -induced mucosal lesions [1004].

8.10 Mutagenicity of Hydrogen Peroxide

Hydrogen peroxide can induce mutations. Hydrogen peroxide was investigated for its potential to induce gene mutations in V79 Chinese hamster cells [1005]. Exposure of $2\text{--}3 \times 10^6$ cells/100-mm dish to 0.5–4.0 mM H_2O_2 for 1 h resulted in a concentration-dependent increase in the frequency of 6-thioguanine-resistant clones. At 4 mM H_2O_2 the mutation frequency was increased about sixfold above that in controls, and survival of the cells was reduced by 50%. Cytotoxicity was markedly increased at lower cell densities. The results showed that mutagenicity of H_2O_2 in mammalian cells in vitro previously escaped attention because the concentrations tested were too low, presumably because the likely toxicity of H_2O_2 to V79 cells treated at high cell densities was overestimated.

In bioassays conducted under controlled, comparable conditions, weak direct mutagenicity responses were observed for hydrogen peroxide in the standard (Ames test) agar plate incorporation bioassay with *Salmonella typhimurium* strains TA97, TA98, TA102, and TA1537, in a 20-min preincubation test with strains TA97, TA98, TA100, TA102, TA1537, and TA1538, and in a liquid incubation modification using strain TA1537 [1006]. These results conclusively demonstrated that hydrogen peroxide is a weak mutagen, especially in strains that are sensitive to oxidative damage under suitable bioassay conditions.

Hydrogen peroxide is genotoxic to bacteria as tested in the standard Ames test. Hydrogen peroxide is also genotoxic to mammalian cells in culture, inducing sister chromatid exchange, deoxyribonucleic acid (DNA) single-strand breaks (gene mutations), chromosomal aberrations, micronuclei, unscheduled DNA synthesis, and transformation. However, the genotoxic potential of hydrogen peroxide is dependent upon direct contact with genetic material. Direct contact of cells with hydrogen peroxide is usually only at the site of initial contact during whole-body exposure, while cells in culture are

all uniformly exposed without the benefit of the body's ability to metabolize hydrogen peroxide [985].

Hydrogen peroxide had a mutagenic effect on fungi and bacteria (e.g., Ames test), but not on insects or mammalian cells in vitro. Chromosome aberrations (mainly chromatid breaks or micronuclei) were induced in V79 cells, Chinese hamster cells, human embryonic fibroblasts, human leucocytes, Syrian hamster, and Balb/c mouse cells after in vitro treatment with H_2O_2 . H_2O_2 induced DNA-repair in *Escherichia coli*, *Salmonella typhimurium* in the presence of metabolic activation, catalase, or superoxide dismutase (SOD); no effect was observed in the DNA-repair test or the SOs chromotest using *E. coli* strains. H_2O_2 induced DNA single-strand breaks in bovine lens epithelial cells, rat intestinal epithelial cells, leukemia cells, rat hepatocytes, human lymphocytes, and human bronchial epithelial cells [985].

Oxidative DNA damage caused by hydrogen peroxide was enhanced by copper zinc superoxide dismutase (CuZnSOD) in a concentration-dependent manner, as reflected by the formation of 8-hydroxy-2'-deoxyguanosine (8-OH-dG) and strand breaks [1007]. The effects of CuZnSOD on hydrogen peroxide-induced DNA damage and mutation was attributed to reactive oxygen species, probably hydroxyl-free radicals, formed predominantly by the reaction of hydrogen peroxide and free Cu^{2+} released from oxidatively damaged CuZnSOD.

8.11 Carcinogenicity of Hydrogen Peroxide

The suspected carcinogenicity of hydrogen peroxide has been thoroughly examined in animal tests and actively disputed in the scientific literature, but it has not been classified as a known human carcinogen.

Hydrogen peroxide increased duodenal and upper jejunal carcinogenesis in rats [1008]. A drinking water study in a catalase-deficient mice strain reported the observation of dose-related hyperplasia (at a high incidence) and localized carcinomas (at a low frequency) in the duodenum of the animals [1009–1011]. A solution of 0.4% H_2O_2 was given to the mice as drinking water for about 6 months [1012]. Incidences of duodenal tumor induced by oral administration of hydrogen peroxide (HPO) and catalase activities in the duodenal mucosa, blood, and liver were correlated in four different strains of mice. The results indicated that the incidence of duodenal tumor induction by H_2O_2 is dependent on the individual mouse strain and may be determined by the genes controlling the catalase activities.

These publications triggered a violent scientific debate on the possible carcinogenic potential of hydrogen peroxide and its relevance to humans, and some of its findings have been furiously disputed. A historical and very detailed account of these disputes is given in [969].

According to the Japanese authors all lesions, including tumors, regressed after cessation of the administration of hydrogen peroxide. This finding caused some

doubts on the nature of the observations reported. It appears that the control incidence was lower than other published values in this mouse strain. A subsequent study with different strains of mice showed that there was a strong negative correlation between the incidence of duodenal tumors (hyperplasia or neoplasia) and catalase activities in duodenal mucosa, blood, and the liver [1012]. In a comparable study with rats, drinking water administration of hydrogen peroxide seemed not to be associated with the occurrence of tumors, and there were no tumors in the gastrointestinal tract at all. Studies investigating a possible tumor initiating or promoting activity of hydrogen peroxide consistently showed that hydrogen peroxide is not a tumor initiator and showed contradictory results regarding tumor promotion (promotion or even inhibition of tumors was observed). Under certain conditions a weakly tumor promoting activity cannot be excluded and is likely related to chronic inflammation at continuous exposure. The fact that mammalian cells have built-in defenses against reactive oxygen species arising in endogenous metabolism further reduces the significance of the findings of Ito. Taken together the available data lead to the conclusion that the carcinogenicity of hydrogen peroxide reported in catalase-deficient mice strains is not relevant for humans.

When diluted hydrogen peroxide was given orally to rats, no significant differences in cancer frequency occurred between the two test groups and the control group. No evidence of tumor formation was found 1 year after exposure of mouse skin to 5 mass-% hydrogen peroxide, but benzoyl peroxide was a carcinogen [1013]; see also [1014] and [1015].

A study of the effects of twice weekly topical applications of hydrogen peroxide on the buccal epithelium of Syrian hamsters showed that hydrogen peroxide can, by itself, induce pathologic changes frequently associated with preneoplastic lesions; it may also augment carcinogenesis associated with known carcinogens like 9,10-dimethyl-1,2-benzanthracene [1016]. In animals treated with 30% H_2O_2 alone, histopathologic examination after 22 weeks revealed hyperkeratosis and hyperplasia in all animals with hyperchromatic cells and mild dysplasia in four of nine; no tumors were seen. The DNA damage caused by hydrogen peroxide is enhanced in the presence of trace metals [1017].

Concern regarding carcinogenicity of hydrogen peroxide arises from its ability to act as a strong oxidizing agent in the metabolism and cell division. In short-term genotoxicity tests, H_2O_2 has given predominantly positive results. However, these assays were performed using either bacterial strains engineered to be exquisitely sensitive to oxidant damage or mammalian cells deficient in antioxidant enzymes. Significantly, the addition of antioxidant protective measures (normally present *in vivo*) to these assay systems would protect against H_2O_2 genotoxicity. In most whole animal studies, H_2O_2 exposure neither initiated nor promoted tumors. In mice, however, 0.4% H_2O_2 in drinking water was reported to induce hyperplastic lesions of the duodenum and to erode areas in the glandular stomach epithelium. Owing to the chemistry of dilute H_2O_2 solutions and the anatomy/physiology of the gastrointestinal tract, it is

unlikely that orally ingested H_2O_2 reaches the duodenum. Instead, greatly decreased water consumption and the subsequent mechanical abrasion of the luminal lining on ingestion of pelleted dry rodent chow is the most likely cause of the observed gastric and duodenal lesions following H_2O_2 administration in drinking water. Significantly, when hamsters received high doses of H_2O_2 by gastric intubation (and water intake was not affected), the gastric and duodenal epithelia appeared normal. In-depth analysis of the available data supported the conclusion that oral ingestion of H_2O_2 should not be considered a carcinogenic threat [1018].

8.12 Teratogenicity of Hydrogen Peroxide

So far, no problems associated with reproduction in animals as the result of exposure to hydrogen peroxide have been found [1014].

8.12.1 Genotoxicity of Hydrogen Peroxide

The genotoxicity of H_2O_2 has been studied extensively [969]. This paper by Jacobi has a very good list of references on toxicity, and the following information was copied from that source. Hydrogen peroxide can react directly with isolated deoxyribonucleic acid (DNA) forming hydroxylated DNA bases. In *in vitro* tests, without metabolic activation, H_2O_2 induced gene mutations, primary DNA damage, chromosome aberrations, and micronuclei in mammalian cells, as well as morphological cell transformations. Addition of enzymes like catalase, however reduced or abolished the genotoxic response [1019]. The CEFIC Peroxygen Sector group performed several experiments on animals in order to study the genotoxic potential in mammals *in vivo*. In these studies, efforts were made to maximize exposure of the potential target organs; no chromosomal aberrations or micronuclei were observed in the bone marrow of rats and catalase deficient mice after repeated oral or single intraperitoneal administration. After intravenous administration in rats at the maximal tolerated dose, no unscheduled DNA synthesis was observed in the liver, although such an effect was observed in the rat's liver cells exposed *in vitro* to hydrogen peroxide. In a study of local genotoxicity to mouse skin, 70% hydrogen peroxide did not cause any mutations, hydroxylation of DNA bases, or give an indication of cellular proliferation, thus suggesting that the substance has no local genotoxic potential *in vivo*. In mechanistic studies, it was recently shown that hydrogen peroxide induced controlled cell death (apoptosis) rather than genotoxic lesions in cell cultures of human lymphocytes and did not induce 8-hydroxy-guanosin formation.

8.13 Bacterial Toxicity of Hydrogen Peroxide

The widespread use of hydrogen peroxide as a clean, non-residue disinfectant is based on its ability to kill harmful bacteria, including those causing bad odor from the mouth. Hydrogen peroxide vapor is used in a method like ethylene oxide or ultraviolet light to prevent bacterial contamination during packaging and sealing of sterile surgical supplies and dispensing of IV solutions. Like ethylene oxide, hydrogen peroxide vapor in these industrial settings is an explosion hazard.

The question of the survivability of tough strains of bacteria immersed in varying concentrations of H_2O_2 in water surfaced again during the search for extraterrestrial life. All kinds of life forms have been subjected to simulated conditions like they might exist on Europa or Ganymede.

Hydrogen peroxide concentrations that are not strong enough to kill the bacteria outright may cause unwanted mutations in the survivors [1020]. Externally applied hydrogen peroxide rapidly permeates the bacterial cell and causes at least two classes of potentially lethal damage: Mode one killing appears to be due to DNA damage, has a maximum near 1 to 3 mM H_2O_2 , and requires active metabolism during exposure. Mode two killing is due to uncharacterized damage, occurs in the absence of metabolism, and exhibits a classical multiple-order dose-response curve up to at least 50 mM H_2O_2 . Scavenging enzymes, such as catalase and superoxide dismutase, contribute to resisting oxidative stress [1021].

Hydrogen peroxide has been recommended for cleanup of spilled industrial pollutants in the soil. Under conditions harsh enough to destroy persistent chemicals like trichloroethylene, all bacterial life in the soil would be destroyed also. On the other hand, at lower concentrations, hydrogen peroxide may provide the oxygen that the bacteria need to chew up petroleum products and other nasty chemicals.

Hydrogen peroxide vapor has been evaluated for the external sterilization of spacecraft (before they are sent to other planets) to prevent contamination of extraterrestrial habitats by terrestrial bacteria. So, if HTP is not storable enough to be on the inside of spacecraft sent to other planets, it may at least be useful to sterilize the outside [1022]. Ethylene oxide/fluorocarbon mixtures used to be used for spacecraft sterilization at JPL, but these mixtures stratify if left sitting undisturbed without additional forced convection.

8.14 Occupational Exposure Limits

The accepted occupational exposure limit for H_2O_2 as an 8-h time weighted average (TWA) is 0.14 mg/m³ or 0.1 ppm [973]. The NIOSH REL TWA is 1 ppm (1.4 mg/m³) and the OSHA PEL TWA is 1 ppm (1.4 mg/m³). Short-term exposure limits (STEL, in mg/m³) range from 2.8–4.2 mg/m³ (5–15 min). In the United Kingdom (UK) the STEL is 3 mg/m³ (for 10 min) while the United States (US) does not have an accepted STEL

value. A ceiling is accepted by some countries with a range of 1–2 mg/m³. Neither the UK nor the US have a ceiling value. The maximum concentration from which one could safely escape within 30 min without a respirator has been estimated to be 75 ppm. This concentration is thought not to cause any impairment or irreversible health effects immediately dangerous to life or health (IDLH). The National Institute for Occupational Safety and Health (NIOSH) set an Immediately Dangerous to Life and Health standard (IDLH) of 75 ppm [1023–1025]. That is of the same order of magnitude as hydrazine, although the IDLH of hydrazine was lowered from 80 ppm to 50 ppm in 1995 while the IDLH for H₂O₂ remained unchanged at 75 ppm; see also [1026].

8.15 Epidemiological Studies of Occupational Exposure

In a health surveillance survey of Degussa production staff done at five sites (Europe and USA) they evaluated 110 people, 80 of those had worked there for >10 years (some for a maximum 40 years), and none of the personnel showed any impairment of lung function or other adverse health effects [102].

An industrial hygiene survey was conducted at NASA Stennis Space Center to evaluate personal and area airborne exposure levels to hydrogen peroxide during experimental engine testing [1027]. Survey data were collected during a 3-week period in 1999 for typical operations like obtaining HTP bulk samples for analysis, transfer to oxidizer run tanks (**NOT fuel tank** – as written by Brever) and engine testing. Personal sample results were well below the permissible exposure limit (PEL) of 1 ppm. However, the results of area samples during testing indicated significant short-term elevations above the PEL. Administrative controls such as observation of wind direction and post-test wait time employed were enough to control personal exposures to hydrogen peroxide vapors and should be continued during future testing operations. Personal protective equipment used, such as natural rubber gloves, boots and suits, face shields, goggles, and hard hats, was adequate to protect personnel from potential skin contact with spilled HTP liquid.

8.16 Environmental Fate of Hydrogen Peroxide

A good summary of the environmental fate of hydrogen peroxide was given in the paper by Jacobi [969].

8.16.1 Environmental Fate of Hydrogen Peroxide in the Atmosphere

Natural H₂O₂ concentrations in the atmosphere vary with temperature, solar radiation intensity, humidity, and the presence of scavengers (CH₄, CO, volatile organic

compounds) and inhibitors (SO_2 , NO_2). H_2O_2 emissions to the environment from industrial and domestic sources have little effect due to their rapid decomposition in the wastewater. The amount of H_2O_2 deposited by rainwater into surface waters is greater than that from industrial and domestic sources together.

The atmospheric fate of hydrogen peroxide is governed by simultaneous generation and degradation reactions resulting in a stationary equilibrium [1028]. The formation of atmospheric hydrogen peroxide is photochemically mediated. Consequently, natural concentrations are latitude, altitude, seasonal, and diurnal cycle-dependent and are different in the proximity of industrial pollutants and in a clean atmosphere away from civilization. High solar irradiation leads to high hydrogen peroxide concentrations. Hydrogen peroxide in the atmosphere is produced through free radical reactions. Light, oxygen, hydrocarbons, and free radicals in the atmosphere favor hydrogen peroxide formation. In unpolluted atmospheres, the formation of H_2O_2 is ultimately due to the photolysis of ozone at wavelengths $< 310\text{ nm}$ to give oxygen atoms, which then react with water vapor. About twice as much H_2O_2 is formed at 100% relative humidity than at 50% humidity at ambient temperature.

8.16.2 Environmental Fate of Hydrogen Peroxide in Surface Waters

Hydrogen peroxide has been evaluated as a herbicide for aquatic weeds or algae because it will not leave residues or accumulate in the food chain like other herbicides [1029]. An excellent review with 289 references covers the role of H_2O_2 in natural waters, including determination methods, distribution of H_2O_2 , formation of H_2O_2 in natural waters, H_2O_2 and the redox system, decomposition of H_2O_2 , and natural purification processes in natural waters [1030]. Chemical and biochemical processes defining the H_2O_2 cycle in natural waters and in biological objects were examined. Assessments were given of the inflow of H_2O_2 into surface waters from the atmosphere, and data were collated on the H_2O_2 content of seawater and freshwater. Photochemical, catalytic, and biochemical processes make the main contribution to H_2O_2 formation. The interaction between intracellular redox processes of aquatic microorganisms and the redox state of aquatic media determines the surviving equilibrium concentration. Biotic and abiotic processes for the decomposition of H_2O_2 in natural waters and free radicals connected with the H_2O_2 cycle in the self-purification of natural aquatic media consume and generate H_2O_2 .

The main course of degradation of hydrogen peroxide in natural waters is the degradation by biological material, e.g., plankton and algae. The half-life in water decreases with increasing size of the microbial population in water. Consequently, the half-life of spilled H_2O_2 in natural waters can range from a few hours to several days. Degradation is also catalyzed inorganically by transition metal ions. Direct photolysis does not play a major role in aquatic decomposition.

Seawater contains enough copper and iron ions to catalyze the swift decomposition of hydrogen peroxide just as fast as it forms during sunlight illumination [1031].

8.16.3 Environmental Fate of Hydrogen Peroxide in Wastewater

In municipal wastewater, hydrogen peroxide degrades rapidly because of the content of microorganisms and organic material. Half-lives were reported to be below 15 min or even below 2 min. Hydrogen peroxide is used routinely in the deodorization of wastewater in water treatment plants.

8.17 Aquatic Toxicity of Hydrogen Peroxide

At concentrations <200 mg/L in wastewater, H_2O_2 does not affect the performance of biological wastewater treatment works (activated sludge process). It is quickly degraded and has even been shown to stimulate biodegradation in wastewater treatment works. At higher concentrations (>200 mg/L) H_2O_2 becomes toxic to microorganisms.

Hydrogen peroxide is used to sterilize holding pens in aquaculture farms and, therefore, has the potential to be released from aquaculture facilities when the pens are flushed before a new generation of fish is planted. The release of rinse waters would pose a risk to aquatic invertebrates. A flowthrough, continuous exposure test system was developed to expose *Daphnia magna* to hydrogen peroxide for 21 days [1032]. Hydrogen peroxide concentrations ≤ 1.25 mg/L had no significant effect on *Daphnia* time to death compared to controls and no significant effect on the time to first brood production and the number of broods produced. Concentrations ≤ 0.63 mg/L had no significant effect on the total number of young produced. Concentrations ≥ 0.32 mg/L had a negative effect on *Daphnia* growth.

The 96-h LC50 values for freshwater fish range from 16.4 to 37.4 mg/L H_2O_2 . The 48-h EC50 value for *Daphnia pulex* was 2.4 mg/L and the 24-h EC50 for *Daphnia magna* was 2.3 mg/L. The toxicity of hydrogen peroxide to different species of fish is summarized in Table 65.

Table 65: Hydrogen peroxide toxicity to fish.

Species	Latin name	Effect	Concentration $\mu\text{g/L}$
Rainbow trout, fingerling	<i>Salmo gairdneri</i>	Lethality, 48 h	>40
Squawfish	<i>Ptychocheilus oregonensis</i>	No mortality, LCo, 24 h	10
Channel catfish	<i>Ictalurus punctatus</i>	LCA, 96 h	37.4
Guppy	<i>Lebistes reticulatus</i>	Unharmd	34
Fathead minnow	<i>Pimephales promelas</i>	LC ₅₀ , 96 h	16.4
Fathead minnow	<i>Pimephales promelas</i>	NOEC, 96 h	5

See secondary source, ECETOC [985] for the original source of data.

When assessing the risk of hydrogen peroxide to environmental organisms, the background concentrations in the environment and the capacity of life forms to adapt to increased hydrogen peroxide concentrations must be considered.

9 Explosion Hazards of Hydrogen Peroxide

Hydrogen peroxide can explode in the liquid and in the vapor state. The explosive tendencies of liquid hydrogen peroxide depend on the intensity of the energetic stimulus. Pure 98% H_2O_2 could not be made to explode in the drop weight test or in the bullet impact test. Hydrogen peroxide becomes much more sensitive and more likely to explode in the presence of organic contaminants.

9.1 Drop Weight Impact Sensitivity of Hydrogen Peroxide

Liquid HTP in any concentration between 90 and 99% H_2O_2 could not be made to explode in any of the drop weight impact testers, even in the presence of a gas bubble on top of the liquid.

Drop weight tests are not always very reproducible. More accurate shock impact sensitivity tests can be carried out if the impactor is accelerated not by gravity, but in a compressed gas gun.

A gas-driven two-stage gun was used to produce well-defined shock inputs to understand and quantify the initiation and detonation properties of highly concentrated H_2O_2 [1033, 1034]. Multiple magnetic gauges were used to make *in-situ* measurements of the growth of reaction and subsequent detonation in the liquid. These experiments were designed to be one-dimensional to eliminate any difficulties that might be encountered with large critical diameters. Several experiments were completed on ~98 mass-% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixtures where initiation was observed in some experiments showing homogeneous shock initiation behavior. The initial mechanical shock pressurizes and heats the mixture. After an induction time, a thermal explosion type reaction produces an evolving reactive wave that strengthens and eventually overdrives the first wave, producing a detonation. From such measurements, unreacted H_2O_2 Hugoniot information, times (distances) to detonation (Pop-plot points) that indicate low sensitivity and detonation velocities of high concentration $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ solutions were obtained that agreed with earlier estimates.

9.2 Bullet Impact Sensitivity of Hydrogen Peroxide

Unalloyed titanium, Ti-6Al-4V, Ti-25Zr, and the Ti-19W-11Cr-3Al all-beta alloy have been shown to be impact sensitive in 90% hydrogen peroxide. Impact energies re-

quired to initiate the reaction, however, were considerably higher than those required for LOX. The black oxide films formed on some alloys with long exposures to 90% H_2O_2 did not exhibit pyrophoric properties when scratched or impacted [1035].

9.3 Cap Sensitivity of Liquid Hydrogen Peroxide

Cap sensitivity tests using No. 6 or No. 8 blasting caps were negative. In another test, a 75-L sample of 99.8% H_2O_2 was shocked with a 15-g dynamite booster and did not explode [934]. Only the barrel in which the test was conducted ruptured from the hydraulic shock.

Pure 100% H_2O_2 can only be detonated in sturdy containers with rigid confinement [1036]. It was claimed that aqueous solutions of less than 94% H_2O_2 will decompose explosively if catalyzed but will not detonate.

The following information is quoted only from a second-hand source because the original report [1037] was not available. The test data indicated that detonations in 99% hydrogen peroxide decreased considerably with distance from the booster, and that detonation speeds decreased with decreasing tube diameter. At diameters of less than 1 in., the detonation was quenched inside the tube; 99% HTP tested in a 1-in. ID, 3/16-in. wall CRES tube with a 20-g tetryl booster showed detonation speeds starting at 7060 m/s decreasing to 4715 m/s with an average of 5590 m/s measured across a distance of 1 m. In a similar test with 99% HTP in a 1-in. ID, 3/16-in. wall CRES tube 10-g tetryl booster there was no explosion. The same negative results were obtained with 90% HTP in a 1-in. ID, 3/16 in. wall CRES tube using 20 g tetryl as the booster charge.

The detonation velocity of an 86/14 mass-% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixture was estimated as ca. 6000 m/s (measured using a streak camera). The initial shot temperature and the tube diameter were not specified, but the confining tube material was listed as steel [1038].

The following information is quoted only from a second-hand source because the original report was not available. With both 90 and 99.5% H_2O_2 at 344 K (160 °F), 15 g of #15 Hercomite™ dynamite initiated in the center of 113 kg (250 lb_m) of propellant contained in a metal drum caused only minor damage to drum [1039]. With 98% HTP, a detonation could be initiated in a 1.5-in. schedule 80 CRES pipe by rapid compression, but detonation did not propagate into a 250-lb drum. With 99% HTP, a detonation could be initiated in a 1-in. ID, 0.18 in. wall CRES pipe. The 1-in. pipe was connected to a narrower, 0.5-in. ID, 0.035 in. wall CRES pipe, also filled with 99% HTP. The detonation did not propagate into the 0.5-in. pipe.

The US Bureau of Mines determined the critical diameters of liquid 86.0/14.0 and 90.7/9.3 mass-% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixtures confined in Al-61STS tubes with IDs of 26.7, 31.8, and 40.9 mm and at initial temperatures between 298 and 343 K (25 and 70 °C) [1040]. At 323 K (50 °C) or higher 86% H_2O_2 contained in 1.61 in. ID Al tubes, will detonate at 5600 mm/s when initiated by a strong booster, but not at smaller diameters. For the

86% material, the critical diameter was ca. 40.6 mm at 323 K (50 °C) and 35.6 mm at 343 K (70 °C) and, for the 90.7% material, the critical diameter decreased from 40.6 mm at 298 K (25 °C) to 20.3 mm at 343 K (70 °C). Rough detonation speed measurements gave speeds in the range of 5500–6000 m/s. The gap over which the 90.7% solution will propagate detonation increased with increasing temperature.

The *Fedoroff Encyclopedia of Explosives and Related Items* contains a good summary of the explosive properties of hydrogen peroxide and its mixtures [1041].

Hydrogen peroxide is an unusual explosive as it contains only hydrogen and oxygen. This makes spectroscopic studies of shock-induced reactions and decomposition of the molecule simpler than those for conventional nitrogen-containing explosives. UV/visible emission spectroscopy was used to follow the buildup of detonative reaction in pure hydrogen peroxide [1042]. Spectra were captured on a nanosecond timescale, and the data supported the proposed shock-induced reaction pathway. This was then compared to the reaction scheme found for hydrogen peroxide decomposition at room temperature and pressure.

The failure diameter and detonation speed for 90.5 mass-% H_2O_2 confined in thick seamless 304 stainless steel tubing and fired at ca. 303 K (30 °C) was measured [225]. The geometry of the sample holder tube was as follows: ID 45.47 mm, OD 50.88 mm, and length 610 mm. The measured density of the H_2O_2 sample was $1.390 \pm 0.002 \text{ g/cm}^3$ at 297.4 K (24.3 °C); this corresponds to 90.5 mass-% H_2O_2 . The shots were strongly boosted with SE-1 detonators, PBX-9407 pellets, and a piece of PBX-9404 of 51 mm diameter and 44 mm high. The detonation speed and knowledge of the diameter effect curves of other liquid explosives were then used to estimate the infinite-medium (i.e., plane wave) detonation speed of this material. Ambient condition sound velocity measurements and the universal liquid Hugoniot form were used to obtain the unreacted Hugoniot of the 90.5/9.5 mass-% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixture. This Hugoniot and the Rayleigh line obtained from the estimated infinite medium detonation wave speed were used to predict the von Neumann spike pressure of the material. Estimates of the fully reacted (i.e., products) Hugoniot, the C-J detonation pressure, and the C-J detonation speed for other $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixtures were obtained using the CHEETAH equilibrium thermochemical code. In Figure 59, the lower points are the calculated C-J detonation speeds for $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixtures at an initial temperature of 296 K (23 °C), as obtained with the CHEETAH code using the Becker-Kistiakowsky-Wilson (BKW) product library. A general analytical expression is given for the corrected primary shock Hugoniot of any $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixture at 295.7 K (22.6 °C). A least squares fit line has been drawn through the data points. The solid line corresponds to the equation

$$v_{\text{D CJ}} = 2.019 + 0.0412 \times C_{\text{H}_2\text{O}_2}$$

where $v_{\text{D CJ}}$ is the detonation velocity in km/s, and $C_{\text{H}_2\text{O}_2}$ is the hydrogen peroxide concentration in mass-%. The dashed line corresponds to the equation

$$v_{\text{D CJ}} = 2.56 + 0.0412 \times C_{\text{H}_2\text{O}_2}$$

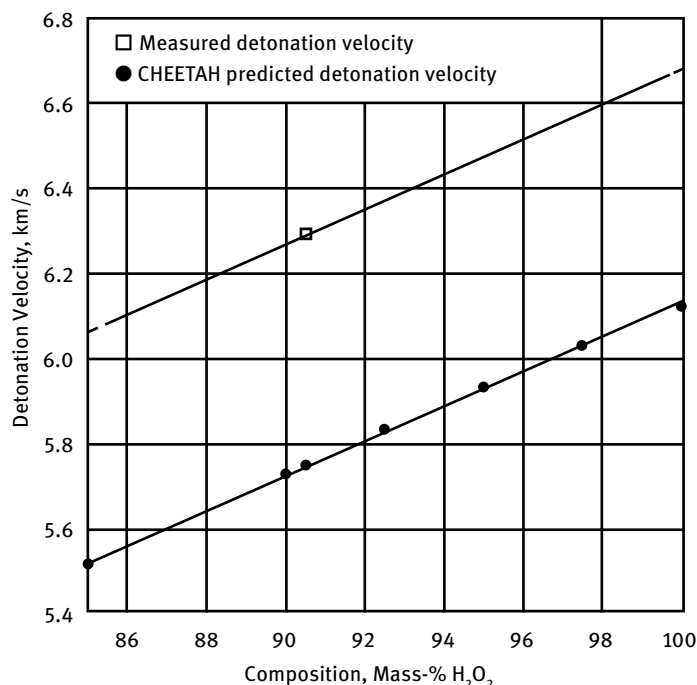


Figure 59: Calculated and measured C-J detonation speeds for $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixtures at an initial temperature of 296 K (23 °C). (Reprinted and modified from [225], with permission from © 2000 American Chemical Society; permission conveyed through RightsLink.)

where v_{DCJ} is the detonation velocity in km/s, and $C_{\text{H}_2\text{O}_2}$ is the hydrogen peroxide concentration in mass-%. The lonely square data point on the dashed line is the measured detonation velocity of 6.294 km/s (after applying temperature and infinite diameter corrections). The dashed line through the experimental point is a translation (holding the slope constant) of the lower line, providing an estimate of the expected detonation speed as a function of chemical composition. The (corrected) experimental detonation speed is 9% higher than the CHEETAH calculation of 5.75 km/s, which is a rather large difference.

Extrapolating from 90.5% H_2O_2 to 100% H_2O_2 , neat H_2O_2 is predicted to have a detonation velocity of 6.68 km/s and a C-J pressure of 130 kbar.

Hydrogen peroxide was shock compressed at pressures up to the von Neumann pressure for a steady detonation wave, using ultrafast laser-driven shockwave methods [1043]. At higher laser drive energy, evidence of exothermic chemical reactivity occurring in less than 100 ps after the arrival of the shockwave in the sample were found. The results were consistent with molecular dynamics simulations and analysis and suggested that reactivity in hydrogen peroxide is initiated on a sub-100 ps

timescale under conditions found just subsequently to the lead shock in a steady detonation wave.

Pyroshock from firings of adjacent pyrovalves or explosive separation bolts may initiate explosions in highly concentrated hydrogen peroxide [1044].

9.4 Card Gap Sensitivity of Hydrogen Peroxide

Card gap tests, using an apparatus in which 30 g of liquid sample was separated from a 30 g tetryl charge by a thin (5 to 10 mils) aluminum membrane, indicated no evidence of detonation in 90, 95, or 98% hydrogen peroxide. The results were similar to those resulting from earlier tests conducted by the US Navy [1045] to demonstrate the relative insensitivity of 90, 95.5, and 99.5% hydrogen peroxide at ambient temperatures and 344 K (160 °F).

Results of card gap sensitivity tests with several different concentrations of HTP were described in [1039] (Table 66).

Table 66: Card gap test results with hydrogen peroxide.

H ₂ O ₂ concentration, mass-%	Number of cards required to obtain negative results	
	Ambient temperature	344 ± 3 K = 160 ± 4 °F
90%	0	16
95.5%	7	25
99.5%	9	23
For comparison: Cavea B 110	12	27

Data source: [1039]

However, in the NOL Large Scale Card Gap Test, 98% HTP at 286 K (13 °C) had a 50% point of positive at 35 cards corresponding to an attenuated shock pressure of 90 kbar [1046].

9.5 Boosted Detonation Shock Sensitivity Tests (Without Spacers)

The sample temperature plays a significant role in determining the ability of hydrogen peroxide to propagate a detonation. The temperature necessary to cause a propagating detonation decreases appreciably with increasing concentration of hydrogen peroxide.

From early German investigations in the 1940s, it was reported that the H₂O₂-H₂O system can detonate at velocities of 6000–7000 m/s when the H₂O₂ concentration is

96% or greater. Below 96% it was found to be more difficult to obtain a propagating detonation at ambient temperatures.

Tests at Degussa paralleled earlier work that showed that 99% hydrogen peroxide can be detonated at ambient temperature in a 2 or 4 ft. length of an 1-in. ID pipe (0.17 in. wall thickness) using 20 g tetryl as the initiator [1047]. However, a 10-g charge of tetryl or the use of smaller diameter pipes (0.75 or 0.5 in.) did not induce a propagating detonation.

In tests at Degussa, the card gap test [1048] was modified by using a booster charge of 320 g of RDX/wax/graphite (95/5/0.5) and a thin film of PE and a layer of PTFE tape with a total thickness of about 0.20 mm instead of a stack of cards prepared of cellulose acetate (of thickness 0.19 mm). A propagation of detonation was confirmed for 98.8% H_2O_2 at “zero gap” (0.19 mm, corresponding to one card) yielding a completely fragmented tube (51 fragments, 14% of the tube mass was recovered) and a large hole punched into the lead witness plate [99, 100]. The detonability boundary in a 51-mm (2-in.) diameter charge as a function of H_2O_2 concentration and sample temperature is shown in Figure 60.

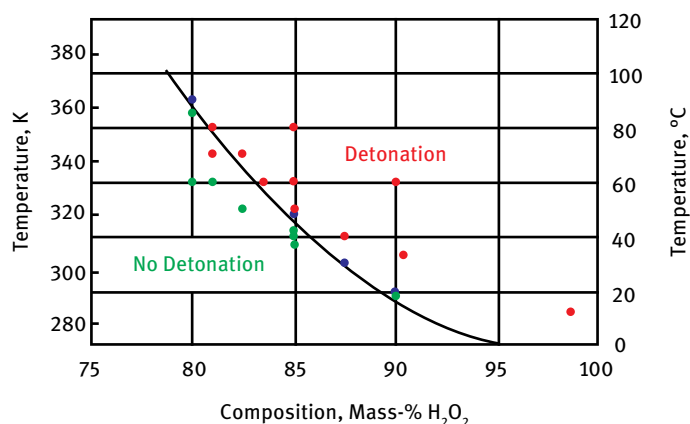


Figure 60: Results of 2-in. diameter steel tube tests as a function of H_2O_2 temperature and concentration. (Reproduced and modified [99], with permission granted by Evonik Operations GmbH.)

Subjecting a sample of identical concentration (98.8%) to the procedure with a PMMA spacer (corresponding to a stack of 240 cellulose acetate cards) did not yield a propagation of the booster detonation. These results showed that the sensitivity of H_2O_2 does not meet the criteria to be classified as an explosive.

9.6 Adiabatic Compression Sensitivity of Hydrogen Peroxide

Adiabatic compression tests with 70% H_2O_2 at ambient temperature and at 334 K (160 °F) showed the material to be insensitive at pressurization rates as high as 231000 psi/s. Even with the more concentrated samples, adiabatic compression tests of 90 and 98% H_2O_2 gave no detonative effects at 294 or 334 K (70 or 160 °F) when subjected to a maximum loading rate of 231000 psi/s [99, 100, 1039].

Somewhat similar tests using 90% H_2O_2 driven with 2000 psi air pressure against the closed end of a 1.250-in. ID pipe were reported by Bellinger [482]. He observed no explosions in these tests or in tests in which the H_2O_2 was driven through a 0.250-in. hole in the end of the pipe. Other tests concluded that 90% H_2O_2 is insensitive to adiabatic compression at all initial liquid temperatures up to 394 K (121 °C = 250 °F) and at pressurization rates up to about 200000 psi/s.

Ordinary shutdown transients and water hammer pressure spikes occurring in the feed system of satellite propulsion subsystems when valves are shut abruptly should not be sufficient to initiate decomposition of hydrogen peroxide but may damage valve seats or rupture burst diaphragms of relief valves [1049]. However, in the X-15 rocket plane, some damage was observed initially before slower acting valves were installed in the HTP system [1050].

9.7 Other Detonation Hazards of Hydrogen Peroxide and Its Mixtures

9.7.1 Other Detonation Hazards of Hydrogen Peroxide

According to Solvay Interlox, 70% hydrogen peroxide solutions are not detonable, even when boiling at atmospheric pressure. Strengths of 80% and above can be made to explode but only with difficulty. The conclusion of Solvay Interlox is that 85% H_2O_2 is capable of detonation at temperatures of 318 K (45 °C) and above if significant initiation sources are also present. These conclusions are derived primarily from tests that employed initiation by a combination of No. 8 detonator and 50-gram booster charge. This energy of initiation is not judged to be realizable from normally encountered sources associated with chemical handling on a plant (e.g., water hammer, pump malfunction, impact, thermal shock); rather an actual adjacent detonation would be needed (e.g., a mixture of 85% H_2O_2 /organic or some stronger H_2O_2 alone). The question of whether a H_2O_2 vapor explosion (see above) can transmit into a liquid phase detonation was considered by Solvay Interlox, and it was their understanding that this event is not possible, or at worst, extremely remote.

9.7.2 Detonability of Mixtures of Hydrogen Peroxide with Other Oxidizers

Hydrogen peroxide with 90 and 99% H_2O_2 , an oxidizer mixture containing 55% H_2O_2 , 39% ammonium nitrate, and 6% water, and a monopropellant mixture containing

67.8% H_2O_2 , 6.6% diethylene glycol, and 25.6% water were thoroughly characterized in drop weight impact sensitivity, cap sensitivity, boosted detonability, card gap sensitivity, and adiabatic compression sensitivity tests, at room temperature and even at elevated temperature [1051]. It was concluded that all four propellants are so insensitive to mechanical and hydrodynamic shock and to adiabatic compression that might be encountered during field use that no real hazards exist in handling them in the field.

9.7.2.1 Detonability of Liquid Mixtures of Hydrogen Peroxide with Organic Compounds

Mixtures of liquid H_2O_2 with organic compounds must be avoided because they may be shock sensitive and detonable [1052, 1053]. In an effort to increase the specific impulse of hydrogen peroxide monopropellants, mixtures of hydrogen peroxide with ethanol were tested in Germany in the mid-1930s. This resulted in a disastrous explosion, but details of the accident could not be obtained. The explosive limits of hydrogen peroxide mixtures with ethanol, acetone, or glycerol are illustrated in Figure 61.

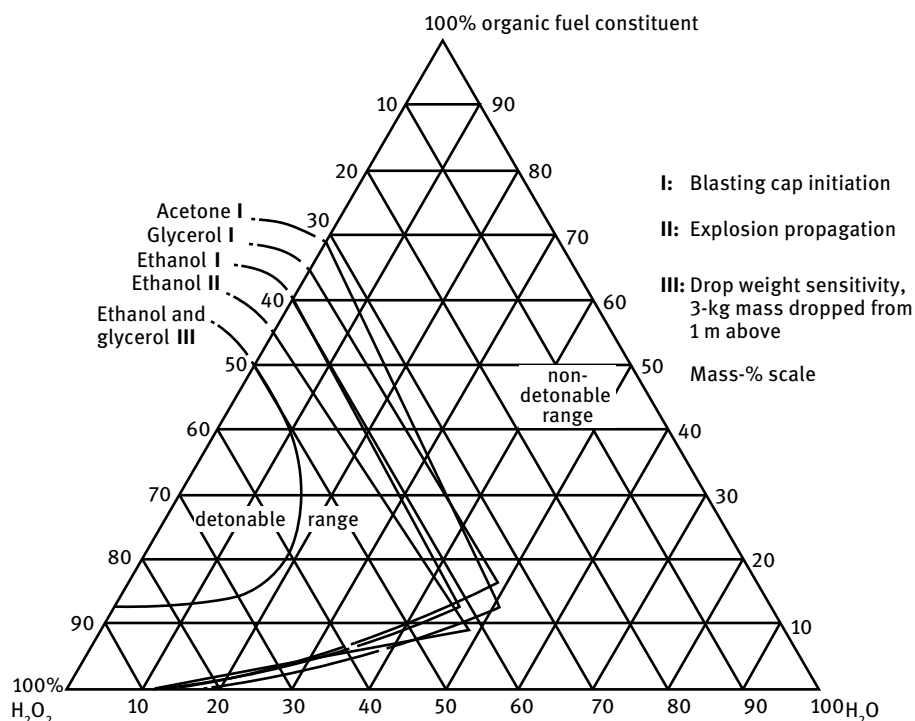


Figure 61: Detonable range in liquid hydrogen peroxide/organic fuel mixtures. (Reproduced and modified from Laporte Chem. Ltd.)

The detonability of mixtures of hydrogen peroxide, soluble organic fuels and water was tested, and a correlation was found between the detonable range and the theoretical heat of explosion [1053, 1054]. The boundaries of the explosive range in the ternary diagram depend on the mode of initiation. The range of drop weight sensitivity is narrower than the range of cap sensitivity. Figure 62 and 63 give the detonable ranges of mixtures of hydrogen peroxide with ethanol or glycerol with water as the diluent and initiation by a blasting cap [1055]. Similar data were available for acetone or tetrahydrofuran as the organic fuel. Similar, but less detailed graphs were shown in publications by Shanley and Greenspan [367] and Shanley and Perrin [1053].

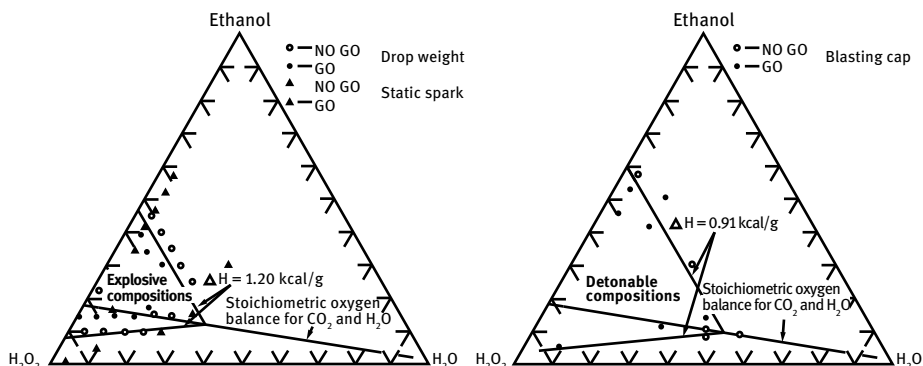


Figure 62: Range of explosive compositions for hydrogen peroxide-ethanol-water mixtures, three different modes of initiation. (Republished and modified from [1053], with permission of © 1958 American Institute of Aeronautics & Astronautics; permission conveyed through Copyright Clearance Center Inc.)

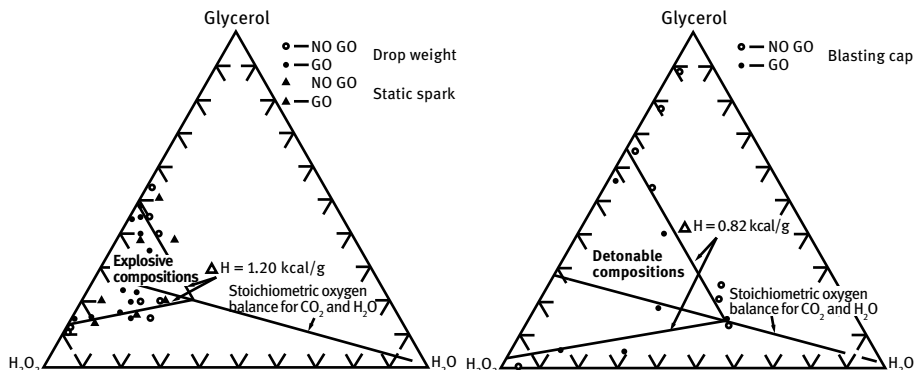


Figure 63: Range of explosive compositions for hydrogen peroxide-glycerol-water mixtures, three different modes of initiation. (Republished and modified from [1053], with permission of © 1958 American Institute of Aeronautics & Astronautics; permission conveyed through Copyright Clearance Center Inc.)

Mixtures of hydrogen peroxide and fuels may detonate with more than one characteristic speed of detonation. Sometimes a transition is observed from one mode of detonation to another as the detonation front propagates through the sample.

The above studies of the explosive limits of hydrogen peroxide/water systems containing methanol, ethanol, or glycerol defined the regions of detonable compositions at room temperature. A subsequent study was made to assess the effect of temperature and type of initiation on mixtures of hydrogen peroxide and water with various organic compounds, such as 2-propanol, all of which are soluble in hydrogen peroxide [1056]. Several types of initiation were used: impact, blasting cap, and a high-velocity shockwave. For some compositions, the overall reaction between the organic materials and hydrogen peroxide can proceed at a rate such that a stable detonation wave is propagated through the liquid. Near the limits determined by impact or blasting cap, however, the reactions are more nearly characteristic of rapid deflagration or explosion than of sustained detonations. In all these instances, the force of the reaction is sufficient to lead to the destruction of containers and considerable damage to the surroundings. Two types of impact testers were used during the investigation: The simpler of these was a modification of the test apparatus described by Bellinger [365]. The piston and cylinder (1.375 in. and 1 in. long, respectively, and 0.3 ± 0.0002 in. in diameter, lapped to fit) were of hardened tool steel for greater reproducibility of the impact shock. The striking blow was delivered by a 360-gram weight falling from a height of 180 cm. The other apparatus was designed to study the effect of higher temperatures on the explosion limits. A 500-g weight falling 200 cm was to drive the piston into the chamber containing the test solution. The steam jacket around the cavity allows the rapid attainment of elevated temperatures (within 20 to 30 s) just prior to the moment of impact. The packing gland prevented evaporation of liquid from the hot sample.

The limits of explosion for the 2-propanol-aqueous hydrogen peroxide mixtures were measured by impact test at 294 and 406 K (21 and 133 °C), using the second tester described above. Increasing the temperature of the system to 406 K (133 °C) resulted in a small widening of the limits of explosion as measured by impact tests. Similar results were obtained when 2-propanol was substituted with a mixture of 75% 2-propanol and 25% acetone. Other organics tested included methanol, formaldehyde, acetaldehyde, propionaldehyde, formic acid, and 70% acetic acid.

The third method for initiating explosion of H_2O_2 /organics mixtures was by means of a high-energy shockwave like a card gap test without spacers. A 1- to 4-L sample was placed in a cylindrical tube on top of a booster charge consisting of a 2-in.-thick block of Composition B high explosive, which has a detonating pressure of approximately 270 kilobars. The Composition B pad was initiated with a plane wave generator. The mixtures of hydrogen peroxide and organic material that underwent steady detonation maintained detonation velocities as high as 6500 m/s. This compares to the high-velocity detonation of 7700 m/s reported for nitroglycerin.

Figure 64 shows the drop weight impact and cap sensitivity explosion limits in the ternary $\text{H}_2\text{O}_2/i\text{-C}_3\text{H}_7\text{OH}/\text{H}_2\text{O}$ system. The stoichiometric reaction taking place in these mixtures is

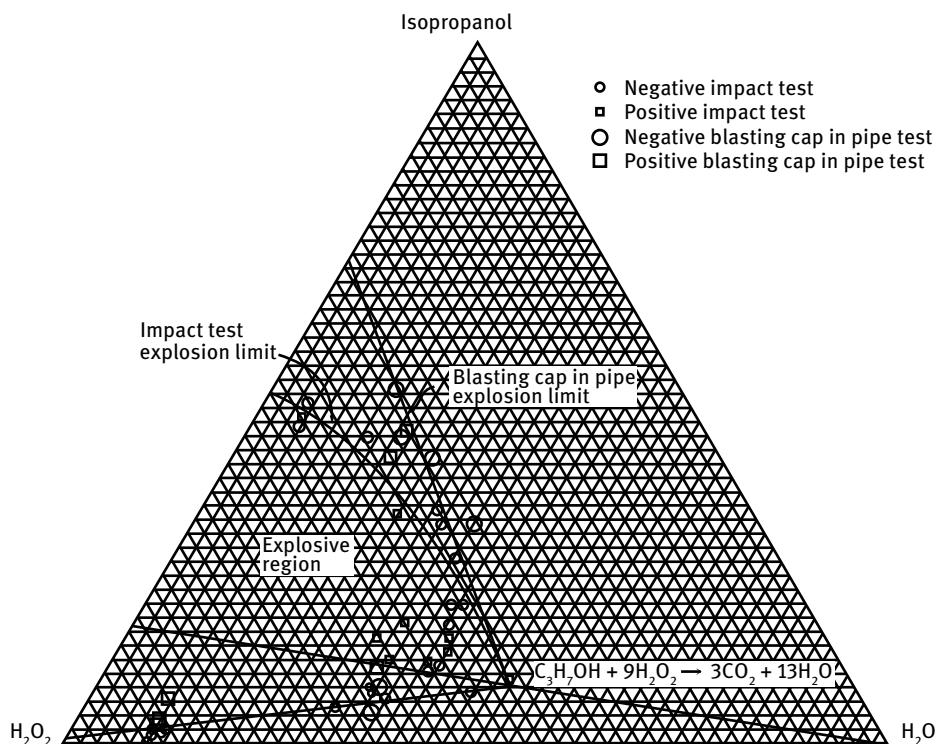
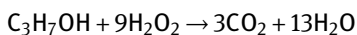


Figure 64: Drop weight impact and cap sensitivity explosion limits of ternary $\text{H}_2\text{O}_2/i\text{-C}_3\text{H}_7\text{OH}/\text{H}_2\text{O}$ mixtures. (Reproduced and modified from [1055].)

Since combustible organic liquids are used in the production of hydrogen peroxide by oxidation methods, hazards may be created by the presence of the combustibles in the peroxide liquid and vapor during such a process [1057]. The flammability of vapor mixtures of hydrogen peroxide at 427 K (154 °C) and 101 kPa with *o*-xylene and water was measured in a 1-in. diameter by 15-in. length Pyrex[®] tube. Hydrogen peroxide solutions with 55–70 mass-% H_2O_2 in mixtures with formic acid, acetic acid, or tartaric acid or xylene were tested for detonability in the card gap test, and the results presented in a triangular diagram and also as a function of carbon content. A sample with 67.5% H_2O_2 detonated. Thus, certain purge liquors formed in hydrogen peroxide

production can detonate when adequately stimulated if the organic material is permitted to build up to a sufficiently high concentration.

The detonability of hydrogen peroxide/glycerol mixtures was examined at the US Bureau of Mines [1058].

The use of hydrogen peroxide as an oxidant for organic chemical reactions (e.g., epoxidation) in the chemical processing industry can cause serious hazards. Some incidents due to runaway reactions of hydrogen peroxide with organics are described in [1059].

The explosive properties of mixtures of aqueous H_2O_2 and several different alcohols like 2-propanol, 2-methyl-2-propanol, 2-methyl-2-butanol, and 2-methyl-2-pentanol have been investigated [1060]. Among others, the potential hazard of such mixtures may be characterized by their ability to react to different stimuli leading to an explosion in the condensed phase, e.g., a thermal explosion or a detonation. Accordingly, the mixtures were tested either by heating them up under confinement in different autoclaves or by exposing them to a shockwave impact applying the steel tube test. The results are summarized in Figure 65.

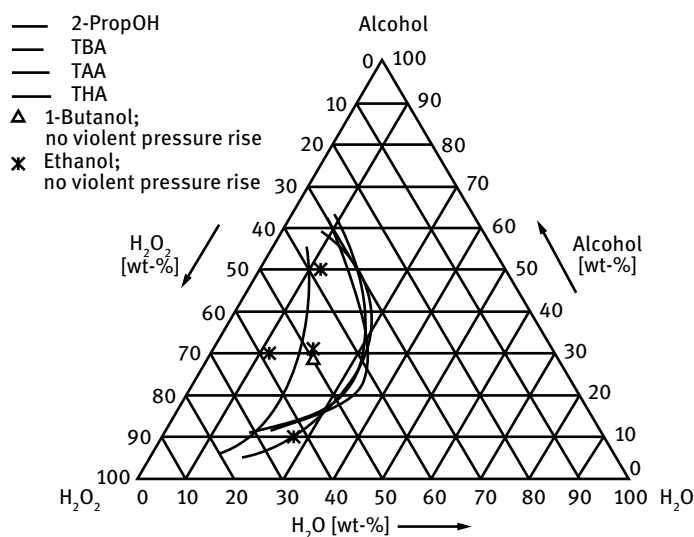


Figure 65: Thermal explosion ranges of H_2O_2 /alcohol mixtures obtained in TEVT version B. (Republished and modified from [1060], with permission of © 2004 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

Sadly, mixtures of hydrogen peroxide and alcohols and mixtures of hydrogen peroxide with solid fuels have been used by terrorists in bombing attacks [1061].

Cook-off experiments performed on 70% H_2O_2 and sucrose compositions, as well as an acid-sensitized mixture showed that at soak temperatures of 355 to 361K

(82 to 88°C) the time to cook-off was 3010 to 3560 s [1062]. The experiments were performed in 10.16 cm (4 in.) diameter by 10.16 cm (4 in.) high, sealed aluminum containers heated externally with electric heating tape wrapped radially around the container. There were four internal and five external thermocouples to control the heater and to record sample temperature and exotherms. The energetic mixture was composed of four parts 70% H_2O_2 and one part sucrose. The mass used was 993 g (794 g H_2O_2 , 199 g sucrose), which filled 750 mL of a total internal volume of 825 mL. One experiment used a fuel mixture containing mostly sucrose, but with some citric and ascorbic acid. After assembly, the apparatus was heated to a predetermined soak temperature of either 361, 357, or 355 K (88, 84, or 82°C) and held there isothermally, until the energetic material ignited. The acid-sensitized mixture, when soaked at 355 K (82°C), reacted much faster than even the 361 K (88°C) acid-free experiment and burst the apparatus after just 2450 s. The acid caused the material to be thermally sensitized.

Mixtures of HTP with organic fuels have been considered as industrial explosives with low NO_x emission levels, suitable for underground mining [1063].

Difficulties with ignition of aerosolized HTP and kerosene led to a more detailed study of two-phase detonation properties of HTP/kerosene aerosols [1064]. Experimental attempts to generate a detonation in a liquid fuel drop (kerosene)-liquid oxidizer drop (50% hydrogen peroxide in water)-inert gas-environment were not successful. A vertical detonation tube, 4.1 cm (1 5/8 in.) diameter and 3.65 m (12 ft) long, was used for these studies. The blast wave was generated by the detonation of GH_2 and GO_2 at initially elevated pressures. While it was difficult to judge in some cases, the conclusion reached was that detonation of the aerosol mix was not realized. Stronger peroxide solutions, other liquid combinations, smaller drop sizes, and larger detonation tube cross section would be appropriate to demonstrate detonability of such aerosol suspensions.

9.8 Detonation of Hydrogen Peroxide Vapors

Whereas it is difficult to get liquid hydrogen peroxide to detonate, H_2O_2 vapors can detonate only too readily and sometimes unexpectedly. The situation is, thus, like that with hydrazine liquid and hydrazine vapors.

A vapor detonation is a chemical reaction coupled with a multiple shockwave system that propagates at supersonic velocities in reference to the unreacted vapor. After initiation, the thermal energy of the reaction sustains the shockwave, and the shockwave compresses the unreacted material to sustain the reaction. To assess a potential explosion hazard due to detonation, the following information must be known:

- pressure and temperature of H_2O_2 vapor
- atmosphere diluents, presence of incompatible or reactive materials and their concentrations

- ignition sources and the amount of energy released by the source
- type of confinement

Early investigators working with H_2O_2 vapors reported somewhat contradicting results for explosive decomposition limits, depending on the type of apparatus used, the presence or absence of non-inert surfaces, and the mode of initiation. In a 3-cm diameter Pyrex[®] tube at 373 K (100 °C), thermal decomposition flames and explosions were very readily initiated by a hot wire or a spark when the pressure was about 2.6 kPa (20 mm Hg) or higher [1065]. At atmospheric pressure the explosion was very violent and potentially initiated by catalytic spots on imperfectly cleaned glassware. The minimum temperature to which a wire must be heated to cause immediate ignition of the vapor at atmospheric pressure was about 873 K (600 °C).

The explosive characteristics of hydrogen peroxide vapor at atmospheric and sub-atmospheric pressures, including values for the ignition limit over this pressure range and the effect of the nature of diluent gases and the method of initiation on the limit have been reported by several authors [770, 771, 1066]. Most studies bracketed the concentration, pressure, and temperature envelope within which the H_2O_2 decomposition (not necessarily the detonation) can propagate. At atmospheric pressure, vapors containing 26.0 mol-% or more hydrogen peroxide could be exploded by initiation with a hot wire or spark gap. The ignition limit was unchanged by the system of ignition used, by varying the temperature of the hot wire between 1350 and 1750 K or by changes in the hydrogen peroxide-oxygen ratio in the diluent gas. The ignition limit increased to 33 mol-% hydrogen peroxide at 26.6 kPa (200 mm Hg) total pressure and to 55 mol-% hydrogen peroxide at 5.3 kPa (40 mm Hg). Vapors lying within the explosive composition region at 1 atmosphere total pressure may be exploded by contact with catalytically active material initially at room temperature or by “non-catalytic” materials like aluminum at temperatures of 423 K (150 °C) or higher. Decreasing the system volume by packing it with Raschig rings shifted the ignition limit to higher H_2O_2 concentrations.

The term “ignition limit” as used here is defined as the minimum concentration of hydrogen peroxide in a vapor mixture below which powerful external ignition cannot initiate a self-propagating reaction. The self-propagating reaction must not but can be a detonation. The propagation must not necessarily be a detonation, as will be discussed below.

The explosive limits of hydrogen peroxide vapors were examined at various partial pressures and in dilution with different inert gases [729, 779]. Based on those experiments, the lower limit of detonability at sea-level atmospheric pressure is 25.6 mol-% H_2O_2 (balance is H_2O steam). If the pressure is increased, the limit is lowered to 20.7 mol-% H_2O_2 and remains at that level for pressures from 202 to 606 kPa (2 to 6 at). At 26.6 kPa (200 mm Hg) pressure the $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ vapor mixtures become detonable only if they contain 33 mol-% H_2O_2 . If the pressure is lowered further to 5.3 kPa (40 mm Hg), the mixture must contain at least 55 mol-% H_2O_2 to

sustain a detonation. Ignition can occur not only with a hot wire and a spark gap, but also by contact with catalytic materials. Inert gases have no different effect (no different than steam). Only carbon dioxide appears to have a weak inhibiting effect on ignition and the boundary of detonability is shifted toward higher H_2O_2 concentrations.

Satterfield and coworkers extended the pressure range over which the explosion limit was previously established to the range of 101 to 653 kPa (14.7 to 95 psia.) [772, 1067]. Instead of starting with H_2O_2 of the desired concentration, the experiment was part of a still in which 40 mol-% H_2O_2 could be concentrated until the explosive limit in the vapor phase was reached. The test vessel was a 300-mL borosilicate glass bulb at the top of a distillation column. The entire apparatus could be placed inside a pressure vessel, pressurized with nitrogen, and operated remotely. Ignition was done with a spark between electrodes connected to a Tesla coil. The only materials that came in contact with H_2O_2 vapor were borosilicate glass, aluminum wire, and Teflon. Between 202 and 606 kPa (2 and 6 atm) pressure, the ignition energy limit was found to be constant at 20.7 mol-% H_2O_2 in the vapor. The minimum concentrations for explosive propagation were found to be 25.6 mol-% at 101 kPa (1 atm) and 20.7 mol-% in the 202 and 606 kPa (2 and 6 atm) region.

Quenching distances and minimum ignition energies of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ vapor mixtures were studied in a flow system in which liquid $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ was fed to a boiler where it completely vaporized and then passed through the explosion vessel holding the ignition source [1068]. The quenching distances and minimum spark ignition energies of mixtures containing between 35 and 50 mol-% H_2O_2 were determined at pressures between 3.3 and 26.6 kPa (25 and 200 mm Hg) at temperatures 9°C above the condensation temperature. The quenching distances varied between 0.51 and 1.63 cm and the ignition energies between 0.53 and 25.5 millijoules, decreasing with increasing H_2O_2 content and pressure. The observed minimum energy for ignition is related to the quench distance by:

$$E_{\min} = 3.84 \times d_q^{3.04}$$

where $E_{\min}$ is the minimum ignition energy in millijoules, and d_q is the quench distance in cm.

Earlier work by Satterfield et al. had measured explosion limits in the $\text{H}_2\text{O}_2/\text{H}_2\text{O}/\text{diluent}$ system only at pressures near 0.7 kPa (1 psia). Monger et al. [1069] expanded the measurements over a wider pressure range from 0.7 kPa to 6.8 MPa (0.1 to 1000 psia). Three types of apparatus were used: **(1)** A stainless steel apparatus that measured 17.8 cm (7 in.) O.D. and 66 cm (26 in.) in length. **(2)** A 300-mL glass bulb with and without a glass coil. **(3)** The other apparatus was made of aluminum, had an I.D. of 49 mm (1.939 in.) and was 2.43 m (8 ft.) long but was used only for lower pressure tests. Ignition was achieved with a spark from two 28 μfarad capacitors in series charged to 1500 V. In a few cases, the vapors ignited on their own by contact with a hot spot on a wall. Instead of having a stagnant vapor reservoir in the test

chamber, the hydrogen peroxide vapor flowed constantly through the apparatus to make sure that it was always fresh and had not deteriorated before the spark was energized. The only damage to the equipment occurred as the result of a test at 20 kPa (2.9 psia) using 77.8 mol-% H_2O_2 in the 300-mL glass bulb. Upon sparking, there was a sharp report, and the entire coil and the reboiler section were shattered. A 35 mol-% H_2O_2 mixture will detonate at 2037 m/s (6700 ft/s) at 101 kPa (1 atm). The ignition limit under these conditions is about 30 mol-% H_2O_2 vapor. The superatmospheric and subatmospheric pressure ignition limits of hydrogen peroxide are illustrated in Figure 66 and 67.

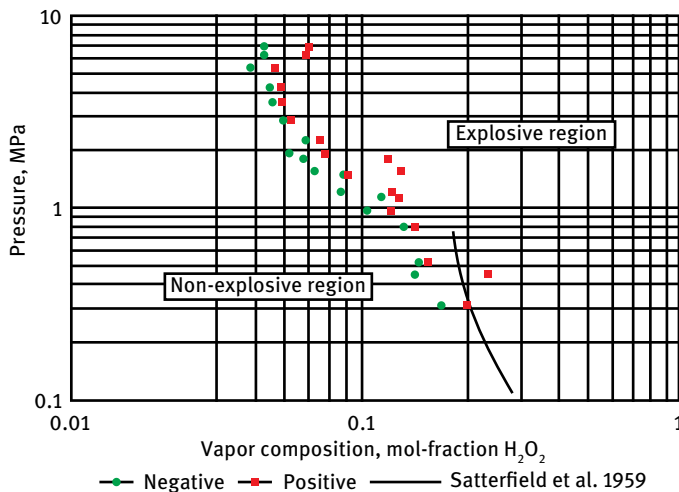


Figure 66: Ignition limit of hydrogen peroxide vapors at above atmospheric pressure. (This chart was created by Schmidt 2020 based on data from [1069].)

Note: The open symbols indicate negative tests (no detonation), and the solid symbols indicate positive tests (detonation). The dashed line in Figure 67 indicates the earlier data from Satterfield, which agree quite well with Monger's data.

The vapor space above 90% H_2O_2 becomes detonable only if the liquid is heated to at least 390 K (117 °C). If the vapor space above 100% H_2O_2 is tested, detonability will not be achieved unless the liquid is heated to at least 383 K (110 °C). These temperatures are not normally encountered during storage and transportation of HTP. Facilities for manufacturing and rocket engine testing with HTP will have to take the necessary safety precautions to prevent collateral damage in the event of an unexpected explosion.

Other experiments were conducted at 19.95, 46.6, and 101 kPa (2.90, 6.77, and 14.7 psia) in order to study the detonation characteristics of hydrogen peroxide vapor [1070]. Liquid $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ solutions of the necessary concentration were fed to

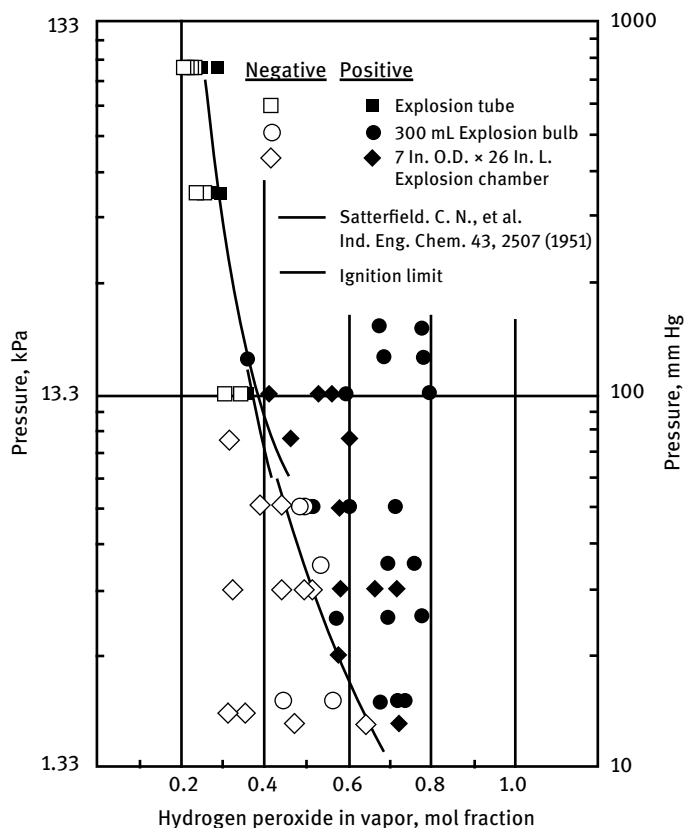


Figure 67: Ignition limit of hydrogen peroxide vapors at below atmospheric pressure. (Reprinted and modified from [1069], with permission from © 1964 American Chemical Society; permission conveyed through RightsLink.)

a reboiler and the vapor passed through a detonation arrestor into the test section. Three different methods of initiation were used: One consisted of a 3500-V capacitive spark from the discharge of two 28 mfarad condensers across a 0.8-mm (0.031-in.) gap between two tantalum electrodes with hemispherical ends. Another form of initiation was provided by 1-in. firecrackers ignited with a resistance wire. Sometimes the mixture would ignite spontaneously before the other mode of initiation could be activated. The detonation tube was a length of 51-mm (2-in.) OD Sched. 80 Type 6063-T6 aluminum pipe fitted with a tee and blowout disk at each end. The inside diameter of the pipe was 49 mm (1.939 in.), and the assembled length was 2.43 m (8 ft.) The tube was radiatively heated with external heating rods to temperatures up to 423 K (150 °C). Within the experimental conditions employed, no detonations were observed at 19.9 and 46.6 kPa (2.90 and 6.77 psia). At atmospheric pressure,

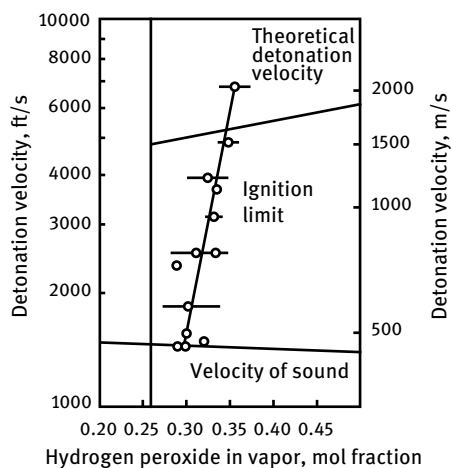


Figure 68: Detonation velocity of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ vapor mixtures at atmospheric pressure. (Reprinted and modified from [1070], with permission from © 1964 American Chemical Society; permission conveyed through RightsLink.)

detonation with a velocity of 2037 m/s (6700 ft/s) was observed in vapor with a composition of 35 mol-% hydrogen peroxide. The mixtures became detonable as the H_2O_2 concentration was increased from 30 to 35 mol-%. Between 30 and 35 mol-%, several concentrations were tested in 1% increments. Compositions above 35 mol-% could not be tested because they had a tendency to explode prematurely before the spark could be energized. The data (Figure 68) showed a gradual, linear transition from the velocity-of-sound decomposition wave to the detonative mode. At the two lower pressures, decomposition waves propagated through the mixtures near or below the velocity of sound, but substantially below the calculated, theoretical CJ detonation velocity. Such decomposition events, if they happened in a distillation tower or in a storage tank, would still be quite destructive, but they would not be true detonations in the exact sense of the word.

Addition of aluminum powder to 98% H_2O_2 makes a very powerful explosive [1071]. In an experiment, 40 μm amorphous aluminum powder was suspended by gelling 90% hydrogen peroxide with a carboxy polyvinyl chloride. Stable detonation rates were measured for well-confined compositions of both types balanced stoichiometrically to alumina and steam. The concentration of hydrogen in the reaction products of a series of aluminum-hydrogen peroxide charges with oxygen balances rising toward zero decreased and became negligible. Pressures of 95 kilobars or higher were achieved by this mixture when initiated with 100 g tetryl. Experimental results from these charges were compared with Ruby code calculations of reaction products for a charge balanced to alumina and steam and also with data from experiments with water immersed torpexes. As part of this program, the detonation rate of aqueous hydrogen peroxide (97.5%) by itself without any fuel added was measured and compared with values found in prior German work and with a Ruby code calculation. Detonation velocities of aq. H_2O_2 (96+%) without fuel addition under heavy confinement and strong boosting were measured by a smear camera

under the following conditions: A 1530 g charge, 7.6 cm diameter, 24.0 cm length, was loaded in a glass cylinder (2.5 mm wall) confined by a tightly fitting, mild steel sleeve (3 mm wall). Initiated by 100 g tetryl, the charge reacted at 6440 m/s with no measurable drop in velocity over its length. A 2.54 cm thick steel witness plate under the charge was perforated to a diameter about equal that of the charge. The sensitiveness of aq. H_2O_2 (97.5%) to shock initiation was measured by the large-scale gap test. In this test, 230 g aq. H_2O_2 (97.5%) were confined in a steel cylinder of 3.66 cm ID, 0.56 cm wall, and separated from a standard tetryl donor by a cellulose acetate gap. The cellulose acetate thickness was varied in successive shots to obtain a 50% initiation gap. This gap for aq. H_2O_2 (97.5%) was 35 cards or 0.35 inches and is compared with gap sensitivities of two well-known explosives and a double-base propellant in Table 67.

Table 67: Comparison of large scale gap sensitivities of aqueous H_2O_2 (97.5%) and other energetic materials; 50% initiation probability gap.

Composition	Density	% Theoretical maximum density	No. of cards
AHH double-base propellant	1.60		36
Aqueous H_2O_2 (97.5%)	1.44		35
TNT (cast)	1.62	98	138
Composition B (cast)	1.70	99	201

Data source: [1071]

9.9 Explosive Yield of Hydrogen Peroxide in the Lead Block Test

In addition to the go/no go detonability tests discussed above, the explosive power of 85.5% H_2O_2 mixtures with methanol, ethanol, and glycerin was measured in the Trauzl lead block test, and the detonation velocity was measured as well [1038]. The lead block indentations approached those measured with nitroglycerin and exceeded those of picric acid.

9.10 Bonfire Tests of Hydrogen Peroxide Tanks

The H_2O_2 tanks in which a foreign hydrogen peroxide product was to be shipped were to be constructed from 99.5% aluminum. The US Coast Guard does not normally allow the use of aluminum for tank construction because of its poor high temperature strength. In this case, however, pure aluminum was necessary to minimize the decomposition rate of the cargo. Engineering estimates were made to study the effect of a vigorous external fire on a nominal 15 m^3 (4000 gallon) bare aluminum tank con-

taining 70% hydrogen peroxide [396]. Decomposition rates of 70% hydrogen peroxide over a temperature range up to and above the normal boiling point (398 K = 125 °C for 70 mass-% H_2O_2) were measured. Previously reported work on hydrogen peroxide stability was done mostly with 90% material. Reproducibility of results was a problem at 373 K (100 °C) and above, and therefore a lower temperature was commonly employed for these tests, for example 323 K (50 °C). In this analysis, the problem decomposition rates of significance are those at: **(1)** the ambient temperatures encountered in transportation and **(2)** the temperatures resulting from a fire situation, especially the decomposition rate up to the boiling point at the relief pressure of the 4000-gallon tank. Pressure is said to have no effect on the rate of decomposition. The decomposition reaction of hydrogen peroxide is not reversible.

10 Oxonium and Peroxonium Salts

Peroxonium salts are of interest as solid propellant oxidizers and as potential sources of singlet atomic oxygen for chemical lasers. The peroxonium salts discovered so far are not very stable, and additional work is required to develop proper stabilization techniques.

The first known examples of peroxonium salts $[\text{H}_3\text{O}_2]^+ [\text{Sb}_2\text{F}_{11}]^-$, $[\text{H}_3\text{O}_2]^+ [\text{SbF}_6]^-$, and $[\text{H}_3\text{O}_2]^+ [\text{AsF}_6]^-$ were prepared by protonation of H_2O_2 in anhydrous HF solutions of the corresponding Lewis acids [1072, 1073]. These salts would be powerful oxidizers and are a means to store H_2O_2 in solid form. They were isolated as metastable solids, which underwent decomposition to the corresponding H_3O^+ salts and dioxygen, in the temperature range 293–323 K (20–50 °C). The $[\text{H}_3\text{O}_2]^+$ salts were characterized by vibrational and NMR spectroscopy. Attempts to protonate both oxygen atoms in H_2O_2 to form $[\text{H}_4\text{O}_2]^{2+} [\text{SbF}_6]^-$ resulted in $[\text{H}_3\text{O}_2]^+ [\text{Sb}_2\text{F}_{11}]^-$ as the only product.

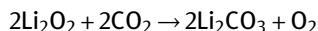
11 Alkali Metal and Alkaline Earth Metal Peroxides

The alkali and earth alkaline metal peroxides are strong oxidizers, but they are not used as solid rocket propellants due to their moisture sensitivity. A common use of several of these materials is in breathing air regeneration oxygen cartridges where the acidity of exhaled carbon dioxide along with moisture of exhaled air releases breathable oxygen.

11.1 Lithium Peroxide

In the group of alkali metal peroxides, lithium peroxide, Li_2O_2 , CAS RN [12031-80-0] surprises by its poor solubility in water (8%). Lithium peroxide solutions are stable but

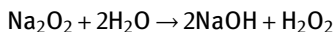
will decompose in the presence of manganese or iron salts or silver catalysts [1074]. Lithium peroxide is used in air revitalization life support units where weight (mass) is important and justifies the higher price of Li_2O_2 compared to the use of Na_2O_2 , e.g., in crewed spacecraft (Apollo) to absorb carbon dioxide and release oxygen in the reaction:



This reaction is the same for the other alkali metal peroxides. Lithium peroxide absorbs more CO_2 than the same mass of lithium hydroxide and offers the bonus of releasing breathable oxygen.

11.2 Sodium Peroxide

Most metals when burning in oxygen or air would result in the formation of the metal oxide. Not so with sodium and some of the other alkali and earth alkaline metals. Sodium metal burning in oxygen or air will result in the formation of sodium peroxide Na_2O_2 and not sodium oxide Na_2O . Sodium peroxide, Na_2O_2 , CAS RN [1313-60-6] is a yellowish solid, often supplied in spherical granules. Sodium peroxide dissolves in water with the release of heat, initially forming a hydrate $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ and on further dilution slowly hydrolyzes to an alkaline solution of NaOH and H_2O_2 :



Other hydrates and peroxohydrates formed are $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$, and $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}_2$. Organic materials in contact with sodium peroxide may autoignite.

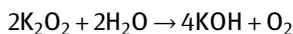
When used in air revitalization units to absorb CO_2 , an intermediate compound $\text{Na}_2\text{C}_2\text{O}_6$ may form before all oxygen is released.

Waterless reactions between solid alkali metal or alkaline earth peroxides and hydrogen (deuterium) halide gases can produce singlet Δ oxygen for a chemical laser in a non-liquid medium [1075–1078]. These reactions occur under ambient conditions without the need for an external energy source. The production of singlet Δ oxygen was verified by direct emission spectroscopy at $1.27\text{ }\mu\text{m}$ with a calibrated optical multi-channel analyzer. These reactions overcome the quenching problems encountered in liquid-phase reactions and the dangers/inconvenience associated with the use of basic hydrogen peroxide liquids for the chemical oxygen iodine laser (COIL).

11.3 Potassium Peroxide and Potassium Superoxide

Potassium forms five types of oxides: potassium oxide K_2O , CAS RN [12136-45-7], potassium peroxide K_2O_2 , CAS RN [17014-71-0], potassium superoxide (“potassium hyperoxide”), KO_2 , CAS RN [12030-88-5], the less common potassium trioxide K_2O_3 , and

potassium ozonide KO_3 . In dry air, potassium oxide K_2O absorbs oxygen and transitions into potassium peroxide K_2O_2 . Potassium peroxide hydrolyzes readily with water to form potassium hydroxide and oxygen:



Potassium superoxide can be produced by burning molten potassium metal in pure oxygen. It is a yellow solid. When dissolving potassium superoxide in water, an unidentified short-lived, blue-colored intermediate can be observed. Potassium superoxide is often used as an oxidizing agent in industrial chemistry, as a CO_2 scrubber and oxygen generator in rebreathers, spacecraft, submarines, and spacesuit life support systems. Potassium ozonide, KO_3 , is a dark red solid that is produced when potassium metal is burned in ozone.

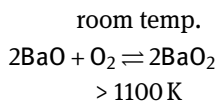
11.4 Calcium Peroxide

Calcium peroxide, CaO_2 , CAS RN [1305-79-9], is an off-white solid peroxide. It is practically insoluble in water but will dissolve in acidic water to form hydrogen peroxide. When in contact with water it will slowly decompose, releasing oxygen. In the bread baking industry calcium peroxide is used as a flour bleaching agent, but mixtures of calcium peroxide and flour in the wrong ratio are potentially explosive.

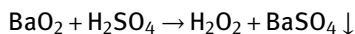
11.5 Barium Peroxide

Barium peroxide, BaO_2 , barium dioxide, CAS RN [1304-29-6], is a gray-white solid. Barium peroxide is an oxidizing agent, which can be used for bleaching of cellulosic materials, fabrics, and as an oxidizer in pyrotechnic formulations.

Barium peroxide is formed during the combustion of barium metal in oxygen or by the reversible absorption of atmospheric O_2 by barium oxide. The oxygen is released if barium peroxide is heated above 1100 K



This reaction was the basis for the now-obsolete Brin process for separating oxygen from the atmosphere and the first process for production of hydrogen peroxide:



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Hydroxylammonium Salts

Books on rocket propellants have undergone significant changes during updating in the twenty-first century. One of the most prominent changes is the inclusion of new chapters on hydroxylammonium salts, which were never even mentioned in the old books but have now evolved into an interesting family of potential rocket and liquid gun propellants.

Because the hydroxylammonium cation contains one more oxygen than the ammonium cation, salts of hydroxylamine with oxidizing acids make better oxidizers than ammonium salts. In the form of their aqueous solutions they can be used in monopropellants, liquid gun propellants, and torpedo propellants (*Encyclopedia of Monopropellants*). Concentrated solutions of hydroxylammonium salts can also be used as liquid oxidizers in bipropellant engines or in hybrid rockets. This chapter on hydroxylammonium salts is preceded by a short summary of information on the free hydroxylamine base. Although too unstable to be used as a rocket propellant, hydroxylamine free base plays an important role in the slow and fast decomposition of hydroxylammonium salts. Aqueous solutions of the free hydroxylamine base can also be used as a starting reagent in the preparation of hydroxylammonium salts. This is why it is included here. The most important hydroxylammonium salt in this rocket propellant category is hydroxylammonium nitrate, $[\text{NH}_2\text{OH}^+][\text{NO}_3^-]$, HAN, and consequently the majority of the current chapter is devoted to it. Hydroxylammonium nitrate aqueous solutions must be maintained slightly acidic to prevent formation of hydroxylamine free base. The unwanted and uncontrolled presence of hydroxylamine free base accelerates the premature decomposition of HAN during storage.

1 Hydroxylamine Free Base

Hydroxylamine free base, NH_2OH , CAS RN [7803-49-8], HA (antiquated names are oxammonium and oxyammonia), is not used as a rocket propellant, but because it is either an intermediate or additive in the production of hydroxylammonium salts (for comparison: NH_2OH^+ ion, CAS RN [62675-55-2]) or closely related to some of the decomposition mechanisms of hydroxylammonium salts, we are including a tutorial chapter on it here. This serves as an introduction to the more detailed sections on hydroxylammonium salts, which have more practical uses than the free base. A HAN-based monopropellant has flown in a satellite propulsion system to demonstrate the feasibility of less toxic monopropellants. Hydroxylamine free base can be used for the preparation of HAN. Some of the hazards encountered when preparing and using hydroxylammonium salts are closely tied to the instability of the parent amine, hydroxylamine free base. For this reason, we are including in this book on propellant oxidizers two sections on the decomposition of hydroxylamine free base, first discussing the

mechanisms (which are closely interrelated with the mechanisms of decomposition of HA salts as monopropellants) and thermal decomposition kinetics. A discussion going beyond plain decomposition of HA, where actual experimental decomposition and actual flame studies are conducted, are included in a volume on monopropellants (*Encyclopedia of Monopropellants*). Hydroxylamine or hydroxylammonium are intermediates in the bacterial oxidation of ammonia to form nitrite and nitrate and in the reduction of nitrate by another set of bacteria. Nitrification in nature is a two-step oxidation process of ammonium (NH_4^+) or ammonia (NH_3) to nitrate (NO_3^-) catalyzed by two different types of bacteria. The first reaction is oxidation of ammonium to nitrite by ammonia-oxidizing bacteria (AOB) represented by the *Nitrosomonas* genus. These steps are carried out by two different groups of organisms, the ammonia-oxidizing bacteria and the nitrite-oxidizing bacteria. A key enzyme in nitrification is ammonia monooxygenase, which oxidizes ammonia to hydroxylamine. Another enzyme in action is hydroxylamine oxidoreductase. Hydroxylamine may exist in the gut of animals eating a nitrate-rich diet. There are thousands of tons of hydroxylamine in circulation in the bacterial world at any one time. There is plenty of ammonia in interstellar space and planetary ices, as well as hydroxyl radicals. Their reaction could lead to hydroxylamine, which would accumulate in the condensates at low temperature because it is less volatile. Hydroxylamine in interstellar space may react with acetic acid to form amino acids, the building blocks for life.

We discuss hydroxylamine free base here because even in salts of HA with strong acids, as in HAN, reverse dissociation that liberates a small amount of the free base in equilibrium with its salt is responsible for a lack of thermal stability in many hydroxylammonium salts in solution. The free base itself in the anhydrous state lacks sufficient thermal stability to be considered as a propellant or for any other application in the pure state by itself. In the pure state, it is better characterized as an explosive.

A short summary of hydroxylamine chemistry is contained in *Ullmann's Encyclopedia of Industrial Chemistry* [1], but it does not even mention HAN.

1.1 Preparation of Hydroxylamine Free Base

It is unlikely that rocket propellant chemists will need to prepare hydroxylamine free base in the laboratory, but the synthesis of some of the more energetic hydroxylammonium salts may start with the free base and an acid, doing a simple neutralization reaction.

Historically, the economic incentive for producing hydroxylamine solutions was driven by the desire to produce polyamides (nylon 66, etc.) in large quantities to satisfy the needs of the textile industry. Once one has a cheap source of hydroxylamine free base, it would be easy to produce all the other HA salts (HAN, hydroxylammonium perchlorate [HAP]) by a simple neutralization and concentration process. The polymer industry would use the free base to prepare cyclohexanone oxime, an inter-

mediate in nylon synthesis. In many industrial installations the hydroxylamine is not isolated as such, but dilute solutions of HA free base or hydroxylammonium salts are immediately processed into oximes and isolated as such. More than 95% of all hydroxylamine produced is used to make cyclohexanone oxime or caprolactam. The global production capacity of hydroxylamine is estimated to be 800000 metric tons/year. Industrial use and transport of hydroxylamine is not as the free base but is mainly as the sulfate salt, supplied as both an aqueous solution and solid crystalline material. Aqueous solutions of hydroxylammonium sulfate can be shipped in tank cars made of stainless steel or polyethylene. Crystalline hydroxylammonium sulfate is packed in polyethylene sacks. A small amount of HAN in the form of 24% HAN solutions is used for the reprocessing of nuclear reactor fuel elements.

Hydroxylamine free base in 50% aqueous solution is used for cleaning and photoresist removal of silicon chips in the production of integrated circuits and memory chips. It was during production of a 50% HA solution for this semiconductor application that two devastating explosions occurred in two different continents within a few years of each other. Distillation of hydroxylamine free base is a **hazardous** operation.

Hydroxylamine free base is sometimes used for the preparation of hydroxylammonium salts by neutralization with the acid of choice. But hydroxylammonium salts prepared from the free base may contain contaminants (stabilizers) carried over from the HA production process. Commercially available hydroxylamine free base as a 50% solution often contains proprietary stabilizers that would interfere with subsequent use of HAN in catalytic monopropellant reactors. If anhydrous hydroxylamine free base is needed, the commercially available aqueous 50% hydroxylamine solution can be dehydrated by distillation with *n*-butanol. This is a hazardous operation.

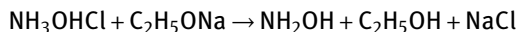
Methods for the production of hydroxylamine free base without starting with hydroxylammonium salts include the reduction of nitrate, the catalytic oxidation of ammonia [2], reaction of ozone with ammonia, reduction of NO/NO₂ in a solution of ammonium sulfite, reduction of NO with H₂ over a platinum catalyst, and many others.

1.1.1 Preparation of Hydroxylamine Free Base from Hydroxylammonium Salts

If small samples of pure hydroxylamine are needed for spectroscopic or other analytical purposes, they can be prepared by the historical method described by Hurd and Brownstein. This method starts with preparing a solution of sodium butoxide in *n*-butanol, which is then reacted with a dispersion of finely ground hydroxylammonium chloride in butanol while stirring, and observing the pH with a phenolphthalein indicator. The insoluble sodium chloride is filtered and washed with butanol, and the filtrate is chilled to 263 K (−10 °C). Hydroxylamine free base precipitates in large white flakes. It is collected on filter paper, washed with butanol and then with diethyl ether, and dried in a desiccator. The yield is 50% of theory.

The same method is described in a patent [3] (which also describes various stabilizing additives), although no credit was given to Hurd and Brownstein.

An older method is very similar and used sodium ethoxide instead of sodium butoxide

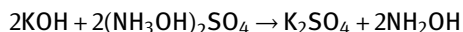


with essentially the same results [4].

Small amounts of hydroxylamine free base and also its deuterium isotopologue can be prepared by vacuum decomposition of hydroxylammonium orthophosphate, $(\text{NH}_3\text{OH})_3\text{PO}_4$, in partial vacuum with a stream of purge nitrogen [5].

The reaction of hydroxylammonium sulfate with sodium hydroxide gives a mixture of free base and sodium sulfate. The mixture is cooled to precipitate the sodium sulfate, and the filtrate can be distilled at reduced pressure in a stripper column with steam at $\sim 353\text{ K}$ ($\sim 80^\circ\text{C}$) to give a salt-free hydroxylamine distillate containing 8% NH_2OH that can subsequently be concentrated in a different distillation column such that 50% NH_2OH can be withdrawn at the bottom [6]. This is a **hazardous** operation.

The process as it was operated at Concept Sciences, Inc. in Pennsylvania and at Nissin Chemical in Gunma Prefecture in Japan consisted of a continuous stirred tank reactor (CSTR), multiple filtration units, and a packed distillation tower. The CSTR was fed with stoichiometric amounts of potassium hydroxide (KOH) and hydroxylammonium sulfate. The two streams combined in the reactor according to the following equation:



Preliminary studies indicate that KOH catalyzes the decomposition of HA; therefore, the mixture must be well mixed, and the reactants must be metered in slowly. The product stream from the reactor is fed to a filtration unit to remove the solid potassium sulfate. An accumulator may be used to isolate the preceding process (reaction and filtration) from the distillation. A heat exchanger with an outlet temperature control is also employed to achieve a suitable feed temperature for this stream, which consists of approximately 30 mass-% HA. The 30% HA stream is then fed to a vacuum distillation tower to concentrate it to 50 mass-% HA at the bottom. A packed distillation tower operating at 33 kPa (250 mm Hg) and a reflux ratio of 0.5 should enable the desired separation to obtain 50 mass-% HA product. This is a **hazardous** operation, and accidents that have occurred at facilities using this process are discussed in Section 1.4.

A high-purity aqueous solution of hydroxylamine free base can be obtained by treating an aqueous solution of a hydroxylammonium salt with a base such as ammonia at low temperatures [7]. The ammonium salt side product can be separated from hydroxylamine by low-temperature filtration and a resin-exchange process. The concentration of the hydroxylamine product is further increased by a distillation process that produces a high-purity and high-concentration hydroxylamine product with reduced risks of explosion.

A cation exchange resin can be loaded with hydroxylammonium ions from a solution of any hydroxylammonium ion, washed with water to remove contaminants, washed with a dilute hydroxylamine free base solution, and then treated with caustic having a dissociation constant greater than 10^{-7} (ammonia) to liberate the purified hydroxylamine free base. For preparation of free base by ion exchange from hydroxylammonium salt solutions, see [8–12]. An alternate use would be to extract the cation resin with strong nitric or perchloric acid to prepare the corresponding ammonium salts in high purity (albeit with an excess of acid).

An electrodialysis process using a bipolar cation exchange membrane starting with hydroxylammonium salts and liberating the free base at the cathode is described in a patent [13].

1.1.2 Preparation of Hydroxylamine Free Base from Nitric Oxide

There are several dozen patents for the preparation of hydroxylamine free base from nitric oxide, which is a cheap starting reactant. An excellent review of hydroxylamine production methods by reduction of nitric oxide was written by Tauszik and Crocetta [14]. The reduction of nitric oxide with hydrogen is carried out over platinum catalysts in sulfuric acid solution and would not lead to the free base but to a hydroxylammonium salt [15]. One type of catalyst is platinum deposited on activated charcoal with platinum contents in the range of 1.2–11.3 mass-% [16]. Similar methods aimed at hydroxylammonium salts instead of free base are discussed in Section 3.2.8.

Hydroxylamine can be made by partial reduction of nitric oxide. However, continuing the reduction of nitric oxide past the desired product, with hydroxylamine as the reductant, leads to ultimately useless nitrogen and water [17, 18].

The reduction of nitric oxide, NO, on gold electrodes in alkaline solutions leads directly to free HA [19]. This reaction can even be carried out in a fuel cell, where it produces electricity as an additional bonus in a cogeneration scheme [20]. The electrochemical cell typically consists of a porous gas-diffusion anode and cathode placed in two compartments that are separated by a proton-exchange membrane [21–23].

Among the several cathode electrocatalysts tested, iron-phthalocyanine impregnated in graphite was the most favorable one for selective synthesis of hydroxylamine [24].

1.1.3 Electrochemical Methods for Production of Hydroxylamine

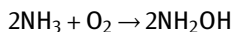
The electrolytic reduction of NO may go through N_2O , HONO, and $(HONO)_2$ as intermediates. Polarographic measurements of electrode potentials show a multi-step process. The first polarographic step (0.8 to 0.65 V) corresponds to the formation of N_2O . The second step (0.45 to 0.22 V) is the reduction to NH_3OH^+ and NH_4^+ . The reduction of NO on gold electrodes in alkaline solutions leads directly to free HA [25]. A somewhat different apparatus uses a flow-through mercury-plated nickel electrode [26]. See also

[27–29]. Other investigators reduced nitric oxide on a porous platinum electrode to obtain hydroxylamine (or its salts) in good yields [30, 31].

A three-compartment cell with anion-selective membranes and cation-selective membranes separating the center compartment is fed with a solution of a hydroxylammonium salt to produce a solution of the free base in the catholyte [32]. One method for reducing the acid content of a solution and for converting a hydroxylamine salt to hydroxylamine uses an electrolysis cell consisting of an anolyte compartment containing an anode, a catholyte compartment containing an oxygen-consuming cathode, and an anionic membrane divider separating the two compartments. An aqueous solution of an acid is fed to the anolyte compartment, and an aqueous solution comprising the hydroxylamine salt is fed to the catholyte compartment. An oxygen-containing gas is bubbled through the cathode compartment [33]. This can be combined with a nitrate-reducing cell to produce the free base from nitric acid in a continuous process. In this case, the cell consists of a feed compartment between the cation-selective membrane and the anion-selective membrane, a recovery compartment between the cathode and the cation-selective membrane, and an acid compartment between the anion-selective membrane and the anode. Electrochemical processes for the production of HAN are described in Section 3.2.2.

1.1.4 Formation of Hydroxylamine Free Base by Oxidation of Ammonia

The most direct method for synthesis of hydroxylamine would be the oxidation of ammonia with oxygen or even with air:



Unfortunately, this reaction is not feasible, but a similar reaction with ammonia and hydrogen peroxide in the liquid phase over a titanium silicate catalyst is supposed to give some hydroxylamine [2]. Similar processes have been patented for the production of hydroxylammonium salts (Section 3.2.9). Ammonia oxide NH_3O forms as an intermediate during ammonia oxidation and quickly isomerizes to hydroxylamine [34], but both intermediates are too unstable to be isolated under the highly exothermic conditions of ammonia combustion. The problem is at least as difficult or even more difficult than the direct oxidation of methane to methanol.

The research in stabilization of hydroxylamine has been reviewed [35]. The decomposition mechanism, influence factors, and inhibition means of hydroxylamine and its salts are important for their use as propellants. The characteristics of related stabilizers were discussed and analyzed to provide guidance for stabilization research of energetic oxidizers such as HAN.

1.2 Physical Properties of Hydroxylamine Free Base

1.2.1 Physical and Mechanical Properties of Hydroxylamine Free Base

The introduction of one oxygen atom changes the properties of ammonia drastically. No longer is it a gas at room temperature that boils at 240 K (−33°C), but the new compound is now a solid at room temperature with a melting point of 306 K (+33°C). As such, it is the highest-melting compound with the low molecular mass of 33.0298 g/mol. This change in physical properties is due to the extensive formation of hydrogen bonds. Hydrogen bonds can be measured by spectroscopic methods (discussed later).

The boiling point of HA is 343 K (70°C) at a reduced pressure of 60 mm Hg. The distillation of HA is a **hazardous** operation because the vapors **and the liquid** may detonate [36]. Hydroxylamine cannot be distilled at atmospheric pressure. Physical properties of hydroxylamine free base are summarized in Table 1.

Table 1: Physical properties of hydroxylamine free base.

Property	At	SI units	Other units	References
Melting point		306.2 K	33.05°C	[36]
Melting point		305.2 K	32.05°C	[36]
Boiling point	22 mm Hg	329–330 K	56–57°C	[36]
Boiling point	60 mm Hg	343 K	70°C	[36]
Vapor pressure	0°C	35.9 Pa	0.27 mm Hg	[37]
Vapor pressure	32°C (melting point)	704 Pa	5.3 mm Hg	[37]
Vapor pressure	47.2°C	1.33 kPa	10 mm Hg	[37]
Vapor pressure	64.6°C	5.3 kPa	40 mm Hg	[37]
Vapor pressure	77.5°C	13.3 kPa	100 mm Hg	[37]
Density, solid	0°C		1.2255 g/mL	[36]
Density, liquid	33°C		1.204 g/mL	[36]

The vapor pressure of hydroxylamine in the range from 261 to 280 K (−12 to +7°C) can be expressed by the equation (Back and Betts [37])

$$\log p = 11.7102 - \frac{3352.6}{T}$$

where p is the vapor pressure in mm Hg and T is the temperature in kelvin. Vapor density measurements showed that NH_2OH vapor consists of single molecules (no association of binary or multiple clusters in the vapor space) at 36 Pa (0.27 mm Hg) and 298 K (25°C).

1.2.2 Optical Properties of Hydroxylamine Free Base

1.2.2.1 Absorption Spectra of Hydroxylamine Free Base

The absorption spectra of hydroxylamine free base are of interest as a means to analyze HA and HA salt solutions and to determine its molecular structure. Thermodynamic data needed for rocket performance calculations with HA and its salts are derived from spectroscopic data. Attempts have been made to ignite HAN-based propellants with lasers, and before one can select a laser for this task, one must know the absorption spectra of the compound that needs to be ignited.

Based on absorption spectra in the gaseous and solid states in the range 1.5–25 μ , it was concluded that the free base NH_2OH molecule is symmetrical and that *cis* and *trans* forms coexist [38]. The infrared (IR) spectrum of HA vapor is shown in Figure 1. The N–H and N–O bands were recorded at high resolution, and because NH_2OH is a relatively simple molecule, it was possible to assign bonds and types of vibrations to all of the bands observed. The thermodynamic functions of HA vapor could be derived from the IR absorptions. The same paper also contains an IR spectrum of solid hydroxylamine. Once the absorption bands of the free base hydroxylamine are known, it is also easier to assign absorption bands in HAN and other hydroxylammonium salts.

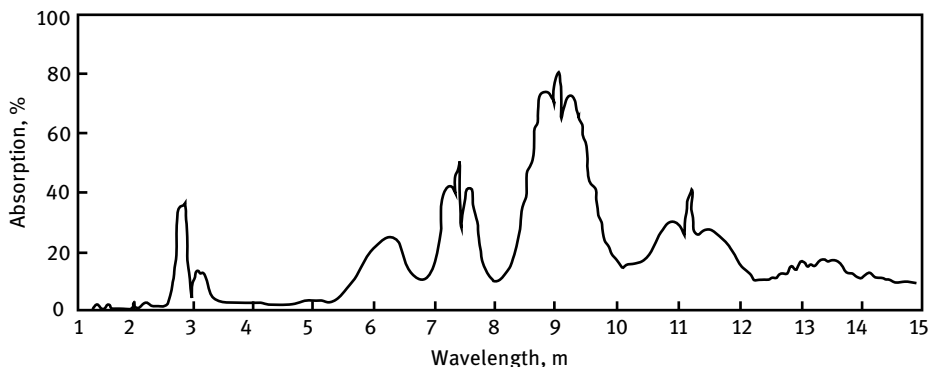


Figure 1: Infrared spectrum of hydroxylamine vapor. (Republished from [38], with permission of © 1952 Canadian Science Publishing; permission conveyed through Copyright Clearance Center, Inc.)

The infrared spectra of thin films of solid H_2NOH and D_2NOD were obtained at 195 and 83 K (–78 and –190 °C) in the region 4000–500 cm^{-1} [39]. Two distinct types of spectra resulted, depending on whether the films were formed at 195 K (–78 °C) or at 83 K (–190 °C). The spectra obtained when the films were formed at 83 K were characterized by broad overlapping bands; those formed at 195 K gave much narrower bands, some of them splitting into two or more distinct components. The latter type of spectrum is representative of the stable crystalline form at low temperature. This spectrum could not be correlated with a postulated ammonia oxide isomeric form of hydroxylamine, $\text{H}_3\text{N}=\text{O}$. Satisfactory vibrational assignments could be made for a model with symme-

try of the point group C_3 , H_2NOH . If *cis*- and *trans*-rotational isomers coexist in the solid, they must possess very nearly the same potential energy or at least a high potential barrier between them. The O—H stretching vibration in the solid was found at a very low frequency, 2867 cm^{-1} , indicating a very strong hydrogen-type bond with an energy of about 54.4 kJ/mol (13 kcal/mol).

Infrared spectra of HA trapped in a matrix of solid nitrogen or solid argon were very helpful for studying the role of hydrogen bonding in forming HA dimers in crystals, melts, solutions, and vapors [40]. Absorption bands were assigned to fundamental vibrations based on the isotope effect in deuterated HA [41]. Photolysis of the $NH_3\text{-}O_3$ complex, formed by reagent co-deposition with excess argon at 10–14 K, gave hydroxylamine as the sole product. Fundamental frequencies were obtained for hydroxylamine isotopes by using deuterium or ^{15}N -enriched NH_3 or ^{18}O -enriched O_3 precursors. Normal isotopic hydroxylamine and both fully and partially deuterated hydroxylamine were also produced in high yields from the thermal decomposition of the tertiary hydroxylammonium phosphate salt, $(NH_3OH)_3PO_4$. All of the fundamental vibrations except the NH_2 rocking were observed for normal isotopic hydroxylamine. The experimental force field of hydroxylamine was constructed from the IR data, and it indicated that the (unobserved) NH_2 rocking occurs in the 1300 cm^{-1} region, as has been predicted by *ab initio* calculations.

IR-optical double resonance studies of the $7\nu_{OH}$ level of hydroxylamine observed spectral features 14 cm^{-1} wide in the vibrational overtone spectra of rotationally selected hydroxylamine [42]. The vapor was flowed through a sample cell at $50\text{ mTorr}=6.6\text{ mPa}$ and was excited with two lasers operating at different wavelengths. The $7\nu_{OH}$ level of NH_2OH is above the N—O dissociation threshold; the finite lifetime of the molecule will broaden the vibrational overtone transitions.

Substitution of the hydrogen in water by various ligands with increasing electron affinity causes shifts in the IR spectra wavelengths and intensities [43]. The atomic polar tensors of the H atom for ROH molecules where $R = H, CH_3, NH_2, HO$, and F, were calculated by the *ab initio* method using the 4–31G basis set. The results were interpreted in terms of the charge, charge flux, atomic dipole flux, and homopolar dipole flux contributions.

The UV spectrum of HA starts at 255 nm and shows a first maximum at 182.5 nm [44]. A minimum at 170 nm is followed by increasing absorption toward shorter wavelength. It may be difficult to record UV spectra of HA because at the shorter wavelength the sample starts decomposing while its spectrum is being recorded. One has to maintain a flow of fresh vapor through the sample cell in order to avoid interference from decomposition products. Nitrous oxide is the main decomposition product, and it is already forming while the spectrum is being recorded. The absorption maximum at 182.5 nm probably corresponds to the dissociative excitation of the lowest excited singlet state. A second dissociative process becomes dominant at wavelengths shorter than 170 nm.

1.2.3 Thermodynamic Properties of Hydroxylamine Free Base

The enthalpy of formation of HA free base is important for calculating the potential energy release in accidental explosions of this chemical and for calculating the enthalpy of formation of HAN if it is made by neutralization of HA free base with nitric acid. Thermodynamic properties of hydroxylamine free base are summarized in Table 2.

Table 2: Thermodynamic properties of hydroxylamine free base.

Property	At	SI units	Other units	References
Enthalpy of formation, solid	298 K	-106.7 kJ/mol	-25.5 kcal/mol	[45]
Enthalpy of formation, vapor	298 K	-47.7 ± 4.6 kJ/mol	-11.4 ± 1.1 kcal/mol	[46]
Enthalpy of formation, vapor	298 K	-42.26 kJ/mol	-10.1 ± 0.3 kcal/mol	[47]
Enthalpy of formation, vapor	298 K	-42.68 kJ/mol	-10.2 kcal/mol	[48]
Heat of vaporization	305 K	47.7 kJ/mol	11.4 kcal/mol	[49]
Heat of vaporization		61 kJ/mol	14.6 kcal/mol	[50]
Enthalpy of sublimation	273 to 305 K	64.18 kJ/mol	15.34 kcal/mol	[49]
Enthalpy of sublimation		64 kJ/mol	15.3 kcal/mol	[50]
Heat capacity of vapor	298 K	$46.7 \text{ J K}^{-1} \text{ mol}^{-1}$	$11.17 \text{ cal } ^\circ\text{C}^{-1} \text{ mol}^{-1}$	[51]
Heat of fusion	305 K	16.48 kJ/mol	3.94 kcal/mol	[49]
Entropy of sublimation	273 to 305 K	$169 \text{ J K}^{-1} \text{ mol}^{-1}$	$40.4 \text{ cal } ^\circ\text{C}^{-1} \text{ mol}^{-1}$	[49]

Actually, HA is a solid at 298 K, but the samples used by early investigators probably were not completely water-free and thus they may have been liquid at 298 K.

Based on a set of *ab initio* calculations, an estimated value of -47.7 ± 4.6 kJ/mol (-11.4 ± 1.1 kcal/mol) for the gaseous HA enthalpy of formation at 101 kPa and 298.17 K was reported [46].

Coupled-cluster *ab initio* calculations through non-iterative triple excitations were used to compute optimized structures, harmonic vibrational frequencies, atomization energies at 0 K, and heats of formation at 298 K for hydroxylamine (NH_2OH) and three related compounds (NH_3 , HNO , and H_2O_2) [47]. The use of basis sets as large as augmented sextuple- ζ resulted in small extrapolations to the complete basis set limit in order to achieve acceptable accuracy (± 1 kcal/mol) in the thermodynamic properties. Excellent agreement with experiments was found for the heats of formation of NH_3 , HNO , and H_2O_2 . For NH_2OH , the best current estimate of the heat of formation at 298 K is -42.26 ± 1.2 kJ/mol (-10.1 ± 0.3 kcal/mol), which falls roughly midway between two experimental values at -50.2 ± 10 kJ/mol (-12.0 ± 2.4 kcal/mol) and -33.0 ± 6.3 kJ/mol (-7.9 ± 1.5 kcal/mol). Other sources [48] give the enthalpy of formation of the vapor as -42.68 kJ/mol = -10.2 kcal/mol. Hydroxylamine is a weak base with a $\text{p}K_{\text{b}}$ of 8 (Table 3).

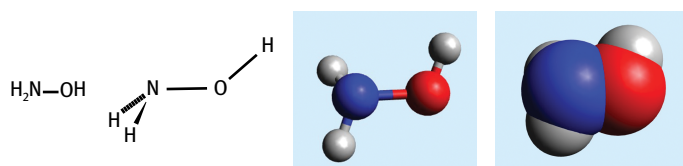
Table 3: Dissociation properties of hydroxylamine free base.

Property	At	SI units	Other units	References
Dissociation constant	293 K	1.07×10^{-8}		[36]
Dielectric constant		77.63–77.85		[36]
Proton affinity			211 kcal/mol	[36]
pK_a (NH_3OH^+)	293 K	6.04		[52]
pK_b	293 K	8.13		[52]

Because H_2NOH is a relatively simple polyatomic molecule, it has been used for many model calculations in comparison to isoelectronic or similar molecules such as HOOH or H_2NNH_2 . For instance, calculations of chemical interactions give rotational energy profiles and test the rules of additivity and the role of bond–bond, bond–lone pair, and lone-pair–lone-pair interactions [53]. From these calculations, one can predict the enthalpy of formation of the molecule in the vapor phase.

1.2.4 Molecular Structure of Hydroxylamine Free Base

Hydroxylamine is derived from ammonia by replacing one of the hydrogens in the molecule by a hydroxyl group (Figure 2).

**Figure 2:** Molecular structure of hydroxylamine free base

The unique physical and chemical properties of hydroxylamine and its derivatives can be explained through its molecular structure and arrangement of atoms in the molecule. The bond energies of the N–O and N–H bonds are a key parameter in evaluating the stability and the potential explosivity of this molecule.

Based on absorption spectra in the gaseous and solid states in the range 1.5–25 μ , it was concluded that the molecule is symmetrical, belongs to point group C_s , and that *cis* and *trans* forms coexist [54]. At room temperature, no *cis* isomer is observed. Force constants, moments of inertia, rotational constants, and molecular parameters have been evaluated. Thermodynamic functions of the gaseous substance were calculated between 298.16 and 1200 K. The N–O distance was found to be 1.46 Å, and the O–H and N–H distances have nearly the same values as those in water and NH_3 , respectively. The O–H bond with 1.06 Å is slightly longer than in the free radical and lies in the plane of the C_s symmetry.

Microwave spectroscopy and electron diffraction studies have established the *trans* equilibrium structure of NH_2OH belonging to the C_s group, as illustrated in Figure 3.

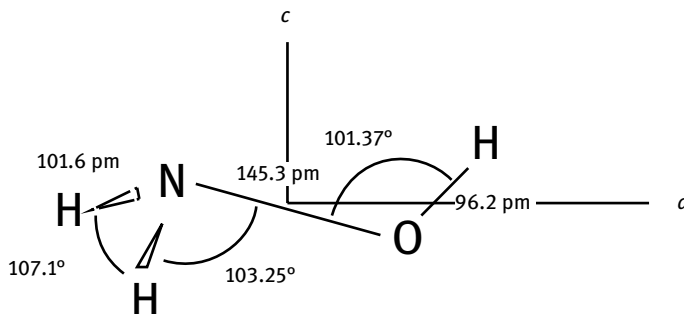


Figure 3: Hydroxylamine equilibrium geometry. (Based on data from [55].)

The best experimentally determined values for the N—O bond length in hydroxylamine and its N-protonated form are, respectively, 1.453(3) and 1.411(2) Å, the latter being derived from a redetermination of the crystal structure of hydroxylammonium chloride [56]. The data are in good agreement with those from *ab initio* molecular orbital (MO) calculations reported in the literature. The chloride salt crystallizes in space group $P2_1/n$, with $a = 6.954(2)$, $b = 5.943(1)$, $c = 7.286(2)$ Å, $\beta = 114.12(2)^\circ$, and $Z = 4$.

The N—O bond dissociation energy of hydroxylamine was calculated at the level of CCSD(T)/6-31G + (d,p)//MP2/6-31G + (d,p) to be approximately 251 kJ/mol (60 kcal/mol), which suggests that the N—O bond is too strong at ambient temperature to be broken at a significant rate. This number is in good agreement with earlier estimates of 256.5 kJ/mol (61.3 kcal/mol) by Back and Betts [37]. The most likely decomposition pathway was proposed to be the bimolecular isomerization of hydroxylamine into ammonia oxide. Water is a catalyst for the isomerization of HA to ammonia oxide. The activation barrier for this reaction in the gas phase was calculated to be about 108.8 kJ/mol (26 kcal/mol) above the hydroxylamine bimolecular complex, and this reaction in aqueous solution is slightly exothermic, with an energy barrier of only 67 kJ/mol (16 kcal/mol).

A Monte Carlo simulation of liquid hydroxylamine gave theoretical values for the heat of sublimation (64 kJ/mol = 15.3 kcal/mol), the heat of vaporization (61 kJ/mol = 14.6 kcal/mol), the dipole moment of 0.59, and the dielectric constant (predicted for HA 77.7, compared to that predicted for water 78.5) [50].

Using the quantum mechanical software Gaussian 03, HA bimolecular or water-catalyzed HA isomerization to ammonia oxide in aqueous solution was identified as a possible decomposition pathway [57]. With the improvement of computer resources and computational chemistry, molecular simulation has become a powerful and reli-

able tool to complement and guide experimental thermal stability testing. Ammonia oxide is very unstable but survives long enough to play a role in hydroxylamine decomposition and ammonia oxidation [58].

Quantum mechanical calculations were carried out in an effort to predict the enthalpy of formation and bond energies in the hydroxylamine molecule and its proton affinity [59]. Similar calculations were performed to predict the instability of the molecule and explain its explosive behavior.

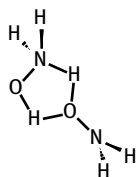
Hydroxylamine, hydrazine, hydrogen peroxide, methylamine, and methanol all share the same dumbbell shape of the molecule backbone, and calculations of the bond energies and hindrances to free rotation will reveal why some of the molecules will autodecompose and others will not [60]. An energy decomposition scheme in terms of quasi-classical, interference, and charge transfer interactions between non-orthogonal, strictly local molecular orbitals (NOLMOs) was applied to the study of the barriers to internal rotation. It was found that the barriers in these molecules essentially arise from a combination of a number of predominant quasi-classical and interference effects.

1.2.4.1 Hydrogen Bonding in Hydroxylamine Free Base

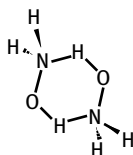
Hydroxylamine free base has the highest melting point, 306 K (33 °C), of any chemical compound with the same molecular mass. Molecules with similar molecular masses are either liquids or even gases at the same temperature. The reason for the exceptional behavior of HA and many of its salts is the strong hydrogen bonding between the hydrogen atoms of the $\text{H}_2\text{N}-$ group and its neighboring O and N atoms. Because these intermolecular forces affect the physical properties and energy content of HA and its salts, they need to be discussed here in a little more detail.

1.2.4.2 Hydrogen Bonding in Anhydrous Hydroxylamine Free Base

The first step of association of HA molecules leads to formation of dimers (also called homodimers), which may exist in the crystal structure of solid HA, in melts, in solution, or in the vapor phase. The dimerization energies and IR band-wave numbers of dimers of HA were calculated based on the self-consistent field molecular orbital theory [61]. There are three possible structures: a linear alignment with a C_s symmetry and two cyclic dimers with a C_{2h} symmetry. The cyclic dimers can form either five-membered or six-membered rings:



Five-membered ring dimer



Six-membered ring dimer

Of the three possibilities, the six-membered ring is the most likely structure. Calculations were performed assuming that one of the hydroxyl groups in water is the proton donor and that the lone pair of electrons on the nitrogen is the electron donor. The computed IR spectra of the dimers and complexes showed the red wave number shifts and intensity enhancements of O—H and N—H stretching bands typical for hydrogen bonding. Fundamental vibrations calculated for this structure agreed well with bands assigned in IR spectra of HA trapped in a matrix of solid nitrogen or solid argon [40, 41].

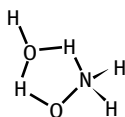
Based on X-ray diffraction (XRD) data, four molecules of hydroxylamine are in an orthorhombic unit cell of symmetry $P2_12_12_1$ with the unit cell dimensions $a = 7.20 \text{ \AA}$, $b = 4.39 \text{ \AA}$, and $c = 4.88 \text{ \AA}$ [62]. The N—O bond length is $1.47 \text{ \AA}$.

1.2.4.3 Hydrogen Bonding in Aqueous Hydroxylamine Free Base Solutions

It is known that ammonia has a strong interaction with water when it is dissolved in water. Similar to ammonia, HA dissolving in water acts as a weak base, and the solution is alkaline. When anhydrous HA dissolves in water, some of the dimers and other clusters are broken up because water molecules arrange themselves between the HA molecules and actively participate in the hydrogen bonding. This is why HA solutions have such a low vapor pressure and are very viscous.

The IR spectra of water and hydroxylamine, co-deposited in solid nitrogen and argon matrices at 17 K, confirmed the predictions of *ab initio* theoretical studies that the monomers interact to form a cyclic hydrogen-bonded complex, stabilized by both $\text{OH}\cdots\text{N}$ and $\text{OH}\cdots\text{O}$ bonds [63]. The experimental wave number shifts were compared with those calculated theoretically, and an encouraging degree of agreement was observed.

Molecular orbital calculations of 1:1 $\text{NH}_2\text{OH}\cdots\text{H}_2\text{O}$ associates were carried out using the 6-31G** basis set [64]. The first question was how the formation of the adduct would affect the IR spectra of either HA or the water. It was possible to predict the vibrational wave numbers of H_2NOH and its adduct with a fair degree of accuracy. The most stable structure of the adduct is a five-membered ring with the free O—H group of the water rotating out of the plane of the ring:



As the result of the adduct formation, the N—O bond length is reduced by 0.5 pm, and the O—H bond length is extended by 0.9 pm. In the water molecule, the H—O—H angle widens by 0.5° .

Hydroxylamine free base forms a similar, but less stable, hydrogen-bonded adduct with anhydrous ammonia [65].

Two analytical pair-potential radial distribution functions for $\text{NH}_2\text{OH}\cdot\text{H}_2\text{O}$ have been derived using 6-31G and 6-31G** basis sets for *ab initio* calculations of the interaction energy surface [66]. The results of *ab initio* calculations, and of Monte Carlo simulations performed with these potentials, proved the importance of the polarization functions in potential construction. The structure of hydration solvent molecules surrounding the NH_2OH was shown to consist of a sphere in which up to 18 water molecules are arranged under the influence of H_2NOH . In general terms, the system structure around NH_2OH appears as a large hydration shell ($R = 4.5\text{--}5.0 \text{ \AA}$) involving an average of 16 or 17 water molecules distributed in two semi-shells, each containing eight water molecules, and being oriented around the O and N atoms of the hydroxylamine molecule. This high coordination number can be attributed to the rather large size of the hydroxylamine molecule and the low stabilization energy of hydrogen-bonded structures. In addition, there are interactions between two neighboring H_2NOH molecules arranging themselves head to tail.

1.3 Chemical Properties of Hydroxylamine

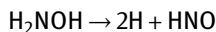
1.3.1 Photolysis and Photodissociation of Hydroxylamine

Photolysis of hydroxylamine and its salts is of interest for the laser ignition of rocket and gun propellants. One of the several ways to entice unstable molecules into decomposition is to create vibrationally excited molecules at one frequency (energy level of the light) and subsequently to excite the vibrationally energized molecule into a dissociative electronic state. From then on, the reaction intermediates and ultimate products can be followed by absorption spectrophotometry or laser-induced fluorescence using less energetic (non-dissociating) spectroscopic probes. Because the initial vibrational excitation can strongly influence the motion of the vibrationally excited molecule on the potential energy surface, this process is called vibrationally mediated photodissociation. It provides more information than a single-shot excitation (one-photon photolysis). In the two-step photodissociation, neither photon has sufficient energy to dissociate the molecule from its vibrational ground state, and even the combined energy of two photons is not enough to reach the electronically excited state. Hydroxylamine is a good candidate for studies of vibrational overtone excitation in vibrationally mediated photodissociation of simple molecules [67]. It has both O—H and N—H stretching vibrations that are acceptable to vibrational overtone excitation. One of the decomposition products is hydroxyl free radical, which can easily be detected by laser-induced fluorescence. The one-photon photolysis of hydroxylamine at 240 nm produces NH_2 and OH.

Ultraviolet (UV) light from a mercury lamp (253.7-nm resonance line) becomes much more effective in causing decomposition of HA if the HA vapor contains a trace of mercury vapor as a sensitizer [68]. The product composition is quite different for the direct photolysis and the mercury-sensitized photolysis. The direct photolysis yields

much hydrogen with some N_2O . The Hg-sensitized photolysis gives mostly ammonia with very little H_2 or N_2O . Both reactions form water.

Photolysis of HA vapor with a laser at 193 nm leads to rapid dissociation [69]. The main dissociation channel leads to $\text{H} + \text{H} + \text{HNO}$, with a quantum yield of greater than one. Another channel leads to excited OH and NH_2 . At 193 nm, close to the first maximum in the UV absorption spectrum, the formation of H atoms via



is by far the most important channel, with the N—O bond dissociation contributing less than 10%.

Photoionization mass spectrometry of NH_2OH and ND_2OD showed that the species observed at $m/e = 31$ are HNO^+ and NOH^+ , and that produced at $m/e = 32$ is H_2NO^+ [70]. From the appearance potentials (photon energy expressed in eV), one can derive the bond energies and dissociation energies of the hydroxylamine molecule.

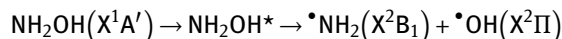
Hydroxylamine photodissociation can be studied in two ways: **(1)** by direct single-photon dissociation and **(2)** by two-photon vibrationally mediated photodissociation. In the vibrationally mediated photodissociation experiments, hydroxylamine excited in the third or fourth O—H stretch overtone state is photolyzed by a second photon of sufficient energy to dissociate only vibrationally excited molecules. Vibrational overtone spectra for the second, third, and fourth overtones of the O—H stretch were obtained via photoacoustic spectroscopy and simulated to obtain rotational constants and line widths [71]. Strong vibrational coupling arising at an energy between the third and fourth overtones and persisting thereafter led to a sharp increase in line width. Ground-state *ab initio* calculations indicated that Fermi coupling between the O—H stretch and NOH bend is significant. They also showed the presence of a barrier to isomerization to ammonia oxide (NH_3O) near the energy of the fourth overtone.

Single-photon dissociation at 240 nm releases most of the excess energy to relative translation (53%) and NH_2 internal energy (40%), with little to OH internal energy (7%). *Ab initio* calculations of the excited state of hydroxylamine showed a small barrier to dissociation because of an avoided crossing and a change in equilibrium geometry from *trans* to bent upon electronic excitation.

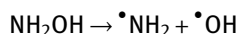
The photodissociation of NH_2OH is a useful tool to study interactions between NH and OH free radicals and the recombination of NH_2 and OH radicals. The photodissociation of hydroxylamine following direct single-photon and vibrationally mediated two-photon excitation below 42000 cm^{-1} showed that in all cases the lowest dissociation channel [$\text{NH}_2(\text{X}^2\text{B}_1) + \text{OH}(\text{X}^2\Pi)$] dominates [55]. Single-photon dissociation at 240 nm releases most of the excess energy into relative translation (53%) and NH_2 internal energy (40%, mostly vibrational). OH carries little internal energy (7%), most of it in the form of rotational excitation. One- and two-dimensional potential functions explain the OH product state distributions observed in different experiments in terms of the geometry relaxation of NH_2OH upon electronic excitation. The formation of OH and NH_2 in their electronic ground states is the main channel of the photodissocia-

tion of hydroxylamine at wavelengths above 240 nm. A presumably small proportion of NH_2 radicals are formed in the first excited state. The NH_2 fragments are produced with significant internal energy, accounting for half of the available energy at 240 nm, most likely in the form of vibrational excitation.

Hydroxylamine is a particularly interesting example for the study of non-adiabatic effects in photodissociation. It has a weak N—O bond, with a bonding energy of about 259 kJ/mol (~62 kcal/mol) that can be broken photochemically:



Conical intersections of two states of the same symmetry are usually considered rare and are not frequently observed. The existence of conical intersections of two states of the same symmetry was investigated for the four lowest electronically excited states of NH_2OH using computational methods based on configuration interaction wave functions [72]. The calculation results indicate the existence of “same-symmetry” conical intersections, which may play a role in the photodissociation of HA:



Although the ground electronic state has C_s symmetry (with two equivalent hydrogens), less symmetrical configurations play a role in NH_2OH photodissociation. Similar effects may take place in photolysis of HAN.

1.3.2 Reactions of Hydroxylamine Free Base

1.3.2.1 Reactions with Inorganic Substances

Alkaline solutions of HA free base autoxidize quite readily when exposed to air [73, 74].

Analytical methods for hydroxylamine free base are discussed in a following chapter describing analytical methods for the most important (for rocket applications) hydroxylammonium salt, hydroxylammonium nitrate. The analytical methods for the free base and for its salts are very similar. Hydroxylamine may act as an acid and form salts with sodium or calcium metal in which the analogs to sodium amide or calcium amide are formed, but these salts are unstable and not well characterized.

NH_2OH reacted with ClO_3F at 203 to 293 K (–70 to +20 °C) in EtOH to form $(\text{NH}_3\text{OH})\text{F}$ and unstable $(\text{NH}_3\text{OH})\text{ClO}_3$. $(\text{NH}_3\text{OH})\text{ClO}_3$ decomposed to $(\text{NH}_3\text{OH})\text{NO}_3$ and ClO_2 [75].

Redox Reactions of Hydroxylamine

Hydroxylamine is a reducing agent. The reducing potential depends on the pH of the solution and is strongest if the solution remains caustic, which would liberate some hydroxylamine as the free base. Redox reactions of hydroxylammonium salts, including HAN, are of interest as analytical methods and for the disposal of surplus HAN. Redox reactions catalyzed by traces of transition metals may be responsible for the

limited storage stability of hydroxylamine free base. The most commonly encountered contaminant metal ion is iron in its bivalent state as Fe^{2+} , which forms complexes with hydroxylamine. The working principle of stabilizers and iron scavengers such as α, α' -dipyridyl is based on formation of such complexes.

A study of the kinetics of redox reactions of hydroxylamine and hydroxylammonium with Fe(III) showed that the results obtained were consistent with a mechanism dependent on the relative iron(III)-to-hydroxylamine concentrations [76, 77]. An excess of iron(III) gave a stoichiometry of 2:1 for the total reaction and N_2O as the oxidation product, whereas at equal amounts or excess of hydroxylamine, the stoichiometry reduced to 1:1 with N_2 as the main product.

Reactions with Acids

Acid–base reactions of hydroxylamine free base with various acids lead to the corresponding hydroxylammonium salts. This is the most straightforward and most versatile method for preparing hydroxylammonium salts (Section 3.2.1), but chemically it is not very exciting (as long as one keeps the solutions cool enough to prevent runaway reactions). The most important reactions of hydroxylamine free base are redox reactions in which the amine is the fuel and an associated anion is the oxidizer. These reactions are intermediate steps in the decomposition of hydroxylammonium salts, HAN in particular. A more detailed discussion of HAN decomposition reactions is offered in Section 1.3.5.

1.3.2.2 Reactions with Nitrous Acid

The reaction of hydroxylamine (hydroxylammonium ion) with nitrous acid is an important step in the decomposition of HAN [78]. The reaction of hydroxylammonium hydrochloride and ^{15}N -enriched sodium nitrite in solution in ^{18}O -enriched water led to formation of equal quantities of $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{14}\text{N}^{16}\text{O}$. When the same reaction was carried out at a pH of 1, an excess of $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ was produced. In both experiments, the concentration of $^{15}\text{N}^{15}\text{N}^{16}\text{O}$ was accounted for on the basis of the reaction of nitrous acid with hydroxylamine to yield nitrous oxide molecules containing one nitrogen atom from each source. ^{18}O exchange occurred to a greater extent in acidic media, and the double-tagged N_2O so produced was mainly $^{14}\text{N}^{15}\text{N}^{18}\text{O}$ rather than a mixture of the isomers $^{14}\text{N}^{15}\text{N}^{18}\text{O}$ and $^{15}\text{N}^{14}\text{N}^{18}\text{O}$. These observations led to the conclusion that in neutral solutions, most of the nitrous oxide produced is formed by dehydration of a symmetrical intermediate, probably hyponitrous acid ($\text{HO}-\text{N}=\text{N}-\text{OH}$). In acidic media, a competitive dehydration of an unsymmetrical intermediate plays an important role. Mechanisms involving nitroxyl as an intermediate are less likely. Oxygen exchange is acid-catalyzed and occurs exclusively with nitrous acid or with an unsymmetrical intermediate formed in the course of this reaction. Oxygen atoms from either nitrous acid or hydroxylamine appeared in the product nitrous oxide. See also [79, 80].

1.3.2.3 Reactions with Organic Compounds

For reactions of organic compounds with hydroxylamine free base, the most important reactions are those with ketones and aldehydes, leading to ketoximes and aldoximes. These compounds are less soluble and are often used as intermediates in the isolation, identification, and purification of ketones and aldehydes because they can be hydrolyzed to release the pure ketone or aldehyde. In addition, the rearrangement of cyclohexanone oxime to ϵ -caprolactam is an important method for the production of nylon-type polyamides.

1.3.2.4 Proton Affinity of Hydroxylamine and Reverse Dissociation of Hydroxylammonium Salts

Reverse dissociation is part of the hydrolysis of salts in aqueous solution. The pK_b of hydroxylamine is 8.13. There have been investigations trying to explain why the pK of hydroxylamine is so high. It has been attempted to explain this abnormality by the strong hydrogen bonding and ion clustering in concentrated solutions.

1.3.2.5 Basicity Constant of Hydroxylamine Free Base

Hydroxylamine is a weak base and is less caustic than its parent base, ammonia. The proton affinity of hydroxylamine and the basicity constant have been studied extensively (Table 4). This parameter is important for the thermal and long-term storage stability of all propellants based on hydroxylammonium salt solutions because a very small percentage of free base exists in an equilibrium even in an acidic medium, and it may be the reason for lack of storage stability. Thus, if the basicity could be increased by synthesizing HA derivatives, it might lead to more storable propellants.

The pH in a solution of hydroxylamine is determined by

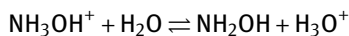
$$\text{pH} = \frac{1}{2}pK_h - \frac{1}{2}\log(Cf_{H^+} - a_{H^+})f_{\text{NH}_3\text{OH}^+}$$

where C is the concentration of NH_2OH , a_{H^+} is the activity of the H^+ ion, and f_{H^+} and $f_{\text{NH}_3\text{OH}^+}$ are the activity coefficients of H^+ and NH_3OH^+ ions [83]. On average, K_h was reported as 1.04×10^{-6} at 298 K. From this, K_a was calculated as $K_a = a_{\text{NH}_3\text{OH}^+}a_{\text{OH}^-}/a_{\text{NH}_2\text{OH}} = 0.97 \times 10^{-8}$, which corresponds to $pK_a = 8.02$, which is quite different from later results.

Table 4: Summary of basicity and acidity constants of hydroxylamine free base.

pK_0	Ionic strength	Remarks	References
6.04	1 M	Spectrophotometric	[52]
6.09		Colorimetric	[81]
5.95		At 298 K, glass electrode	[82]
5.98			[83]

The protolysis of hydroxylamine takes place by the following equilibrium:



The ionization constant for this system is

$$K = \frac{[\text{H}^+][\text{NH}_2\text{OH}]}{[\text{NH}_3\text{OH}^+]}$$

The ionization constants of NH_2OH in aqueous NaClO_4 solutions were determined by potentiometric titration at 288, 293, 298, and 308 K (15, 20, 25, and 35 °C) [82]. The thermodynamic values, pK_0 , of the ionization constant of nitrous acid were obtained by extrapolating the pK values to zero ionic strength. NH_2OH was titrated at four different ionic strengths, 0.04, 0.25, 1.00, and 2.25, with ~0.1M NaOH in NaClO_4 solutions. The pK value follows from

$$pK = \text{pH} - \log \left\{ \frac{(C_B + [\text{H}^+])}{[C - (C_B - [\text{H}^+])]} \right\}$$

where $\text{pH} = -\log [\text{H}^+]$, C_B is the total concentration of the added strong base, and C is the total concentration of the NH_2OH . The pK of NH_2OH depends on the ionic strength, I , of the solution in a linear fashion: $pK = pK_0 + BI$, where K_0 is the thermodynamic ionization constant and B is a constant, both depending on the temperature. The thermodynamic protolysis constant K_0 of NH_2OH depends on the temperature, as in

$$\log K_0 = -\left(\frac{a}{T}\right) - cT + b$$

where the constants a , b , and c for hydroxylamine were calculated by the least-squares method based on the values of pK_0 found by titration and obtained as $a = 2.7757 \times 10^{-3}$, $b = 5.8899$, and $c = 8.4782 \times 10^3$. The values of the $-\log K_0$ found were practically linear in $1/T$ and showed the acid strength of the weaker acid, NH_2OH , to increase more rapidly than that of HNO_2 . The pK_a of hydroxylamine at 298 K was 5.95.

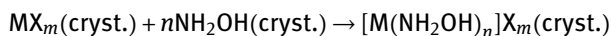
Changes in standard free energies, entropies, enthalpies, and heat capacities of the protolytic reactions of NH_2OH could be calculated once the values of a , b , and c were known. For instance,

$$dH^\circ = 2.303 R(a - cT^2)$$

where $R = 1.9873 \text{ cal K}^{-1} \text{ mol}^{-1}$; dH° is positive, and hence the ionization reactions are endothermic; dH° decreases slightly with increasing temperature; $-\log K_0$ has a minimum value at a certain temperature, $T_{\min.} = (a/c)^{0.5}$. NH_2OH has a $T_{\min.}$ of 572 K at $\log K_{0\min.} = -3.81$, which is in the same temperature range as for H_2O .

1.3.3 Hydroxylamine Free Base as a Ligand in Complexes

Similar to aquo and ammino complexes with water or ammonia as ligands in the hydration (complexation) sphere surrounding metal cations, hydroxylamine free base can form hydroxylammino complexes with many cations [84]. Those involving oxidizing cations (nitrate, perchlorate) are explosive and can potentially be used as propellant ingredients, but they may be too sensitive to be produced in large quantities. The shock sensitivity and thermal stability of these compounds has not yet been measured. In the case of lithium, three or one hydroxylamine fill the solvate sphere, and in the case of earth alkaline metals, the number of NH_2OH ligands can be 6, 3, 2, or 1, depending on the size of the cation and the method of preparation. Starting with complexes containing the highest number of ligands, lower complexes can be obtained by slowly evaporating the volatile ligand under vacuum at temperatures below the explosive ignition temperature. In order to calculate the enthalpy of reaction and the standard enthalpies of formation, the heat of sublimation of solid hydroxylamine had to be known. This number was assumed to be 64.18 kJ/mol (15.34 kcal/mol), and the standard enthalpy of formation of hydroxylamine free base was assumed to be -115 kJ/mol (-27.5 kcal/mol), based on some antiquated measurements. The uncertainties with these numbers are carried over into the subsequent calculations. The enthalpies of the reactions



and the standard enthalpies of formation of a group of hydroxylammino complexes with oxidizing anions X in the solid state were calculated and measured calorimetrically [85, 86]. The results are summarized in Table 5 in comparison to the heats of formation of the metal salts from which they were derived. The data were calculated assuming an enthalpy of formation of -115 kJ/mol (-27.5 kcal/mol) for solid hydroxylamine, which is an antiquated number. It would be of interest to compare the thermal stability of the hydroxylammino complex nitrates and perchlorates to that of HAN and perchlorate. Is the complexation in a sphere of solvation, or is the protonation more effective in stabilizing the otherwise unstable hydroxylamine molecule? The strength of ligands bonding in the sphere of coordination of lithium and alkaline earth-metal perchlorates decreases in the order $\text{N}_2\text{H}_4 > \text{NH}_2\text{OH} > \text{NH}_3 > \text{H}_2\text{O}$. The stability of the complexes also influences their heat of dissolution in water, which was also measured and tabulated (but not displayed here).

Table 5: Standard enthalpies of formation of hydroxylammino complexes and the metal perchlorates from which they are derived.

Formula of complex	Molecular mass	Enthalpy of reaction		ΔH_f , crystalline MX_m		ΔH_f , crystalline $[M(NH_2OH)_n]X_m$	
		kJ/mol	kcal/mol	kJ/mol	kcal/mol	kJ/mol	kcal/mol
$[Li(NH_2OH)_3]ClO_4$	205.48	-72.8	-17.4	-381.2	-91.12	-799.1	-191
$[Mg(NH_2OH)_6](ClO_4)_2$	421.39	-203.8	-48.7	-563.6	-134.71	-1457.7	-348.4
$[Ca(NH_2OH)_6](ClO_4)_2$	437.16	-107.9	-25.8	-735.4	-175.76	-1533.9	-366.6
$[Ca(NH_2OH)_3](ClO_4)_2$	338.07	-75.7	-18.1	-735.4	-175.76	-1156.5	-276.4
$[Ba(NH_2OH)_3](ClO_4)_2$	336.24	-40.2	-9.6	-774.3	-185.06	-1159.8	-277.2
$[Mg(NH_2OH)_2](ClO_4)_2$	289.27	-104.6	-25	-563.6	-134.71	-898.3	-214.7
$[Ba(NH_2OH)](ClO_4)_2$	369.27	-8.8	-2.1	-774.3	-185.06	-898.3	-214.7
$[Li(NH_2OH)]NO_3$	101.96	-10.5	-2.5	-483.1	-115.47	-608.8	-145.5
$[Mg(NH_2OH)_2](NO_3)_2$	214.38	-71.1	-17	-876.5	-209.5	-1092.4	-261.1
$[Ca(NH_2OH)_2](NO_3)_2$	230.15	-61.5	-14.7	-938.6	-224.33	-1230.1	-294

Data source: [85, 86]

1.3.4 Analysis of Hydroxylamine Free Base

For rocket applications it will be relatively rare that one has to analyze hydroxylamine free base, but the analysis of any hydroxylammonium salt can be performed using the same methods by first bringing the sample to an alkaline pH, liberating the free base. There is another section on analysis of hydroxylammonium salts in Section 3.4.4.

Hydroxylamine ($<3 \times 10^{-3}$ mol/L) can be quantified by UV spectrophotometry after reaction with an excess of formaldehyde in a buffered solution at pH 12.2. The absorbance of the formaldoxime produced is measured at 218 nm when hydroxylamine is alone but at 230 nm when monochloramine is present, which may interfere with the analysis [87].

Hydroxylamine can be determined by its oxidation to nitrite with a known excess of bromine [88]. Bromine in acidic medium bleaches the dye methyl red. A known excess of bromine when treated with hydroxylamine is reduced to bromide, and the unreacted bromine is determined using methyl red. The method obeys Beer's law in the range 0–5 μ g of hydroxylamine in an overall aqueous volume of 25 mL. The relative standard deviation is 2.7% ($n = 10$) at 3 μ g of hydroxylamine.

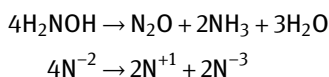
Hydroxylamine in mixtures with other hydroxylamines or hydrazines can be analyzed by first derivatizing the mixture with acetone, extracting the oximes and hydrazones with ether, drying, stripping the solvent, and injecting the extract into a gas chromatograph [89].

1.3.5 Thermal Decomposition of Hydroxylamine Free Base

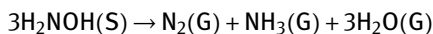
This is one of two sections in this book on the decomposition of hydroxylamine. This is the one discussing only the mechanisms (which are closely interrelated to the mechanisms of decomposition of HA salts as monopropellants) and thermal decomposition from a more academic point of view. The section following this one discusses the explosive hazards in the production and handling of HA free base. In the wake of several industrial accidents with hydroxylamine free base, the thermal decomposition of hydroxylamine and hydroxylamine solutions has been thoroughly investigated. At this point, there does not seem to be any plan to use hydroxylamine free base as a rocket propellant (and that is for a good reason!). But it may be used as an intermediate in the preparation of hydroxylammonium salts for other monopropellants, and that is one reason why we write here about hydroxylamine free base. For actual experimental decomposition and flame studies with hydroxylamine free base, see a later chapter on monopropellants (*Encyclopedia of Monopropellants*).

The useful life of HAN-based monopropellants is limited by the slow decomposition of HAN, often associated with gas evolution and the potential of overpressurizing a storage tank. One of the proposed mechanisms for HAN decomposition puts the blame of insufficient stability not on HAN but on the small amount of HA free base present in the hydrolysis equilibrium. This is why we included a chapter on the decomposition of HA free base in this book. In order to better understand the decomposition of HAN, we will need to look at the decomposition of HA free base first, and then examine what stabilizing effect (if any) the protonation of HA has. It appears that the presence of even a small amount of HA free base significantly decreases the thermal stability of HAN.

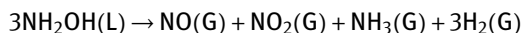
It is best to store pure hydroxylamine free base samples in a refrigerator or freezer. The pure, anhydrous hydroxylamine molecule is not stable at room temperature but decomposes slowly to nitrous oxide, water, and ammonia:



The heat of reaction according to the equation

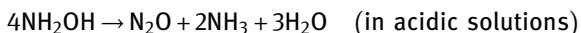
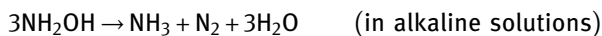


is 4.3 kJ/g, which is very close to the heat release observed in differential thermal analysis (DTA) and differential scanning calorimetry (DSC) experiments with HA and HA solutions. Another reaction sequence allows for formation of hydrogen



but the energy release of this reaction (between 117 and 133 kJ/mol [28 and 32 kcal/mol], depending on which source of information is trusted) is in disagreement with the exothermicity of HA decomposition under many different conditions (with and without the presence of catalysts).

Additional references describe the complex nature of the HA decomposition reaction system by addressing the possibility of different distinct pathways depending on the pH:



Both of these reactions are exothermic.

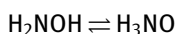
Calorimetric data for the thermal decomposition of 50 mass-% hydroxylamine/water (HA) in air, both with and without added stabilizers, were measured in closed cells with an automatic pressure-tracking adiabatic calorimeter (APTAC) [90, 91]. The explosive hazard potential was assessed based on the onset of exotherm temperatures, reaction order, activation energies, pressures of non-condensable products, thermal stability at 373 K (100 °C), and effect of HA storage time on stability. The catalytic effects of carbon steel, stainless steel, stainless steel with silica coating, Inconel, titanium, and titanium with silica coating on the reaction self-heat rates and onset temperatures were examined. In borosilicate glass cells, HA was relatively stable at temperatures up to 406 K (133 °C), where the HA decomposition self-heat rate reached 0.05 °C/min. In borosilicate glass cells, there was no significant difference in the onset temperature of HA thermal decomposition reaction with or without stabilizers. The onset temperatures were 406 K (133 °C) and 409 K (136 °C), respectively. The added stabilizers appeared to reduce HA decomposition rates in glass cells and at ambient temperatures. The tested metals and metal surfaces coated with silica acted as catalysts to lower the onset temperatures and increase the self-heat rates. An older sample without stabilizer stored for more than 5 months exhibited a much more energetic decomposition, with an onset temperature of 340 K (67 °C) and a maximum self-heat rate of 132 K/min (132 °C/min), compared with an onset temperature of 409 K (136 °C) and a maximum self-heat rate of 5 K/min (5 °C/min) for a recently received or “new” sample. In both stainless steel and titanium sample cells, the maximum self-heat rate of the HA with stabilizers was lowered by a factor of ~8 compared to the HA without stabilizers. The overall decomposition reaction was modeled with first-order kinetics and indicated an activation energy of ~121–142 kJ/mol (~29–34 kcal/mol).

In continuation of this work, the thermal stability of several members of the hydroxylamine family was studied using adiabatic calorimetry [92]. The study included aqueous solutions of hydroxylamine free base, hydroxylammonium chloride, hydroxylammonium sulfate, and hydroxylamine-*O*-sulfonic acid of concentrations typically used in industry. The catalytic effect of metal surfaces of stainless steel, carbon steel, and titanium was examined. From all the solutions studied, HA free base was the most reactive, displaying higher maximum temperature, pressure, non-condensable pressure, and shorter delay times to maximum rate. The HA free base maximum heat rate was at least about three times faster than that of the other solutions studied, and the pressure rise rate was about 13 times faster. The decomposition reactions of all samples were catalyzed by stainless steel, but only HA free base was catalyzed

significantly by titanium metal. Solid hydroxylammonium chloride, hydroxylammonium sulfate, and hydroxylamine-*O*-sulfonic acid exhibited some stability but only up to ~333 K (~60 °C). A violent reaction occurred with solid hydroxylammonium sulfate that generated a heating rate of >500 K/min (>500 °C/min) and pressure-rise rate >35.8 MPa/min (>5200 psia/min) before the sample cell was completely destroyed by the generated pressure.

Under adverse conditions, the decomposition of pure HA free base compound can take place with explosive force, as several manufacturers of hydroxylamine free base have, unfortunately, found out the hard way (Section 1.4 below).

The rate of HA decomposition and its reaction pathway is dependent on the presence of acids or other bases [93, 94]. This is of particular interest for the study of the decomposition of HAN and other HA salts. The thermokinetic data, such as onset temperature, heat of reaction, maximum self-heat rate, maximum pressure-rise rate, and non-condensable gas pressure, were compared with those of hydroxylamine solution without added impurities. The study showed that the thermal decomposition behavior of hydroxylamine free base is affected by the presence of acid/base, and mixing of hydroxylamine with acid/base may cause inadvertent thermal decomposition at lower than expected temperatures. One of the postulated intermediates in HA decomposition is its isomer and tautomer, ammonia oxide [58, 95]:



Ammonia oxide, a zwitterionic tautomer of hydroxylamine, has been scrutinized as an intermediate to explain the high reactivity of NH_2OH . Some evidence has shown that ammonia oxide exists in the condensed phase and aqueous solution [96]. Ammonia oxide may play a role not only during decomposition of hydroxylamine but also during synthesis of hydroxylamine by oxidation of ammonia. Thermochemical parameters of ammonia oxide were calculated, under standard conditions, using isodesmic reactions at several theoretical methods and several basis sets in comparison to hydrogen peroxide [97]. The quantum chemistry calculations predict the value of molar enthalpy of formation to be 55.7 ± 2.9 kJ/mol and molar Gibbs energy of formation to be 103.8 ± 2.9 kJ/mol, for gaseous ammonia oxide at 1 atm and 298.15 K. The determined molar entropy and molar heat capacity at constant volume, also at 1 atm and 298 K, are 221.1 ± 0.1 J mol⁻¹ K⁻¹ and 28.9 ± 0.3 J · mol⁻¹ · K⁻¹, respectively.

Hydroxylamine isothermal decomposition measurements were performed in the temperature range of 353–433 K (80–160 °C) using an isothermal calorimeter equipped with a pressure-resistant glass reactor and an APTAC employing glass and titanium cells [98]. Reaction products were identified via UV, high-performance liquid chromatography (HPLC), and ion chromatography. Dilute aqueous solutions of hydroxylamine free base (<50% NH_2OH) and HAN solutions (<18% NH_3OHNO_3) were kept at constant temperature for different lengths of time in closed glass cells in an APTAC at 403, 413, and 413 K (130, 140, and 150 °C) and in a closed titanium cell at 403 K (130 °C). There was no evidence of HA decomposition in a glass cell at 403 K (130 °C) during

the 1200 min of the experiment. At 413 K (140 °C), a measurable rate of decomposition started at approximately 300 min. At 413 K (150 °C), decomposition started faster and resulted in immediate reactor venting. In titanium instead of glass, the HA decomposition reaction developed as soon as the cell was heated to reach the desired temperature of isothermal operation, 403 K (130 °C), and its very rapid pressure rise activated the pressure-relief system.

In the wake of several industrial accidents involving hydroxylamine, several studies were devoted to the effect caused by possible contaminants in the reacting mixtures, such as transition metal ions and, in particular, iron ions.

The thermal behaviors of HA free base, hydroxylammonium chloride, and HAN solutions under redox reaction conditions were investigated using a small-scale reaction calorimeter and UV-visible spectroscopy [99]. Generally the free base was more reactive than its salts. The reactions were triggered by aqueous solutions of transition metals, including Cr^{3+} , Cr^{6+} , Mn^{7+} , Co^{3+} , Co^{2+} , and Cu^{2+} . All exothermic reactions were accompanied by precipitation or a change in the UV-visible spectra. The UV-visible spectra indicated that the transition metals, such as Cr^{6+} and Mn^{7+} , were reduced in solutions of NH_3OHCl or NH_3OHNO_3 . HA as a weak base provided precipitation of hydroxides upon contact with all metals. All metals, except Cr^{3+} , continuously reacted with HA. An induction period was observed for the reaction of HA with Co^{3+} .

In the case of reaction of HA and its salts with iron ions, Fe^{3+} was found to trigger an exothermic reaction, especially in HA [100]. The finding on the effect of iron on the decomposition of 50% HA solution is particularly relevant in the effort to explain the causes of several explosions involving HA solutions where iron contamination was suspected.

The thermal decomposition behavior of 50% HA in contact with iron in the form of iron(III) oxide, ferrous ion, and ferric ion was quite different from that of pure HA solutions [101]. HA in contact with iron ion (Fe^{3+} or Fe^{2+}), even in small concentrations and at ambient temperatures, reacted violently to produce a bubbling, foamy system. A great amount of energy, close to 4 kJ/g, was released in a very short period of time, which resulted in boiling of the reaction mass. The measured heat of reaction for hydroxylamine without iron ion was 3.78 kJ/g. Rust caused heterogeneous iron catalysis of the reaction, which was not as violent as homogeneous iron catalysis, where even 0.0004 mol-% (10 ppm) of iron ion added at room temperature triggered the complete decomposition of hydroxylamine.

The transition-metal-catalyzed oxidation (not only decomposition) of HA has been used to analyze solutions with parts-per-billion (ppb) concentrations of ions by thermometrically measuring the rate of heat evolution that is proportional to the amount of contaminating ions (iron or copper).

The runaway-reaction gaseous decomposition products of 50% HA in the absence of air are H_2 , N_2 , N_2O , NO , and NH_3 , with traces of NO_x possible [102]. The presence or absence of air does not have much effect on the product composition: The gas-phase HA decomposition products under runaway conditions for samples run with and with-

out air were N_2O , N_2 , NO , and H_2 . Ammonia was detected in the liquid condensate. Water may be a reaction product, but because the mixture contained water to start with, its source cannot be determined.

One possible source of ignition of HA during vacuum distillation could be the intrusion of air. However, based on APTAC data, the overall kinetics, onset temperatures, non-condensable pressures, times to maximum rate, heat and pressure rates vs. temperature, and mixture vapor pressures for the experiments in vacuum were similar when compared to the corresponding data for HA decomposition in air [103, 104]. The overall activation energy of $119 \pm 8 \text{ kJ/mol}$ ($29 \pm 2 \text{ kcal/mol}$) is low compared to the 257 kJ/mol (61.3 kcal/mol) required to break the $\text{H}_2\text{N}-\text{OH}$ bond reported in the literature. The availability of oxygen from air did not affect detected runaway decomposition products, which were H_2 , N_2 , N_2O , NO , and NH_3 , for samples run in vacuum or with air in contact with the sample. A heat of reaction ΔH_{rxn} of -117 kJ/mol (-28 kcal/mol) was estimated for the HA decomposition reaction under runaway conditions.

Hydroxylamine thermal decomposition proceeds via a network of parallel and sequential reactions involving short-lived intermediates. The type of intermediates and the rates of their formation and destruction are dependent on the operating conditions of the reactor. One cannot operate with pure hydroxylamine at atmospheric pressure because the reaction would be too fast to be analyzed. One has to use a diluent or operate at reduced pressure. Because of its thermal instability and the high pressures produced by its decomposition, for safety reasons the hydroxylamine sample sizes must be small. Because of the very small samples, the potential analytical techniques that can be employed for the identification and quantification of unstable, and even some stable, intermediates must be very sensitive and rapid. Liquid samples of less than 0.5 mL can be withdrawn from the glass reactor to be further analyzed via UV, HPLC, and ion chromatography. The simultaneous identification and quantification of coexisting ammonia, nitrates, nitrites, and other nitrogen bases is difficult.

The thermal decomposition of hydroxylamine was studied via isothermal and isoperibolic calorimetric measurements in a glass and in a metal reactor [105]. Identification of stable intermediates such as ammonia, nitrates, or nitrites during the course of the reaction did not provide any conclusive results about the reaction mechanism. Calorimetric measurements revealed condition-dependent endothermic and exothermic reaction steps that were consistent with previous results based on computational chemistry. These findings corroborate previously reported theories, according to which the NH_2^- moiety (the formation of which is favored in strongly basic solutions) may trigger runaway reactions.

While most of the previous studies used only dilute solutions of HA with a maximum concentration of 50 mass-%, the following study included work with higher concentrations of HA free base. The thermal decomposition of HA/water solutions was studied based on calorimetric data obtained using DTA, a miniature closed-bomb pressure vessel test (MCPVT), a pressure vessel test (PVT), and a steel

tube test [106, 107]. The exotherm onset temperatures using untreated stainless steel cells were more than 70 K below those measured using a glass apparatus. This implies that the exotherm onset temperature depends on the materials of the sample cells. On the other hand, the heat of reaction did not depend on the materials of the sample cells. The intensity of the thermal decomposition increased greatly when the HA concentration was beyond 80 mass-% in the MCPVT. The thermal decomposition of 70 mass-% HA solutions was very violent in the PVT. In addition, HA/water solutions containing more than 80 mass-% HA could detonate in the steel tube test; 80 mass-% HA was easily detonated by a detonator without RDX booster in the steel tube test.

In addition, the decomposition hazard of HA/water solution by the metal ion and iron powder was investigated in this study. The thermal stability of 85 mass-% HA/water solution with iron ion or iron powder was expressed by the exotherm onset temperature by DTA. The exotherm onset temperatures decreased when the concentration of the iron ion or iron powder increased in the DTA measurements. The reactivity of HA/water solution with metal ions of iron, manganese, nickel, chromium, and copper was examined by measuring the mass loss of HA/water solution after the metal ion was added to it at room temperature. The reactivity of HA/water solution with the iron powder was also studied. Ferrous ion, ferric ion, and iron powder reacted vigorously with HA/water solutions [108]. Ignition was spontaneous when the 0.2 mass-% ferric ion solution was added to 85 mass-% HA/water solution. The decomposition reaction of 85 mass-% HA/water solution with Cu^{2+} was calm compared to that of the iron ion. HA/water solutions did not react with Mn^{2+} , Ni^{2+} , or Cr^{3+} at room temperature.

In a DTA apparatus with both gold-plated sample holder cells and plain stainless steel sample holders, 50% HA solutions showed an onset of exotherm at 339 K (66 °C) in the stainless steel cell and 414 K (141 °C) in the gold-plated cells [109].

Several types of carbon catalyze the decomposition of hydroxylamine free base or hydrazine free base [110]. The hydrazine decomposition involves the formation of the diazene $\text{HN}=\text{NH}$ intermediate. The hydroxylamine decomposition probably involves nitroxyl (HNO) or its dimer as an intermediate. HA decomposition is catalyzed by metals on carbon to give N_2 , NH_3 , N_2O , and hyponitrite in varying proportions depending on the catalyst and conditions. The reaction mechanisms of hydrazine and hydroxylamine decomposition are quite different.

Measurements of the heat of explosion of hydroxylamine free base were performed in a metal reactor, employing 30–80 mL solutions containing 1.4–20 g of pure hydroxylamine free base [111]. The measurements showed that increased concentration or temperature resulted in higher global enthalpies of reaction per unit mass of reactant. At 423 K (150 °C), specific enthalpies as high as 8 kJ per gram of hydroxylamine were measured, although in general they were in the range of 3–5 kJ/g.

Because NH_2OH is formed as an intermediate in the metabolism of nitrate-reducing and ammonia-oxidizing bacteria, it was of interest to study the disproportionation of HA solutions in abiotic, anaerobic media [112]. The catalytic disproportionation of NH_2OH has been studied in anaerobic aqueous solutions at pH 6–9.3 and 298 K (25 °C), with $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ as a precursor of the catalyst $[\text{FeII}(\text{CN})_5\text{H}_2\text{O}]^{3-}$. The oxidation products are N_2 , N_2O , and NO^+ (bound in the nitroprusside ion, NP), and NH_3 is the reduction product. The yields of $\text{N}_2/\text{N}_2\text{O}$ increased with pH and with the concentration of NH_2OH . An intermediate absorbing at 440 nm was always observed, whose formation and decay depend on the medium conditions. It was identified by UV-visible and ^{15}N nuclear magnetic resonance (NMR) spectroscopies as the diazene-bound $[\text{FeII}(\text{CN})_5\text{N}_2\text{H}_2]^{3-}$ ion.

Several density functional and *ab initio* methods were used in conjunction with several basis sets to theoretically investigate the initial thermal decomposition steps of HA, including both unimolecular and bimolecular reaction pathways [113]. The theoretical investigation showed that simple bond dissociations and unimolecular reactions are unlikely to occur. The energetically favorable and most likely initial step of decomposition pathways was a bimolecular isomerization of hydroxylamine into ammonia oxide with an activation barrier of 104.6 kJ/mol (25 kcal/mol). Solvent effects on the initial decomposition pathways were also studied using water-cluster methods and the polarizable continuum model. In water, the activation barrier of the bimolecular isomerization reaction decreased to 67 kJ/mol (16 kcal/mol). The results indicated that the bimolecular isomerization pathway of hydroxylamine is more favorable in aqueous solutions than in the anhydrous material. The bimolecular nature of this reaction means that more dilute aqueous solution will most likely be more stable.

It is not likely that gold will ever be used as a catalyst, but a combined anion photoelectron spectroscopic study and density functional theory computation of the reaction between a single hydroxylamine molecule and a single gold atomic anion, Au^- , showed that an Au^- anion can activate a hydroxylamine molecule by inserting into its N–O bond [114]. This reaction is facilitated by the presence of two minimum-energy crossing points, i.e., spin flips, along the reaction pathway. Other metal anions may have similar activity.

1.4 Explosive Hazards of Hydroxylamine Free Base

The explosive hazard of hydroxylamine free base has been known for a very long time, and precautions for handling this material have been advised in the literature [115]. Hydroxylamine free base would not be used as a rocket propellant, but it is a very useful intermediate in the preparation of hydroxylammonium salts, which are used as rocket or torpedo propellants.

Despite all precautions, two explosions within a few years of each other occurred during the production of 50% HA solutions by distilling HA under reduced pressure.

On 19 February 1999 at 8:14 P. M., a process vessel containing several hundred pounds of HA exploded at the Concept Sciences, Inc. (CSI) production facility in Hanover Township near Allentown, Pennsylvania (Figure 4). Employees were distilling an aqueous solution of HA and potassium sulfate, the first commercial batch to be processed at CSI's new facility. After the distillation process was shut down, the HA in the process tank and associated piping explosively decomposed, most likely due to high concentration and temperature. Four CSI employees and a manager of an adjacent business were killed. Two CSI employees survived the blast with moderate to serious injuries. Four people in nearby buildings were injured. Six firefighters and two security guards suffered minor injuries during emergency response efforts. The production facility was extensively damaged. The force of the explosion produced a crater 4 feet deep and approximately 18 feet in diameter in the floor of the CSI plant. The Federal Emergency Management Agency/U.S. Fire Administration Accident Investigation Board has issued a detailed accident investigation report on this event [116]; also [117]. Immediately prior to the accident that destroyed the CSI plant, the final step in their routine production of HA from hydroxylamine sulfate was a vacuum distillation at 323 K (50 °C), which is well below the temperatures for significant decomposition rates of HA in glass cells reported by various other investigators.



Figure 4: Aerial view of the CSI plant after the explosion. (Photo courtesy of David Lesak, Chief of Lehigh County Hazmat Team – Retired.)

Shortly after the CSI disaster, on 10 June 2000, a factory at Nissin Chemical in Gunma Prefecture in Japan was destroyed by a similar explosion [118–120]. The explosion in a factory where HA/water solutions were manufactured damaged all houses within a radius of 1500 m (4500 ft), and broke many windows. The explosion killed four people and injured 58 others. In a distillation fractionation tower, 50% HA was produced and purified by distilling an 85% HA solution under reduced pressure. The 85% solu-

tion was not a commercial product and existed only as a process stream at this factory. A vessel containing the 85% HA solution was completely destroyed by the explosion. The post-accident investigation concluded that the initial detonation occurred in the 750–800 L of 85% HA solution and the piping leading to and from the reboiler.

In the wake of these two back-to-back explosions, the chemical industry worldwide scrambled to develop a safer process and build replacement production facilities. A quantitative risk assessment is useful for analyzing what went wrong and for developing a safer process if facilities are to be repaired and rebuilt [36].

Because of the explosion hazard and transportation safety restrictions, hydroxylamine free base is available commercially only as a 50 mass-% solution (with a proprietary stabilizer). A common abbreviation for this chemical product is FH-50 (free hydroxylamine–50% solution). It is widely used in the semiconductor integrated circuit industry to remove photoresist masks without leaving any residues. See also [121, 122].

1.5 Experimental Studies on HA as an Energetic Substance

In studying the detonation behavior and as part of the accident investigation, samples containing various concentrations of HA were placed in glass or polyethylene cylinders inside a steel tube and subjected to confined detonability tests [109]. The sample size was either 40 mL in a 25-mm–inner diameter (ID), 200-mm–long glass tube or 980 mL in a 50-mm–diameter, 500-mm–long polyethylene bag in a steel tube. The initiation was with RDX charges or, in one case, with a blasting cap without a booster charge. When detonation occurred, the steel tube was fragmented into six or more pieces. The results are summarized in Table 6.

Table 6: Detonability of hydroxylamine free base solutions

NH ₂ OH concentration, mass-%	Ignition method	Result
90	Detonator + 10 g RDX	Detonation
85	Detonator alone, no RDX	Detonation
85	Detonator + 2 g RDX	Detonation
80	Detonator + 10 g RDX	Detonation
70	Detonator + 10 g RDX	No detonation
50	Detonator + 50 g RDX	No detonation
0 (blank test)	Detonator + 10 g RDX	No detonation

Data source: [109]

As of 2016, FH-50 was available from BASF (Germany), Hangzhou Dayangchem Co. Ltd. (China), and CellMark AB (Sweden), among others. The same three companies also offered HAN solutions.

1.5.1 Theoretical Studies on HA as an Energetic Substance

Several publications describing computational chemistry studies of the molecular structure of the H_2NOH molecule can serve as a base for subsequent hazard analysis and were described in Section 1.2.4. Once the enthalpy of formation of an energetic molecule is obtained by either computer models or calorimetric experiments, the data can be plugged into a reactive hazard analysis model such as CHETAH to calculate the explosion pressure.

1.6 Stabilizers for Hydroxylamine Free Base

Commercially used stabilizers for FH-50 are usually not identified on the product label. That is deplorable because if the HA solution is to be used in making hydroxylammonium salts for monopropellants, the stabilizers are carried over into the salt solution and may act as catalyst poisons. There are numerous stabilizers for HA described in the patent literature, including the trisodium salt of *N*-hydroxyethyl-ethylenediaminetriacetic acid; the tetrasodium salt of ethylenediaminetetraacetic acid; polyvinylpyrrolidone and poly-*N*-vinyl-5-ethyl-oxalidinone [3]; and pyridine or pyridone salts, such as the sodium salt of 2-hydroxypyridine-*N*-oxide, 2-hydroxy-4-methoxy-pyridine-*N*-oxide, 1,2-dimethyl-3-hydroxy-pyridine-4-one, 4-methyl-pyridine-*N*-oxide, 6-methyl-pyridine-*N*-oxide, 1-methyl-3-hydroxy-pyridine-2-one; and combinations thereof [123] or complexones [124]. Some of these may also be suitable for stabilization of hydroxylammonium salt solutions. Stabilizers patented by Heitner 1992 are all sulfur compounds [125] and would definitely have to be avoided in monopropellant rocket applications with catalytic reactors.

1.7 Strand Burning of Hydroxylamine Free Base

Hydroxylamine free base solutions containing 74 mass-% NH_2OH were burned in capillary glass tubes of 2 and 4 mm ID at atmospheric pressure [126]. The regression rate was 1 mm/s. The solutions burn with a yellow flame, and ammonia is one of the decomposition products. Nitric oxide NO was not observed.

1.8 Toxicity of Hydroxylamine Free Base

Although free HA base will most likely never be used as a rocket propellant, the toxicity of HA is listed here because it is closely related to that of its salts such as HAN. The toxicity of hydroxylammonium salts is mostly determined by the cation, protonated hydroxylamine free base, and not so much by the anion. Before hydroxylammonium salts are accepted by the propulsion community as “non-toxic” replacements for hy-

drazine, one must examine the toxicity of hydroxylamine-derived compounds to make sure that one does not unwittingly replace one toxic compound with another. The type of toxicity hazard with hydroxylamine and its salts may be different from that of the well-advertised hydrazine toxicity but may represent a toxicity hazard nevertheless. Hydroxylamine is a natural intermediate in the metabolism of ammonia-oxidizing and nitrate-reducing bacteria. So if the bacteria can live with it, it cannot be that toxic.

Toxicity tests are usually conducted in buffered media. Only very rarely will tests be conducted in strongly alkaline media with hydroxylamine free base, which would have pH values near 11. Once the media are buffered, one would have a mixture of free base and its salts. Therefore, it is difficult to separate the discussion of toxicity into that of the free base and that of its salts. In many cases the title of a publication reads “hydroxylamine,” when in fact the test was conducted in a buffered solution with pH near neutral or below, with very little free base in the equilibrium present. There is a substantial overlap between this current chapter and the one on toxicity of HAN, discussed in more detail in Section 3.11.

Although hydroxylamine is a product of normal cellular metabolism, it is also a potent mutagen *in vitro*. However, in spite of this potential, it has not been shown to possess carcinogenic capabilities. In fact, this chemical has demonstrated carcinostatic activity against certain tumors in animals. Of course, the same has also been said about hydrazinium(2+) sulfate. Hydroxylamine has been shown to inactivate or inhibit a number of cellular enzymes and some viruses *in vitro*. It is also a skin irritant and sensitizer. It causes dermatitis and is corrosive to the eyes. Acute and chronic exposures to hydroxylamine have caused methemoglobinemia and sulfhemoglobinemia [127].

1.8.1 Acute Toxicity of Hydroxylamine Free Base

The lethal dose for 50% of the animals tested (LD_{50}) of HA in mice by oral administration is 408–419 mg/kg.

1.8.2 Mutagenicity of Hydroxylamine Free Base

The mutagenicity of hydroxylamine free base and hydroxylammonium salts has been thoroughly investigated. Hydroxylamine free base interferes with deoxyribonucleic acid (DNA) replication by reacting with various amines that are DNA building blocks. Similar activity was expected for some of its salts.

Hydroxylamine free base has been used in the past by biologists to introduce random mutations by switching base pairs from A to G, or from C to T, which is one of the reactions used to identify genes in DNA sequences. This was done in wheat in an effort to breed more productive varieties. It must be assumed that hydroxylammonium salts would exhibit the same mutagenic activities.

The *Drosophila* wing somatic mutation and recombination test was evaluated for its suitability in genotoxicity screening by testing 30 chemicals, including hydroxyl-

amine [128]. Of the two crosses used, the mwh-flr3 cross turned out to be more convenient than the previously used mwh-flr cross. A qualitative evaluation of the genotoxicity of a compound in the wing assay was possible with as few as 1–2 different exposure concentrations.

In order to generate mutants randomly in the *E. coli uncA* gene (encoding the α -sub-unit of F_1 -ATPase), plasmids carrying *uncA* were treated *in vitro* with hydroxylamine [129]. Restriction fragments of the mutated *uncA* gene were then reconstructed into plasmid pDP34, which expresses all of the F_1F_0 structural genes, and the reconstructed mutant plasmids were expressed in a strain carrying a deletion of chromosomal *uncA*. Each of the mutations was characterized by DNA sequencing, growth assays and biochemical assays of membrane preparations.

One of the series of publications on the mutagenicity of hydroxylamine continued for several years and included at least 14 consecutive publications. A group of Russian authors led by Budowsky published a long series of publications covering a span of ten years from 1969 to 1979 dealing with the mechanisms of the mutagenic action of hydroxylamine and *O*-methylhydroxylamine in a variety of assays [130]. The replication of the phage MS2 in the presence of either hydroxylamine or *O*-methylhydroxylamine (mutagenesis *in vivo*) results in an increase in the reversion frequency of two amber mutations in the maturation protein. When acting on the extracellular phage (mutagenesis *in vitro*), the mutagens do not affect the reversion frequency. The most probable mode of mutagenic action of the hydroxylamines on the vegetative MS2 phage involves the enzymic formation of modified precursors and their incorporation into RNA [131]. Hydroxylamine may react with the adenine, uridine, or cytidine, which are part of the RNA molecule [132]. We are referencing here only a few of the more recent examples of those publications, assuming that the reader will have to pick up the remaining 12 publications from the reference list therein.

The cytotoxic and mutagenic properties of hydroxylamine were studied in *Drosophila* over a wide dose range (0.005–1 M) on adult males up to 125 mM and on embryos for higher concentrations [133]. The effects on adults were examined for two HA derivatives: the hydroxamate dihydroxyurea (DHU) and methoxyamine (MOA). HA at high concentrations (≥ 1 M) was tolerated only by the embryonic test system, where it induced cytostatic and cytotoxic effects such as arrested cleavage and embryonic lethality. At a concentration of 1 M, the regression of embryonic survival leading to egg hatchability on time of treatment indicated that the cytotoxic lesions could be an outcome of a single chemical reaction dependent on the HA concentration. HA proved to be mutagenically inactive over the dose range investigated in both the adult and embryonic test systems. Of the tested derivatives of HA, the hydroxamate DHU was also mutagenically inactive, but the oxy ester MOA was decisively effective in the induction of mutations. The molecular basis of the biological activities of HA and its derivatives were interpreted in the light of known chemical reactions of this chemical series with cellular macromolecules.

A total of 133 compounds including hydroxylamine were tested in the micro-screen assay, which is a multi-endpoint assay and utilizes *E. coli* WP2s(λ) instead of *Salmonella typhimurium* [134]. These included 111 compounds that had been tested in the *S. typhimurium* assay and 66 compounds for which both rodent bioassay and *S. typhimurium* assay data were available. Exposure of *E. coli* WP2s(λ) takes place in serial dilutions of the test compound in microtiter wells (250 μ L), followed by sampling from wells in which growth has occurred (i.e., those where cytotoxicity has not killed the viable material). Although a number of different endpoints can be measured, only the prophage induction endpoint has been extensively tested. The concordance for the microscreen assay and the *S. typhimurium* assay was good (71%). For this group of compounds, the sensitivity of the microscreen assay in detecting carcinogens was 76%, compared with 58% for the *S. typhimurium* assay. However, the *S. typhimurium* assay was somewhat more specific (69%) compared with the microscreen (56%).

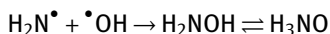
Here we are mostly concerned about the potential mutagenicity and carcinogenicity of rocket propellant ingredients such as hydroxylamine and its salts. We were surprised to see a study in which the authors actually suspected that, due to its antioxidant properties, hydroxylamine might be suitable as a preventive treatment against cancer. The effect of administration of hydroxylamine to male and female mice was studied because of reports suggesting an anti-carcinogenic effect and an enhancement of lifespan [135]. In this study, two C3H sub-line breeds were used: the C3H/HeN, which carries a germinal provirus of the mouse mammary tumor virus, and the C3H/HeJ(+), which also carries the milk-transmitted exogenous virus. Lifetime administration of 10 mM HA in the drinking water resulted in a decrease in mammary neoplasm incidence in female C3H/HeN mice but not in female C3H/HeJ(+) mice. Ovarian neoplasms and cysts were common in all groups, indicating ovarian dysfunction, but these were not affected by treatment. The incidences of other cryptogenic neoplasms found in controls in significant numbers, i.e., liver carcinomas, lymphomas, lung adenomas, and adrenal cortex tumors, were only marginally affected in either direction by the treatment. However, an increased incidence of vascular neoplasms of the spleen in hydroxylamine-treated female C3H/HeN mice and vascular neoplasms of the lymph nodes in hydroxylamine-treated male C3H/HeJ(+) mice indicated a sub-line-related action of HA on the reticuloendothelial system. The survival of control mice was 35–58% at 2 years, and this was not increased in either sub line by hydroxylamine, which is interpreted to indicate that this antioxidant does **not** increase lifespan of animals under conditions of maintenance that are adequate for good survival, but it did not kill the mice prematurely, either.

In a study of the bacteriostatic action of hydroxylamine, the results showed that hydroxylamine is bacteriostatic for a number of microorganisms [136]. In some cases, the toxicity may take effect before mutagenicity can be tested. Exposure of cells to high concentrations of hydroxylamine resulted in immediate cessation of DNA, RNA, and protein syntheses. The synthesis of specific proteins (i.e., inducible enzymes) was inhibited to the same extent as total protein synthesis. This also applied to the produc-

tion of constitutive enzymes. DNA isolated from bacteria treated with hydroxylamine did not display altered physicochemical properties, but hydroxylamine prevented the incorporation of amino acids into s-RNA as well as the formation *de novo* of ribosomal, messenger, and s-RNA. The ribosomes as well as the s-RNA prepared from hydroxylamine-treated bacteria were inhibited in their ability to participate in the synthesis of polyphenylalanine.

1.9 Other Occurrences of Hydroxylamine Free Base

Hydroxylamine H_2NOH and its isomer ammonia oxide H_3NO have been postulated as potential short-lived intermediates in the oxidation and combustion of ammonia. Hydroxylamine can form by recombination of hydroxyl and amino radicals



but, of course, that reaction is reversible and is also a path of hydroxylamine decomposition.

Because HAN-based monopropellants are advertised as “green” (environmentally friendly) propellants, they have undergone extensive scrutiny to make sure that they have no such hidden hazards, as some of the hydrazines and perchlorate ion do. When hydrazines and perchlorates were first introduced as rocket propellants, there was less concern about the environmental impact or about occupational hygiene for the handling and disposing of these propellants, or it may be that some of the ramifications of introducing these propellants into rocket test and launch sites were not completely understood. This is why hydroxylamine and its salts were examined before being used as gun or rocket propellants.

Hydroxylamine is an intermediate in many naturally occurring bacterial oxidation and reduction cycles. NH_2OH is an intermediate in biological nitrification. The oxidation of ammonia is mediated by hydroxylamine oxidoreductase. Although this is not a book on microbiology, we thought it would be of interest here to mention the natural occurrence of hydroxylamine and its salts in the biosphere when one has to prepare an environmental impact statement on the use of hydroxylammonium salt in rocket propellants. If we can show that hydroxylamine is a natural intermediate in many nitrogen cycles, then there will be less concern about it accumulating in and damaging the environment. One of the best proofs of this proposition is the fact that some naturally occurring bacteria thrive in a nutrient broth that contains hydroxylamine.

Nitrosomonas europaea, *Nitrosomonas nitrosa*, and *Nitrosococcus oceanus* were successfully grown in a nutrient broth containing hydroxylamine [137]. Significant cell yields were obtained in growth media containing ammonia supplemented with successive small additions of hydroxylamine. The molar growth yield on hydroxylamine, measured as formation of cell protein per unit of substrate oxidized, was found to be approximately twice that on ammonia. In respiration experiments, the oxygen con-

sumption was 1.5 mol O₂ per mol ammonia, and 1.0 mol O₂ per mol hydroxylamine oxidized to nitrite.

Hydroxylamine is an intermediate in the bacterial oxidation of ammonia to nitrite. Cells of *Nitrosomonas europaea* are capable of growing in nutrients with ammonia and hydroxylamine [138]. The molar growth yield on hydroxylamine (4.74 g mol⁻¹ at a growth rate of 0.03 h⁻¹) was higher than expected. Aerobically growing cells of *N. europaea* oxidized ammonia to nitrite with little loss of inorganic nitrogen, while significant inorganic nitrogen losses occurred when cells were grown on mixtures of ammonia and hydroxylamine. In the absence of oxygen, hydroxylamine was oxidized with nitrite as electron acceptor, while nitrous oxide was observed as a by-product. This may be an important natural route to nitrous oxide, a greenhouse gas.

Although the following discussion of the bacterial oxidation of hydroxylamine belongs more in a later chapter on the environmental effects and degradation of hydroxylamine in the environment, the information is presented here because it immediately follows other studies of bacterial interactions that either generate or consume hydroxylamine. As it turns out, there is more hydroxylamine by several orders of magnitude in one form or another already in the environment at any given time than the U.S. Army has ever consumed in its liquid gun propellant development.

Six strains of aqueous heterotrophic bacteria belonging to the genera *Arthrobacter*, *Pseudomonas*, *Aquaspirillum*, and *Macromonas* were found to be capable of hydroxylamine oxidation to nitrites via one or several intermediate products [139]. *A. siderocapsulatus* produced bound hydroxylamine as an intermediate product. The rate of oxidation of that intermediate was lower than that of free hydroxylamine. Hydroxylamine at a concentration greater than 10 mg/L suppressed the bacterial growth (beginning cytotoxicity). *A. siderocapsulatus* and *P. fluorescens* oxidized hydroxylamine. *A. siderocapsulatus* and *P. putida* could not oxidize hydroxylamine when the buffering action of the growth medium decreased.

Hydroxylamine oxidation by *Arthrobacter siderocapsulatus* occurs under aerobic conditions and is intensified in the presence of respiration substrates [140]. The process is specifically inhibited by iron chelating agents and sulfhydryl group reagents. The activity of oxidation rises at the stationary phase of *A. siderocapsulatus* growth parallel to the content of cytochromes B and C, the activity of catalase and peroxidase.

Alcaligenes faecalis var. *nitrificans* was shown to oxidize ammonium via hydroxylation involving electrons directly from the respiration chain [141]. The mechanism of oxidation is similar to that in *Nitrosomonas*, but the source of electrons for hydroxylation is hydroxylamine in the autotrophic bacterium and organic compounds in the heterotrophic bacterium. The enzyme system of *A. faecalis*, which oxidizes ammonium to hydroxylamine, is supposed to be similar to tyrosinase.

An enzyme capable of the oxidation of hydroxylamine to nitrite was isolated from the obligate methylotroph *Methylococcus capsulatus* Bath [142]. The absorption spectra in cell extracts, electron paramagnetic resonance spectra, molecular weight, covalent attachment of heme group to polypeptide, and enzymatic activities suggested

that the enzyme is similar to cytochrome P-460, an iron-containing protein previously observed only in *N. europaea*. The native and sub-unit molecular masses of the *M. capsulatus Bath* protein were 38900 and 16390 Da, respectively; the isoelectric point was 6.98. It is interesting to note that the enzyme has approximately one iron and one copper atom per sub-unit, and these ions also catalyze the autoxidation and decomposition of HA and HAN *in vitro*. Hydroxylamine may even be an intermediate of bacterial activity in the intestinal tract [143]. It was suggested that hydroxylamine may be an intermediate in the oxidative conversion of L-arginine to nitric oxide, a vasorelaxant.

We have a hard time preventing hydroxylamine free base from decomposing in the laboratory under terrestrial conditions. So the last place one would go to look for hydroxylamine would be interstellar space, with its harsh radiation environment. However, the list of complex inorganic and organic molecules detected in interstellar space continues to grow. Ammonia is there. The possibility of NH_2OH to survive under these conditions and its potential to become protonated has been assessed, but the probability of its existing under these conditions is low [144].

1.9.1 Substituted Organic Hydroxylamines

Because hydroxylamine free base is too unstable to be considered as a rocket propellant, its methyl derivatives were at one time evaluated as propellant ingredients. There are two places on the H_2NOH molecule where methyl groups or other organic groups can be attached: One can be attached to the oxygen atom, and up to two can be attached to the nitrogen atom. Several of these derivatives, O-substituted as well as N-substituted alkylhydroxylamines, are known, and a few of them have been evaluated as rocket propellants. Properties of alkyl-substituted hydroxylamines and salts prepared from them are described in Section 6 in this chapter. Hydroxylamine can react at both the nitrogen and the oxygen atoms. For preparation of O-substituted hydroxylamines, the nitrogen atom must be protected to avoid N-alkylation. Monopropellants containing these organic hydroxylamines are described in *Encyclopedia of Monopropellants*.

Hydroxylamine free base is very sensitive to contamination, and several explosions have been blamed on contamination by iron ions. Along the same line, O-methylhydroxylamine and other alkylhydroxylamines are also sensitive to iron(III) contamination [145].

2 Hydroxylammonium Salts

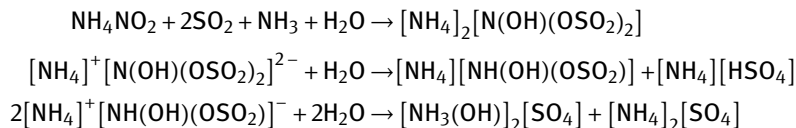
Although hydroxylammonium salts are not typically used as oxidizers in solid propellants, they are discussed here adjacent to ammonium nitrate (AN), ammonium perchlorate (AP), ammonium dinitramide (ADN), and hydrazinium nitroformate (HNF) because in the pure state these compounds are crystalline solids. A few solid propel-

lants have been formulated with solid HAN or hydroxylammonium perchlorate, but they were found to be impractical due to lack of thermal stability. It is also very difficult to obtain hydroxylammonium salts in the water-free state. Therefore, hydroxylammonium salts are used mostly in aqueous solutions.

One of the peculiar properties of hydroxylammonium salts is their extreme hygroscopicity, which makes it difficult to prepare the salts in the pure, dry state. The last traces of water are tenaciously held by these salts, and that makes it difficult to determine their physical properties in the anhydrous state. It takes only a few percent of water to convert hydroxylammonium salt crystals to a viscous liquid. While this may be a hindrance to studying these compounds in the pure, anhydrous state, it is a welcome method for creating liquid oxidizers with relatively high useful oxygen content, low water content, high density, and low freezing points. Compared to the corresponding ammonium salts, hydroxylammonium salts are much more soluble in water than their ammonium counterparts.

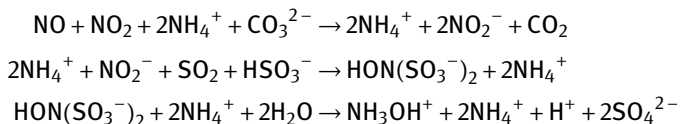
The most commonly produced hydroxylammonium salt is hydroxylammonium sulfate, which is the easiest and the most stable form to store and to transport hydroxylamine compounds in the solid state. Much of the hydroxylamine going into production of caprolactam goes through the intermediate state of the sulfate salt and ends up as polyamide elastomers such as nylon.

Hydroxylammonium sulfate can be produced by reduction of aqueous ammonium nitrite with $\text{HSO}_4^-/\text{SO}_2$ as the reductant at 273 K (0 °C). This yields a hydroxylamido-*N,N*-disulfate anion, which can be hydrolyzed to give $(\text{NH}_3\text{OH})_2\text{SO}_4$:



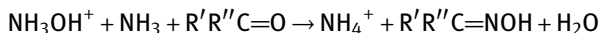
Hydroxylammonium sulfate is an important intermediate in the synthesis of cyclohexanone oxime, which can be converted to caprolactam, which is a precursor in the production of nylon. Initially, it was also the most frequently used intermediate in the production of HAN, but sulfate contamination was a continuing concern, particularly once HAN was beginning to be used as a monopropellant in catalytic thrusters. Sulfate and sulfur would act as catalyst poisons.

The Raschig synthesis of hydroxylamine

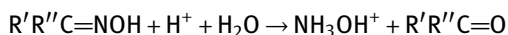


is an economical method for producing hydroxylamine for use as an intermediate in the manufacture of oximes. The end product of the Raschig synthesis is an aqueous

solution of hydroxylammonium ions (~1.8 N), ammonium ions (~4.7 N), and hydrogen ions (~1.9 N) balanced by sulfate and, to a minor extent, nitrate ions. The separation of pure hydroxylammonium salts and especially of hydroxylamine free base solutions from the mixtures of salts obtained in the Raschig synthesis presents some difficulties. Fractional crystallization of these mixtures generally fails because of the relatively high proportion of other salts. One method has been to use the Raschig synthesis solution (after neutralization) to prepare the oxime of a volatile ketone:



The resulting ketoxime is separated from the aqueous salt solution by distillation and is subjected to hydrolysis in the presence of a strong acid. This produces a solution of the hydroxylamine salt of the acid and the ketone, which can be recycled:



This method has several drawbacks. The hydrolysis of ketoximes is reversible even at low pH, and continuous removal of liberated ketone is required in order to complete the reaction in the desired direction (and minimize side reactions). Also, hydroxylamine base or salts of hydroxylamine with weak or oxidizing acids cannot be produced directly with this method.

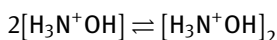
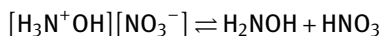
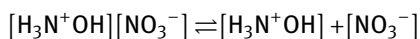
Ion-exchange methods have been used to separate hydroxylamine free base from the reaction mixture [9, 146]. A cation exchange resin can first be loaded with ammonium and will then absorb hydroxylammonium from the product mix. Hydroxylammonium ions in aqueous acidic solutions displace ammonium ions from sulfonic acid resins. In the last step, hydroxylamine liberated by ammonia treatment of the ion-exchange resin in a column elutes later than ionic components present in the resin [8].

Nomenclature. When conducting literature searches, it has been noted that many authors and librarians have misspelled hydroxylammonium nitrate as “hydroxyl ammonium nitrate” in three words. The incorrect name “hydroxylamine nitrate” is also occasionally found in the literature. It is therefore recommended that literature searches be conducted for both or all three spellings.

3 Hydroxylammonium Nitrate

Hydroxylammonium nitrate, also known as hydroxyammonium nitrate, hydroxylamine nitrate, hydroxyazanum nitrate, NH_3OHNO_3 , $\text{N}_2\text{H}_4\text{O}_4$, CAS RN [13465-08-2], HAN, is the most important hydroxylammonium compound for rocket applications. In comparison, the other hydroxylammonium salts have only limited interest, but we list them here for comparison.

Hydroxylammonium nitrate solutions contain an intimate mixture of hydroxylammonium ions, nitrate ions, associated ion pairs, ion clusters, some undissociated HAN, and traces of free hydroxylamine in equilibrium:



In addition to information on solid propellant oxidizers, the properties of the aqueous solutions of these salts are included here for further reference since they are the main reason for the recent popularity of these compounds as liquid oxidizers, and all solid propellant oxidizers start out as aqueous solutions in one point of their lives. Again during demilitarization at end of life and the eventual recycling of ingredients, aqueous solutions of solid propellant oxidizers are an important part of the recycling process. The properties listed in the following chapters are thus not restricted to those of solid compounds, but they also include their aqueous solutions. Concentrated solutions of HAN and its mixtures with other water-soluble oxidizers can be used as liquid oxidizers in bipropellant rocket engines, bipropellant liquid-propellant guns, hybrid rocket engines, and for achieving the complete combustion of fuel-rich torpedo propellant exhaust to minimize the wake signature of torpedoes under water.

3.1 Literature on Hydroxylammonium Nitrate

A good summary of the properties of HAN and HAN-based liquid propellants is contained in a series of conference proceedings published by the Ballistics Research Laboratory entitled “__th Annual Conference on HAN-Based Liquid Propellants.” Five of these conferences were held during the period 1985–1990 [147–149].

3.2 Production of Hydroxylammonium Nitrate

Most rocket propellant chemists will prefer to purchase their ingredients from a reliable chemical supplier and not have to worry about how to manufacture these energetic materials themselves. However, once in a while, it may be difficult to find a chemical with the desired purity or in the necessary quantities, and the propellant chemist may have to make decisions about alternate suppliers and alternate methods of production. In any case, contaminants carried over from various production processes may result in lack of thermal stability or lack of storage stability when a propellant chemist begins to formulate a new propellant. Contaminants (e.g., mercury carried over from electrolytic processes) may make it more difficult to

dispose of process wastes. For most of the chemicals discussed as rocket propellants in this book, a short note about the methods of production will suffice. For HAN and also for ADN, we made an exception and are providing a more detailed description of production methods. Before using any chemical as a rocket propellant, it helps to know how the chemical was made and which contaminants to watch out for. If rocket propellant or liquid gun propellant applications are the only industrial use of an oxidizer, industry may decide to discontinue production if the military consumption of a specific oxidizer suddenly drops below the point where it is economical and profitable to continue to operate a large production facility. In those instances, the rocket propellant chemist will have to search for alternate methods to produce the needed chemical.

The supply situation for HAN in the United States has changed dramatically in both directions during the past 20 years. At the beginning of the 1990s, there was only one commercial source for HAN in the United States, Southwestern Analytical Chemicals in Austin, Texas (currently called Sachem Inc. [150]). The highest concentration initially offered was only 24% (4.8 M) HAN. Under the tradename Tronos 415, a 2-M (18%) HAN solution was offered at one time for printed circuit board processes. This solution was stabilized by an excess of 0.05–0.3% HNO_3 . It was assumed that Sachem used an ion exchange method for its product, which was mostly supplied to the nuclear reactor fuel element reprocessing industry. In 1992, Olin Chemicals brought the first electrolytic reduction HAN production plant on line under a U.S. government contract that supplied HAN for RLPG testing for several years. The HAN produced by the electrolytic reduction of nitric acid is a higher-purity product than HAN produced by metathetical reactions. At the same location, Olin also operated a concentrating plant that produced 13-M HAN. In late 1997, the U.S. Army transferred ownership of the HAN production facility at the Olin Chemicals complex in Charleston, Tennessee, to Olin. Under a previous contract with the Army, Olin had built and operated this HAN plant while the Army explored alternatives to traditional solid gun propellants. Based on proprietary technology developed by Olin in 1984, the plant was initially built to explore the potential use of HAN as a safe liquid propellant for artillery weapons. After the cancellation of the U.S. Army Crusader regenerative liquid propellant gun (RLPG) program, Olin discontinued HAN production at the Charleston plant and, in a company-structure reorganization, spun off the specialties chemicals line (including the hydrazines business) as Arch Chemicals. Arch Chemicals was acquired by Lonza in 2011, the HAN propellants products line was discontinued, and the production facility was dismantled.

Hydroxylammonium nitrate can be produced by several methods, including neutralization of hydroxylamine free base with dilute nitric acid, electrolysis of nitrate ions, catalytic reduction of nitrous oxide, metathetical reactions, and ion exchange reactions. Hydroxylammonium nitrate solutions offered by some suppliers were found to have a high sulfate content, which made it impossible to use this material in mono-propellant reactors with platinum group catalysts.

Most of the methods described here result in only dilute aqueous solutions of HAN. Therefore, the method of concentrating dilute HAN solutions to concentrations that make them useful as rocket propellants is a critical step in developing the overall technology. During the early years when HAN-based propellants were first developed and tested in small quantities, there have been accidents when HAN solutions were heated under vacuum to drive off the water.

When HAN began to be evaluated as an ingredient for liquid monopropellants in rocket engines in the early 1990s, the rocket and space program benefited from the experience that had been gained by the U.S. Army and its contractors in developing HAN-based liquid gun propellants for its RLPG during the preceding two decades. For several years, a new 155-mm self-propelled howitzer (AFAS “Crusader”) was based on this gun concept, and the chemical industry was gearing up to produce HAN-based liquid gun propellants in large quantities.

The Advanced Field Artillery System (AFAS) was conceived as a 155-mm self-propelled howitzer system that was supposed to provide a significant increase in artillery survivability/lethality, mobility, and operational capability and effectiveness through the use and integration of advanced technology in its sub-systems and combat components. For a long time, the baseline AFAS critical technologies and capabilities included an RLPG and XM46 insensitive liquid propellant. The LP cannon promised greater range and lower per-round cost but stretched the AFAS schedule by 2 years or more. Both liquid-propellant AFAS and solid-propellant Crusaders were to have multiple-round simultaneous impact (MRSI) capability.

When the AFAS Crusader switched from liquid propellants to solid propellants (Uni-Charge) in 1994, there was an abundance of unused HAN production capacity that was eventually idled because there were few other uses for this chemical. One of the other commercial uses of HAN was in the reprocessing of spent nuclear reactor fuel rods in the Purex process, where it was used along with hydrazinium nitrate solutions to separate uranium and trans uranium elements, but that process uses only a fraction of the amount of HAN that would have been consumed by a fully fielded AFAS RLPG program. Other countries may still be pursuing liquid propellant guns; see [151].

3.2.1 Production of Hydroxylammonium Nitrate by Neutralization of Hydroxylamine Free Base

The most difficult part of this method is not the neutralization but the preparation of the dilute hydroxylamine free base solution that goes into the process (Section 1.1). The dilute hydroxylamine free base solution can be obtained by a number of processes, many of which are described in patents.

Once hydroxylamine free base solutions started being used for the removal of photomasks on integrated circuits, they became available in the commercial open market from several vendors. It would be easiest to use such commercially available hydroxylamine free base solutions and neutralize them with the acid of choice to make any

hydroxylammonium salt wanted. When using commercially available 50% free base solutions, one must remember that these contain a non-volatile stabilizer that may contaminate the HAN product if the 50% free base solution is used without prior distillation. Distillation of 50% HA free base is a **hazardous** operation. The distillate no longer has the benefit of the stabilizer and will decompose faster than the commercially available HA solution. Stabilizers are usually chelating agents. The exact nature of the stabilizer is proprietary information – it may not even be listed in the Material Safety Data Sheet (MSDS) – but it has been speculated that it might be EDTA, 8-hydroxyquinolin, pyrogallol, or ascorbic acid.

A simple process for the production of concentrated and high-purity HAN has been described in which diluted nitric acid is slowly added to a solution containing excess aqueous hydroxylamine while the resultant mixture is agitated to obtain uniform mixing to avoid locally high concentrations of nitric acid. The batch is cooled to keep the temperature below 333 K (60 °C) [152] or even 323 K (50 °C) [153]. Conversely, addition of hydroxylamine to nitric acid causes spontaneous decomposition of the product HAN, even when the nitric acid has been diluted to less than about 50 mass-%.

A HAN production process patented to Thiokol [154–156] first distills the free base liberated from hydroxylammonium sulfate with alkali under reduced pressure at temperatures below 338 K (65 °C) without alcohol auxiliary fluids to obtain a solution containing 10–50 mass-% hydroxylamine, and then neutralizes the base with 20–70 mass-% HNO_3 at 223–293 K (–50 to 20 °C). The patent claims emphasize that the process is carried out without alcohols. Apparently, earlier processes distilled the free base while the vapor was diluted with a high-boiling alcohol to prevent explosions. Some of the alcohol carried over into the product, which was an undesirable contaminant. Another, older process extracted HAN with butanol, in which it is more soluble than hydroxylammonium sulfate.

A method described in a different patent also distills the free base from caustified hydroxylammonium chloride or sulfate and then neutralizes the distillate with nitric acid [157]. A similar process treats hydroxylammonium sulfate with sodium hydroxide, separates the free base, and neutralizes it with nitric acid in aqueous solution [158].

The easiest way to convert readily available hydroxylammonium sulfate into other, more valuable rocket propellant ingredients is by ion exchange: The first step is to produce a solution of pure hydroxylamine [159], which is then neutralized with the acid of choice (either nitric acid, perchloric acid, or dinitramide) to obtain a solution of the high-performance rocket propellant ingredient in high purity.

Instead of using sodium hydroxide to liberate the free base from a suspension of finely ground $[\text{NH}_3\text{OH}]_2[\text{SO}_4]$ in methanol or ethanol, one can also use ammonia [160] to liberate hydroxylamine free base in an alcoholic solution and then neutralize it with nitric acid or perchloric acid to obtain HAN or HAP.

The other method is to use sodium alkoxides (sodium methoxide or sodium ethoxide) in alcoholic solution as the base to react with finely ground hydroxylammonium sulfate [161]. Once one has a solution of HA free base in ethanol, HAN or HAP can

be obtained by carefully neutralizing this solution with nitric acid or perchloric acid. The excess alcoholic solution of unreacted hydroxylamine may be recycled and used as starting material for the next batch.

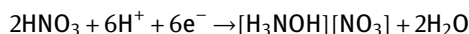
If the hydroxylamine free base to be neutralized contains some ammonia contamination, the resulting HAN will be contaminated by ammonium nitrate. The ammonia contamination in the reactant free HA base can be removed by sparging with an inert gas before neutralizing the solution [162].

Commercially available 50% solutions of hydroxylamine free base (FH-50) contain a proprietary stabilizer, most likely an organic complex-forming chelator, which may interfere with intended applications of HAN solutions prepared by neutralization of FH-50 with nitric acid.

Hydroxylammonium nitrate prepared via a neutralization reaction of hydroxylamine free base and nitric acid at different pH levels was analyzed using Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) [163]. Based on TGA, the decomposition temperatures of HAN samples synthesized at pH 5–7 were in the range of 393–413 K (120–140 °C), and the sample synthesized at pH 8 decomposed at a decomposition temperature higher than 413 K (140 °C).

3.2.2 Production of Hydroxylammonium Nitrate by Electrolytic Reduction of Nitrate Ions

The most direct method for production of HAN is the electrolytic reduction of nitrate ion in nitric acid solutions:



Possible intermediates in this reaction are nitrite and hyponitrite.

Based on its extensive experience with membrane cells for chlorine and alkali production, Olin Corporation developed an electrolytic HAN process and built a pilot production plant at Charleston, Tennessee, for the large-scale production of HAN. This process initially used a 300-A electrolytic cell with horizontal membrane and opposing mercury pool cathode and produced 3.0 molar HAN at 3.35 kg/d, 77% cathode current efficiency, and 92% yield from nitric acid at 1.5 kA/m². The excess free nitric acid was removed from the product using weak base anion-exchange resins, and the final product contained less than 2.5 ppm transition metals, 0.5 mass-% ammonium nitrate, and less than 0.1 mass-% excess free nitric acid [164–166]. Seventy percent electronic-grade HNO₃ was reduced in a high-hydrogen–overvoltage mercury cathode horizontal membrane cell and produced a 24 mass-% (3M) HAN solution in excess nitric acid [167–170]. This was a continuous process. Each cell had a cathode area of 6 m² and operated at a current density of up to 3 kA/m². Maintenance of the correct nitric acid concentrations in the two electrolyzer compartments was critical to proper operation of the reactor. At low nitric acid concentrations, hydroxylamine would be reduced at the cathode to ammonia, which is undesirable. At high nitric acid concentrations, HAN would be oxidized to NO_x, which is even worse. Either deviation

is undesirable. A mercury cathode was used on top of a conductive plate that was also the top of the cooling compartment. One design entailed the use of additional space for the separate cooling compartment and did not provide for high circulating catholyte flow rates or against the possible loss of the mercury cathode from the cell. The need to employ special precautions to prevent human exposure to mercury and the potential for contamination of the HAN with mercury were disadvantages of the electrochemical process. This process also required more than 2 mols of high-purity nitric acid for each mol of HAN produced, as well as a separate step to remove excess nitric acid before the HAN could be concentrated for use in propellants. Also, the HAN concentration produced electrolytically was limited to about 3.5 molar and required an additional concentration process to make 13-M HAN.

A balance of the nitric acid concentrations between the two compartments was required to allow water transport across the membrane and to maximize the efficiency of the cell. The product leaving the cathode chamber had to contain excess nitric acid. The product leaving the electrolyzer contained typically 25% HAN and 2.8% nitric acid. The excess nitric acid in the product stream could be evaporated or neutralized by addition of free HA or by passing the solution over a cation-exchange resin saturated with hydroxylammonium ions from a hydroxylammonium sulfate solution [171]. A highly acidic ion exchange resin had to be found that was compatible with HAN and HNO_3 . IONAC CFP-110 (Sybron Chemicals) was one of the ion exchange resins that met these requirements. The HAN solution was then concentrated to 81% (13-M) HAN. See also [172].

HAN solutions as produced by electrolytic reduction of nitric acid contained a substantial excess of free nitric acid that had to be removed or neutralized so that it would not adversely affect the stability of the HAN product. One method to neutralize it without introducing a third component was to neutralize it with free hydroxylamine base or at least a solution of HAN containing an excess of free hydroxylamine base [173]. The solution of hydroxylammonium salt containing free hydroxylamine was made by contacting a portion of the solution of the hydroxylammonium salt substantially free of excess acid with a weak base ion exchange resin. This avoided deterioration of the ion exchange resin by contact with free nitric acid. A similar process used a multi-stage electrochemical reactor with an ion exchange membrane in the last stage, loading it electrolytically with hydroxyl ions, which then neutralized the excess free nitric acid [174].

An electrolysis cell with a mediator compartment or coating prevents mixing of anolyte and catholyte during the electrolysis [175]. Selectivity and yield can be improved by forming a film on the intermediate membrane. Film-forming additives are organic polyamines [176]. The nitrate ion is reduced to a hydroxylammonium salt in the presence of a mediator or a film formed by the mediator. The hydroxylammonium salt can be recovered as such or can be electrochemically converted to hydroxylamine free base.

3.2.3 Production of Hydroxylammonium Nitrate by Electrolytic Reduction of Nitric Oxide

Instead of starting with a nitrate (nitric acid) solution, one can pass nitric oxide through a gas diffusion cathode and obtain either HAN or hydroxylamine free base [177, 178]. Intermediates in this reaction are HNO and H_2NO [179]. In one variation of the nitrate reduction process, nitric oxide, NO, is bubbled through the cell, thereby increasing the yield per Joule [180]. Ammonium ion is present as proton donor. The extent of NO reduction decreases with decreasing proton donor concentration because of a lower rate of NO protonation and higher contribution of a competing pathway in which NO^- is converted to N_2O .

Hydroxylamine was produced in a trickle bed cell by passing nitric oxide gas and sulfuric acid catholyte co-currently downward through a cathode bed of tungsten carbide particles [181]. The dependence of hydroxylamine concentration and current efficiency on cathode activity and the particle size, flow rate, composition of gas and catholyte, bed height, reactor temperature, and pressure was quantified, and operating conditions were optimized. Hydroxylamine concentrations of up to 0.18 mol/L were produced at 62% current efficiency in a single pass through a 0.375-m-high cell operated at atmospheric pressure and a current density of 213 A/m^2 . The hydroxylamine concentration increased with cell pressure and gas flow rate and decreased in catholyte flow. It could be raised to 0.4 mol/L by recycling the catholyte for several passes through the system. The process appears to be controlled by mass transfer at current densities of over 400 A/m^2 and by electrochemical reaction below 300 A/m^2 .

The electroreduction of nitric oxide on smooth platinum in aqueous perchloric and sulfuric acid solutions was studied using linear potential sweep and rotating disc electrode techniques [182]. Three potential peaks were observed with linear sweep voltammetry. The first was a well-resolved peak at $E = 0.25 \text{ V}$. Analysis gave a Tafel slope of approximately 0.110 V, which was independent of acid concentration, and a pseudo-first order rate constant that varied linearly with hydrogen ion activity. The results were dependent on electrode reduction pre-treatment and the state of the platinum surface. A second peak at 0.1 V was not well resolved, but evidence was presented suggesting that this peak may be related to nitrogen formation at a zero-oxidation state on a reduced electrode. A third peak at -0.1 V appeared to be a mixed diffusion-adsorption peak associated mainly with ammonia synthesis. The rotating disc electrode experiments supported these conclusions.

A most extraordinary electrochemical method for producing hydroxylamine from nitric oxide and hydrogen does not consume electricity but instead generates electricity in a fuel cell [183]. Hydroxylamine is the reaction product, and electricity is a by-product. This method for the synthesis of hydroxylamine uses a laboratory-scale nitric oxide-hydrogen fuel cell with 3.5-M sulfuric acid electrolyte, nanocrystalline platinum gas-diffusion electrodes, and a proton exchange membrane. Operating conditions are varied and optimized for different voltages and different NO flow rates. The highest current efficiencies of NH_2OH production obtained were above 80% and were

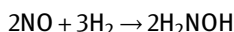
NO flow-rate dependent. The maximum current density of NO reduction was about 5 mA cm^{-2} in the fuel-cell voltage region from 0.2 V down to very low voltages, in which the highest selectivity of hydroxylamine formation was also obtained.

The waste stream from a HAN electrolysis cell may contain traces of mercury that must be removed before the water can be released to surface water bodies. Thus, after hydroxylammonium ion has been destroyed by oxidation with hypochlorite, the excess of hypochlorite must be removed with a reductant such as sodium hydrosulfite before mercury can be precipitated as mercury(II) sulfide by addition of sulfide ion [184].

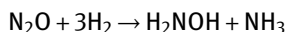
3.2.4 Production of Hydroxylammonium Nitrate by Catalytic Reduction of Nitric Acid, Nitric Oxide, or Nitrous Oxide

Instead of electrochemical reduction, catalytic reduction in the presence of hydrogen gas is another method for producing HAN. It is interesting to note that HAN and hydroxylamine free base can not only be produced by catalytic reduction of nitrous oxide with hydrogen gas but that nitrous oxide is also one of the intermediates in the decomposition of HAN and hydroxylamine free base. The two compounds are thus closely related.

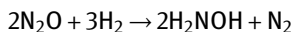
The first step in the reduction of nitric oxide (NO) to NH_2OH in nitric acid solution follows the reaction



The first step in the reduction of nitrous oxide (N_2O) to NH_2OH in nitric acid solution follows one of the reactions



or



One of the earliest patents for the production of HAN by catalytic reduction of nitric oxide is the BASF patent [185]. BASF at that time was pioneering the production of nylon from ω -caprolactam. An aqueous solution of ~10% HAN was produced by catalytic reduction of nitric oxide with hydrogen in acid solution over a selectively poisoned platinum catalyst at elevated pressure. The $\text{NO} + \text{H}_2$ feed gas has to be diluted with nitrogen to render it less flammable and less explosive. Nitric acid was continuously supplied during the reaction in an amount necessary for the end-concentration of HAN [186]. Using nitric acid instead of sulfuric acid resulted in less ammonia as a by-product.

The platinum catalyst was used as a suspension in sulfuric acid at 1.5 bar and 313 K (40 °C) in a six-stage reactor, and the emerging mixture of hydroxylammonium sulfate, ammonium sulfate, and catalyst was filtered off before processing the hydroxylammo-

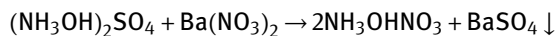
nium salt solution obtained as the filtrate. It was important to recover the expensive platinum on graphite catalyst by redissolving the filter cake and allowing the catalyst to settle so it could be reused [187]. Filtration and sedimentation are very slow processes. In one version of the process, 13% of the nitric oxide was converted to nitrous oxide, an undesirable by-product.

Another patent describes a process for preparing hydroxylammonium salts through catalytic reduction of nitrate ions in an acid (pH 1–4) medium in the presence of a palladium and/or platinum catalyst supported on a carrier in which at least 0.00025 mmol halogen ions are present per m² of palladium and/or platinum area [188]. The hydrogen pressure is between 0.5 and 2 MPa.

In many instances [189, 190] the dilute HAN solution is not isolated as such but is directly reacted with cyclohexanone to produce cyclohexanone oxime for later conversion to ω -caprolactam and polyamides like nylon.

3.2.5 Production of Hydroxylammonium Nitrate by Metathetical Reactions

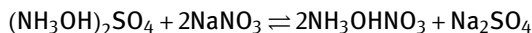
Hydroxylammonium sulfate is a good starting point for the synthesis of other hydroxylammonium salts because it is available in large quantities as an industrial commodity commonly used for the synthesis of nylon and similar polyamide polymers. It is possible to convert hydroxylammonium sulfate to HAN by a metathetical reaction or by ion exchange. Metathetical reactions work only if it is possible to shift the equilibrium in the desired direction by forming and precipitating an insoluble salt. Thus, HAN can be formed by reaction of barium nitrate with hydroxylammonium sulfate, where the barium sulfate precipitates as sparsely soluble white precipitate:



There is concern about contamination of the product by barium ions and sulfate. The precipitate is so fine that normal filtration and washing are practically impossible, and settling is extremely slow, usually taking 8–16 h.

In a variation of this process that uses less water, a hydroxylammonium salt is slowly added to a well-agitated saturated slurry of either barium nitrate or barium perchlorate [191]. The agitation must be sufficiently vigorous so as to ensure that the hydroxylammonium salt goes into solution and reacts with the dissolved barium salt and does not come into direct contact with the slurried barium salt. Should this undesirable direct contact occur, the soluble salt will receive an insoluble coating, and the reaction will be prematurely curtailed.

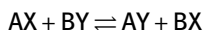
Another method to remove HAN from the equilibrium



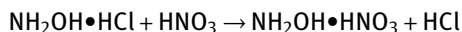
is to extract it with butanol or an ether in which it is quite soluble [192]. Either *n*-butanol or isobutanol is suitable for this application. The HAN is recovered from the organic phase by countercurrent water extraction or solvent evaporation.

In a similar method, the viscous reaction mixture of the two salts in a little water is heated until it is homogeneous, allowed to cool, and extracted with ethanol. The unwanted salts are precipitated from the extract by adding diethyl ether to the solution, filtering, and slowly evaporating the solvents from the filtrate until HAN crystallizes out. The last two steps are repeated several times for purification [193].

Another method to carry out metathetical reactions is to use electric current as the driving force in electrolysis cells separated by semipermeable membranes. Another electrochemical method for the production of HAN is the electrodialytic process [194]. The process may be superior to some previously employed methods such as the cation-exchange process of Wheelwright [195] in some aspects. It can produce HAN with a low free acid content, a high HAN concentration, and a high chemical yield without recycling, and the capacity of the production facility can be varied over a wide range by changing the current density and flow rate – and all of that can be achieved without any deterioration of product quality. These electrodialytic methods are generally applicable to any ionic metathetical reactions of the type



This conversion can be carried out through a double decomposition electrodialytic reaction, e.g., starting with hydroxylamine hydrochloride and nitric acid:



With semi-permeable membranes of high selectivity now available, one can obtain products of high purity. With bipolar membranes, the concept can be extended to water-splitting triple decomposition reactions; e.g., starting with hydroxylammonium chloride and sodium nitrate



and replacing nitric acid with the less expensive sodium nitrate salt. The multi-compartmented cell for the water-splitting triple decomposition reaction consists of bipolar membranes, which can be made by several different methods. A simple and effective method is to fuse together an anion- and a cation-exchange membrane with heat and pressure. In a multi-cell assembly, consisting of repeating sequences of six different cells, a solution of hydroxylammonium chloride is fed into compartment number 2 and a solution of sodium nitrate goes into compartment number 4. When current is passed, the key product HAN is produced in compartment number 3, while the by-products, hydrochloric acid and sodium hydroxide, are produced in compartments 1 and 5, respectively. Each repeating unit of six cells consists of a bipolar membrane, two anion-exchange membranes, two cation-exchange membranes, two feed compartments, and three product compartments. The electrolytes are recirculated, and the product is withdrawn as soon as it achieves the most economical concentration.

The overall current efficiency drops with increasing concentration of HAN in the product cell number 3. Homogeneous membranes (e.g., CMV and AMV) give a much better yield than heterogeneous membranes (e.g., MC 3470 and MA 3475).

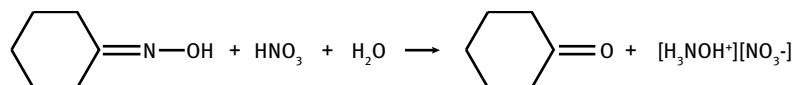
3.2.6 Production of Hydroxylammonium Nitrate by Ion Exchange Reactions

Hydroxylammonium sulfate is converted to HAN by passing an aqueous hydroxylammonium sulfate solution through a cation-exchange resin bed that absorbs the hydroxylammonium ion, washing the excess sulfate ion from the resin bed, and eluting the hydroxylamine as HAN with nitric acid [195, 196]. This process does not go through the intermediate step of liberating HA as the free base.

Hydroxylammonium nitrate can be made in an electrodialysis unit that has a tank divided into chambers by cation-exchange membranes, containing an aqueous solution of hydroxylammonium sulfate and a solution of nitric acid in adjacent chambers [197]. An electric potential is applied so that the NH_3OH^+ and H^+ ions pass through the membrane, and the nitric acid is converted to HAN as desired product.

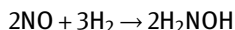
3.2.7 Preparation of Hydroxylammonium Nitrate by Hydrolysis of Oximes

Cyclohexanoneoxime is a major industrial product used in the synthesis of polyamides (nylon). Hydrolysis of cyclohexanone oxime with dilute nitric acid gives solutions of HAN [198]. The effects of the molar ratio of cyclohexanone oxime to nitric acid, the amount of water, the reaction temperature, the reaction time, and the extraction solvent on the hydrolysis reaction were investigated. The results indicate that the conversion of cyclohexanone oxime can reach 62 with 97% selectivity to HAN and 97% selectivity to cyclohexanone under the optimal reaction conditions.

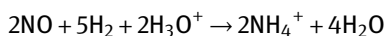
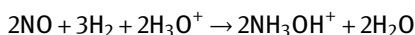
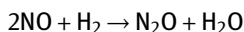


3.2.8 Catalytic Hydroxylamine Production Methods

The catalytic reduction of NO is a convenient route for the production of hydroxylammonium salts:



However, the reaction is not as simple as it seems. In acidic solutions, three competing reactions take place



of which only the second one gives the desired product. The selectivity among the three products depends strongly on the partial pressure of NO in the gas phase. Increasing the partial pressure of NO causes the rates of NH_3OH^+ and NH_4^+ formation to increase, reach a maximum, and finally drop to nil, while the rate of N_2O formation continues to increase all the way. There is only a narrow partial pressure regime (around 0.02 MPa) where NH_3OH^+ and NH_4^+ are produced. Most processes use a platinum catalyst supported on activated carbon, suspended in diluted (<6 N) sulfuric acid. These methods produce hydroxylammonium salts instead of hydroxylamine free base. Of those, the method producing HAN by electrolytic reduction of nitrate ion is the one receiving the most interest and it is discussed in detail in Section 3.2.3.

3.2.9 Production of Hydroxylammonium Nitrate by Oxidation of Ammonia

An integrated process was developed for the synthesis of hydroxylammonium salts with ammonia and hydrogen peroxide as raw materials [199]. This is similar to the process that was aimed at hydroxylamine free base instead of its salts (Section 1.1.4). In this process, hydroxylamine is produced from a combination process of cyclohexanone ammoximation and cyclohexanone oxime hydrolysis, whereby cyclohexanone and its corresponding oxime, which is circulated, act as the “reaction carrier.” Solid hydroxylammonium salts were obtained through the integrated process, which corresponds to an overall yield of 64.2% with respect to ammonia. An intriguing feature of the process is that the reaction carrier, as well as the catalyst employed, can be recycled in the process. This process reminds one of the Produits Chimiques Ugine Kuhlmann (PCUK) process for production of hydrazine hydrate, which also starts with hydrogen peroxide and a ketone as the intermediate. The main objective of these processes was to make cyclohexanone oxime for conversion to caprolactam and polyamides, not to produce hydroxylammonium salts. In this case, both the nylon industry and the rocket propellant makers may benefit from the same invention.

An alternate ammoximation process uses cyclohexanone and ammonium chloride instead of free ammonia as the source of nitrogen and titanium silicalite as catalyst [200]. This new process should now be adapted to the synthesis of HAN instead of cyclohexanone oxime. This process uses a titanium silicalite zeolite with a controlled number of crystal defects as the catalyst [201]. The catalytic mechanisms of titanium species in TS-1 zeolite for the hydroxylamine formation have been investigated using density functional theory. The reaction process for making hydroxylamine can be divided into two steps: **(1)** the H_2O_2 decomposition over the Ti species to produce the peroxo titanium species, and **(2)** the NH_3 oxidation over the generated oxidizing species. The results indicated that defective Ti sites in the TS-1 zeolite are the dominant catalytic sites for H_2O_2 decomposition rather than perfect Ti species, leading to the formation of Ti—OOH species as oxygen-donating intermediates for the NH_3 oxidation reaction. This process can be carried out as a continuous process in a microreactor [202].

3.2.10 Purification of HAN Solutions

The storage life of HAN solutions and propellants prepared therefrom is limited by contaminants introduced inadvertently during their preparation or leached from container materials during storage. The feasibility of removing transition metal contaminants (trace quantities of iron and copper ion) from HAN solutions by cathodic reduction and some non-electrochemical techniques has been experimentally evaluated [203]. A high-mass-transfer packed-bed electrochemical reactor was designed and built for removing the trace metals by cathodic plating. Several bed and electrode materials were evaluated, including lead and amalgamated copper, varying electrode potentials, and solution pH. Although cathodic plating of copper worked quite well with a removal efficiency of 93%, iron was not so easily removed. Lead was unsuitable as a substrate, but amalgamated copper was a candidate substrate material. Both electrochemical and non-electrochemical techniques for removing metal ions as a hydroxide precipitate were investigated. Co-precipitation using alumina as a coagulation agent at a pH of 3.1 seemed to work for iron removal.

HAN prepared by electrolytic reduction of nitric acid by the Olin process may contain traces of mercury as a contaminant. Mercury contamination can be removed by precipitation as mercury sulfide [204, 205].

3.2.11 Concentrating of HAN Solutions

Commercially available 24% HAN solutions can be concentrated in a Rotavapor under vacuum (12 mm Hg) from a bath temperature of 323 K (122°F). This process has been scaled up to a 50-gallon batch process [206]. At room temperature, water will dissolve up to 95 mass-% HAN [207].

One must remember that the storage stability of HAN solutions is improved by maintaining a small, controlled excess of free nitric acid. During distillation, any free nitric acid that may have been in the starting product is lost with the water. The free nitric acid content in the concentrated residue may have to be adjusted again to improve the storage stability of the product. Samples of 92% HAN kept in a thermostatted 338 K (65°C) bath for several days showed a gradually increasing free acid content and fumed off after several days in test.

Concentrated solutions of inorganic hydroxylammonium salts, including HAN, can be safely produced in a continuous process by contact with a semipermeable membrane having a sorption side and a desorption side [208, 209]. The dilute solution is in contact with the sorption side of a membrane, which is substantially permeable to the solvent and impermeable to the solute of the solution. The solvent can flow through the membrane to the desorption side and will then be desorbed by a purge. This process does not require direct heating of the solution and is much safer than distillation methods.

3.2.12 Preparation of Solid Hydroxylammonium Nitrate

Because it is very difficult to remove the last few percent of water from a very concentrated HAN solution, and because the solutions have a tendency to supercool, solid HAN is not often prepared. There are not many applications that would need pure anhydrous HAN. Some investigators needed pure solid HAN to record its spectra and determine crystal structures, but for rocket applications one would hardly ever want to prepare solid HAN.

In one case where solid HAN was prepared, the water was removed by vacuum drying over a **3-month** time period, but the sample still contained some impurities [210]. The impurity level calculated from the change in melting temperature with fraction melted was 0.040 mol fraction. Chemical analysis indicated that the sample contained 0.005 mol fraction HNO_3 and 0.007 mol fraction NH_4NO_3 , with $\text{N}_2\text{H}_5\text{NO}_3$ absent for sure. The remainder of the impurity could have been water, but this is not known for certain.

Few rocket propellant preparations need HAN in the solid state. It is usually very difficult to obtain dry HAN from aqueous solutions. Solid HAN can be obtained by operating in alcoholic instead of aqueous solutions, by slowly adding HNO_3 to an alcoholic solution of hydroxylamine [211]. This procedure forms a HAN precipitate. However, if more HNO_3 is added, the precipitate dissolves before the stoichiometric amount of acid can be added. Therefore, only just-sufficient HNO_3 is added to form a maximum amount of solid HAN precipitate. The solid HAN is then isolated by conventional means (e.g., filtration or centrifugation), possibly preceded by chilling of the solution. The excess alcoholic solution of unreacted hydroxylamine may be recycled and reused as starting material for the next batch. Formation of methyl nitrate must be avoided because methyl nitrate is a sensitive explosive. Another method adds a water-miscible solvent (an alcohol) in which HAN is not soluble to an 80-% aqueous HAN solution, causing the salt to precipitate [212]. This idea should have been no longer patentable in 1997 because it has been described in prior-art open literature.

Solid HAN can be prepared by metathetical reactions of hydroxylammonium chloride with zinc nitrate, silver nitrate, lead(II) nitrate, or chromium(III) nitrate in ethanol, an ethanol/methanol mixture, or diethyl ether, where the HAN precipitated and the metal chloride remained in solution [213]. The purity of the product was verified by ion chromatography. Melting point, DSC traces, and isochoric, isothermal reactor pressure traces of a 90% solution of this product were identical to those of HAN prepared by neutralization of a 50% HA solution with HNO_3 .

A dual-solvent extraction method was used to obtain HAN in solid particulate form [214]. The dehydrated crystals obtained from an aqueous HAN solution were washed with dual organic solvents, including acetone and ethanol.

3.3 Physical Properties of Solid HAN and HAN Solutions

The physical properties of HAN are summarized in Table 7.

Table 7: Physical properties of hydroxylammonium nitrate.

Property	SI units	Other units	References
Molecular mass	96.04 g/mol	10.4123 mol/kg	
Melting point, α -HAN	308.77 ± 0.65 K	35.72 ± 0.65 °C	[215]
Melting point, β -HAN	320.88 ± 1.69 K	47.73 ± 1.69 °C	[215]
Density at 298 K	1.841 g/cm ³		
Enthalpy of formation	−366.5 kJ/mol	−87.6 kcal/mol	[216]

3.3.1 Melting Point of Solid HAN

Literature data for the melting point of pure, anhydrous HAN vary widely because it is extremely difficult to remove the last traces of water, which can cause a strong melting-point depression. Based on a melting endotherm of 2–3 mg HAN samples during DSC, a melting point of 315.4 K (42.2 °C) was reported [217].

Other sources give the melting point of pure HAN as 321 K (48 °C) [218]. With this low a melting point, it would be impractical to attempt to make solid composite propellants with HAN. Gelled HAN-based propellants have been cast into the shape of solid propellant grains instead.

Crystalline HAN exists in two modifications, α -HAN and β -HAN [215]. Measurements by DSC determined that the onset of melting of α -HAN was at 308.77 ± 0.65 K (35.72 ± 0.65 °C), and the onset of melting of β -HAN was at 320.88 ± 1.69 K (47.73 ± 1.69 °C).

3.3.1.1 Freezing Points and Melting Points of Binary Systems

It is very difficult to experimentally determine freezing points of HAN solutions because the solutions supercool and do not give a sharp freezing point. The solutions become more and more viscous and then solidify to a transparent glass. The temperature at which this happens is called the glass transition temperature. It can be determined by measuring other properties (heat capacity) of the mixture while the solidification takes place. The processes taking place during the solidification of HAN solutions are discussed in more detail in the sections on viscosity and molecular structure of HAN solutions, Section 3.3.3 and 3.3.8.2

The HAN/water binary phase diagram is a simple eutectic type with the eutectic at 231.5 K (−41.7 °C) and a HAN mol fraction of 0.281 (mass fraction HAN = 0.676) (Figure 5) [210]. The melting temperature for an impure sample of HAN was 315.9 K (42.7 °C). The melting point corrected to zero impurity was 317.7 ± 1 K (44.5 °C). The enthalpy of fusion of the HAN was determined from the solid and liquid results to be 11 ± 2 kJ/mol.

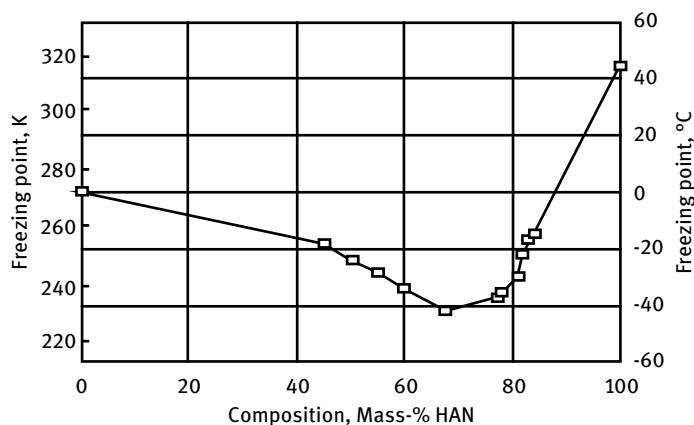


Figure 5: Freezing-point diagram for the HAN/water system. (Chart created by Schmidt 2016, based on data from [219].)

DSC studies of melting and phase transitions of HAN/water solutions over the range of 123–293 K (–150 to +20 °C) measured in glass ampoules with flat bottoms (Mettler DSC crucibles, in order to avoid interference by corrosion of metal crucibles commonly used in DSC), showed that HAN/water solutions have the properties of dilute aqueous solutions at low HAN concentrations and the properties of molten salts at high HAN concentrations [220]. The molten salt behavior continues to appear at HAN concentrations below 11 M, but it disappears at and below 0.4 M. The glass transition temperatures and the change in heat capacity are summarized in Table 8.

Triethanolammonium nitrate (TEAN)/water solutions behaved very similarly, with an exotherm occurring at 200 K (–73 °C). The data suggest that more than one

Table 8: Glass transition temperatures of HAN solutions.

HAN concentration mol/L	Glass transition, °C		ΔHeat capacity	
	Onset	Complete	Cal g ^{–1} °C ^{–1}	J g ^{–1} K ^{–1}
15.8	–90.1	–84.6	0.264	1.104
14	–98.3	–92.6	0.301	1.259
12	–105.2	–99.2	0.399	1.669
11	–108.7	–102.3	0.364	1.523
10	–111.5	–105.1	0.416	1.741
9	–114.1	–107.8	0.414	1.732
8	–101.8	–96.2	0.215	0.900
4	–102.8	–96.6	0.123	0.515
2	–103.5	–101.2	0.025	0.105
0.8	–105.5	–95.0	0.058	0.243
0.4	none observed		—	—

Data source: [220]

crystal form of the salt is obtained, possibly with different numbers of water of hydration.

The solubility of HAN in water at various temperatures is given in Table 9. This is based on a melting temperature of pure HAN of 321 K = 48 °C and the coordinates of the eutectic point (73 mass-% HAN, 234 K = -39 °C) (Figure 6 and 7) [221].

Table 9: Solubility of HAN in water.

Temperature, °C	-20	0	10	20	30	40
Temperature, K	253	273	283	293	303	313
Solubility, mass-% HAN	81.5	85.3	91.6	94	97	98.5

Data source: [221]

The freezing and melting points of HAN solutions with 10 to 83.7 mass-% HAN were measured in gold DSC pans at temperatures down to 205 K (-68 °C) [222]. All HAN solutions exhibited weak supercooling effects, independent from the HAN concentration, that were much less pronounced than those of TEAN solutions evaluated as part of the same study. The peaks during heating were always much broader than the peaks during cooling. A eutectic point could not be found because the equipment did not cool below 205 K. A 93% HAN solution may contain both liquid and solid phases. Fig-

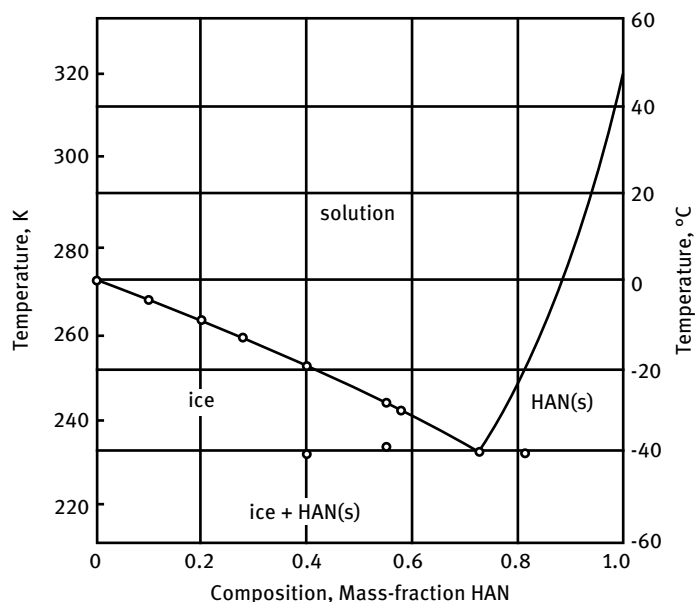


Figure 6: Phase diagram of the HAN/water system with mass-fraction abscissa scale. (Republished and modified with permission of American Institute of Aeronautics and Astronautics, Inc. from [221]; permission conveyed through Copyright Clearance Center, Inc.)

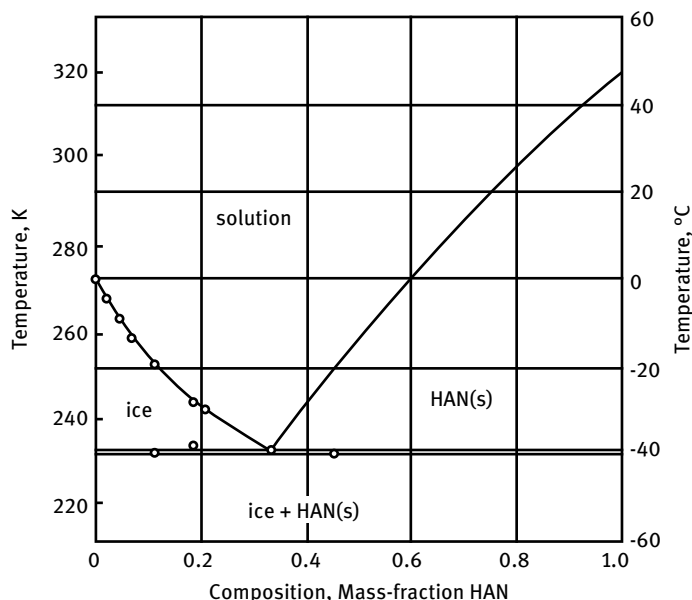


Figure 7: Phase diagram of the HAN/water system with mole-fraction abscissa scale. (Republished and modified with permission of American Institute of Aeronautics and Astronautics, Inc. from [221]; permission conveyed through Copyright Clearance Center, Inc.)

ure 8 shows a comparison of measured and calculated melting temperatures of HAN solutions in the range of 10 to 65% HAN. The solid line is the theoretical freezing point assuming the dissociation into two ions. Similar measurements were made for TEAN and LP-1845, as well as with added water. The melting temperatures of the HAN solutions at some specified concentration range were predicted rather well using the two-electrolyte assumption.

The following two HAN/H₂O melting-point diagrams (Figure 9 and 10) show a eutectic at about 230 K (−43 °C) and a HAN mol fraction of 0.28 [223]. These graphs are very similar to Figure 6 and 7.

The dependence of the glass transition temperature (T_g) of the binary system HAN-H₂O on the water content was investigated using DSC [224, 225]. It was found that T_g of the binary system exhibits the colligative property in the concentration range of 25–82 mol-% HAN, and when the HAN concentration is decreased as low as 25 mol-%, the property disappears, and the T_g rises surprisingly and is concentration independent. An attempt has been made to interpret this behavior in terms of the molecular clusters formed by various mol ratios of HAN/H₂O, which change with the content of H₂O in the system. It is considered that at most three molecules of H₂O can be incorporated with one HAN to form into the cluster, but when the content of H₂O increases as high as 75 mol-% (the mol ratio of HAN/H₂O is 1:3), only clusters of 2:3 mol ratio of HAN/H₂O are formed, and they are the most stable. See also [226].

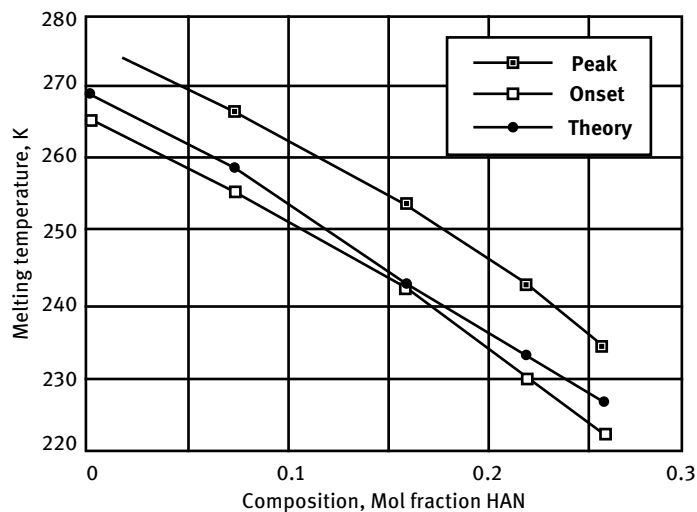


Figure 8: Comparison of measured and calculated melting temperatures of HAN solutions. (Republished and modified from [222], with permission of © 1991 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

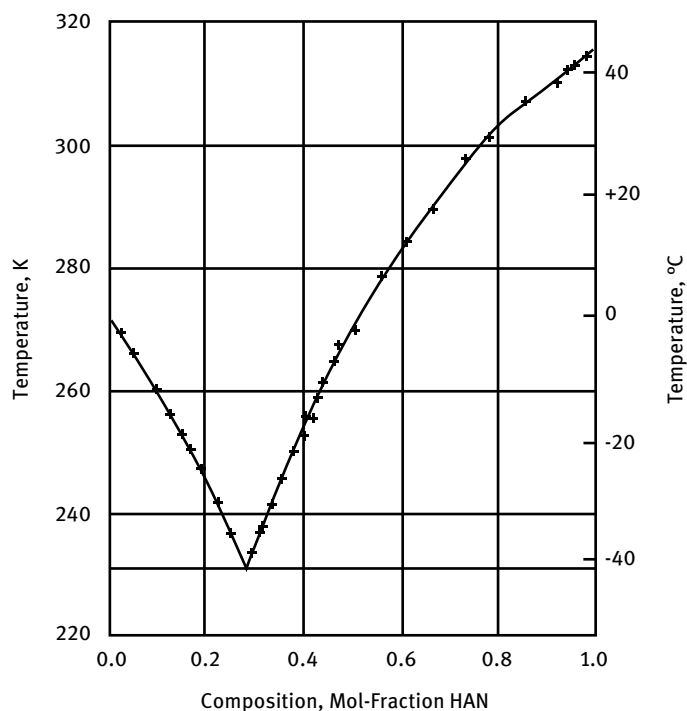


Figure 9: Melting-point phase diagram of the HAN/H₂O system, Abscissa: Mol fraction. (Reproduced and modified from [223].)

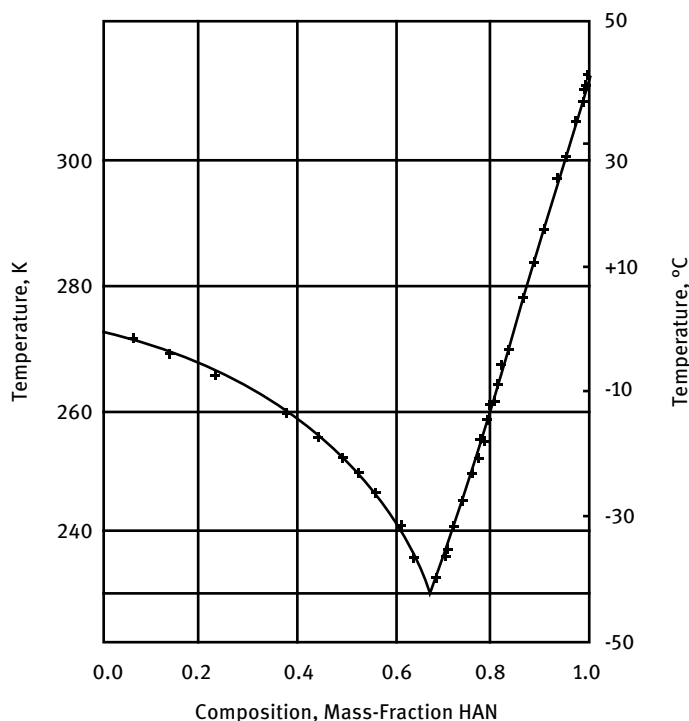


Figure 10: Melting-point phase diagram of the HAN/H₂O system, Abscissa: Mass fraction. (Reproduced and modified from [223].)

3.3.1.2 Freezing Points and Melting Points of Ternary Systems

Ternary systems containing HAN, a solvent, and another oxidizer were developed as liquid oxidizers with the potential of becoming “green” replacements for other, more corrosive oxidizers such as N₂O₄ and red fuming nitric acid (RFNA). They were proposed as gas generants in oxygen generators (oxygen for welding or breathing air) and as oxidizers in bipropellants, hybrid propellants, and gelled solid propellants. In an effort to achieve low-freezing liquids, the melting-point diagrams of the ternary systems were graphed first, and they served to illustrate the choices that could be made in the selection process. Many of the compositions with the lowest freezing points chosen were close to eutectic points.

A family of low-melting eutectic salt mixtures was developed at Aerojet. Some of these oxidizer melts were later gelled with polyvinyl alcohol or similar water-soluble polymers, energized with metal powders, and cast into shapes like solid propellant grains. Others were mixed with water-soluble fuels to make liquid monopropellants. We are summarizing in this chapter here only the properties of eutectic nitrate melts (without added fuels or binders). The solution and emulsion propellant mixtures using these liquid oxidizers are discussed in *Encyclopedia of Monopropellants*.

A series of patents [227, 228] cover combinations of inorganic nitrates as oxidizers for rocket propellants, such as the following:

- ammonium nitrate, hydrazinium nitrate (HN), and hydroxylammonium nitrate
- ammonium nitrate and hydroxylammonium nitrate
- hydrazinium nitrate and hydroxylammonium nitrate
- ammonium nitrate, hydrazinium nitrate, and lithium nitrate

The melting points and safety properties of some of these low-melting oxidizers are summarized in Table 10.

Table 10: Melting points and hazard properties of eutectic oxidizer combinations.

	AN/HN*	AN/HAN	HN/HAN	AN/HN/HAN	AN/HN/LiN
Mol ratio	1 : 2	1 : 2	1 : 2	1 : 2 : 2	1 : 1.2 : 0.5
HAN, mol-%	0	67	67	40	0
AN, mol-%	33	33	0	20	37
HAN, mass-%	0	71	67.2		
AN, mass-%	29.3	39	0		
Melting point, °C	~45	~5	~5	~5	~28
Density, g/cm ³		1.806	1.796	1.782	
Bureau of Mines Impact Test (cm @ 2 kg), 50% point	69	>100	>100	>100	>100
DSC exotherm onset, °C	>200	158	171	165	>200
DSC exotherm peak, °C	>200	176	199	192	>200
Spark sensitivity, J	>1.0	>1.0	>1.0	>1.0	>1.0
Friction sensitivity (g @ 2000 rpm)	>4000	>4000	>4000	>4000	>4000
Detonability, NOL sleeve @ 0 cards	Pos	Neg	Neg	Neg	Neg
Detonability, NOL sleeve @ 69 cards	Neg	Neg	Neg	Neg	Neg

*This is a known eutectic, included for reference only.

Data source: [227, 228]

Of the five mixtures tested, the three containing HAN resulted in the lowest melting combinations. One advantage of the eutectic formulations is that they have better thermal stability than HAN by itself, as shown by DTA and TGA measurements. The stability can be improved further by the addition of stabilizers: ammonium dihydrogen phosphate and 2,2'-dipyridyl, typically adding 1 mass-% each, based on the amount of HAN present. An oxidizer mixture containing these stabilizers called S-HAN5 (stabilized HAN with 5% AN) was widely used for formulating gelled solid propellants and monopropellants. It is interesting to note that the addition of as little as 1% of organic material may noticeably increase the drop-weight sensitivity.

The S-HAN patents by Bruenner are very similar to the OXSOL patents by Wagonman.

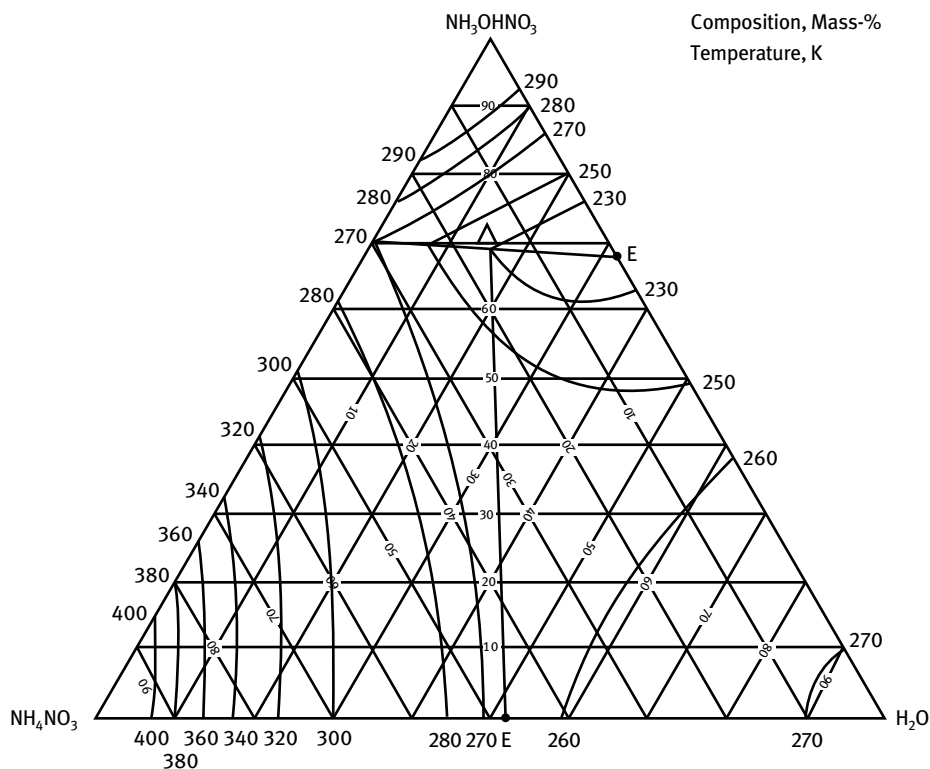


Figure 11: Melting-point diagram of the ternary HAN/AN/H₂O system. (Based on data from [229] and other sources.)

The melting-point diagrams of the ternary HAN/AN/H₂O and HAN/HN/H₂O systems were studied in the search for a low-melting liquid oxidizer that would be a non-toxic substitute for N₂O₄ or RFNA. The approximate contours of ternary melting-point diagrams of the HAN/AN/H₂O and HAN/HN/H₂O systems are shown in Figure 11 and 12, based on freezing-point data tabulated in [219].

There are insufficient data points to draw the isotherm lines with moderate accuracy. The lines drawn in Figure 11 and 12 require a lot of imagination and are shown only to illustrate the trend. The composition marked with an open triangle in Figure 11 is that of the preferred liquid oxidizer called OXSOL-1, containing 70% HAN, 15% AN, and 15% H₂O. Likewise, the composition marked with an open triangle in Figure 12 is that of the liquid oxidizer called OXSOL-2, containing 65% HAN, 22% HN, and 13% H₂O. A continuation-in-part of an earlier patent application by Wagaman was issued as U.S. patent 6299711 [230]. It is similar to the Mueller and Wagaman patent dated 1999, except it does not use HAN but also includes methylhydrazinium nitrate as a constituent. OXSOL-3 is a mixture containing AN, HN, and water (no HAN).

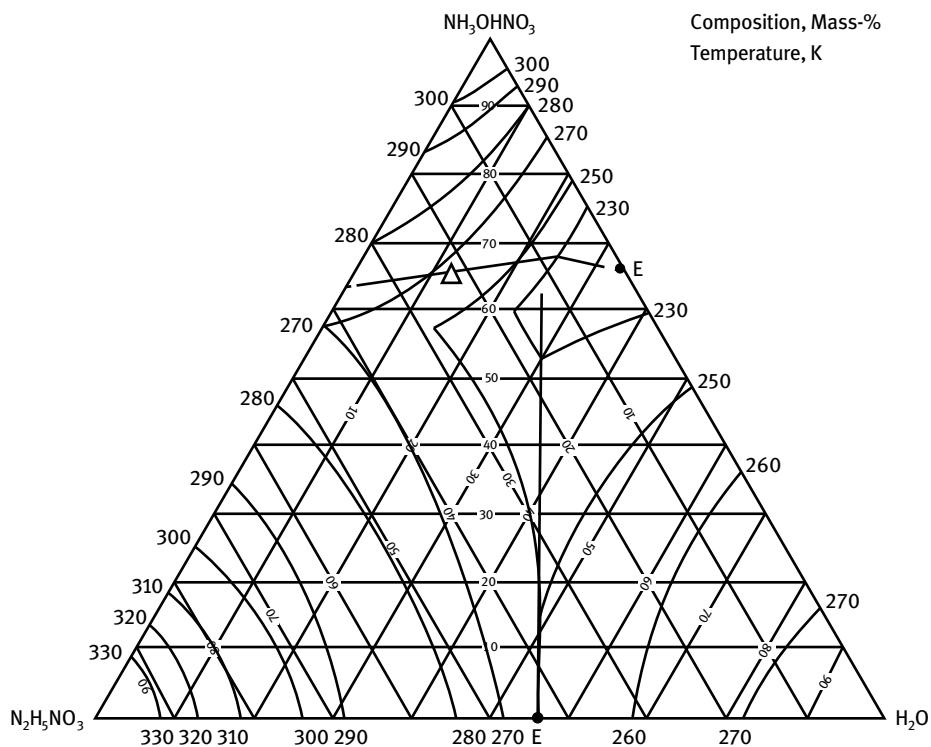


Figure 12: Melting-point diagram of the ternary HAN/HN/ H_2O system. (Based on data from [229], and other sources.)

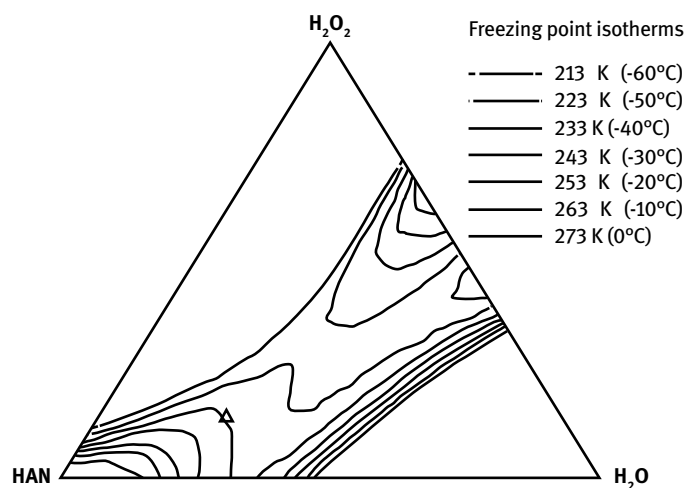


Figure 13: Freezing-point diagram of the $\text{HAN}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ system. (Reproduced and modified from [230].)

Another patent covers solutions of HAN in hydrogen peroxide/water solvents [229, 230]. These oxidizers are called “PERHAN.” The freezing-point diagram of the HAN/H₂O₂/H₂O system is shown in Figure 13. The freezing point of a preferred PERHAN composition (62% HAN, 12.5% H₂O₂, 25.5% H₂O) is 233 K (−40 °C).

The freezing points and densities of binary HAN/H₂O and ternary HAN/HNO₃/H₂O mixtures were examined, and the activity coefficients of such solutions were compared to those of HN/HNO₃/H₂O mixtures [231]. Binary data (water activity as a function of the molal concentration) at 298 K (25 °C) for HAN and HN in nitric acid aqueous media were determined by direct water-activity measurements. Density deviations at 298 K (25 °C) were also observed. Ternary systems involving these nitrate salts and nitric acid were studied from the standpoint of simple solution theory. It was found that the HN/HNO₃/H₂O system did not exhibit simple behavior, which was due to hydrazinium(2+) dinitrate N₂H₆²⁺ formation. On the other hand, the system HAN/HNO₃/H₂O, which did not undergo major chemical interactions, satisfactorily followed the simple-solution rule as long as the water activity was higher than 0.84. No such abnormality was observed with HAN in HNO₃/H₂O solutions. For ternary simple solutions, it was possible to predict activity coefficients for each component.

Another series of monopropellant blends was made from hydrazinium nitrate, hydroxylamine, and water, and the code name was MHF-9, but these mixtures were not very stable [232] (*Encyclopedia of Monopropellants*).

3.3.2 Density of HAN

The density of solid HAN is 1.841 g/cm³ (from X-ray data). It is thus denser than ammonium nitrate or hydrazinium nitrate. Other sources give the density at 298 K as 1.830 g/cm³ [233].

3.3.2.1 Density of Binary HAN Solutions

The knowledge base for the density of HAN solutions in water as a function of concentration has evolved, and data have been refined over the course of several decades. Density has often been used as a quick indication of HAN assay during preparation and concentration of HAN solutions. The accuracy of this method suffers from contamination by nitric acid and ammonium nitrate.

The first approximation, derived from 1 to 13-M HAN solutions at room temperature, was

$$\rho = 1.0000 + 0.0369M$$

where ρ is the density in g/cm³ and M is the molarity (Sasse, 1976, unpublished data). Extrapolating to 100% HAN would point to a density of 1.81 g/cm³, a number that was

used by many investigators in the 1970s. Later data from Thiokol [206] indicated that the density is not a true linear function of the molarity. An equation for the mid-range from 2.1 to 17.3-M HAN was fitted to the data, but extrapolation to either end was discouraged:

$$M = 26.04\rho - 26.38$$

$$\rho = 1.013 + 0.0384M$$

The main interest was in solutions near the target concentration of 13 M. Thus, a more accurate set of data was created [206] for the range from 11.7 to 14.3 M and is represented by

$$\rho = 1.12292 + 0.03099M$$

where ρ is the density in g/cm^3 and M is the molarity (as quoted by Decker et al. [220]). This curve fit was made to give an optimum match over a medium range, but it was not forced to go through the known points at 0 and 99.9% HAN.

The density of HAN solutions as a function of HAN concentration is shown in Figure 14 [234]. A single data point for LP1846 = XM46, marked with an $\times$, is shown for comparison.

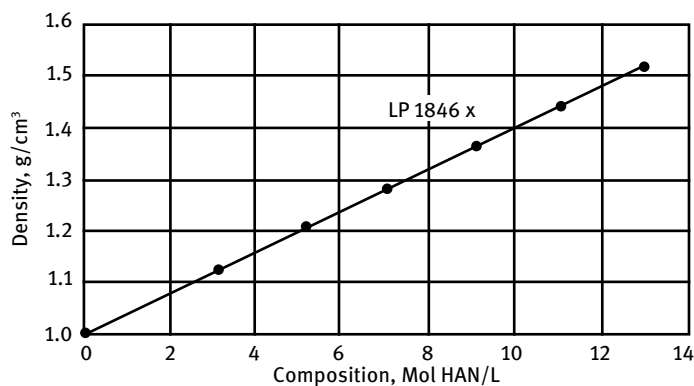


Figure 14: Density of HAN solutions as function of molarity. (Reproduced and modified from [234].)

Figure 15 gives a comparison of four sets of density data for HAN solutions developed during the period 1976 through 1989. A similar comparison of HAN solution-density data from three different sources was compiled and curve-fitted [235]; see Figure 16.

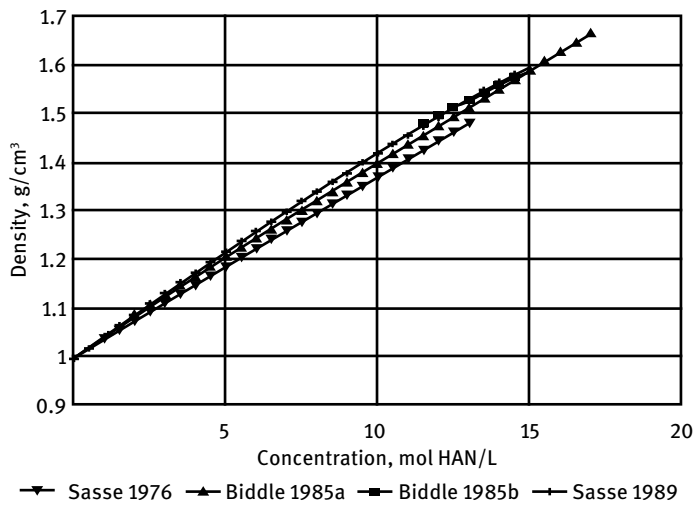


Figure 15: Comparison of data for density of HAN solutions in water at room temperature (Image created by Schmidt 2020.)

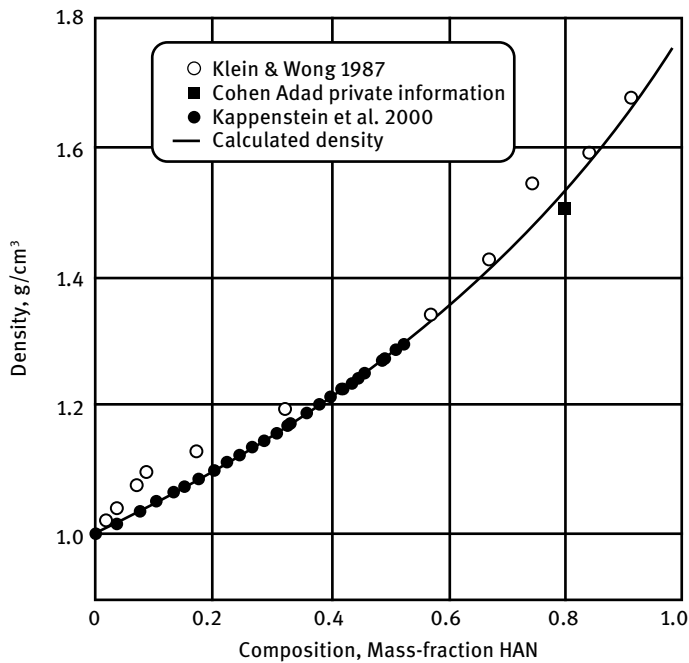


Figure 16: Comparison of density data of HAN solutions. (Reproduced and modified from [235].)

Table 11: Density of HAN solutions

HAN concentration, molarity	Density at 293 K, g/cm ³
13	1.537
10.7	1.449
9	1.382

Table 12: Density and molecular weight of HAN/H₂O solutions.

HAN/H ₂ O mixture, M	Density, g/cm ³ , at 293 K (20 °C)	Molecular mass, kg/mol (g/mol)	Mol fraction HAN	Mol fraction water
0.0 (pure H ₂ O)	0.99963			
0.5	1.02341			
2.781	1.12533			
3.12	1.128	0.02297 (22.97)	0.0635	0.9365
5.2	1.211	0.02709 (27.09)	0.1163	0.8837
5.232	1.22919			
6.858	1.29636			
7.02	1.284	0.03142 (31.42)	0.1718	0.8282
8.839	1.37548			
9.1	1.367	0.03748 (37.48)	0.2495	0.7505
11.05	1.445	0.04466 (44.66)	0.3415	0.6585
12.622	1.52306			
13	1.523	0.05394 (53.94)	0.4604	0.5395
16.338	1.65569			
17.5 ^a	1.680 ^a			
19.17 ^b	1.841 ^b			

^aAnhydrous melt^bFor comparison: value for a crystalline solid

Data source: [236, 237]

Other data points for densities of HAN solutions are listed in Tables 11 and 12.

If the density of HAN solutions is plotted against the mass fraction, the curve is slightly concave. This is typical for electrolytes where the ions are surrounded by a sheath of water molecules in a tightly held structure. Figure 17 shows the density of aqueous HAN solutions at 298 K in comparison to densities of two other oxidizers [238]. The AN data were measured at higher than room temperature (323 K) because AN is less soluble in water than the other two oxidizers.

The partial molar volumes of HAN and other oxidizers were measured so that the theoretical density of oxidizer/fuel/water mixtures in monopropellants could be calculated assuming additive behavior of the partial molar volumes in mixtures. As

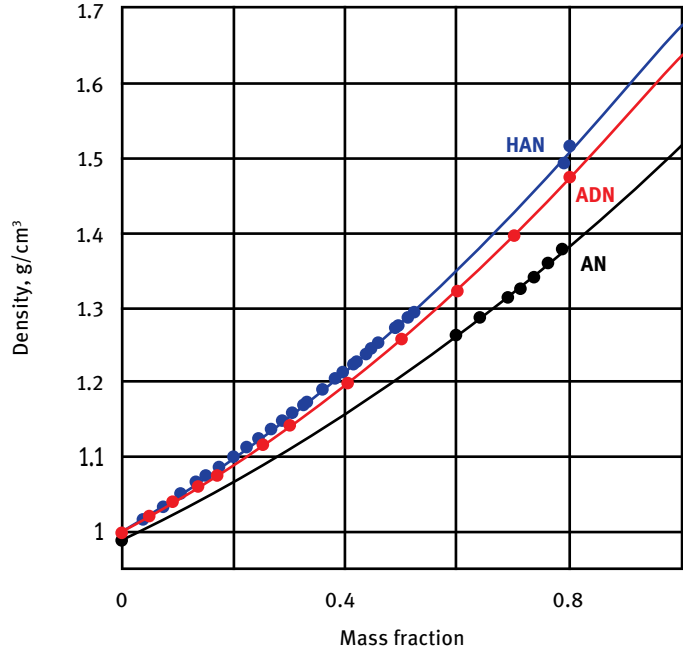


Figure 17: Density of aqueous HAN solutions in comparison to other oxidizers. (Reproduced and modified from Kappenstein, Batonneau, Perianu and Wingborg [238] with permission from Dr. Charles Kappenstein.)

a start, the reciprocal density (i.e., the specific volume) was plotted vs. the mol fraction of oxidizer, as shown in Figure 18.

The curves in Figure 18 are straight lines, such that their shape can be expressed by a simple linear function

$$V_m = V_{m\text{H}_2\text{O}} \times X_{\text{H}_2\text{O}} + V_{m\text{HAN}} \times X_{\text{HAN}}$$

$$V_m = V_{m\text{H}_2\text{O}} + (V_{m\text{HAN}} - V_{m\text{H}_2\text{O}}) \times X_{\text{HAN}}$$

The partial molar volumes of the salts are derived from the intercept of the lines. The results are summarized in Table 13.

Table 13: Extrapolated partial molar volume and density of pure ionic liquid oxidizers.

Compound name	Formula	Molar volume, cm ³ /mol	Density of pure ionic liquid (no solvent), g/cm ³
Ammonium nitrate	NH ₄ NO ₃	52.00(15) ^a	1.539(5) ^a
Ammonium dinitramide	NH ₄ N(NO ₂) ₂	74.06(13)	1.675(3)
Hydroxylammonium nitrate	NH ₃ OH NO ₃	55.45(19)	1.732(6)

^aNumbers in parentheses designate the standard deviation of the last digits.

Data source: [238]

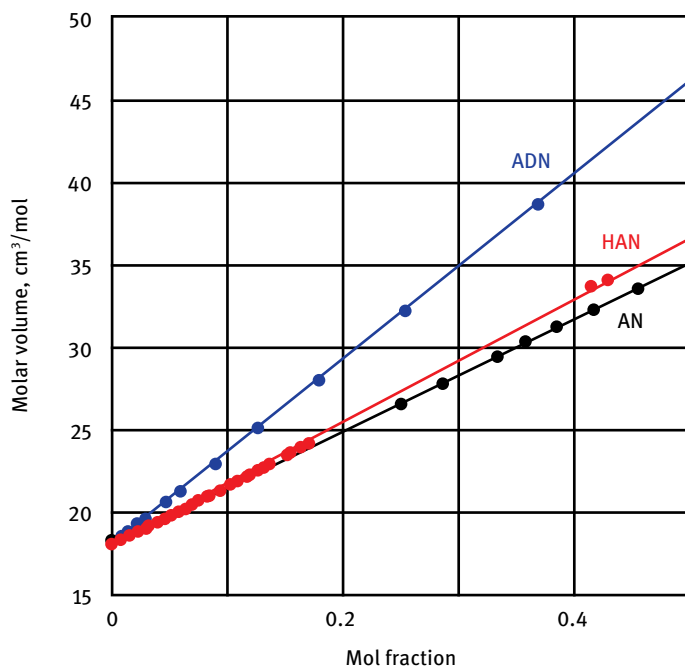


Figure 18: Molar volume of aqueous HAN solutions vs. mol fraction HAN, in comparison to other oxidizers. (Reproduced and modified from Kappenstein, Batonneau, Perianu and Wingborg [238] with permission from Dr. Charles Kappenstein.)

The apparent molar volume of a solution is obtained by assuming that it is made up of two additive contributions, one from the water solvent and the other from the solute. The partial molar volume of the solute can be calculated by subtracting the volume of water from the density of the solution and subtracting the density of the solute:

$$V_s = \frac{1000\left(\frac{1}{D} - \frac{1}{D_i}\right)}{G + \frac{E}{D}}$$

where

V_s = apparent molar volume of solute, cm³/mol

D = density of solution, g/cm³

D_i = density of solvent, g/cm³

G = molality of solution, mol/1000g

E = molecular mass of solute, g/mol

The conversion of molarity to molality is done by

$$G = \frac{1000M}{(1000D - ME)}$$

where M is the molarity of the solution. The mol fraction X of the solute is obtained from

$$X = \frac{G}{\left(G + \frac{1000}{B}\right)}$$

where B is the molecular mass of the solvent (H_2O ; $B = 18.0153$). Instead of plotting the partial molar volumes against the reciprocal density, a better correlation can be obtained by plotting the partial molar volumes against a concentration parameter χ

$$\chi = \frac{\sqrt{X}}{1 + \sqrt{X}}$$

where X is the mol fraction HAN. This correlation was used at Olin Chemicals for calculating the densities not only of the HAN solution products but also of feedstock and mixed electrolytes at various stages of the HAN production process [239]. The slope of the linear function (X coefficient) shown in Figure 19 is 19.2226. The intercept at infinite dilution is at $47.1141 \text{ cm}^3/\text{mol}$. The density at the pure HAN end (1.68 g/cm^3) is closer to that of molten HAN than crystalline HAN. The same method was also used for AN and TEAN solutions. The method is useful for obtaining densities of solutions at constant temperature over a wide range of concentrations if only the density of the solid salt and one density point of the solution are available.

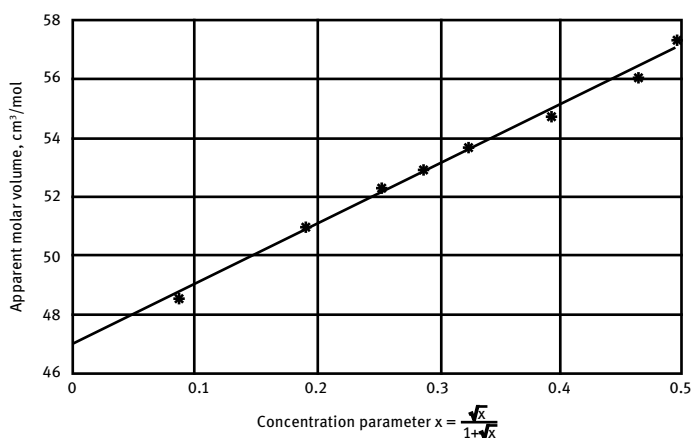


Figure 19: Apparent molar volumes of HAN at 20 °C as a function of concentration parameter χ . (Reproduced and modified from [162].)

Density measurements at the U.S. Army's Ballistic Research Laboratory (BRL) by Sasse et al. [236, 240] were made not only on HAN in water but also on its deuterium analog in heavy water; see Table 14.

Table 14: Density of HAN/water and HAN-D4/heavy-water solutions at 293 K (20 °C).

NH₃OHNO₃/H₂O		ND₃ODNO₃/D₂O	
Density, g/cm³	Concentration, M	Density, g/cm³	Concentration, M
0.99963	0.0 (pure water)	1.1053	0.0 (pure D ₂ O)
1.02341	0.500	1.1662	1.336
1.12533	2.781	1.1904	1.875
1.22919	5.232	1.2761	3.936
1.29636	6.858	1.4488	8.321
1.37548	8.839	1.6137	12.74
1.52306	12.622	1.69694	15.86
1.65569	16.338	—	—
1.68	17.5 ^a	1.841	18.40 ^a
1.841	19.17 ^b	1.916	19.15 ^b

^aAnhydrous melt

^bCrystalline solid, from X-ray data, [241]

Data source: [236], except data points marked with^b

The data in Table 14 have been curve-fitted to a second-order polynomial instead of a linear progression formula.

For HAN in H₂O:

$$\rho = 0.9935 + 0.04630M - 0.0004007M^2$$

For HAN-D4 in D₂O:

$$\rho = 1.1045 + 0.04646M - 0.0005581M^2$$

Figure 20 shows the data from Table 14 and a second-order polynomial curve fit for the mid-range. The standard deviation for density using the quadratic equation is three times smaller than for data approximated by the linear equation.

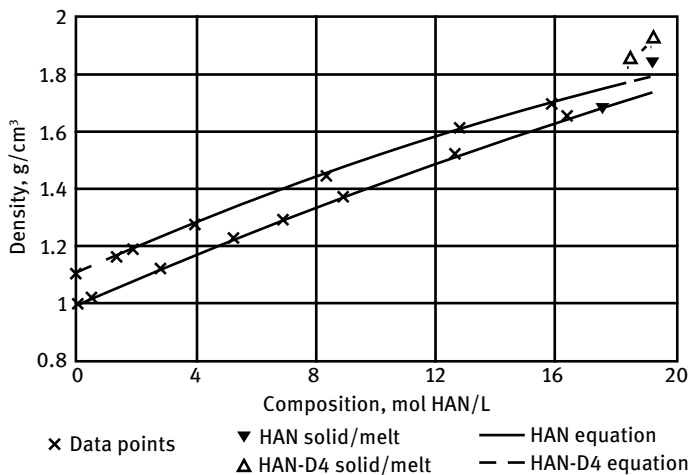


Figure 20: Comparison of solution densities for HAN/H₂O and HAN-D₄/D₂O. (Image created by Schmidt 2020 based on data from [236].)

3.3.2.2 Density of Ternary HAN Solutions

In addition to binary HAN/water solutions, ternary mixtures of HAN/AN/H₂O, HAN/HN/H₂O, and HAN/H₂O₂/H₂O have been formulated as liquid oxidizers. The measured density of OXSOL-1 at 296.2K (23.1°C) is 1.539g/mL. The patent [242] contains tabulated density data for a wide range of HAN/AN/H₂O mixtures in

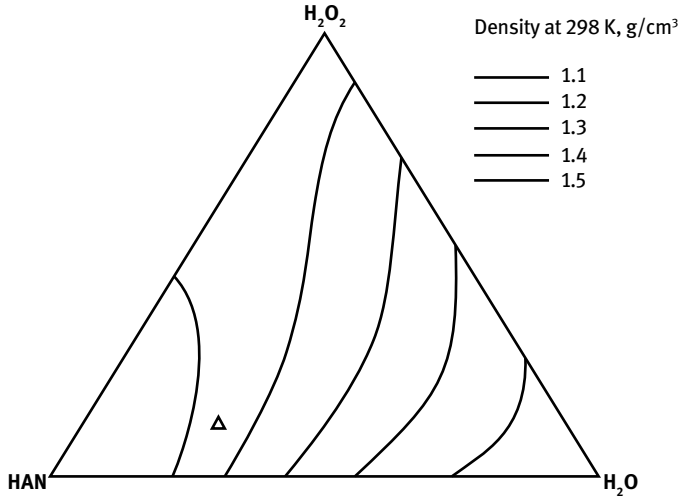


Figure 21: Density of HAN/H₂O₂/H₂O solutions. (Reproduced and modified from [229, 230].)

addition to that of OXSOL-1. The measured density of OXSOL-2 at 296.2 K (23.1 °C) is 1.552 g/mL.

Densities of ternary HAN/H₂O₂/H₂O solutions are graphed in Figure 21. The density of PERHAN (62% HAN, 12.5% H₂O₂, and 25.5% H₂O, marked with a triangle Δ) is 1.439 g/mL at 298 K.

3.3.3 Viscosity of HAN Solutions

The viscosity of HAN solutions increases abruptly as the temperature of the solutions drops to close to the glass transition temperature T_g . Viscosity measurements as a function of water content and temperature were conducted to validate theoretical models in an attempt to represent the molecular structure of ion clusters in solution.

The viscosities of HAN solutions as a function of concentration based on data from van der Hoff, Bunte, and Donmoyer 1986 [243] are summarized in Table 15. Additional density and viscosity data are in Table 16. Table 17 gives viscosity of HAN solutions with different concentrations at various temperatures.

Table 15: Viscosity of HAN solutions as a function of concentration.

Concentration	Viscosity at 293 K (20 °C)	
M	mPa s	cPs
0 (pure water)	1.002	1.002
0.1	1.02	1.02
0.5	1.06	1.06
1	1.06	1.06
3	1.23	1.23
5	1.52	1.52
7	2.14	2.14
9	3.05	3.05
11	4.80	4.80
13	7.11	7.11

Data source: [244]

Table 16: Viscosity and density of HAN solutions as a function of concentration.

Concentration	Temperature	Density	Dynamic viscosity	
Mass-% HAN	K	g/cm ³	mPa s	cPs
0	298	1.0	0.89	0.89
83.3	298	1.528	9.09	9.09
90.2	298	1.591	15.9	15.9
94.0	298	1.608	20.0	20.0

Data source: [206]

Table 17: Viscosity of aqueous HAN solutions as a function of concentration and temperature.

HAN mixture Molarity	Temperature		Dynamic viscosity	Viscosity correction factor	References
	K	°C	$\text{mNs m}^{-2} = \text{mPas} = \text{cPs}$	$\eta^\circ/\eta; \eta^\circ = 1.002$	
0.1	293	20	1.02	0.98	[244]
0.5	293	20	1.02	0.95	[244]
1	293	20	1.06	0.95	[244]
3	293	20	1.23	0.81	[244]
3.2	273	0	1.94		[245]
3.2	288	15	1.44		[245]
3.2	298	25	1.21		[245]
5	293	20	1.52	0.66	[244]
7	293	20	2.14	0.47	[244]
9	293	20	3.05	0.33	[244]
11	293	20	4.8	0.21	[244]
13	293	20	7.11	0.14	[244]
13	273	0	15.5		[245]
13	288	15	9.62		[245]
13	298	25	7.62		[245]

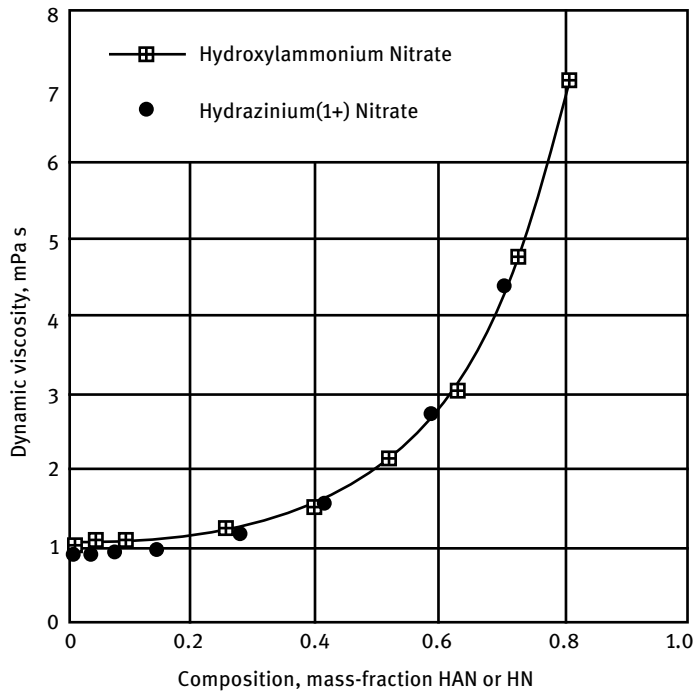


Figure 22: Dynamic viscosity of HAN and HN solutions at 273 K. (Reproduced and modified from [235].)

The curves obtained when plotting the dynamic viscosity of HAN solutions vs. the mass fraction in comparison to that of HN solutions show that solutions of the two salts in water behave very similarly (Figure 22) [235]. The viscosity increases steeply as the concentration approaches saturation.

The kinematic viscosity of 13-M HAN as a function of temperature is shown in Figure 23.

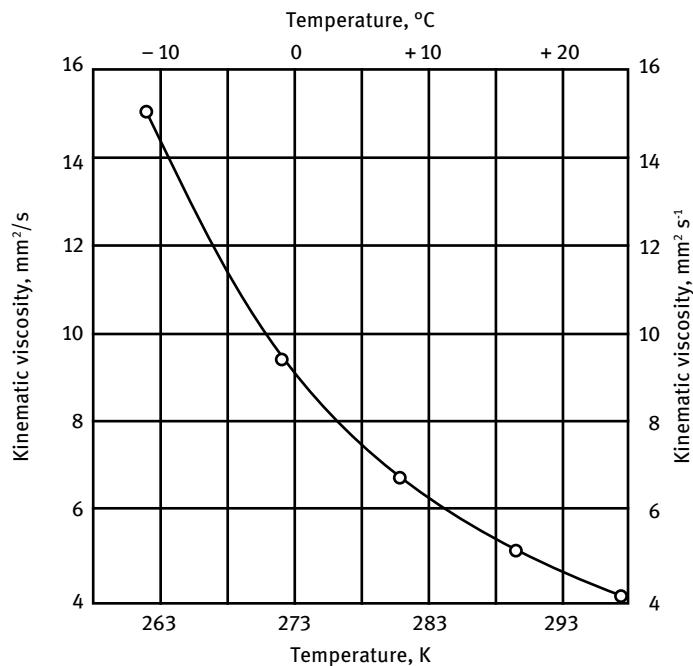


Figure 23: Kinematic viscosity of 13-M HAN as a function of temperature. (Reproduced and modified from [235].)

3.3.4 Vapor Pressure and Boiling Point of HAN Solutions

The vapor phase above HAN solutions consist essentially only of water. HAN itself is not volatile as long as there is some water in the solution.

Because of a lack of thermal stability, one will generally avoid heating HAN solutions to the boiling point for any length of time. However, because most HAN is produced in dilute solutions and has to be concentrated for use as a propellant, the boiling behavior of HAN solutions has been studied in detail [246]. Two sets of experiments were conducted, one in an open system (allowing water to escape) and the other in an open system with a reflux condenser that returned all water vapor to the sample. Both were done under inert gas because the presence of oxygen may cause acceleration of “fizz” reactions. The potentially **hazardous** tests were conducted with

10-mL samples in 30-mL glass flasks and extended for up to 3 h. A sample of 12.48-M HAN was refluxed and analyzed before and after the experiment. The boiling point was 405 K (132°C) at the beginning and 402 K (129°C) at the end of the 2.5-h experiment. The analysis showed a 6% loss in HAN and a gain of water. The gases escaping were nitrogen and nitrous oxide in a mol ratio of 1:2. The boiling points for different HAN concentrations are given in Table 18.

Table 18: Boiling points of HAN solutions.

Composition, molarity		Boiling point	
HAN	Water	K	°C
0	55.56	373.15	100
4.0	43.72	380.15	107
9.0	28.99	388.15	115
12.0	20.16	400.15	127
12.48	16.72	405.15	132
13.0	17.21	402.15	129
13.0	17.21	407.15	134
15.8	8.97	418.15	145

Data source: [236]

Pure HAN does not have a measurable vapor pressure. Hydroxylammonium nitrate solutions are ionic liquids, and as such have been proposed as working fluids for electric colloid thrusters, which operate only in vacuum. In such electrospray thrusters, the HAN solution would have to be introduced as an aerosol, which can then be ionized to create a plasma and then be accelerated in an electric field, similar to an ion engine [247]. A modeling effort was started to better understand the ionization processes of vaporized ionic liquid mixtures. Differences were noticed between decomposition reactions at elevated pressures and those occurring when HAN was vaporized and ionized in vacuum. The species in the vacuum decomposition spray were analyzed with a residual gas analyzer and showed a large percentage of nitric oxide. A mixture of 1-ethyl-3-methylimidazolium ethyl sulfate ([Emim][EtSO₄]) and HAN is an energetic monopropellant potentially suitable in a multi-mode chemical-electric microtube-electrospray micropropulsion system [248].

3.3.5 Compressibility of HAN Solutions

Liquid-propellant guns operate at much higher pressures than rocket engines. For this reason, the compressibility of HAN, HAN solutions, and HAN-based propellants has been investigated. Although this is not needed for normal rocket propellant opera-

tions, certainly not without prior addition of a fuel, the data are listed here nevertheless, just in case they are needed.

3.3.5.1 Velocity of Sound in HAN Solutions

The velocity of sound is easier to measure than the compressibility of fluids, and the two properties can be converted by simple equations. There are substantially more data on velocity of sound and compressibility measurements of formulated, mixed HAN-based propellants than on the ingredients by themselves.

A cell for high-pressure sound velocity measurements of liquids in a Birch-Bridgman pressure vessel was used to determine the velocity of sound in 2, 4, 9, and 13-M HAN and in several TEAN solutions at room temperature at pressures up to 4000 bar (55 ksi) [249–251]. The velocity of sound as a function of pressure and concentration is shown in Figure 24.

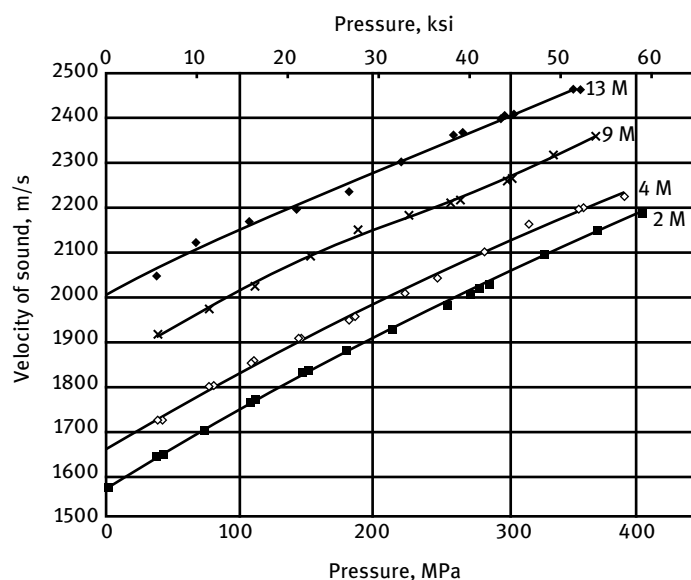


Figure 24: Velocity of sound of HAN solutions as a function of pressure and concentration. (Reproduced and modified from [251].)

The velocity of sound and the attenuation of sound in HAN solutions was measured at 203 to 294 K using ultrasound and Rayleigh-Brillouin scattering methods in the frequency ranges of 10 MHz and 8–14 GHz [252, 253]. The data were curve-fitted to obtain the dependence of the velocity of sound on the sample temperature. Similar measurements were performed on TEAN solutions.

3.3.6 Gas Solubility in HAN Solutions

During the evaluation of HAN-based monopropellants as liquid gun propellants, inadvertent ignition due to adiabatic compression of gas bubbles was an ongoing concern. The release of gas bubbles is most likely a worst-case scenario if the propellant is saturated with gas. Therefore, the solubility of gases in HAN and HAN-based monopropellants has been investigated (*Encyclopedia of Monopropellants*).

3.3.7 Thermodynamic Properties of Hydroxylammonium Nitrate

3.3.7.1 Heat Capacity of HAN Solutions and Solid HAN

Abrupt changes in the heat capacity of HAN solutions occur when the temperature is lowered close to the glass transition temperature. Heat capacity measurements were used as a sensitive indication of changes taking place in the molecular structure of the associations of ions and solvates in clusters. The interpretation of these measurements is given in Section 3.3.8.2 (molecular structure).

It has been attempted to derive the heat capacity and other thermodynamic functions of solid and molten HAN from the spectroscopic and XRD data using statistical thermodynamics and a Monte Carlo method. A formula not previously found in the literature was derived for the heat capacity at constant pressure for a system at given density and temperature from a single Monte Carlo run [254]. X-ray and neutron diffraction measurements have been made of HAN and/or deuterated HAN. The crystalline structure has been determined for a wide range of temperatures. The X-ray and neutron diffraction data have been jointly analyzed to display the details of the valence electron distribution in HAN. X-ray and neutron liquid scattering experiments have yielded the total structure factor of molten HAN. Theoretical models of the partial structure factors (and from them, the total structure) of molten HAN have been made using the Percus-Yevick hard-sphere model. As a beginning approach to a perturbation theory of the system, a system of rigid ellipses was studied [255].

Other heat-capacity data points for three different HAN concentrations at one temperature are listed in Table 19. Heat-capacity data for two different HAN concentrations at five different temperatures are listed in Table 20.

Table 19: Heat capacity of HAN solutions.

HAN concentration, molarity	Heat capacity at 293 K, J kg ⁻¹ K ⁻¹
13	1570
10.7	1553
9	1733

Table 20: Heat capacity C_p of HAN solutions.

Temperature, K	Temperature, °C	3.2-M HAN		13-M HAN	
		J g ⁻¹ K ⁻¹	cal g ⁻¹ °C ⁻¹	J g ⁻¹ K ⁻¹	cal g ⁻¹ °C ⁻¹
310	37	3.30	0.789	2.25	0.538
315	42	3.39	0.811	2.25	0.53
320	47	3.39	0.811	2.25	0.538
325	52	3.41	0.815	2.27	0.542
330	57	3.39	0.811	2.27	0.543

Data source: [245]

3.3.7.2 Enthalpy of Fusion of HAN

The enthalpy of fusion of HAN was determined from solubility and phase diagram results to be $11 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ [210].

Direct measurement of the enthalpy of fusion was done in a calibrated differential scanning calorimeter [215]. The onset of melting of α -HAN was at $35.72 \pm 0.65^\circ\text{C}$, and the average heat of fusion was $26.97 \pm 2.05 \text{ cal/g} = 112.8 \pm 8.6 \text{ J/g}$. The onset of melting of β -HAN was at $47.73 \pm 1.69^\circ\text{C}$, and the average heat of fusion was $26.72 \pm 1.81 \text{ cal/g} = 111.8 \pm 7.6 \text{ J/g}$. There was no significant difference between the latent heats of fusion of the two crystal modifications.

3.3.7.3 Enthalpy of Formation of HAN

The enthalpy of formation of solid HAN is mostly of academic interest since HAN is almost never used in the solid state as a rocket propellant. We really need the enthalpies of formation of various HAN solutions and of HAN in solution together with other ionic species serving as fuels in monopropellants.

3.3.7.4 Enthalpy of Formation of Solid Hydroxylammonium Nitrate

The most frequently quoted number for the standard enthalpy of formation of solid HAN is $366.5 \text{ kJ/mol} = 87.6 \text{ kcal/mol}$ [256, 257]. The source of this number is most likely [216].

PEPCODED.DAT has an enthalpy of formation of HAN of $-843.0 \text{ cal/g} = -80.96 \text{ kcal/mol} = -338 \text{ kJ/mol}$ [258]. The source of this number is not known.

Kounalakis and Faeth [259] estimated the enthalpy of formation of HAN and TEAN from the Doraiswamy group contribution method and predicted 399 kJ/mol (95.3 kcal/mol) for HAN and -776 kJ/mol (-185.5 kcal/mol) for TEAN.

Kuwahara calculated the theoretical performance of AP/HTPB/Al, AN/HTPB/Al, and HAN/HTPB/Al solid propellants and used an enthalpy of formation of -4358 kJ/kg [217]. That translates into -418.4 kJ/mol .

Other sources (Ashcraft, Raman, and Green [260]; Meng et al. [261]) quote the enthalpy of formation as $-333.4 \text{ kJ/mol} = -79.68 \text{ kcal/mol}$, but that may be for dissolved

HAN in aqueous solutions at infinite dilution. The enthalpy of dissolution of HAN in water was reported as 22.5 kJ/mol, which partially accounts for the difference in these numbers.

3.3.7.5 Enthalpy of Formation of Hydroxylammonium Nitrate Solutions

The difference between the enthalpy of formation of solid HAN and the enthalpy of formation of HAN solutions is the enthalpy of dissolution. Table 21 gives the enthalpy of dissolution of HAN compared to that of other high-energy oxidizers [262]. All of these salts cool off when dissolved in water, a phenomenon that is used with advantage with ammonium nitrate (AN) in two-component instant ice packs for first aid in sports injuries.

Table 21: Standard enthalpy of dissolution of HAN compared to that of other oxidizers.

Compound	Standard enthalpy of formation, kJ/mol		Enthalpy of dissolution, kJ/mol
	Solid	In solution at infinite dilution	
NH_3OHNO_3	-366.5	-344.8	+22.5
NH_4NO_3	-365.4	-339.9	+25.3
$\text{N}_2\text{H}_5\text{NO}_3$	-246.9	-215.1	+31.8

Data source: [262]

3.3.7.6 Enthalpy of Formation of Hydroxylammonium Nitrate Vapor

Various computational chemistry methods have been used to predict the enthalpy of formation of HAN vapor from its molecular structure. Although HAN vapor would exist only during the sublimation of HAN at very low pressures, this condition can be simulated successfully with modern computational methods. We cite one of these methods here as an example of how the potential hazards of energetic materials can be predicted without getting one's fingers wet (or burned) in the laboratory. The calculated gas-phase heats of formation at 298 K were -271 and -242 kJ/mol (-64.8 and -57.8 kcal/mol) using AM1 and PM3 methods, respectively [263]. In order to validate the results, the high-level quantum mechanical method G2MP2 from the Gaussian 03 suite of programs was also used to calculate the heat of formation of HAN. The suggested heat of formation of -255 kJ/mol (-61 kcal/mol) is about the average of the results using the AM1 and PM3 methods. One must know the heat of sublimation to convert these numbers to the enthalpy of formation of solid HAN.

3.3.8 Molecular Structure of Hydroxylammonium Nitrate

3.3.8.1 Molecular Structure of Solid Hydroxylammonium Nitrate

The molecular structure of the ion pair used for modeling is illustrated in Figure 25.

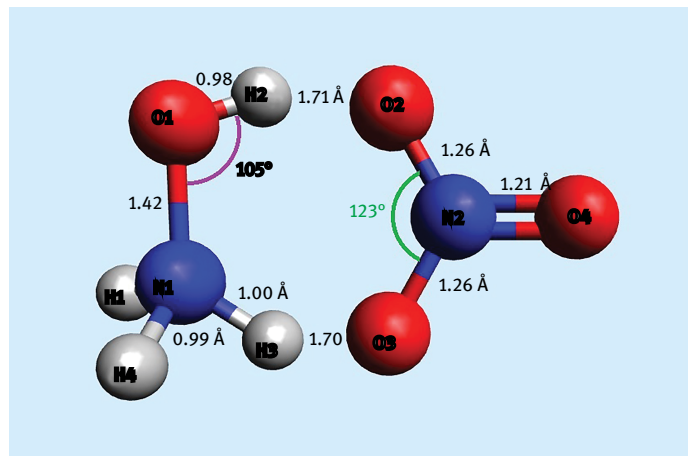


Figure 25: Molecular structure of a HAN ion pair in the gas phase. (Patterned after [263].)

The crystal and molecular structures of pure HAN and HAN-D4 were obtained by single-crystal X-ray diffraction (XRD) [264]. Hydroxylammonium nitrate crystallizes in monoclinic crystals $P2_1/c$ with the lattice parameters of $a = 4.816 \text{ \AA}$, $b = 6.800 \text{ \AA}$, $c = 10.728 \text{ \AA}$, and $\beta = 99.35^\circ$ [265, 241]. HAN and its perdeuterated homolog HAN-D4 are isostructural and have very similar crystal parameters, bond distances, and bond angles. The local environment of the NH_3OH^+ ion is shown in Figure 26 in an illustration copied from [266].

All of the hydrogen (or deuterium) atoms are involved in hydrogen bonding to neighboring oxygen atoms, with H(2) being bifurcated between O(2) and O(3). The hydrogen-bond contacts are shown as dashed lines. The strongest hydrogen bonding is between the hydrogen on the $-\text{OH}$ group and one of the oxygens on a neighboring nitrate ion.

The theoretical electron-density analysis of five crystals including HAN was calculated using molecular orbital computational chemistry methods [267]. The theoretical results were compared to the experimental results available from XRD. The theoretical calculations give electron-density distributions in good agreement with the experimental results for some compounds, but obvious differences between the calculated electron-density distributions and experimental density distributions for HAN were noted. Some improvement in agreement between experimental and calculation results can be achieved when the basis sets are changed from STO-3G to 3-21G.

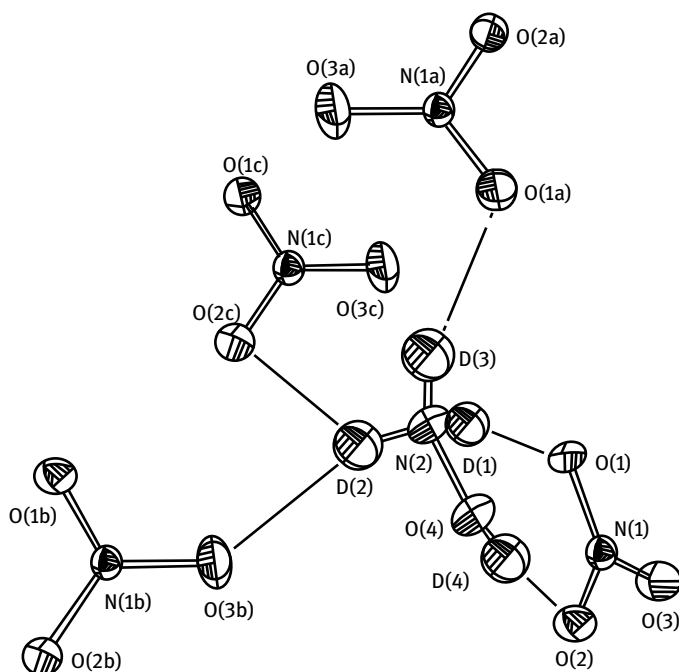


Figure 26: The microenvironment of $\text{ND}_3\text{OD}^+\text{NO}_3^-$ ions in crystalline HAN. (Reprinted from [266], with permission from © 1986 American Chemical Society; permission conveyed through RightsLink.)

X-ray and neutron diffraction measurements have been made of HAN and/or deuterated HAN [254, 255, 268]. The crystalline structure was determined for a wide range of temperatures, looking for phase changes similar to those occurring in AN. The X-ray and neutron diffraction data were jointly analyzed to display the details of the valence electron distribution in HAN crystals.

Electron-density distributions in four compounds were analyzed by simultaneous modeling of X-ray and neutron diffraction data [269]. The model compounds, HAN, and three other molecules represented a wide range of atom–atom interactions and provided a stringent test for a single electron-density model. It was found that the X-ray and neutron models converge to a single model when appropriate considerations have been included and that the X + N technique is helpful in reaching a higher level of confidence. Model considerations that were explored included anharmonic thermal motion (third-order and fourth-order), secondary extinction correction, proper weighting of the two data sets, and application of charge constraints.

3.3.8.2 Molecular Structure (Clusters) in Hydroxylammonium Nitrate Solutions

Hydroxylammonium nitrate solutions contain hydroxylammonium ions, nitrate ions, water, undissociated HAN, and very small amounts of hydroxylamine free base and

free nitric acid. The ions are highly associated, connected by hydrogen bonds and water molecules forming bridges. The ions associate in clusters. Ion pairing can be observed in solutions with concentrations as low as 2-M HAN. Cluster formation is responsible for many of the unique properties of HAN solutions, e.g., their high viscosity and the rate of proton exchange.

The intermolecular distances of hydrogen-bonded oxygen atoms in HAN solutions can be derived from the sharpness of IR peaks [270]. At 308 K (35 °C) and 9.5-M HAN, the O—H band of water is very broad, corresponding to a wide variation of O...O distances. The distribution narrows with increasing concentration and shifts to lower frequencies (shorter O...O distances) with decreasing temperature. At 213 K (−60 °C) there is an abrupt shift due to the formation of a glassy state. The intermolecular distance of O...O in $\text{H}_3\text{NOH}\cdots\text{O}$ is very sharp at 2.63 Å, and the distance in $\text{HO}-\text{H}\cdots\text{O}$ varies widely depending on temperature and concentration, centered around 2.9 Å. A large H-bond shift and its narrow distribution suggest a highly ordered ion-pair configuration in the liquid.

HAN is fully dissociated into the hydroxylammonium and nitrate ions in dilute aqueous solutions. As the salt concentration increases past 2 mol/L, beginning ion pairing is observed, the ion pair being formed between the hydrogens of NH_3OH^+ and the oxygens of NO_3^- . Computational chemistry molecular modeling studies can describe the structure of these ion pairs and the clusters that form as HAN concentration is increased and can explain the fate of the water solvent tucked away and immobilized between the ions. The properties of concentrated HAN–water mixtures are quite different from those of aqueous solutions and are readily explained with the assistance of these molecular modeling studies.

Ion clusters can be studied in solution or in the gas phase. Compounds that are not stable enough in the gas phase for experimental study of cluster formation can be modeled by computational chemistry to obtain images of their spatial arrangements minimizing the free energy.

The glass transition temperatures of HAN/ H_2O solutions were determined by DSC [271]. It was found that T_g behaves as a colligative property and remains nearly constant at 372.85 K (−99.7 °C) in the concentration range of 25–82 mol-% HAN. When the HAN concentration is lowered to below 25 mol-% HAN, T_g rises surprisingly, and for a wide range it is independent of the HAN concentration. Researchers have attempted to explain this behavior by the formation of clusters [272, 273]. It was assumed that three molecules of water at most can be incorporated in a cluster with HAN. The most stable clusters are those containing three molecules of water for every two molecules of HAN, which form when the HAN concentration is below 25 mol-%.

Structures and energies of gas-phase HAN clusters can be determined using density functional theory (DFT). Three stable cluster configurations were found for HAN that involve strong hydrogen bonding between hydroxylamine and nitric acid molecules and their ions [274]. In the most stable configuration, both the oxygen and the nitrogen of hydroxylamine were found to be hydrogen bonded to sites on

the nitric acid molecule. In the less stable HAN structures, only the oxygen or the nitrogen of hydroxylamine are hydrogen bonded. There are two stable structures for the $(\text{HAN})_2$ complex. The more stable structure is ionic, with the nitric acid proton having transferred to the nitrogen of hydroxylamine. Strong electrostatic and hydrogen-bonding interactions stabilize this structure. The other stable form of $(\text{HAN})_2$ has fewer hydrogen bonds and is composed of interacting neutral nitric acid and hydroxylamine molecules. Proton exchanges are very fast for the HAN configurations. The saddle points for the proton exchange process are ionic forms of HAN with interacting HONH_3^+ and NO_3^- moieties. These ionic structures are 13.5 and 13.6 kcal/mol higher in energy than the neutral hydrogen-bonded complexes of HONH_2 and HNO_3 from which they are formed. The electrostatic attractions between the ions are sufficient to stabilize the ionic form of $(\text{HAN})_2$, whereas in the HAN “monomer” the interaction energy for single HONH_3^+ and NO_3^- ions is not sufficient to compensate for the energy required for proton transfer from nitric acid to the hydroxylamine group. Alkylation of the NH_2 group changes the proton transfer barriers; see Section 6 on alkylhydroxylamines.

The images used for illustrating the appearance of HAN clusters here are only two-dimensional on paper. In reality, this is a three-dimensional (3-D) network. It would require some 3-D software to illustrate clusters on a computer screen and enable the viewer to rotate the molecule and view it from different angles.

HAN clusters become even more complex after the addition of water-soluble fuels in an effort to create monopropellants. Many of these fuels are ionized salts or are molecules that actively participate in the formation of hydrogen bonds.

Theoretical models have been developed to explain the unusual behavior of the viscosity of HAN solutions (and ternary mixtures containing HAN, water, and a fuel) as the temperature of the liquid approaches the glass transition point. Anharmonic effects in ammonium nitrate and HAN clusters due to hydrogen bonding are responsible for the unique properties of their aqueous solutions [275]. The covalent and ionic clusters of ammonium nitrate and hydroxyl ammonium nitrate were characterized using DFT and second-order vibrational perturbation theory. The most stable structures are covalent acid–base pairs for the monomers and ionic acid–base pairs for the dimers. The hydrogen-bonding distances are greater in the ionic dimers than in the covalent monomers, and the stretching frequencies are significantly different in the covalent and ionic clusters. Calculations of geometries, frequencies, and shielding constants have provided insight into the significance of anharmonic effects in ionic materials, as well as data that will be useful for the illustration of molecular mechanical force fields in ionic liquids. Anharmonic effects are particularly important for the study of proton transfer reactions in ionic materials, such as those that initiate the decomposition of HAN.

3.3.9 Optical Properties of Hydroxylammonium Nitrate

3.3.9.1 Spectra of Hydroxylammonium Nitrate Solutions and Solid Hydroxylammonium Nitrate

Absorption spectra of HAN solutions in the UV and IR regions have been taken for several reasons: They are useful in studying the unique properties of ionic, highly associated (clustered) liquids, and they are used as analytical methods to verify the nominal composition of propellant mixtures containing HAN and to detect unwanted contaminants. Another reason that the spectra of HAN and HAN-based propellants over the entire range of the electromagnetic spectrum needs to be known is the proposed use of laser or microwave heating as a method for igniting these hard-to-ignite propellants. The amount of energy absorbed depends on choosing the correct frequency for the source of radiation, matching the laser output with the absorption spectrum of the compound to be ignited. Spectra discussed here cover a wide range of the electromagnetic wave spectrum. A separate section also includes induced methods such as nuclear magnetic resonance (NMR) and electron spin resonance spectroscopy.

UV Spectra of Hydroxylammonium Nitrate Solutions

The UV and IR spectra of HAN solutions and propellants are of interest for laser-ignition studies. Because HAN-based propellants are ultimately safe, and some will not ignite even if hit with the flame of a welding torch, various alternate ignition methods have been studied for ignition in liquid guns or rocket engines. This includes laser ignition.

IR Spectra of Hydroxylammonium Nitrate Solutions

Infrared spectra of HAN solutions are valuable diagnostic tools to monitor HAN concentrations during its synthesis, to verify the absence of contaminants, and to identify and analyze decomposition products formed during extended storage or intermediates formed during rapid heating to the point of ignition. Infrared spectroscopy is an ideal method for analysis of HAN and HAN contaminants in the solid state or in aqueous solutions [276]. The mid-IR spectrum of HAN solutions contains several distinct, non-overlapping peaks that are characteristic for its ingredients. The line broadening of the peaks indicates strong hydrogen bonding of several of the species in aqueous solution. Infrared spectra of HAN solutions at atmospheric pressure were obtained by placing a capillary film between AgCl windows. Changes in the IR spectra of all three components, NH_3OH^+ , NO_3^- , and H_2O , provided a consistent picture of the interactions between these species. The nitrate spectrum was most sensitive to inter-species interactions because distinctive bands due to ion pairing and hydration were observed.

The bands below 2000 cm^{-1} are due to intramolecular vibrations of water, NH_3OH^+ , and NO_3^- ions. Spectra at high pressures were obtained using a variable temperature diamond anvil cell. From these spectra, qualitative and quantitative

information about hydrogen bond lengths and the interspecies distance distributions in aqueous HAN solutions was obtained as a function of concentration (7 to 17 M), temperature (153 to 333 K = -120 to +60 °C), and pressure (0.1 to 7100 MPa). Absorption bands were identified using isotopic uncoupling techniques (deuterium analogs) for the O—H...O and N—H...O hydrogen bonds in conjunction with frequency–distance correlations [277]. Replacing hydrogen with deuterium shifts the absorption bands that are due to N—H bonds and O—H bonds, as seen in Figure 27, which shows IR spectra of normal and deuterated HAN (dHAN).

Infrared spectra of aqueous solutions of dHAN (11M ND₃ODNO₃ (= dHAN) in D₂O) were recorded at pressures ranging from 0.101 kPa to 1.767 GPa [278]. Comparing absorption bands of isotope-substituted dHAN to those of normal HAN allows

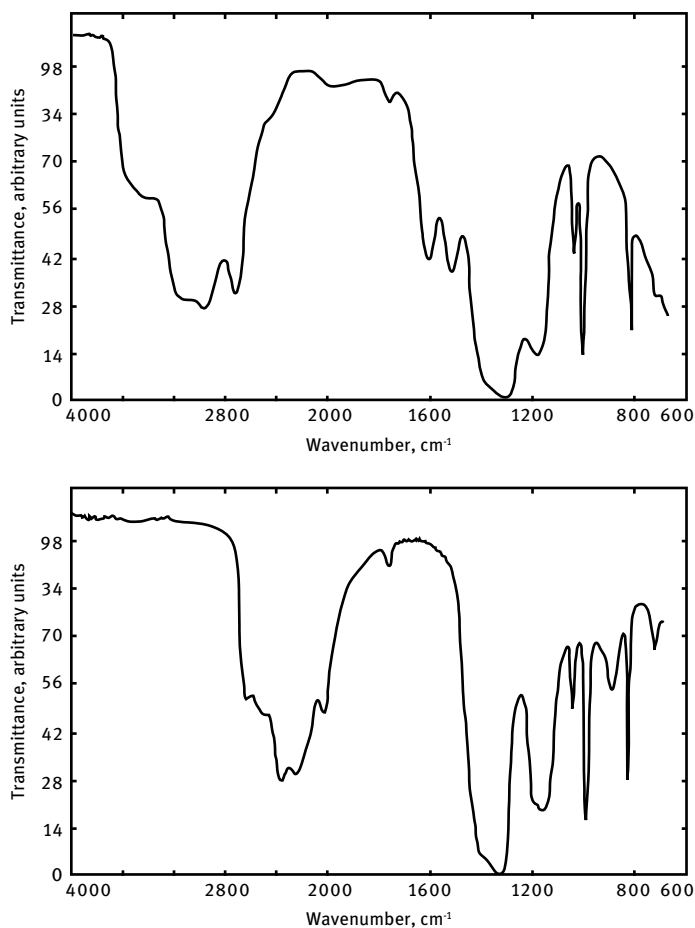


Figure 27: Transmittance IR spectra for 13-M HAN and deuterated HAN. (Republished and modified from [270] with permission of © 1988 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

one to measure hydrogen (deuterium) bond distances between OD (OH) groups and neighboring O atoms. Compressing the solution in a diamond anvil cell to extremely high pressures shifted the IR absorption bands in response to the changing interatomic distances. As a result of the pressurization, the N—O stretch shifted from 991.7 to 1012.2 cm^{-1} , and the NO_3^- bending mode shifted from 825.7 to 816 cm^{-1} .

The broad absorption band at 2730 cm^{-1} resulting from the $-\text{NH}_3^+$ bending combination mode of HONH_3^+ has been used in kinetic studies of aqueous HAN thermal decomposition [279].

The IR spectrum of an 85% HAN solution shown in Figure 28 is very useful because the exact wave numbers were written next to the peaks [280].

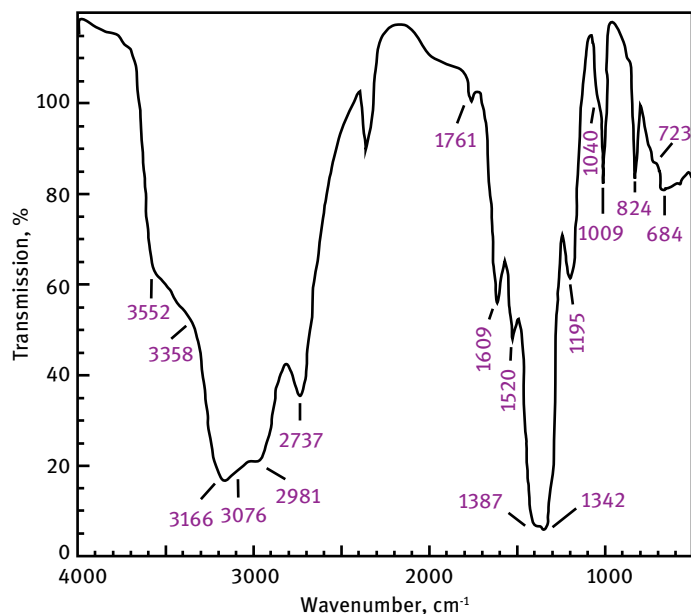


Figure 28: IR spectrum of 85% HAN solution. (Reprinted and modified from [281].)

The vibration bands at 3166, 3076, 2998, 2981, 1761, 1520, 1195, and 1009 cm^{-1} were assigned to the NH_3OH^+ group by analogy with NH_3OHCl . The intense band at 2737 cm^{-1} is a combination of the rotation band and the symmetrical deformation band of NH_3OH^+ (1195 and 1520 cm^{-1} , respectively). The stretching vibrations of the O—H bond are identified at 3552, 3358, 1609, and 684 cm^{-1} . The influence of the hydrogen bonding manifests itself in the position of the stretching vibration band and the deformation band of the O—H groups. The N—O bond has a doubly degenerate band at 1387–1342 cm^{-1} and a deformation band at 824 cm^{-1} . The concentration of the HAN solution seems to influence the vibrational bands position in the IR range.

Thus, an increasing water concentration shifts the characteristic bands of N—H to higher wave numbers. For the stretching vibrations of the N—O bond, the dilution effects a slight increase in band wave numbers located at 1387–1342 and 684 cm^{-1} . The stretching vibrations of O—H bonds (3552 and 3358 cm^{-1}) undergo an expansion that increases with dilution.

IR Spectra of Solid Hydroxylammonium Nitrate

Solid and water-free HAN is relatively difficult to obtain, and it is difficult to prevent it from absorbing water from the atmosphere while the sample is being prepared and mounted in the spectrometer.

Infrared studies of HAN and HAN-D4 spectra conducted in the 1980s often fail to give proper credit to an earlier study of deuterated hydroxylammonium salts, including the nitrate and perchlorate (Rocchicciolo [282]). The IR band assignments for HAN from this precedent source are summarized in Table 22. All bands, with the exception of the νNO band and those of the anions, are affected by deuteration. A similar table for HAP is presented in a later section of this book.

Table 22: IR absorption-band assignments for HAN and d-HAN spectra.

Wavenumber		Assignment
Hydrogen	Deuterium	
3045(f)	2380	νOH
2995(F)	2240	νNH_3^+ anti-symmetric
2900(F)	—	νNH_3^+ symmetric
2665(m), 2380, 1895(f)	2020	Combinations
1580(F), 1559(f)	1142	δNH_3^+ degenerate
1505, 1480, 1470(m)	1120	δNH_3^+ symmetric
1193(F)	903	Rotational NH_3^+
1165(F)	870	δOH
998(F)	990	νNO
529(m)	—	Torsional OH
1365(F), 830(m), 724(f)	—	NO_3^-

Data source: [282]. Absorption band strength legend: (F) very strong, (f) strong, (m) medium.

Deuterating any hydrogen-containing compound and observing the isotope shift in IR absorption lines is a useful tool in assigning IR bands. HAN and HAN-D4 are isostructural and possess similar bond distances and angles. There is no water of crystallization in the crystal lattice. The IR spectrum of HAN and its fully deuterated analog HAN-D4 was measured between 170 and 470 K [266]. Twenty-four bands between 800 and 3140 cm^{-1} were resolved, and about half of them were tentatively assigned to fundamental vibrations. In addition to the fundamentals, a number of overtone/com-

bination bands appear that have become enhanced by N—H and O—H vibrational anharmonicity caused by hydrogen bonding. Figure 29 presents the mid-IR spectrum of partially dry solid and melted HAN. A shoulder at 3140 cm^{-1} depends on the amount of water in the sample.

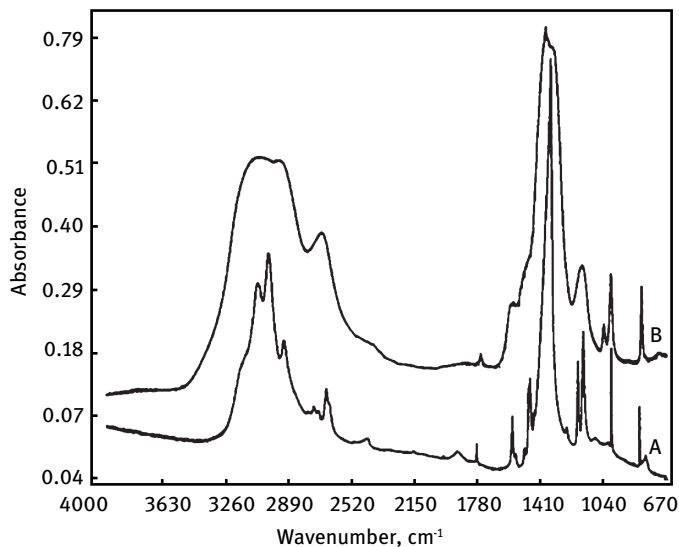


Figure 29: Mid-IR spectrum of partially dry solid (A) and melted (B) HAN. (Reprinted and modified from [266], with permission from © 1986 American Chemical Society; permission conveyed through RightsLink.)

There has been some uncertainty about the assignment of absorptions in the $2620\text{--}2750\text{ cm}^{-1}$ range of aqueous HAN. At one time it was proposed that these may be due to $\nu(\text{OH})$ of a very short $\text{NH}_3\text{OH}^+\cdots\text{ONO}_2^-$ contact ion pair, but Cronin and Brill now assign this to $-\text{NH}_3^+$ combination bands rather than to an OH fundamental. Solid HAN that was relatively water-free was cooled to 170 K while its IR spectrum was recorded. There were normal frequency shifts but no visible solid–solid phase transitions. Solid HAN was then heated through its melting point. All of the bands broadened upon melting.

IR spectra of HAN and its decomposition products were used to study the rapid-heating-rate thermal decomposition of HAN and LP1845 using the FTIR/temperature profiling technique [283]. This is part of an eight-part investigation final report in which the investigators also examined model nitrate solutions and compared their spectra to those of HAN. Acoustic levitation was developed as an IR spectroscopy sample-holding technique to develop non-intrusive droplet studies by IR spectroscopy.

Figure 30 shows the IR spectrum of solid HAN obtained by Kuwahara and colleagues [217].

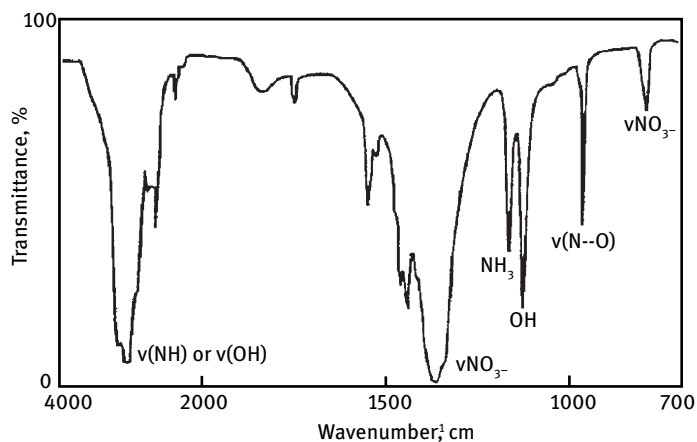


Figure 30: IR spectrum of solid HAN crystals. (From [233], reprinted and modified by permission of American Institute of Aeronautics and Astronautics, Inc.; permission conveyed through Copyright Clearance Center, Inc.)

Raman Spectra of Hydroxylammonium Nitrate Solutions

Raman spectra of HAN solutions and HAN-based monopropellants have been measured mostly for academic interest. There have not yet been any analytical applications of these methods. Raman spectra are useful for studying both the association of ions in clusters and the hydration sphere surrounding the ions. Raman spectra of HAN solutions show concentration-dependent center-frequency and line-width changes similar to those of alkali metal nitrates, but they are different from those of ammonium nitrate [284]. There is no substantial ion pairing in HAN at 0.2M. Markedly different Raman spectra are obtained for solid HAN: The line width decreases, and some bands split. The center frequency of the Raman band in solid HAN is temperature dependent. Raman spectra of XM46 are discussed in *Encyclopedia of Monopropellants*. These XM46 studies often include neat HAN as a baseline.

Slow reactions during the decomposition of 11-M HAN at ambient pressure and at very high pressures were followed by recording the Raman spectra of the solutions [285–287]. The Raman spectra of pure ammonium nitrate were included for comparison. The Raman spectra of an 11-M HAN solution at ambient and unconfined conditions and at elevated pressures were measured using a diamond anvil cell. An Ar^+ laser was used as the radiation source. The 5145 Å line was selected, and the power contained in this line was initially kept at 400 mW, but soon it became apparent that high-intensity laser light caused premature decomposition of the sample, and the beam

was attenuated with neutral density filters to about 10 mW. The pressure in the cell was determined by the pressure shift of the ruby 14405 cm^{-1} line of a ruby chip that was immersed in the sample. Pressure and temperature of the cell were varied over the range of 2–7 kbar and 295–393 K (22–120 °C). At pressures near 6 kbar and temperatures near 363 K (90 °C), a significant and irreversible change in the HAN spectra was observed. This change was interpreted as the result of thermal decomposition occurring within the sample, accompanied by the disappearance of features related to HAN nitrogen–oxygen bonds. Evidence of nitrous oxide formation was found, and some of the nitrous oxide appeared to be present in the solid state at very high pressures. A transient appearance of nitrogen dioxide in an early reaction stage was difficult to verify. Dehydration of HAN-H₂O samples was attempted by evacuating the chamber to approximately 0.1 mm Hg. Raman spectra taken before and after dehydration are shown in Figure 31, together with an H₂O spectrum.

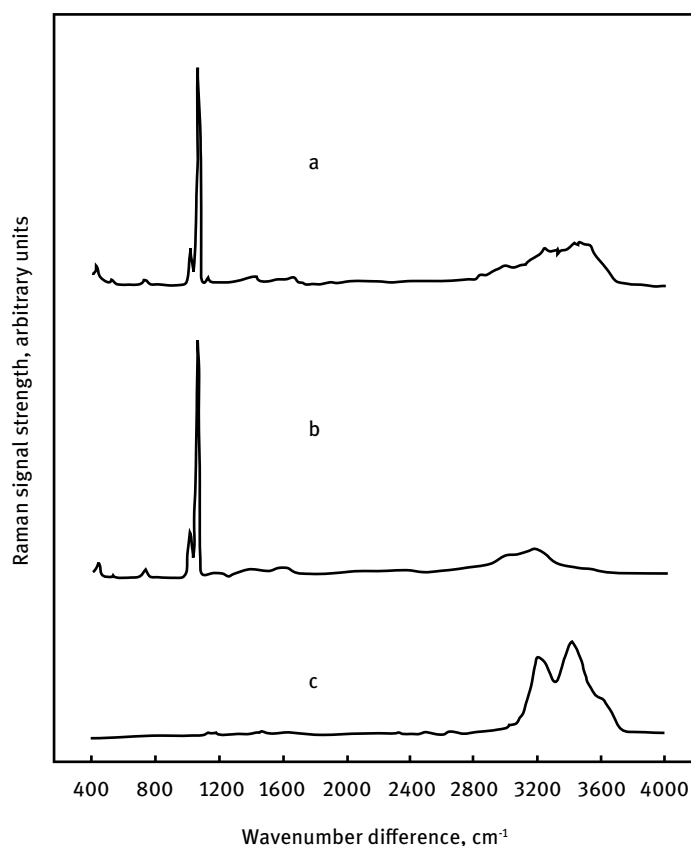


Figure 31: Raman spectra of hydroxylammonium nitrate at ambient pressure conditions. (Reproduced and modified from [287].)

Legend: (a) 50% HAN-H₂O mixture; (b) dehydrated sample; (c) H₂O

The peaks at 3200 and 3430 cm^{-1} and the shoulder at 3600 cm^{-1} diminished as the result of the water being pumping off. The peaks at 3200 and 3430 cm^{-1} and the shoulder at 3600 cm^{-1} have predominant contributions from H_2O , and these features are assigned to the OH stretch mode. The vibration assignments of Raman frequencies are given in Table 23.

Table 23: Assignments for the Raman spectrum of an 11-M HAN- H_2O solution.

Wave number, cm^{-1}	Assignment
730	NO_3^- deformation
1010	N—OH stretching
1050	NO_3^- symmetric stretch
1190	OH bending (from HAN), NH_3 rocking
1420	Asymmetric NO_3^- stretching
1620	NH_3 deformation
2730	NH_3 , rocking and deformation (overtones)
3000	NH_3 N—H stretching
3200	O—H stretching (from both HAN and H_2O)
3430	O—H stretching (from H_2O)
3600	O—H stretching (from H_2O)

Data source: [286]

For comparison, very concentrated aqueous metal nitrate salt solutions were also investigated at high temperature and pressure by Raman spectroscopy to gain an understanding of the properties of NO_3^- under conditions similar to those observed in HAN [288].

3.3.10 Nuclear Magnetic Resonance Spectra of HAN Solutions

HAN concentrations in water were analyzed by H-NMR spectroscopy based on a linear relationship between the normalized chemical shift and the HAN concentration in water, combined with a rapid single-peak scanning method [289].

3.3.11 Electrical Properties of Hydroxylammonium Nitrate

3.3.11.1 Electrical Conductivity of Hydroxylammonium Nitrate Solutions

The electrical conductivity of HAN solutions and propellants based on HAN is an important parameter in the design of electric igniters in rockets and liquid-propellant guns. Ignition may not be due to simple ohmic heating or arcing but may also involve electrolysis and creation of a path of least resistance between the electrodes. Ion mo-

bility also plays a role in the corrosion of metals in HAN solutions, in particular if two different metals are in contact and form a galvanic element. HAN solutions and HAN-based propellants are good electrolytes. The equivalent conductance of HAN solutions has been measured and fitted to the Wishaw-Stokes equation to determine the limiting equivalent conductance and the distance of closest approach for the ions. The electrical conductance of aqueous HAN solutions is similar to that of solutions of monovalent salts.

See also [243, 244]. Those reports contain a very educational introduction to the behavior of ions in dilute and concentrated solutions of weak and strong electrolytes and helps to explain some of the unusual electrolytic behavior observed with HAN solutions. In particular, the importance of ion pair formation to solution behavior is discussed.

Figure 32 shows the specific conductance of HAN solutions as a function of HAN concentration between 0.1 and 13 M at three different temperatures. Kappenstein, Pillet, and Melchior [235] have taken the same data and smoothed the curve connecting the data points.

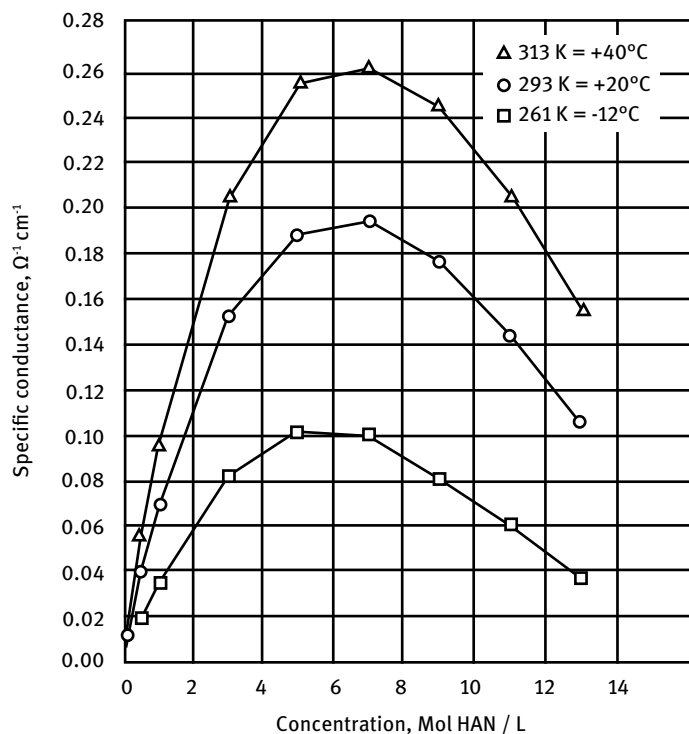


Figure 32: Specific conductance of HAN solutions at -12, +20, and +40 °C. (Reproduced and modified from [244].)

The equivalent conductance of aqueous HAN has been fitted to a Wishaw-Stokes equation to determine the limiting equivalent conductance and the distance of closest approach to the ions. The specific conductance of 11-M HAN as a function of temperature has been fitted to a general third-order polynomial equation. The electrical conductance of aqueous HAN solutions is qualitatively similar to other aqueous solutions of monovalent salts [290].

The specific conductance of HAN solutions in comparison to that of NaNO_3 solutions is shown in Figure 33. The two electrolytes behave very similarly. Sodium nitrate is much less soluble in water than HAN; therefore, the curve goes up to only 8 M.

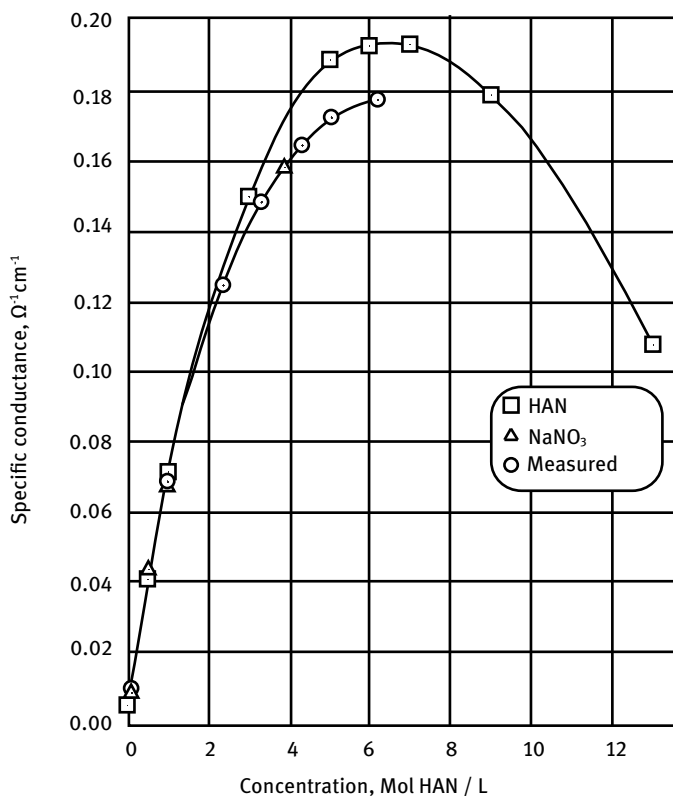


Figure 33: Specific conductance of HAN solutions. (Reproduced and modified from [244].)

The electrical conductivity of 11-M HAN (75 mass-% HAN) solutions as a function of temperature was plotted and curve-fitted, as shown in Figure 34 [235].

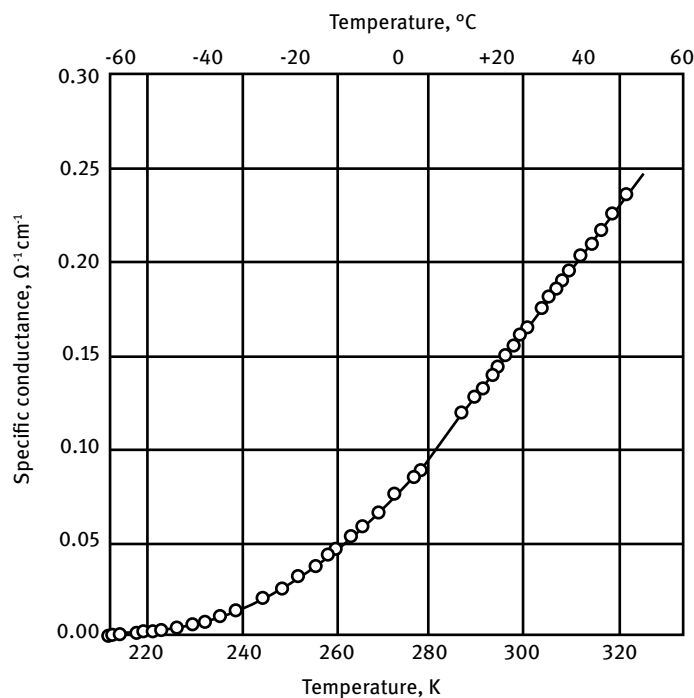


Figure 34: Specific conductance of 11-M HAN as a function of temperature. (Reproduced and modified from [235].)

If the logarithm of the specific conductance λ (units of $\Omega^{-1} \text{ cm}^{-1}$) is plotted against the reciprocal reduced temperature, as shown in Figure 35, one obtains a straight line that is easy to express as a linear function:

$$\ln \lambda = 1.2319 - 423.08x \quad x = 1/(T - T_0) \quad T_0 = 162 \text{ K}$$

Table 24 gives the specific conductance of 11-M HAN solutions as a function of temperature [291].

Table 25 gives the specific and equivalent conductance of aqueous HAN as a function of concentration at three different temperatures.

Electrical conductivity is dependent on the frequency of the alternating current applied. If the frequency is too high, the electrons and ions have a hard time following the rapidly changing electrostatic fields. Measuring electrical conductivity as a function of frequency gives information on the rate of proton transfer and protonation/deprotonation (Table 26).

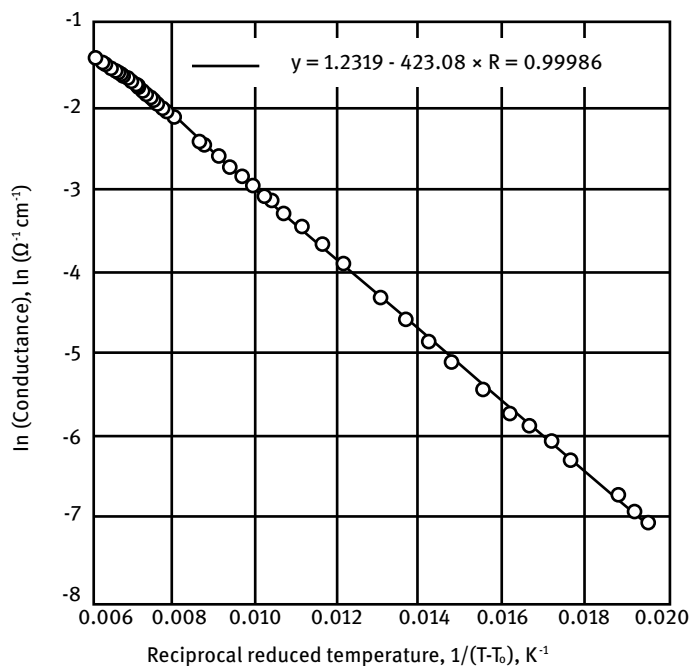


Figure 35: Specific conductance of 11-M HAN as a function of temperature; logarithm vs. reduced temperature. (Reproduced and modified from [235].)

Table 24: Specific conductance of 11-M HAN solutions as a function of temperature.

Temperature		Specific conductance $1/\kappa$	
K	$^{\circ}\text{C}$	Ω/m	Siemens/cm
213.3	-59.9	0.090	0.00090
218.8	-54.4	1.91	0.0191
224.0	-49.2	0.336	0.00336
232.5	-40.7	0.807	0.00807
244.8	-28.4	2.07	0.0207
255.9	-17.3	3.77	0.0377
263.2	-10.0	5.26	0.0526
272.6	-0.6	7.56	0.0756
287.0	13.8	11.9	0.119
293.8	20.6	14.0	0.140
297.5	24.3	15.4	0.154
301.0	27.8	16.5	0.165
307.0	33.8	18.5	0.185
312.4	39.2	20.3	0.203
319.2	46.0	22.5	0.225
327.0	53.8	25.0	0.250

Data source: [220]

Table 25: Specific and equivalent conductance of aqueous HAN as a function of concentration at three different temperatures.

Concentration M	Temperature					
	$T = 261.0\text{ K } (-12.2\text{ }^{\circ}\text{C})$		$T = 293.2\text{ K } (+20.0\text{ }^{\circ}\text{C})$		$T = 313.2\text{ K } (+40.0\text{ }^{\circ}\text{C})$	
	Sp. cond. $\Omega^{-1}\text{ cm}^{-1}$	Eq. cond. $\text{cm}^2\text{ }\Omega^{-1}$	Sp. cond. $\Omega^{-1}\text{ cm}^{-1}$	Eq. cond. $\text{cm}^2\text{ }\Omega^{-1}$	Sp. cond. $\Omega^{-1}\text{ cm}^{-1}$	Eq. cond. $\text{cm}^2\text{ }\Omega^{-1}$
0.1	—	—	0.00924	92.4	0.014	140
0.5	0.0191	38.3	0.039	78.1	0.0555	111
1	0.035	35	0.0693	69.3	0.097	97
3	0.0825	27.5	0.153	51	0.206	68.6
5	0.101	20.2	0.189	37.8	0.255	51
7	0.0998	14.2	0.194	27.7	0.262	37.4
9	0.0802	8.91	0.176	19.6	0.244	27.1
11	0.0608	5.53	0.144	13.1	0.205	18.7
13	0.037	2.85	0.105	8.08	0.155	11.9

Data source: [244]

Table 26: Resistance vs. frequency for HAN solutions using U-tube conductivity cell at 293 K (20 °C).

Frequency, kHz	Resistance, k Ω		
Concentration	0.1-M HAN	1.0-M HAN	13.0-M HAN
0.5	15.69	2.02	1.39
1	15.66	2.014	1.38
2	15.6	2.007	1.37
5	15.59	2.013	1.37
10	15.56	2.024	1.38

Data source: [244]

The electric conductivity of HAN solutions is a key parameter when studying the electrolytic ignition of HAN solutions (no fuel added) in an effort to better understand the electric ignition of HAN/fuel/water propellants [292]. See also [293].

The electric conductivity and electrolytic decomposition of aqueous HAN solutions of various densities were measured as a function of density [294]. The conductivity of aqueous HAN solution had a maximum value of $\sim 57.9\text{ mS/cm}$ at a density of $\sim 1.4\text{ g/cm}^3$. The conductivity decreased at higher concentrations above 1.4 g/cm^3 . In the electrolysis experiments, liquid- and gas-phase temperatures, current, and voltage time history were recorded. It was noted that there are three electrolytic decomposition reaction patterns for HAN aqueous solution, depending on the density/concentration, which can be further correlated with the conductivity of the solution.

3.4 Chemical Properties of Hydroxylammonium Nitrate

3.4.1 Reactions of Hydroxylammonium Nitrate

3.4.1.1 Solvate Formation

Hydroxylammonium nitrate forms solvate complexes with hydroxylamine free base, similar to such complexes formed with hydroxylammonium perchlorate and hydroxylamine. Regardless of an excess of hydroxylamine free base offered, HAN forms a monoligand complex with only one mol of hydroxylamine in its solvate sphere $[\text{NH}_3\text{OH}][\text{NO}_3] \cdot \text{NH}_2\text{OH}$ [295]. Such compound formation should be evident in the melting-point phase diagram of the $\text{NH}_3\text{OHNO}_3/\text{NH}_2\text{OH}$ system. However, HAN/HA mixtures are detonable and extremely shock sensitive [296].

3.4.1.2 Redox Reactions with Hydroxylammonium Nitrate

Hydroxylammonium ion, regardless of the anion it is paired with, is a reducing agent. The reducing potential depends on the pH of the solution and is strongest if the solution is allowed to become caustic, which would liberate some hydroxylamine as the free base. Redox reactions of hydroxylammonium salts, including HAN, are of interest as analytical methods and for the disposal of surplus HAN. Redox reactions catalyzed by traces of transition metals may be responsible for the limited storage stability of HAN-based rocket propellants. The most commonly encountered contaminant metal ion is iron in its trivalent state as Fe^{3+} . Iron in both states of oxidation forms complexes with hydroxylamine, hydroxylammonium, and many other nitrogen bases. The working principle of stabilizers such as α, α' -dipyridyl is based on the formation of such complexes.

3.4.2 Decomposition of Hydroxylammonium Nitrate

Hydroxylammonium nitrate decomposition can occur in the solid, molten, or sublimed state or in solution. The exact mechanism of decomposition of HAN by itself and in the presence of water-soluble fuels commonly used in monopropellants has been the subject of numerous studies, which we will try to organize, summarize, and critique here. The decomposition of HAN, HAN solutions, and HAN-based liquid gun propellants received a substantial amount of investigation during the decades when the RLPGs were in development. This area of scientific inquiry has benefited substantially from the sponsorship of the U.S. Army in its effort to develop a safe and stable liquid gun propellant. The objective of these studies was to determine at which temperature HAN starts to decompose, what the activation energies of the various individual steps of the global reaction are, which intermediates are involved, and what the products of reaction are. In addition, interactions of decomposing HAN with fuels had to be studied. The objective of these studies and the reason for including them here in detail was to prevent premature, unintended decomposition of HAN during storage and heat soak-back after firing of a gun and to achieve more reproducible, on-

command controlled decomposition in a gun or rocket engine. The presence of a fuel in formulated liquid gun propellants did not change the onset of thermal decomposition significantly. One would want to have a complete understanding of the decomposition of HAN by itself (in solution) before starting to examine HAN/fuel blends. The information gained in the past during the development of RLPGs is useful now in evaluating HAN-based monopropellants for applications in rocket propulsion systems.

In addition to decomposition of HAN in guns and rocket engines, there is also a substantial amount of interest in the decomposition of HAN under the conditions of the Purex nuclear fuel element reprocessing process, where it is used as a reductant and complexing agent. Inadvertent HAN solution decomposition during storage was the cause of accidental spills at uranium/plutonium process plants (Section 3.10.3).

The mechanisms of HAN decomposition in the solid and molten states and in concentrated solution are very similar. The decomposition in dilute solutions will result in somewhat different reaction-product compositions. Either condition, molten or dissolved, is affected by the presence of contaminants and catalysts. We will discuss the decomposition of solid or molten HAN first, followed by discussion of the decomposition of HAN in solutions.

3.4.2.1 Slow Thermal Decomposition of Molten HAN

DTA tests with 2–3-mg samples of HAN at a heating rate of 0.17 K/s showed a melting endotherm at 315.4 K and two exotherms at 487.1 and 495.6 K, as shown in Figure 36 [217]. The heat of reaction was 1226 kJ/kg.

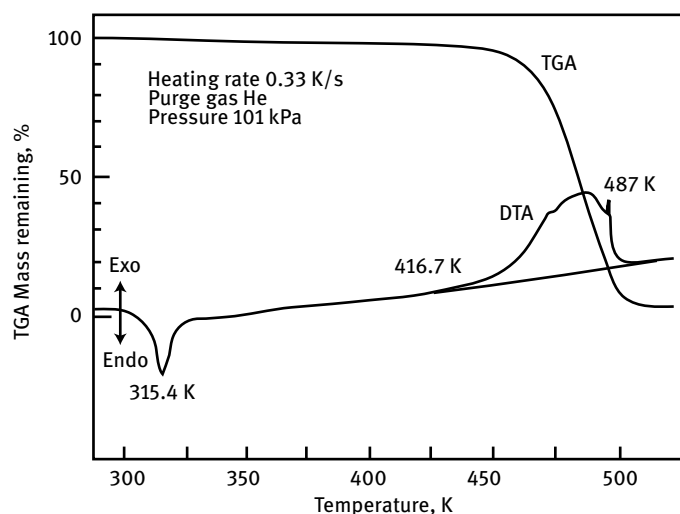
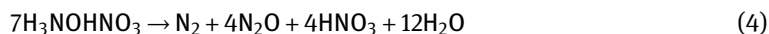
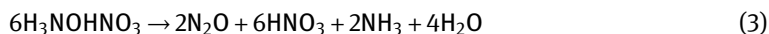
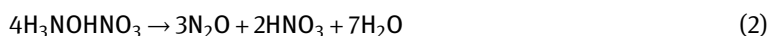
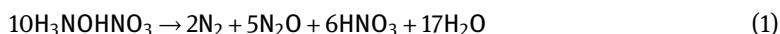


Figure 36: DTA and TGA of solid HAN under He at 101 kPa. (From [217], reprinted and modified by permission of American Institute of Aeronautics and Astronautics, Inc.; permission conveyed through Copyright Clearance Center, Inc.)

The stability of HAN-based liquid propellants and the destabilizing effects of metal impurities were investigated using a DSC thermal stability test [215]. The test involved simultaneous ignition temperature (T_{ig}) measurements for eight samples (2.3 mg each) heated in glass capillaries in a DSC pressurized to 6.9 MPa (1000 psi). Baseline data were for neat propellant LP1845 as well as for samples of propellant “doped” with 3–150 ppm of Fe^{2+} or Cu^{2+} . The results showed that 5 or 10 ppm of either metal leads to a measurable decrease in T_{ig} and that the decrease in T_{ig} per unit metal concentration is greatest at the lowest metal concentrations. From the exo/endo nature and shapes of the DSC peaks under different conditions, it was concluded that when water vaporization was suppressed, there were no detectable endotherms or exotherms prior to ignition and that the first gas-producing reaction was apparently endothermic. When water vaporization was suppressed, the T_{ig} measurements for HAN-based propellants were much higher ($>473\text{ K} = >200^\circ\text{C}$) than previously suspected.

3.4.2.2 Reaction Mechanisms of Thermal Decomposition of Molten HAN

There are several possible overall reactions by which HAN can decompose. All include nitrogen and water as the reaction products, but they vary in the ratio of N_2O to HNO_3 formed:



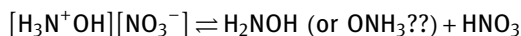
The process described in reaction (5) is the one proposed by Klein in 1983 [297]. The process described in reaction (4) is the one proposed by Klein in a later study [298]. None of these equations accurately represents the stoichiometry of HAN decomposition. The ratio of decomposition products depends on the conditions of the experiment (temperature, pressure, catalysts, solvents). Several investigators have attempted to identify the main path of decomposition by analyzing the products formed, by looking for intermediates in the decomposition reaction, and by timing the rates at which the various products formed and the HAN disappeared. They also gathered evidence that certain catalytically active contaminants may steer the decomposition process in different directions from that typical for an uncontaminated sample.

The dissertation by Lee [299] contains a very good summary of theories developed by other investigators up to that time. The two main theories are those by Klein and those by Oxley and Brower. Klein suggested gaseous species formation by the reac-

tions among NH_3OH^+ , HONO , and HNO . Oxley and Brower proposed HONO and HNO reactions with the NH_2OH intermediate as the cause for formation of gaseous products such as N_2O , N_2 , and H_2O . Lee attempted to clarify these reactions by analyzing the time-resolved sequences of decomposition products of flash-heated samples using FTIR spectroscopy (Section 3.4.2.5).

Reaction Mechanism Proposed by Klein

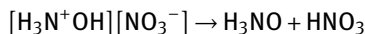
One of the possible sequence of reactions in the thermal decomposition of HAN is described as follows [298, 300]: The initial dissociation is that of a portion of all HAN (in reversal of its formation by neutralization) into free hydroxylamine base and nitric acid:



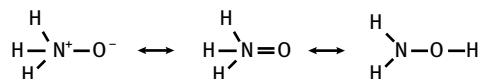
This is an equilibrium reaction determined by the basicity (proton affinity) of the free base. In the presence of water-absorbing media, some of the nitric acid forms hydroxyl ions and nitronium ions:



Another first-step possibility is a proton transfer from $[\text{H}_3\text{N}^+\text{OH}]$ to $[\text{NO}_3^-]$, leaving the free base in the form of its isomer and tautomer, ammonia oxide H_3NO :



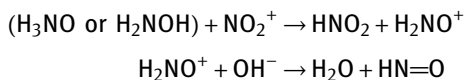
Proton-transfer reactions are generally faster than reactions involving larger ions. The unstable intermediate ammonia oxide was not characterized until recently, when its role in several industrial accidents caused by explosion of hydroxylamine free base was more closely examined; see Section 1.3.5 (free hydroxylamine base). Most of the references quoted in that section dealing with ammonia oxide are less than ten years old. Ammonia oxide is thermodynamically less stable than its tautomer, hydroxylamine, and will quickly rearrange itself to hydroxylamine:



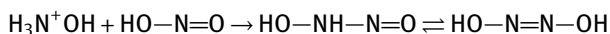
This rearrangement will take place readily only if the molecule is unrestrained and out in the vapor phase by itself. In a strongly hydrogen-bonded cluster, ammonia oxide will survive longer, long enough to undergo an alternate reaction path: A hypothesized (but unproven) hydride ion transfer within the ion cluster with water elimination may lead to nitrous acid HNO_2 and nitroxyl $\text{HN}=\text{O}$:



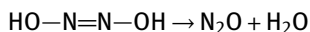
or



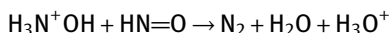
Oxidation states of the nitrogen atoms on the reactant side are ammonia oxide N^{-1} and nitronium N^{+5} , and on the product side the oxidation states of the nitrogen atom are nitroxyl N^{+1} and nitrous acid N^{+3} . This information helps in balancing these redox reactions. Both HN=O and HNO_2 will react with HAN. The reaction of HNO_2 with any amine is a nitrosation, producing HO-NH-N=O , the tautomer of hyponitrous acid,



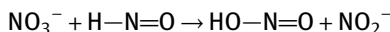
which decomposes to N_2O :



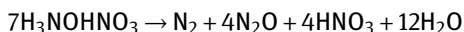
H-N=O could either dimerize and follow the same path, or it could react with $\text{H}_3\text{N}^+\text{OH}$



If both HO-N=O and H-N=O reacted with HAN at the same rate, equimolar yields of N_2O and N_2 would be obtained, but that is not the case. Reduction of nitrate ion by nitroxyl



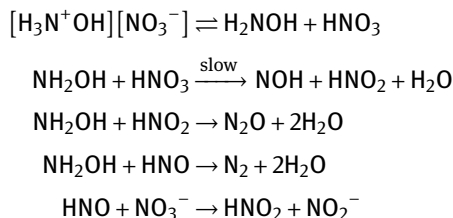
is assumed to proceed at a rate similar to that of the reaction of HAN and nitroxyl, so that slightly more than half of the nitroxyl will be removed by reaction with nitrate. The nitrous acid formed in the latter reaction will then react with more HAN. The overall stoichiometry would be close to



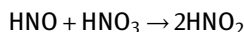
which is the mechanism proposed by Klein in 1990. Salts of hyponitrous acid are stable, but nitroxyl and its dimer (hyponitrous acid) are unstable and rarely identifiable as intermediates. Nevertheless, many investigators have studied the reaction of hydroxylamine with nitric acid and nitrous acid, and all assume hyponitrous acid as an intermediate [301, 302]. It was suggested that the white fog forming above decomposing hot concentrated HAN solutions just prior to a fume-off consists of hyponitrous acid. This would merit additional investigation. A number of variables affect the overall stability of HAN. The effect of these variables on the chemistry of the system is diverse, and the level of control required to produce and maintain stable propellant is, by extension, also diverse. Variables with a significant effect on reaction rates and pathways are acid concentration and transition-metals content.

Reaction Mechanism Proposed by Oxley and Brower

Decomposition of dry HAN resulted in a gas mixture of 83% N₂O and 17% N₂ [303]. This ratio of decomposition products can be explained by the following schematic:



which is essentially the same as



Some NO₂ started appearing only toward the end of the reaction. An alternative, less probable scheme was proposed that involves a hydride transfer step and the formation of hydrazoic acid as an intermediate. An isotope-labeling study starting with ¹⁵NH₃OH⁺ NO₃[−] resulted in equal proportions of ¹⁴N¹⁵NO and ¹⁵N¹⁴NO, indicating that the proton exchange is rapid. It was also attempted to explain the mechanism by adding either ammonium nitrate or hydrazinium(1+) nitrate or hydrazinium(2+) dinitrate to the HAN melt. Although AN by itself does not decompose at 403 K (130 °C), it started to decompose to nitrogen while in a mixture with HAN at 403 K (130 °C). An experiment with ¹⁵NH₄NO₃ showed that NH₄⁺ is exclusively converted to N₂. Hydrazinium(1+) nitrate addition extended the induction period, but hydrazinium(2+) dinitrate shortened it. In both cases, hydrazoic acid was observed in the decomposition products.

3.4.2.3 Experimental HAN Decomposition Studies

Slow reactions during the decomposition of 11-M HAN at ambient pressure and at very high pressures were followed by recording the Raman spectra of the solutions [286, 287, 304]. Pressure and temperature of a HAN sample in a diamond anvil cell were varied over the range of 2–7 kbar and 295–393 K (22 to 120 °C). At pressures near 6 kbar and temperatures near 363 K (90 °C), a significant and irreversible change in the HAN spectra was observed, indicating incipient decomposition.

Hydroxylammonium nitrate and hydrazinium nitrate (HN) are both solids at room temperature, but a mixture of 50% HAN and 50% HN is a liquid at room temperature. Similar to the decomposition of HAN, HNO₃ is observed at about 373 K (100 °C) when this mixture is heated. Ammonium nitrate is indicated in the vapor phase beginning at 503 K (230 °C). At about 525 K (250 °C), another endotherm is observed where HN begins to decompose into HN₃ and other products. Nowhere along this path are there any exotherms.

A very thorough study of the molten HAN decomposition reactions and the reactions of HAN with nitrous acid and nitric acid was performed as part of a PhD dissertation [299]. See also [305, 306]. The apparatus consisted of two resistance-heated pre-heated copper rods with flat ends sequentially moving toward each other and trapping the sample in the middle, allowing a 300- μm gap for the gases to escape to the adjacent FTIR spectrometer. The spectrometer had a time resolution of 0.044 s and a wave number resolution of 1.29 cm^{-1} . Five-milligram (8 μL) samples of XM46, solid TEAN, 13-M HAN, and solid HAN were tested in the apparatus. The evolved species profile was typically recorded for 5 s for up to six species simultaneously. A typical results chart is shown in Figure 37.

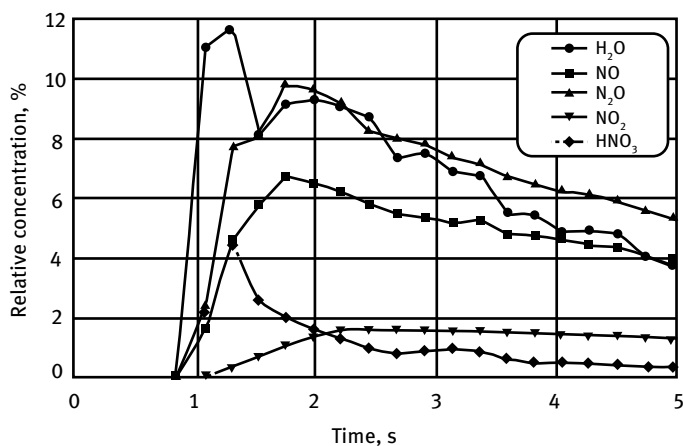


Figure 37: Time-resolved evolution of decomposition products from 13-M HAN at 453 K (180 °C). (Reproduced and modified from [299] with permission by Dr. Hyung Sik Lee granted 14 February 2021.)

The pre-set heater temperatures were selected between 433 and 573 K (160 and 300 °C) in 20° increments. The induction times were plotted against the reciprocal absolute temperature to obtain activation energy data. The two induction time curves for 9-M HAN and XM46 were very similar. The induction times of solid HAN were longer than those of HAN solutions at 393 and 413 K (120 and 140 °C), but they were shorter at 433 and 453 K (160 and 180 °C). For solid HAN, N₂O was the dominant species formed, and HNO₃ concentration was somewhat higher than that in solution at the same temperature.

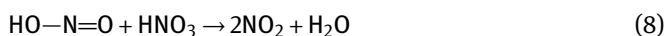
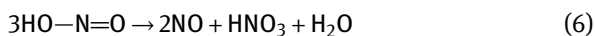
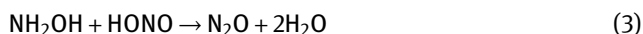
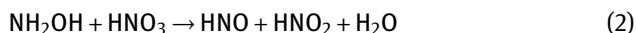
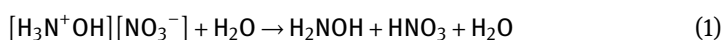
The thermal decomposition of HAN at pressures between 2 μm Hg and 50 μm Hg was studied using residual gas analysis tracing the production of nitrous oxide (N₂O), nitrosamide (H₂NNO), and nitroxyl (HNO) [307]. Initial expectation was that NO and NO₂ would be the primary species producing signals at 30 and 46 m/z, respectively.

Kinetic modeling studies of HAN solution, however, attributed these signals to HNO and H₂NNO, respectively. Thermal decomposition was achieved by injecting an aqueous HAN solution into a flowing thermal capillary and detecting the gas products with mass spectrometry. The results indicated that the formation of N₂O, H₂NNO, and HNO occurs not only in the bulk solution but possibly also on the surface of the aqueous HAN solution and in the vapor phase immediately above the solution surface.

The thermal and catalytic decomposition of aqueous HAN solutions was studied using TGA, DSC, and mass spectrometry [308]. The tests were conducted at heating rates of 1, 2.5, 5, and 10 K/min. The values of the apparent activation energy obtained for thermal decomposition using TGA and DSC were 62.2 ± 3.7 and 57.5 ± 3.5 kJ/mol, respectively, and they were in agreement with the literature data for solid HAN and solutions with high concentrations of HAN. The obtained values of the pre-exponential factor, 2.24×10^4 s⁻¹ for TGA and 3.55×10^3 s⁻¹ for DSC, were lower by six to seven orders of magnitude than those reported in the literature for aqueous HAN solutions, apparently because of full vaporization of water from the HAN solutions at the beginning of the TGA and DSC tests. The use of an iridium/rhodium foam catalyst decreased the temperature of complete decomposition by over 60 °C. The value of the apparent activation energy obtained for the catalytic decomposition using TGA was 63.9 ± 2.5 kJ/mol, and the value of the pre-exponential factor was 3.31×10^5 s⁻¹. Similar tests were also conducted at high pressures [309]. The onset temperature of thermal decomposition of HAN decreased by about 50 °C with increasing pressure from atmospheric to 2 MPa and remained virtually constant with further pressure increase to 15 MPa [310].

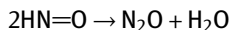
3.4.2.4 Computational HAN Decomposition Studies

The following eight reactions were chosen as the reduced reaction model for HAN decomposition [299]:



Except for reactions (4) and (6), these reactions are the same as in the mechanism proposed by Oxley and Brower. Preexponential factors and activation energies (from the literature) for the various steps were combined in a kinetic model that somewhat

reproduced the species evolution curves. Along with the reaction between NH_2OH and HONO , the dimerization of HNO is another probable pathway of N_2O formation:

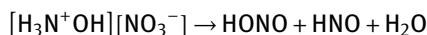


HAN decomposition was studied at very high pressures using confined rapid thermolysis/FTIR spectroscopy over temperatures ranging from 423 to 498 K (140 to 225 °C) and pressures of 0–6.8 MPa (0–1000 psig) [311]. Results showed that the detected major IR-active species in the gas phase of HAN dissolved in water and solid HAN were H_2O , N_2O , NO , NO_2 , and HNO_3 . For solid HAN, H_2O is also the dominant species formed. The sequence of species evolution at atmospheric pressure show a three-stage process: **(1)** proton transfer, which reveals the presence of HNO_3 in the gas phase, **(2)** an induction period involving the rapid formation of nitroxyl and nitrous acid, which subsequently produces N_2O , and **(3)** a delayed evolution of NO_2 , suggesting the presence of competing autocatalytic processes involving HNO_2 . However, as pressure increased, the liquid-to-gas conversion rates also increased, revealing a fourth stage of the decomposition process in which the extent of conversion of the sample into gaseous products was larger, and NO_2 evolution was no longer delayed. Most important and surprising is the role of water in initiating the overall decomposition process of HAN: In experiments with dry, solid HAN, the induction times were typically longer than those conducted with either 9, 10.7, or 13-M HAN. Hence, water appears to play a significant role in altering the molecular structure of the liquid, which affects the proton-transfer process.

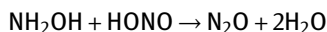
It was attempted to reproduce the sequence and ratios of decomposition product formation during thermolysis of solid HAN and HAN solutions by developing a kinetic model [312]. That model would be composed of interrelated individual reaction steps that work simultaneously to result in the global reaction rate, the one that is easiest to measure. The objective of this study was to propose a reduced model for the condensed-phase reactions of HAN and to determine accompanying Arrhenius-type rate coefficients. For this inverse-based analysis, two kinds of input data were used, measured gas-phase concentrations and the condensed-phase reaction temperatures. The experimental decomposition process was modeled by applying species conservation equations to the condensed-phase and the gas-phase regions separately. The experimental data that were used to deduce the rate coefficient parameters were the gas-phase species concentrations observed during thermal decomposition of 13-M HAN, including HNO_3 , N_2O , NO , and NO_2 [313, 314]. With the best-fit rate constants of the reaction model, the species evolution profiles of 13-M HAN were reasonably recovered, and the condensed-phase mass fractions were predicted. The reaction model, based on the eight reactions shown previously, was applied to the simulation of the species evolutions for solid HAN and HAN-water solutions including 10.7 and 9-M HAN. The simulated, predicted gas-phase concentrations coincided well with the measured data, indicating that the proposed global reaction mechanism captured most of the key reactions of HAN. A major unknown is how much of the gaseous products re-

main dissolved in the condensed phase of reaction products, but their mol fractions should be less than 0.1. See also [315].

Decomposition pathways for aqueous HAN solutions were examined by quantum mechanical molecular orbital computations using a DFT method [316]. Optimized structures were obtained for the reactants, products, and transition states, and the total electron energies of these structures were calculated. Energy barriers in the forward reaction and total energy release were calculated for 42 reactions that can participate in HAN decomposition, also including two self-decomposition mechanisms for HNO_3 . Potential energy diagrams for 20 different reactions were shown to illustrate the energy barriers. In the initial decomposition, the ion + neutral $\text{NH}_3\text{OH} + \text{HNO}_3$ reaction, the neutral + neutral $\text{H}_3\text{NO} + \text{HNO}_3$ reaction, and the HNO_3 self-decomposition pathways were all found to have reasonable energy barriers, with values of 91.7, 88.7, and 89.8 kJ/mol, respectively. The overall reaction resulting from any of these pathways can be written as

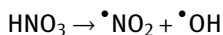


The ionic reaction is dominant during the initial decomposition of HAN in aqueous solution because $\text{H}_3\text{N}^+\text{OH}$ and NO_3^- are the major species in such solutions. The investigators examined six mechanisms, and each of these schemes provided the same global reaction:

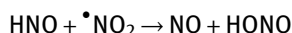
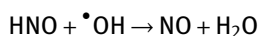
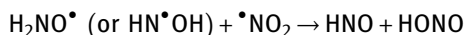
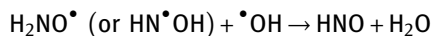
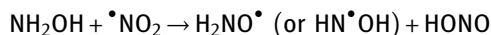


It was concluded that the ion + neutral $\text{H}_3\text{N}^+\text{OH} + \text{HNO}_3$ reaction mechanism is dominant during the initial HAN decomposition in aqueous solution. The associated energy barrier of 91.7 kJ/mol was in good agreement with the activation energy reported in a previous study.

A mechanism for the radical reactions of HAN in the aqueous phase was identified and investigated using *ab initio* computations [317]. Optimized structures for the reactants, products, and transition states were obtained, and the total electron energies of such structures were calculated. The cleavage of HNO_3



was found to trigger the radical reaction. The $\text{H}^\bullet$ abstraction reactions



and other reactions, including decomposition of HONO and HNO, were investigated using *ab initio* computations. HAN has a high reactivity and ignitability compared to AN. $\text{H}^\bullet$ abstraction from NH_2OH has a considerably lower barrier than the one from NH_3 . The differences in reactivity of NH_3 and NH_2OH is the cause of the differences in thermal stability of AN and HAN. The initial reaction that triggers this mechanism had the highest energy barrier (205.0 kJ/mol) of all the reactions investigated in this work. It was concluded that the homolytic cleavage of HNO_3 is the rate-determining step for the decomposition of aqueous HAN solution.

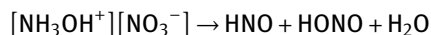
The thermal stability and kinetics of HAN decomposition were studied using DSC, and the thermal decomposition reaction mechanism was modeled using quantum mechanical molecular orbital DFT methods [318]. With the help of parameter values from the non-isothermal DSC curves of HAN, the thermal decomposition activation energies and pre-exponential factors were obtained by the Kissinger and Ozawa methods. The calculated results showed that the values of the activation energy calculated using the Kissinger and Ozawa methods were 67.9 and 70.4 kJ/mol, respectively. The most probable mechanism function was then calculated using the Satava-Sestak method. Seven different paths for the thermal decomposition mechanism of HAN were formulated, and DFT was used to carry out a dynamics analysis for each of these. The seven mechanisms were ranked in the order from the most probable to the least probable mechanism.

A detailed mechanism was developed for thermal decomposition of HAN solutions, based on quantum mechanical calculations using the SMD-B97X-D method [319]. The mechanism described multiple kinetic processes, including nitration and nitrosation of hydroxylamine, HNO dimerization, and HONO-regeneration pathways involving H-abstraction reactions. Rate constants of elementary reactions were estimated using transition state theory with consideration of diffusion effects of all species involved. Kinetic modeling was performed to predict species concentration profiles in 0.1-M HAN in the temperature range of 463–523 K. Results showed reasonable agreement with the experimental data from flow reactor studies. For more concentrated solutions, strong autocatalytic behaviors were predicted with the late emergence of NO_2 and HONO, whose regeneration was considered as the major autocatalytic pathway. Sensitivity analysis results suggested an acid-catalyzed nitration-nitrosation pathway, based on which the autocatalysis should be caused by the rise of solution acidity. A linear correlation can be observed in the previously reported apparent Arrhenius parameters, which may be reconciled via a kinetic compensation effect.

A ReaxFF reactive force field set has been developed for reactive molecular dynamics simulations of the thermal decomposition of HAN [320]. The training set consists of geometries, partial atomic charges, and energy barriers for a number of reactions that participate in HAN thermal decomposition. Geometries and partial atomic charges were calculated in both the gas phase and in solution. The SMD-GIL solvent

model was used to approximate concentrations of HAN in solution and the rate of their change. Transition states for elementary reactions were found at the GIL level of theory. An important autocatalytic pathway for the regeneration of HONO in HAN decomposition was identified. The set from this work can be used to train a ReaxFF force field capable of conducting reactive molecular dynamics simulations of HAN thermal decomposition.

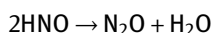
A detailed chemical kinetics model for the liquid-phase reactions of aqueous HAN, based on quantum chemistry calculations, included thermal corrections, formation enthalpies, entropies, and heat capacities of chemical species that were calculated from the partition functions using statistical machinery [321]. Reaction-rate coefficients were determined to allow the application of transition state theory and variational transition state theory to reactions identified in previous studies. Thermal and evolved gas analyses were conducted for 92 mass-% aqueous HAN solution under specific heating conditions. The heat of reaction was measured using a heat flux calorimeter that allowed accurate and reproducible calorimetric measurements with a sensitivity of 5–10 μ W. In each trial, a ~20-mg sample was placed in a glass vial within a high-pressure stainless steel chamber, after which the chamber was purged with argon and sealed. Maximum heat flow occurred at 424 K (151 °C). In addition, a DTA-TGA instrument was connected to a mass spectrometer to analyze the gases formed during decomposition. The new model with 92 reactions had the ability to simulate the thermal decomposition of such a solution, and it successfully predicted the heat of reaction and the gases that result from decomposition under these conditions. This kinetics model also provided a kinetic mechanism for the decomposition of HAN. In this mechanism, the initial reaction



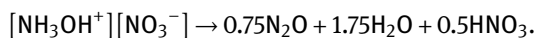
triggers the overall decomposition, while the subsequent reactions



and



are exothermic and accelerate the decomposition. This mechanism can be summarized by the global one-step reaction



3.4.2.5 Rapid Decomposition of HAN

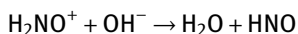
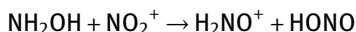
The species that evolve during rapid thermolysis of solid HAN were analyzed by rapid-scanning FTIR spectrometry, with a complete scan performed every 100 ms [266]. This combination of DTA and product analysis is a good method to “unravel” an energetic

molecule step by step and to identify the weak links in a molecule where the reaction starts first. The rapid thermolysis of solid HAN at a heating rate of 35 K/s under 0.69 MPa (100 psi) argon showed nitric acid, followed by N_2O and NO_2 .

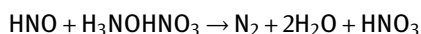
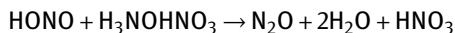
A similar test [322] with 2-mg samples at a heating rate of 100 K/s under 3.44 MPa (500 psi) argon also showed nitric acid first, followed by N_2O and NO_2 and water. The initial endotherm at 353 K (80 °C) leads to proton transfer and release of HNO_3 . A strong exotherm follows, starting at 373 K (100 °C). HAN is the only compound that shows oscillations in the rate of gas evolution during the exotherm. At pressures above 690 kPa (100 psi), the concentrations of the emerging products oscillate during the first few seconds of rapid thermolysis before dampening after 5 s.

3.4.3 Thermal Decomposition of Hydroxylammonium Nitrate Solutions

Based on t-jump FTIR spectrometry of intermediate species, several reaction pathways have been proposed. For instance, the nitronium ion and the hydroxide ion can be involved in the following reactions:



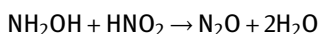
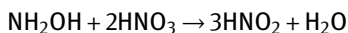
Once HONO and HNO build up in large concentrations, the induction period is near its completion, and NO and N_2O as well as water evolve into the gas-phase region and are detected by their IR absorption. The formation of these species could come from an HONO and HNO attack on HAN via the global steps



A model has been developed for the formation of ammonium nitrate in HAN-based propellants, such as XM46. The amount of ammonium nitrate in aged HAN is an indication of the past thermal history of the propellant.

The following is a summary of publications on HAN decomposition in aqueous solutions, arranged in chronological order.

In aqueous solutions, two reactions compete with each other, one in which nitrous acid is formed and one in which nitrous acid is consumed [323, 324]:



The former is dominant in low HA and high HNO_3 concentrations, and the latter is dominant at higher HA concentrations. The decomposition is characterized by an induction period that depends on the initial concentration of nitrous acid, total acidity, and other reactants present.

Hydroxylamine is oxidized by nitric acid to form nitrous oxide and nitrous acid, the proportions varying with reaction conditions [325]. The reaction is delayed by an induction period, followed by a rapid autocatalytic process. Addition of nitrite eliminates the induction period, while addition of nitrite scavengers completely prevents any reaction. Nitrous acid is an essential catalyst for the reaction, and the initial rate of reaction obeys the equation

$$\frac{d[\text{HNO}_2]}{dt} = K[\text{HNO}_2][\text{NH}_3\text{OH}^+].$$

Hydroxylammonium nitrite is a potential intermediate in the decomposition of HAN. If prepared by other means and isolated, it decomposes quickly [326]. Isotopic experiments using ^{15}N -enriched hydroxylamine showed that virtually all of the N_2O arose from reaction between HNO_2 and hydroxylamine. The mechanism suggested by Pembridge and Stedman [325] involves oxidation of unprotonated hydroxylamine by N_2O_4 to form the nitroxyl diradical HNO ; this is then further oxidized to HNO_2 , which reacts with hydroxylamine to form N_2O .

The yield of a minor product of the reaction between nitrous acid and hydroxylamine, *trans*-hyponitrous acid, has been studied over a wide range of conditions [327]. It has been shown that, for nitrosation of free hydroxylamine by four different neutral nitrosyl compounds, the yield varies with the nature of the reagent: ONBr 27%, ON-NCS 12%, ONNO_2 6%, and ONCl 15%. For nitrosation of the hydroxylammonium ion by the nitrous-acidium ion, the yield is only 2.0%.

Hydroxylammonium ion in HAN is subject to oxidation by both nitric and nitrous acid [328].

A very unusual phenomenon was observed in decomposing HAN solutions: An initially homogeneous solution of hydroxylamine in nitric acid can react to form a two-layer system, a layer of nitrous acid in nitric acid in the top above a layer of hydroxylamine in nitric acid below, with a sharp boundary between them that moves steadily downward as the reaction progresses autocatalytically [329, 330].

The intermediates during reaction of hydroxylamine with nitric acid can be identified by isotope labeling [331]. An isotopic study of the reaction of hydroxylamine with nitric acid showed that a symmetrical intermediate is involved in several steps of the reaction, probably *cis*-hyponitrous acid [332]. The results support a theory that the initial nitrosation is an electrophilic displacement of a proton rather than an addition reaction of the type thought to occur in diazotization and deamination. Hyponitrous acid is a very likely intermediate of HAN decomposition, and its potential formation has frequently been overlooked by other investigators.

A differential scanning calorimeter was modified for high-pressure operation up to 6.9 MPa (1000 psi), and samples of LP1845 and 13-M HAN were analyzed in aluminum and tantalum pans [333]. Tests with LGP1845 in aluminum pans at 6.9 MPa yielded an average $T_{(\text{in})}$ of 393 K (120 °C) with a standard deviation of ± 4 °C, while a higher average $T_{(\text{in})}$ of 397.9 K (124.8 °C) with a standard deviation of ± 2.4 °C was

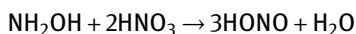
obtained for 13-M HAN (without the addition of fuels) in the presumably more inert tantalum pans at a somewhat lower pressure (5.2 MPa).

Addition of hydrazinium(1+) nitrate to HAN suppressed the decomposition of HAN for several hours [334]. In one instance, a sharp explosion occurred at 413 K. Mass spectrometric analysis showed hydrazoic acid as the pyrolysis product, in particular if hydrazinium(2+) dinitrate instead of the (1+) salt was added to the HAN. The (2+) salt shortened the induction period and accelerated the decomposition reaction of HAN.

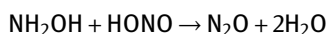
Two unusual phenomena, bistability and fluctuating, pulsating, and oscillating reaction rates occurring in the nitric acid–hydroxylamine continuous-flow stirred tank reactor system, were studied experimentally and theoretically to see how they relate to the decomposition of HAN during industrial uses of this chemical [335, 336]. Stationary concentrations in the stirred reactor were plotted vs. inlet concentrations to derive reaction mechanistic theories. Similar oscillations were observed in the oxidation of hydroxylamine by other oxidizers.

A computer model was developed to simulate the decomposition of 5.2 to 9.1-M HAN solutions [337]. This model can also be applied to deflagration of hydroxylammonium perchlorate. The theory considers the chemical kinetics, energetics, and fluid dynamics of the combustion zone, making use of asymptotic analysis to decide which combustion mechanisms are consistent with available data. The model is useful in conjunction with experimental results to obtain frequency factors and overall activation energies for HAN decomposition. Results suggested that deflagration rates are controlled by condensed-phase combustion, with production of water dominating the heat release, and that phase and chemical equilibrium are not approached in the condensed-phase combustion zone. The mass consumption rate of HAN was assumed to follow a zero-order expression, with an activation energy of about 63–73 kJ/mol (14.5–17 kcal/mol), which is close to that of proton transfer. These results support the postulate that the rate of HAN decomposition is controlled by the rate of proton transfer from NH_3OH^+ to NO_3^- .

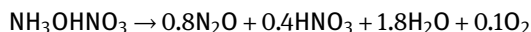
In a later study at the University of Delaware, researchers used a Nd:YAG laser at 1.064 μm to excite Raman spectra of decomposing HAN solutions in a sapphire window flow-through cell at up to 500 K and 295 bar [338]. The exothermic decomposition of aqueous HAN solutions was investigated as a function of temperature, concentration, and flow rate. Rapid decomposition occurred as soon as the samples reached 460 K, causing a sharp drop of HAN concentration. From the induction times, apparent activation energies of 129 ± 29 and 66 ± 8 kJ/mol were estimated at HAN concentrations of 0.9–1.5 and 1.6–1.7 M, respectively. It was suggested that at low concentrations the decomposition proceeds via



whereas at higher concentrations (>1.52 M) the reaction



becomes more important. The overall reaction was proposed to be



Comparing the FT Raman spectra of samples before and after passing through the heated cell showed that the N—OH stretch of H_3NOH^+ was completely absent after reaction, whereas NO_3^- had been only partially consumed. N_2O was the only nitrogen-containing gaseous product. The decomposition of HAN is autocatalyzed by HNO_2 .

Using a similar flow-through cell but measuring IR absorption in an FTIR spectrometer instead of Raman excitation, the rate of decomposition of 0.1 to 0.2-M HAN solutions at 463–523 K and 27.5 MPa was measured and the intermediates identified [339]. The loss of NH_3OH^+ and the formation of N_2O occurred at the same rate under these conditions and could be fitted to a first-order rate expression. From the slope of the averaged NH_3OH^+ concentration and residence time curves, an activation energy of 103 ± 21 kJ/mol was derived. This is similar to the numbers obtained from the Raman spectra. See also [340].

The rapid thermolysis studies of HAN and other energetic materials were tested in a confined rapid thermolysis/FTIR apparatus using about 8 μL of a 13-M HAN solution at heating rates exceeding 1500 K/s to a set temperature (403 or 433 K), where decomposition occurred [313, 314]. The rapid heating was achieved as a result of confining the sample between two closely spaced isothermal surfaces instead of just placing it on a heated filament ribbon. The gaseous decomposition products (H_2O , N_2O , NO , HNO_3 , NO_2) departed from the confined space through a rectangular slit into the region that was traversed by the IR beam. The evolved gases were quantified using FTIR absorption spectroscopy. The results obtained in this study of the temporal evolution of species concentrations from these ingredients were in reasonably close agreement with results available in the literature. See also [341].

Binary aqueous HAN solutions of different concentrations (20, 60, and 83 mass-%) were thermally (and catalytically, see below) decomposed [221]. The initial reactions of HAN solutions are very similar to those of XM46 propellant. The thermal stability of HAN solutions was measured using a TGA and a DTA apparatus. The thermograms of HAN solutions with three different HAN concentrations are shown in Figure 38 and 39. The onset of exotherms shifts to lower temperatures for higher HAN concentrations.

Figure 40 is a similar set of data except that DTA and TGA are shown on a common time scale [342].

Hydroxylammonium nitrate is an important reagent used in the separation of plutonium and uranium in the Purex process for reprocessing spent nuclear reactor fuel rods. It is used to reduce the plutonium from Pu(IV) to Pu(III), causing a change in solubility and the transfer of the plutonium from an organic phase to an aqueous phase. The aqueous solution used in these separation systems is a concentrated nitric acid

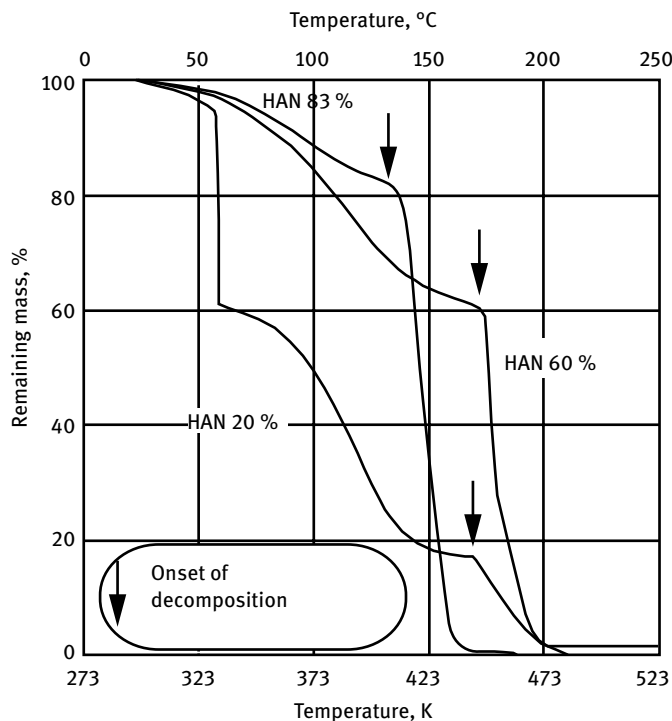
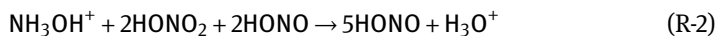
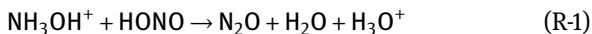


Figure 38: Thermogravimetric analysis of HAN solutions. (Republished and modified from [221], with permission of © 2002 American Institute of Aeronautics and Astronautics, Inc.; permission conveyed through Copyright Clearance Center, Inc.)

solution containing hydroxylammonium ion, trace amounts of nitrous acid, and hydrazinium nitrate as a stabilizing agent. The nitrous acid is an impurity present in nitric acid solutions and acts as an unwanted catalyst in the oxidation of hydroxylamine by nitric acid. Any hydroxylamine that is unwittingly oxidized by nitric acid is lost for the Pu(IV) to Pu(III) conversion. In addition, azide formation is an unwanted byproduct. There have been incidents in which HAN solutions fumed off during storage, causing severe radioactive contamination of work areas.

Hydroxylamine can react autocatalytically with nitric and nitrous acids or act as a nitrous acid scavenger.



Under certain conditions, the combination of (R-1) and (R-2) can lead to rapid evolution of $\text{N}_2\text{O}(\text{G})$; this reaction has been blamed for several vessel ruptures at nuclear facilities. It was therefore of interest to find methods to predict the thermodynamic properties of the reactants and the heat of reaction. An improved understand-

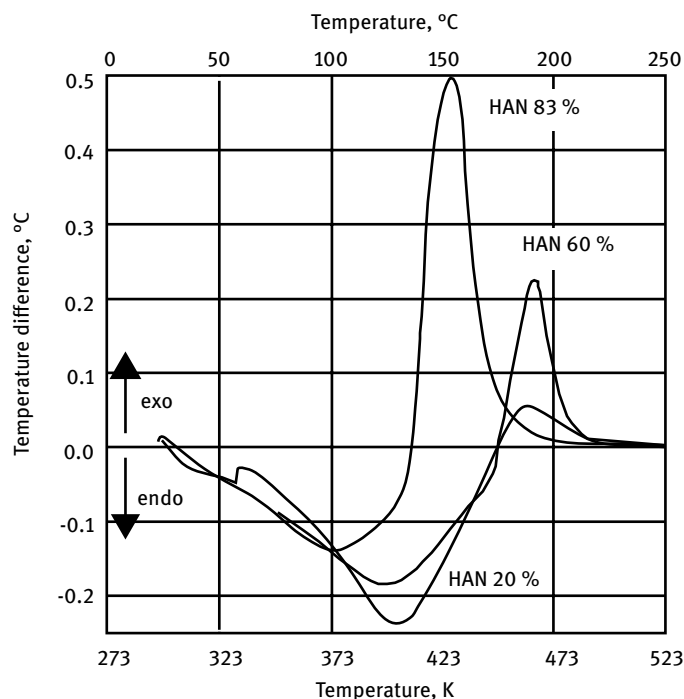


Figure 39: Differential thermal analysis of HAN solutions. (Republished and modified from [221], with permission of © 2002 American Institute of Aeronautics and Astronautics, Inc.; permission conveyed through Copyright Clearance Center, Inc.)

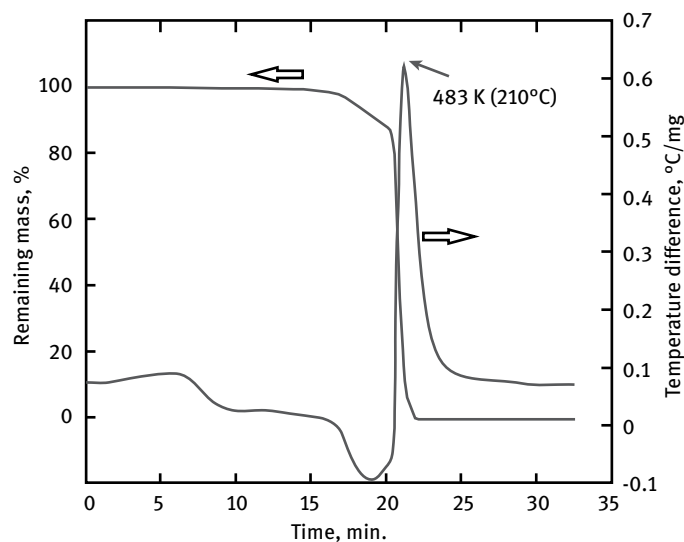
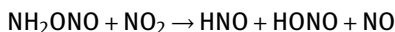


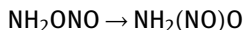
Figure 40: Thermal decomposition of 87.2% HAN solutions. (Republished and modified from [342], with permission granted by © 2006 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center, Inc.)

ing of these reactions is needed to determine the “stability boundary of hydroxylamine” for safe operation of the plutonium–uranium reduction extraction (Purex) process.

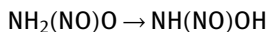
Ab initio molecular orbital (MO) calculations were performed to develop an elementary reaction mechanism for the autocatalytic and scavenging reactions of hydroxylamine in aqueous nitric acid solutions similar to those used for the Purex process [343]. Under the operating conditions of the Purex process (6-M nitric acid), the reactive forms of hydroxylamine are NH_3OH^+ , a trace of NH_2OH , and the complex $\text{NH}_3\text{OH}\cdot\text{NO}_3$, and those of nitrous acid are NO^+ , H_2ONO^+ , N_2O_4 , N_2O_3 , NO_2 , and NO . It was found that in solutions the autocatalytic generation of nitrous acid proceeds through free radical pathways at low-hydroxylamine concentrations from unprotonated NH_2OH via hydrogen abstraction. At high $[\text{NH}_3\text{OH}^+]$, there is a possible involvement of the NH_3ONO^+ intermediate via the reaction



The NH_3ONO^+ intermediate, in turn, is formed via the ion–ion reactions of NH_3OH^+ with NO^+ and/or the reaction between NO^+ and HAN. The intermediates involved in the scavenging reaction of nitrous acid by hydroxylamine are NH_3ONO^+ , NH_2ONO , $\text{NH}_2(\text{NO})\text{O}$, $\text{NH}(\text{NO})\text{OH}$, and HONNOH , and the rate-determining step is the 1,2-NO migration in NH_2ONO leading to $\text{NH}_2(\text{NO})\text{O}$. Reactions



and



were also studied. The rate constants and activation energies for the key reactions were estimated from theoretical considerations.

In continuation of this work, *ab initio* MO calculations were performed and thermochemical parameters estimated for 46 species involved in the oxidation of hydroxylammonium ion in aqueous nitric acid solution [260]. Solution-phase properties were estimated by computational chemistry calculations for physical properties and constants in solution. Hydroxylammonium nitrate solutions will sustain thermal decomposition as long as the concentration is above 40% (5 M) and the pressure is above 5 MPa.

A mathematical model was developed that may be used to determine the safety of HAN solutions used in solvent extraction purification of plutonium [344]. The most significant hazard associated with hydroxylamine use in processing plutonium is its rapid, autocatalytic reaction with nitric acid, which can result in an explosion or pressurization of process vessels with spills of radioactive materials. In addition, heat is produced by the reaction that could potentially ignite organic process solvents.

The HAN decomposition reaction can occur only under specific process conditions (temperature; HAN, plutonium, and nitric acid concentrations), and the model was used to identify worst-case conditions so that they can be avoided. The kinetic model used all of the known significant reactions that could occur in process solutions containing HAN and nitric acid, as well as plutonium and iron. The reaction kinetics data (rate laws, rate constants, activation energies) used in the model were obtained from chemical literature sources. The model shows that the autocatalytic HAN reaction with nitric acid is very rapid and is catalyzed by Pu(III) and Fe(II) in process solutions. High temperatures and nitric acid concentrations also promote the reaction.

Hydroxylammonium nitrate is used to reduce Pu(IV) to Pu(III) in the separation of plutonium from uranium during reprocessing of spent nuclear reactor fuel elements. Hydroxylammonium nitrate becomes unstable under certain conditions and has been known to explode. It is necessary to deactivate HAN once the reduction of plutonium is finished. A report reviews what is known about the chemistry of HAN and various methods to achieve safe destruction of residual HAN in process effluents [345]. There are some areas where additional information is needed to make educated decisions about the handling of HAN in the reprocessing of nuclear fuel elements. Experiments have demonstrated a number of non-radiolytic ways to safely decompose unwanted HAN, including heating in excess HNO_3 , reaction with HNO_2 , photolytic oxidation in the presence of H_2O_2 , and the addition of redox oxidizer such as Fe(III) that will oxidize the hydroxylamine. The report confuses the reactivity of HAN with that of the free base HA, but the Purex process works exclusively in acidic solutions while the extraction with tributyl phosphate is taking place, and there should not be any free base present under those acidic conditions. The report fails to draw on the vast amount of information on HAN solution stability that was generated several decades ago when HAN-based propellants were being evaluated as liquid gun propellants.

3.4.3.1 Activation Energy of the Thermal Decomposition of Hydroxylammonium Nitrate

Several activation energy numbers have been mentioned in the preceding sections. Here we present a few more publications on the same subject. Earlier studies showed that hydroxylamine free base decomposition is well described by a first-order kinetics, with an overall activation energy of 29 kcal/mol [346].

The kinetics of thermal decomposition of molten HAN was measured by the rate of heat release under isothermal conditions in glass ampoules that were initially evacuated [347]. The bath temperatures were in the range of 358 to 394 K (84.8 to 120.9 °C). The decomposition of molten HAN proceeds faster and faster by autocatalysis, and at the point of about 60% decomposition it is 200–300 times faster than at the outset of

the experiment. For up to 60% decomposition, the rate increases with the square of the degree of decomposition η

$$\frac{d\eta}{dt} = k_1(1 - \eta) + k_2(1 - \eta)\eta^2$$

as long as $\eta < 0.6$. Past that point, the rate is less than to the power of two. k_1 is dependent on the loading density m/V . Its temperature dependence at $m/V = 0.0025 \text{ g/cm}^3$ is

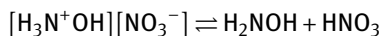
$$k_1 = 4.2 \times 10^4 \exp[(- 16450 \pm 450)/RT]$$

The loading density of the ampoules was varied from 0.001 to 0.0027 g/cm^3 and has a distinct effect on the rate of decomposition. IR analysis of the decomposition products showed them to consist of NO_2 , NO , N_2O , and H_2O . The temperature dependence of the effective rate constant is

$$k_{\text{ef}} = 13.73 \exp[(- 15300 \pm 1800)/RT]$$

where k_{ef} is the rate constant in s^{-1} . The activation energy is $66 \pm 7.8 \text{ kJ/mol}$ ($15.3 \pm 1.8 \text{ kcal/mol}$). The heat of reaction at $\sim 373 \text{ K}$ is 1641 J/g (380 cal/g).

Addition of 5–20 mol-% HNO_3 resulted in vigorous decomposition of the salt even at room temperature. Addition of ammonia delayed the onset of the autodecomposition reaction. It was suggested that this indicates that the process occurs via the molecular forms of the initial base and acid formed by dissociation of the salt

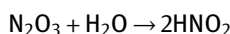
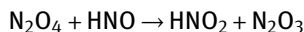
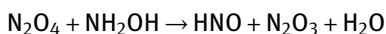
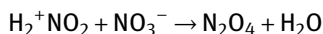


and not through the ionic form because other hydroxylammonium salts decompose more slowly. The HAN decomposition reaction is second order with respect to nitric acid:

$$\frac{d[\text{NH}_3\text{OH}^+]}{dt} = -k[\text{NH}_3\text{OH}^+]_0 \times [\text{HNO}_3]_0^2$$

The fact that the reaction is second order with respect to HNO_3 at the initial stages of decomposition of the pure salt supports a hypothesis that there is interaction between NH_3OH^+ and N_2O_5 or the NO_2^+ nitronium cation.

Other reactions postulated to occur in the background during the decomposition of HAN include



but little proof was offered that they play an important role (if any) in the process.

An activation energy of 69.9 kJ/mol (16.7 kcal/mol) for decomposition of HAN solutions ranging from 5.2 to 9.2 M was calculated [337]. An activation energy for decomposition of solid HAN of 64 kJ/mol (15.3 kcal/mol) was proposed [348].

3.4.3.2 Catalytic Decomposition of Hydroxylammonium Nitrate Solutions

Although it is unlikely that HAN by itself will ever be used as a monopropellant, numerous studies have been conducted to find catalysts that will reproducibly and repeatedly initiate the decomposition of HAN solutions at room temperature, similar to the reaction of S-405 catalyst with hydrazine. Pre-decomposition of HAN prior to injection into a hybrid rocket engine would be a good application of HAN as an oxidizer. The hot, oxygen-rich exhaust from a HAN decomposition reactor might be hot enough to ignite a hybrid fuel grain or to ignite co-injected, otherwise non-hypergolic liquid fuels such as kerosene. Actually, testing catalysts with just HAN without dissolved organic fuels may have the advantage of the catalyst not being fouled by soot or other organic pyrolysis residues. The catalytic decomposition of HAN is a very important initial step in the application of HAN-based monopropellants in catalytic reactors, regardless of the type of fuel present. Many catalysts have been evaluated first with HAN by itself (typically using an 81% = 13-M HAN solution) and later with the actual fuel-containing monopropellant that is closer to the actual application; see *Encyclopedia of Monopropellants*.

The reactions discussed here are the same fundamental reactions that take place in HAN-based monopropellants in the presence of fuels. *Encyclopedia of Monopropellants*, chapter “Hydroxylammonium Nitrate-Based Monopropellants,” in this book series contains a discussion of catalysts for decomposition of HAN solutions not only by themselves but also in the presence of a fuel. Catalysts found to be active in the decomposition of HAN aqueous solutions in the absence of fuels would be equally active with HAN/water/fuel blends, maybe even more so [349]. In the current chapter we are summarizing catalyst studies applicable to HAN solutions, which would result in much lower combustion chamber temperatures than the decomposition of HAN monopropellants. To our knowledge, HAN solutions have never been used as a monopropellant by themselves without the addition of fuels in homogeneous or emulsified mixtures. Tests conducted with catalytic decomposition of HAN solutions by themselves are useful for the evaluation of catalysts for the decomposition of HAN/fuel solutions. They are safer to perform than tests with live monopropellants. There is usually a good correlation of relative activities of catalysts in tests of HAN solutions with and without added fuels.

It was hoped that addition of nanoparticles from TiO_2 or SiO_2 to HAN solutions would lower the decomposition onset temperature and accelerate the strand burning of HAN solutions and monopropellants based on HAN. Synchronized TGA and FTIR measurements were performed to analyze the decomposition characteristics of HAN aqueous solutions with suspended titanium dioxide (titania) nanoparticles [350]. The weight-loss rates as well as gas-generation rates of samples with various TiO_2

loadings in HAN aqueous solutions were measured to gain a better understanding of the influence of nanoparticles on the thermal decomposition of HAN-based propellants. Thermal decomposition tests were performed using a synchronized TGA-FTIR (PerkinElmer STA8000 and PerkinElmer, Spectrum Two). The sample weight loaded for each test was 10 ± 0.5 mg, and the sample was heated from 303 K (30 °C) to 573 K (300 °C) at 10 °C/min in the TGA-FTIR furnace. The purge gas was nitrogen. Resolution of the FTIR spectrum was a modest 4 cm^{-1} to allow higher sampling frequency of the decomposed gas. The onset of decomposition temperature was drastically reduced from 445 K (172 °C) to 393 K (120 °C) as the result of the addition of TiO_2 nanoparticles.

The catalytic decomposition of HAN solutions was investigated using a series of platinum and iridium catalysts supported on mesoporous materials such as MMZY, KIT-6, and SBA-15 [351]. A study of the effects of the active metal loading and the pore structure of the catalysts on decomposition of HAN solution showed that the activity of platinum catalysts supported on mesoporous material was superior to that of iridium catalysts on the same support. The Pt(10)/SBA-15 catalyst showed excellent decomposition activity and was the best among the catalysts tested, which was probably due to its favorable pore structure. Because the pore size of Pt(10)/SBA-15 is larger than that of Pt(10)/MMZY and Pt(10)/KIT-6, it is better for diffusion of reactants and product gases. The activity of the catalyst increased with the Pt active metal loading on the SBA-15 support.

Since most HAN-based monopropellants contain substantially more HAN than fuel, it is a valid assumption that any catalyst active in decomposing 13-M HAN will also be active in decomposing HAN/fuel blends.

It has been difficult enough to gain only a modest understanding of the homogeneous thermal decomposition of HAN solutions. Various theories have been proposed, and kinetic models have been developed to predict the rate of HAN decomposition. It was difficult to do this for a simple solution of HAN in water without any catalytic surfaces. It is considerably more difficult to develop a similar model for the decomposition of HAN solutions on the surfaces of catalysts. In addition to homogeneous liquid-phase reactions, surface-catalyzed and mass-transfer limited mechanisms come into play. Even if a working kinetic theory for one type of catalyst is developed, it will not automatically apply to other catalysts with different active metals.

The development of high-temperature, long-life, capable catalysts for use with HAN-based monopropellants in rocket engines is described in *Encyclopedia of Monopropellants*, chapter “Hydroxylammonium Nitrate-Based Monopropellants.”

HAN Decomposition in Batch Reactors

HAN decomposition in batch and dynamic flow reactors has been studied mostly in academic settings, with the intent of testing the same catalysts in rocket engines at a later time. Platinum catalysts supported on two types of silica-doped alumina carriers were compared for the decomposition of 79% HAN solutions in a TGA and

a closed-bomb microreactor [352, 353]. The supports were prepared by sol-gel synthesis (hydrolysis of alkoxyl aluminum and silicic acid ethyl ester) and dehydrated by subcritical drying (giving xerogels) or supercritical drying with CO_2 (giving aerogels). The 10% platinum was either coprecipitated with the hydroxides before the sol formation (a one-step procedure), or the granular carrier was impregnated with hexachloroplatinic acid solutions and reduced under hydrogen at 673 K (400 °C). The carrier was calcined in air for 5 h at 1473 K (1200 °C) prior to active metal deposition [354].

As an alternative method, the active phase was introduced by impregnation from aqueous platinum precursor solutions or by one-step addition of the precursor before the sol formation. The impregnated catalysts always displayed the best activity, which correlates with the smaller Pt crystallite size that they support. Aerogels have better thermal stability at high temperatures (1473 K = 1200 °C) and are more homogeneously dispersed than xerogels. In spite of this, aerogels were less efficient for the decomposition of HAN solutions at low temperatures. The one-step procedure led to an increase of the thermal stability for the aerogel samples, but the catalytic activity was less efficient. The impregnated catalysts always had the best activity (lowest exotherm in the DTA) in relation to the lower crystallite size of the metallic particles. One of the most important findings of this study was that aerogels can maintain high surface area at high temperatures. The other encouraging result was the possibility to decompose aqueous HAN solutions catalytically at low temperatures (less than 313 K = 40 °C) with a short ignition delay (less than 1 s). The best catalyst was a xerogel catalyst activated by impregnation. The onset of the exotherm of this catalyst in 79% HAN was 345 K (72 °C). After 15 injections of HAN solution into the batch reactor, the active metal content of all catalysts had dropped to half the original value. XRD and transmission electron microscopy (TEM) identified crystallite growth of the platinum crystallites. Active metal loss and crystallite growth combined to cause deactivation of the catalyst after a very short service life. See also [353, 355].

In order to supplement data obtained with the constant volume batch reactor, a dynamic laboratory reactor with online product mass spectrometric analysis was developed to study the thermal or catalytic decomposition of aqueous 20 and 80 mass-% HAN solutions [356]. This reactor allowed the evaluation of catalytic activity of different catalyst-propellant combinations, the qualitative and quantitative time-resolved determination of the reaction products, and control of the selectivity for the formation of nitrogen and nitrogen oxides (N_2O , NO, NO_2). It can be used in isothermal or increasing temperature modes. For dilute solutions (20 mass-% HAN), the thermal decomposition resulted in formation of mostly N_2 and NO as primary products, whereas nitrous oxide N_2O and nitrogen dioxide NO_2 were only formed later (secondary products). The thermal decomposition of concentrated mixtures (80 mass % HAN) gave first N_2 and O_2 during the thermal decomposition, NO being only a secondary product. On the contrary, NO appears to be a primary product in the presence of a catalyst, and NO_2 remains only a minor product (Figure 41 and 42).

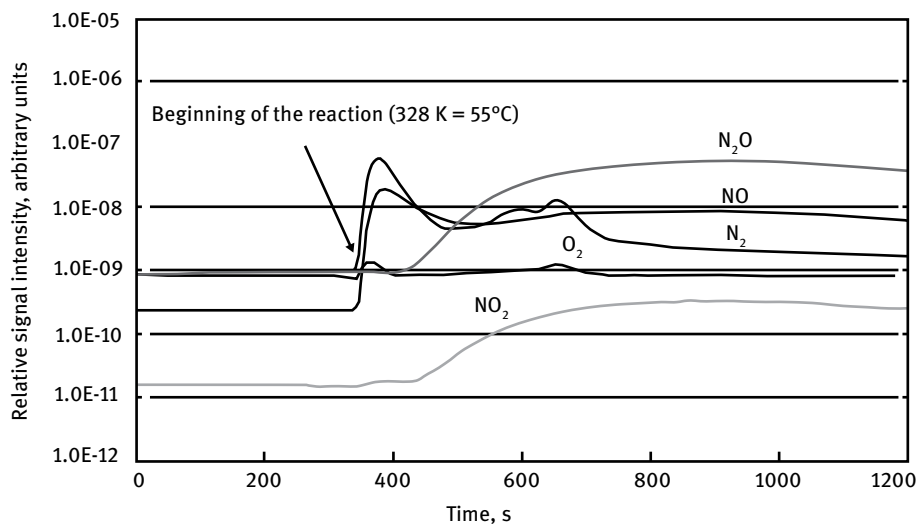


Figure 41: Time-resolved evolution of reaction products from increasing temperature decomposition of 80% HAN on 10% Pt/Al₂O₃/SiO₂ catalyst. (Republished and modified from [356], with permission granted by © 2004 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center, Inc.)

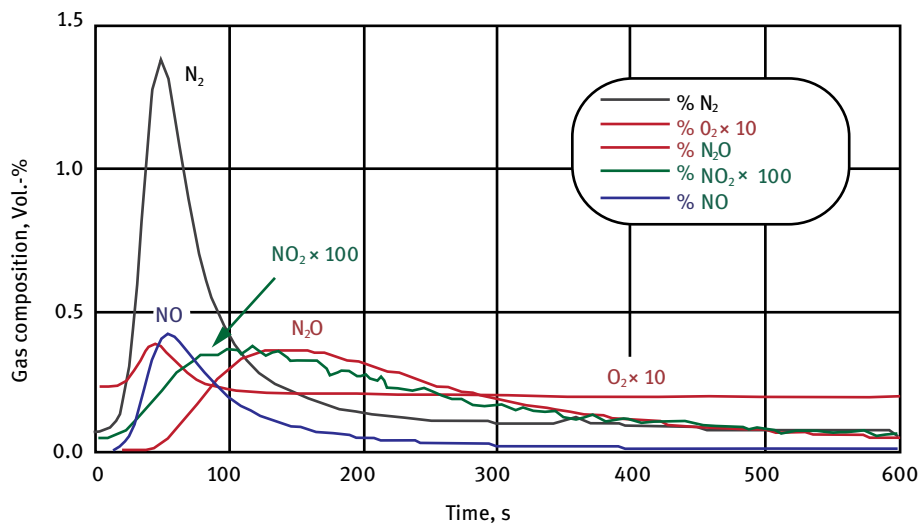


Figure 42: Thermal decomposition of 80% HAN at 473 K = 200 °C. (Republished and modified from [357], with permission of © 2007 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

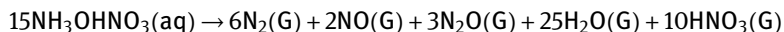
In the downstream section of the dynamic flow reactor, a white powder had sublimed and deposited as a result of decomposing 80% HAN solutions. It was analyzed and found to be ammonium nitrate [357]. The analytical results were supplemented by analyzing the aqueous solutions collected from the condensate by Raman spectroscopy. Based on the species detected in the mass spectrogram, the equations in Table 27 were proposed to describe the decomposition of HAN.

Table 27: Balanced equations for decomposition reactions of HAN.

Eq. no.	Balanced equation	Enthalpy of reaction, kJ/mol	Entropy of reaction, J mol ⁻¹ K ⁻¹	Adiabatic temperature, °C
1	$\text{NH}_3\text{OHNO}_3(\text{S}) \rightarrow \text{O}_2(\text{G}) + 2\text{H}_2\text{O}(\text{G}) + \text{N}_2(\text{G})$	-118.1	624	870
2	$2\text{NH}_3\text{OHNO}_3(\text{S}) \rightarrow 2\text{N}_2\text{O}(\text{G}) + \text{O}_2(\text{G}) + 4\text{H}_2\text{O}(\text{G})$	-36.5	550	309
3	$\text{NH}_3\text{OHNO}_3(\text{S}) \rightarrow 2\text{NO}(\text{G}) + 2\text{H}_2\text{O}(\text{G})$	+63.5	649	
4	$2\text{NH}_3\text{OHNO}_3(\text{S}) \rightarrow 2\text{NO}_2(\text{G}) + 4\text{H}_2\text{O}(\text{G}) + \text{N}_2(\text{G})$	-83.9	564	650
5	$3\text{NH}_3\text{OHNO}_3(\text{S}) \rightarrow 4\text{HNO}_2(\text{G}) + 4\text{H}_2\text{O}(\text{G}) + \text{N}_2(\text{G})$	-61.4	633	484
6	$5\text{NH}_3\text{OHNO}_3(\text{S}) \rightarrow 4\text{HNO}_3(\text{G}) + 8\text{H}_2\text{O}(\text{G}) + 3\text{N}_2(\text{G})$	-128.5	481	911
7	$\text{NH}_3\text{OHNO}_3(\text{S}) \rightarrow \text{HNO}_3(\text{G}) + \text{NH}_2\text{OH}(\text{G})$	+181.7	77	

Data source: [357]

The formation of nitric acid leads to the highest energy release and would be thermodynamically favored. The balanced equation corresponding to the overall thermal decomposition process is a combination of equation 1 and equation 4 from Table 27:



The corresponding enthalpy of reaction is -119.8 kJ/mol. The experimentally obtained $\text{N}_2:\text{NO}:\text{N}_2\text{O}$ ratio was 6:2:2, and it agreed well with the ratio in the above equation. The results were compared to those obtained for ammonium nitrate and ammonium dinitramide decomposition. In both cases, nitric acid formation competes with oxygen formation. Based on equilibrium calculations using HSC Gibbs, nitric acid is a very stable intermediate kinetic product up to about 523 K (250 °C). Above 573 K (300 °C), HNO_3 decomposes into H_2O and NO_2 .

Aqueous solutions of 40 and 79 mass-% HAN were thermally and catalytically decomposed on Pt/SiO₂ catalysts in a batch reactor, and the results were compared to similar tests performed with 40% HNF solutions [358]. The reactions were tracked by TGA and DTA, and the reaction products withdrawn from a batch reactor were analyzed using mass spectrometry. In the presence of a catalyst, HAN displayed a single exothermic peak, whereas HNF showed two separate exotherms. Catalyst removed from the batch reactor after several injections of HAN showed distinct sintering and crystallite growth of the active metal phase.

The stability of 10%Pt/Al₂O₃/SiO₂ and other catalysts during the catalytic decomposition of 79 mass-% aqueous HAN solutions at 313 K (40 °C) was studied by successive, repeated injections of HAN solution onto the catalyst in a constant-volume batch reactor [359, 360]. The four different catalysts remained active with a fast reaction rate, even in the presence of an excess of residual aqueous solution. Of course, the temperature in the reactor never approached the thousands of degrees a catalyst has to survive in a rocket engine.

Catalysts prepared by drying of xerogels or aerogels in supercritical carbon dioxide may have impressively high surface areas in the freshly prepared state, but once exposed to typical operating temperatures of high-performance HAN-based monopropellants, they will quickly sinter into a solid piece of brick with very little remaining activity, despite having been calcined at 1473 K (1200 °C) for 5 h. Aerogels presented much better thermal stability at high temperature and were more homogeneously dispersed than xerogels. What a catalyst chemist [361] calls “a short ignition delay” (<1 s) is still too long by a factor of 20 for practical rocket applications.

The catalytic decomposition processes of 20, 40, and 79 mass-% HAN and 40 mass-% HNF ([N₂H₅]⁺[C(NO₂)₃][−]) solutions were compared in a constant-volume reactor [362]. The reactions were followed by thermal analysis and by pressure-rise measurement in a constant-volume batch reactor. The 79% HAN solution in contact with a Pt(10%)/Al₂O₃/SiO₂ catalyst showed lower pre-heat temperatures (down to room temperature), higher reaction rates, and more gaseous products than any of the other concentrations, giving the most active system. With the same catalyst, HNF solutions gave lower performances than HAN solutions, suggesting that other catalysts need to be found for this oxidizer.

Spherical granule supports from silica-doped alumina with an average diameter of 1.5 mm were prepared using two procedures starting from the same sol-gel silicon-doped boehmite by dripping it into an oil bath, calcining the solidified droplets at 1473 K (1200 °C), and impregnating them with platinum [363–365]. SiO₂-doped alumina supports (Al₂O₃)_{0.88}–(SiO₂)_{0.12} (Si:Al atomic ratio 6:94) were made using a sol-gel procedure with aluminum tri-sec-butoxide (Al(O–CH(CH₃)–C₂H₅)₃) as precursor and silicon tetraethoxide (Si(O–C₂H₅)₄) to introduce Si as the doping element. The resulting boehmite wet gel was dried under sub-critical conditions (oven, 393 K = 120 °C, 12 h, air flow) to form xerogel samples, which were subsequently calcined at 1473 K (1200 °C). The platinum active phase was impregnated onto the surface of the calcined support through incipient wetness impregnation using an aqueous solution of hexachloroplatinic acid H₂PtCl₆. After drying at 393 K (120 °C), temperature-programmed reduction under H₂ at 673 K (400 °C) led to the formation of medium-sized platinum crystallites (17–21 nm). The catalysts were promoted with 10 mass-% Pt and displayed good efficiency and similar catalytic activity for the decomposition of aqueous 79 mass-% HAN solutions. In a DSC apparatus with a heating rate of 10 K/min, the onset of exotherm of 79% HAN with the most active catalyst (MF) was at 331 K (58 °C). The second most active catalyst (OD) showed

an onset of exotherm at 346 K (73 °C). The bare carriers exothermed only at 363 to 403 K (90 to 130 °C). Similar catalysts were later used for the decomposition of HAN/methanol or HAN/glycerol propellants. Monolithic catalysts studied by the same group were tested with hydrogen peroxide but not with HAN.

Binary aqueous HAN solutions of different concentrations (20, 60, 83 mass-%) were thermally and catalytically decomposed in a constant-volume closed-bomb reactor [221]. The initial reactions of HAN solutions were very similar to those of XM46 propellant. It is easier to test catalysts with HAN solutions in the absence of a fuel, so as not to complicate the reactions. The catalysts were prepared by impregnation of pure or doped supports (alumina, zirconia, barium aluminate, magnesium aluminate, or zirconium aluminate) with monometallic or bimetallic active phases (platinum-group metals [PGM] and non-PGM). Evaluation of the catalysts was carried out using a TGA apparatus and a constant-volume batch microreactor. In the microreactor, 50 μ L monopropellant was added to 100–200 mg of catalyst at room temperature with a micro-syringe through a septum and was then heated at a rate of 4–10 K min⁻¹. The pressure and temperature (catalyst and gas phase) were recorded vs. time. The thermal decomposition started only after the water was quantitatively removed, and the onset temperature was 388 K (115 °C) for the 83% HAN solution using the batch reactor. In the presence of a support alone, a catalytic effect was detected for the alumina and silica-doped alumina by a decrease of the decomposition temperature, due to the acidity of the surface; on the other hand, doping with barium lead inhibited this effect. The presence of an adequate PGM active metal phase led to a further drop of the onset temperature (<313 K = <40 °C). It is encouraging that the decomposition can be triggered at room temperature in the presence of water. The catalytic decomposition was an order of magnitude faster than the thermal decomposition.

In a study of the thermal and the catalytic decomposition of ionic oxidizers in aqueous solution such as HAN, AN, ADN, and HNF, the decomposition was followed by DTA-TGA, constant-volume batch reactor, and dynamic flow reactor coupled with a mass spectrometer [366]. The gaseous products were analyzed by mass spectrometry, whereas the condensed products were analyzed by Raman spectroscopy and acid–base titration in order to establish a balanced equation of the thermal or catalytic decomposition of these oxidizers. A 10% Pt/Al₂O₃/SiO₂ catalyst initially developed for HAN-water decomposition achieved only a low catalytic activity toward ADN-water, HNF-water, and AN-water mixtures. Other monometallic and bimetallic catalysts based on Pt, Fe, Cu, and Zn were prepared and tested to decompose these mixtures.

In addition to HAN/H₂O solutions, the decomposition of HAN/H₂O₂ solutions was also tested on monolithic catalysts. It is reasonable to assume that any catalyst capable of decomposing HAN or high-test peroxide (HTP) will also be capable of initiating decomposition of HAN/H₂O₂ solutions that have been considered as oxidizers for bipropellant or hybrid rocket applications. A batch reactor has been used to study the thermal and catalytic decomposition of binary aqueous HAN and ternary aqueous

HAN/H₂O₂ mixtures [281]. The monolithic catalysts were prepared by impregnation of a coated mullite monolith with monometallic active-phase precursor (Pt or MnO_x) and bimetallic active-phase precursors (Pt+MnO_x). The activity of different catalysts was rated by determining the pressure-rise rate and the reaction products. For a ternary mixture consisting of 31.6 mass-% HAN/31.1% H₂O₂/37.3% H₂O, the relative ranking in the order of decreasing activity at room temperature was MnO_x + Pt > MnO_x > Pt.

Binary HAN aqueous solutions have been decomposed thermally and catalytically [349]. Binary HAN/H₂O mixtures were prepared with different concentrations: 95, 80, and 60 mass-% HAN. The catalysts were prepared by impregnation of alumina/lanthanum oxide with iridium and were characterized by XRD, hydrogen chemisorption, and TEM with a resolution of 3.5 Å. The decomposition processes were followed by DTA, TGA, and processing in a constant-volume batch reactor. In the constant-volume batch reactor, 50 μL of monopropellant was added to 80 mg of catalyst at room temperature under 1 bar of argon flow, using a micro-syringe through a septum, and was then heated at a rate of 10 °C/min. The pressure and temperature were recorded vs. time. This reactor can be used to simulate cold starts or injection by pulses, but not stationary monopropellant flow (steady-state studies). The effect of HAN concentrations on reactivity was studied to determine the best “green” propellant formulations for rocket applications. HAN solutions are more active in the catalytic decomposition in the absence of stabilizers that might poison the catalysts. The (10%)Ir/Al₂O₃/La₂O₃ + 95% HAN reaction showed lower decomposition temperatures, higher reaction rates, and higher amounts of gas-phase products than other mixtures tested.

In a differential scanning calorimeter, a 95% HAN solution started to decompose at 428 K (155 °C) in the absence of a catalyst [367]. When an Ir/Al₂O₃/SiO₂ catalyst was added in powdered form, the exothermic reaction started at 320 K (47 °C). It is not quite clear whether subsequent burning-rate tests were done with a HAN/MeOH monopropellant or simply with 95% HAN/H₂O solutions without an added fuel. Both were called “liquid monopropellant.”

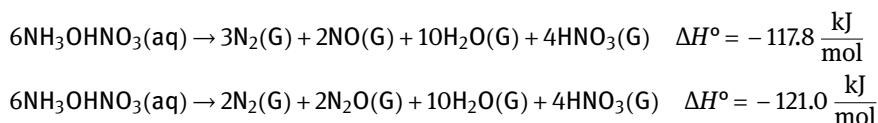
DTA and TGA of aqueous HAN solutions and product gas analysis were conducted for both catalytic and thermal decomposition [368]. These analyses showed that the Ir-based catalyst was effective to reduce the onset temperature of HAN decomposition and that the difference in product gas species was not obvious between catalytic and thermal decompositions. The reaction mechanism of catalytic decomposition was almost the same as that of thermal decomposition. Nitric acid was generated at a lower temperature in catalytic decomposition than in thermal decomposition. The Ir-based catalyst could not change the reaction mechanism but could activate the reaction path of HNO₃ generation.

Dynamic HAN Decomposition Reactors

A dynamic reactor with mass spectroscopy online product analysis was used to study the thermal and catalytically accelerated decomposition of HAN and HAN-based monopropellants [364, 369]. The activity of different catalysts was evaluated by

determining the type and rate of evolution of reaction products (N_2 , O_2 , N_2O , NO , and NO_2). The analysis results were supplemented by Raman spectroscopy of the aqueous condensates collected from the reaction products in a cold trap prior to admitting the non-condensable gases into the mass spectrometer. The thermal and catalytic decomposition of 80 mass-% HAN gave large amounts of N_2 , lesser amounts of NO , and traces of N_2O and NO_2 . A powdered and a granular, spherical catalyst with 10% Pt were tested [370]. The isothermal tests at 323 K (50 °C) gave the best activity, with a powdered catalyst resulting in complete decomposition of the HAN solution. Coarser, sphere-shaped catalysts gave only incomplete HAN decomposition due to channeling of part of the liquid through the catalyst bed. Likewise, the thermal (non-catalytic) decomposition over an inert carrier at 473 K (200 °C) gave only a partial decomposition reaction.

Two parallel reactions were proposed based on the reaction product analysis [363]:



In establishing a model of the HAN decomposition process, 11 reactions were identified as participating in the condensed-phase decomposition reactions of HAN, starting with a proton transfer. The ratio of $\text{N}_2\text{O}/\text{NO}$ generated during HAN decomposition depended on the catalytic surface and temperature. The observed increase in $\text{N}_2\text{O}/\text{NO}$ ratio with Shell 405 catalyst suggest multiple surface-sensitive reaction pathways involving HNO , HNO_2 , and hyponitrous acid $\text{H}_2\text{N}_2\text{O}_2$. It was recommended to study the effects of the SHAN stabilizers in the liquid propellants to determine their roles in the reaction mechanism because they may act as inhibitors and catalyst poisons.

Chinese catalysts intended for the decomposition of HAN-based monopropellants were prepared by incipient wetness impregnation of six different active metals on Al_2O_3 (20–40 mesh; BET surface area 204 m^2/g) or SiO_2 (20–40 mesh; BET surface area 477 m^2/g) with an aqueous solution of the corresponding metal precursors to give an active metal content of 5 mass-% [371]. The catalysts were dried at 353 K (80 °C) for 12h and then calcined at 573 K (300 °C) under N_2 for 5h. Prior to the catalytic tests, the catalyst were *in situ* reduced with H_2 at 623 K (350 °C) for 2h. Two kinds of HAN-based propellants were used to test the catalysts: HAN80 and HANGLY26. The former is a binary mixture containing only 80 mass-% HAN in water and no fuel, and the latter is a ternary mixture composed of 60% HAN, 14% glycine, and 26% water. The catalytic activity was evaluated by three methods: an open-cup (“spot plate”) experiment for rapid screening of catalysts; a thermal analysis method for determining the onset temperature of decomposition; and an isothermal, isochoric batch reactor method for simulating pulse-mode operation in a real thruster with 20 pulses in short sequence. Catalyst temperature and chamber pressure were recorded during each 20-pulse sequence. An 8-mg sample of the catalyst was put into a quartz crucible of the DTA appa-

ratus (Shimadzu DT-20B), and then 30 μL of the 80% HAN solution was added to the catalyst below room temperature by using ice cooling. The catalyst was not spontaneous at room temperature. The crucible was then heated at $10\text{ }^{\circ}\text{C min}^{-1}$ under a purge of N_2 gas, and the first sign of an exotherm was recorded. All the catalysts listed in Table 28 lowered the ignition temperature of 80% HAN to some extent. Both Os and Ir supported on SiO_2 exhibited the best catalytic activities, with the ignition temperatures of 307 K ($34\text{ }^{\circ}\text{C}$) and 294 K ($21\text{ }^{\circ}\text{C}$), respectively. Other supported metal catalysts, such as Pt, Ru, Rh, and Pd, had poor activities, with an ignition temperature of above 343 K ($70\text{ }^{\circ}\text{C}$). This is in contrast to the results obtained by Kappenstein et al., who reported that supported Pt was the most active catalyst.

Table 28: Ignition temperature of 80 mass-% HAN solution on various supported metal catalysts.

	Ignition temperature, $^{\circ}\text{C}$							
	Metal		Ru	Rh	Pd	Os	Ir	Pt
	None	None						
Support								
SiO_2	74	—	69	84	98	34	21	90
Al_2O_3	—	78	78	83	100	—	77	82

Data source: [371]

Some catalysts were soaked in 69% nitric acid prior to the tests and dried, which greatly enhanced their activity to the point that HAN/glycine propellant could be ignited at room temperature.

In tests of 80% HAN decomposition with Ir/ Al_2O_3 and Ir/ SiO_2 catalysts at room temperature, the Ir/ SiO_2 catalysts were more active [372].

3.4.4 Analytical Methods for Hydroxylammonium Nitrate Solutions

The analytical methods described here apply only to oxidizer solutions and not to formulated HAN-based monopropellants containing fuels. Analytical methods for HAN-based monopropellants are described in *Encyclopedia of Monopropellants*, chapter “Hydroxylammonium Nitrate-Based Monopropellants.” See also [373, 374].

A survey of 61 references from the literature resulted in a review of the quantitative methods most widely used to determine hydroxylamine and its salts, including volumetric, electrochemical, and spectrophotometric methods [375].

3.4.4.1 Volumetric Methods

Acidimetric Methods

Because of the different pKs of nitric acid and hydroxylammonium ion, the two can be determined by acidimetric titrations with recording of the pH, typically done in an autotitrator [376].

The free nitric acid content in HAN solutions and in HAN-based monopropellants can be determined by autotitration with electrometric end-point indication. For small acid contents ($<0.5\%$ HNO_3), a known amount of HNO_3 is added before the titration, and the difference is calculated after the titration [377].

Redox Titration Methods

If standardized triphenylphosphonium permanganate solutions are used for titration of hydroxylamine or its salts in pyrophosphate buffers, and if a water-immiscible organic solvent is layered below the water, the end point can be detected by the appearance of a purple color in the organic phase [378].

3.4.4.2 Gas Chromatographic Methods

Hydroxylamine can be derivatized with acetone to form the ketoxime, which is volatile, and can be detected in trace quantities in a gas chromatograph with a flame ionization detector [379].

3.4.4.3 Liquid Chromatographic Methods

Reaction products of HA and HAN decomposition were analyzed using HPLC and ion chromatography using a Dionex P680 system with a Dionex 1024 dio-array detector equipped with an Acclaim C18 5- μm , 120- $\text{\AA}$, 4.6 $\times$ 250 mm column with a 95:5 water:acetonitrile isocratic mobile phase [98]. The method also served to measure the concentration of undecomposed HAN as a function of time. The UV absorption of the HPLC effluents was measured at 201 and 254 nm.

Mixtures of hydroxylamine, *N*-methylhydroxylamine, and *N,N*-dimethylhydroxylamine and their salts can be analyzed by ion chromatography [380].

3.4.4.4 Infrared Spectroscopic Methods

Infrared spectroscopy is an ideal method for the analysis of HAN and HAN contaminants in the solid state or in aqueous solutions [381].

3.4.4.5 UV-Visible Spectroscopic Methods

The total nitrate concentration in HAN and HAN-based monopropellants can be determined by measuring the absorption at 205 nm. This method is useful when monitoring the HAN concentration during the preparation of concentrated HAN solutions from diluted HAN solutions by evaporation of water [382]. It is also useful when monitoring the electrolyte withdrawn from diaphragm HAN production cells [383].

3.4.4.6 Mass Spectrometric Methods

The analysis of HAN for metal ions at the level of 1–10 ppb is possible using inductively coupled plasma-mass spectrometry (ICP-MS) [384]. Sensitivity levels using a Perkin-Elmer model 500 ICP mass spectrometer and appropriate internal standards were approximately 1 ppb. From one prepared and diluted sample, HAN solutions were an-

alyzed for 19 elements, including sodium, magnesium, aluminum, calcium, strontium, barium, vanadium, niobium, chromium, and molybdenum. The analysis was repeated five times per sample and required approximately 3 min for the total analysis. The method can be expanded to include other metals, with the introduction of a set of standards for new analytes. This technique is applicable not only to a finished product but also to all starting reactants and production-process intermediate streams and propellants.

3.5 Ignition of Hydroxylammonium Nitrate Solutions

The same methods that have been tested for the ignition of XM46 were also tried for the ignition of HAN solutions in the absence of fuels, including catalytic, electric, and laser ignition. The ignition of HAN solutions in the absence of fuels is a less energetic reaction. Sometimes HAN solutions ignited by accident rather than on purpose. Because the major part of liquid burn propellants and liquid monopropellants consists of HAN, it is interesting to study the ignition behavior of HAN solutions by themselves in the absence of fuels.

A CO₂ laser was used to initiate and sustain combustion of HAN and TEAN at pressures of 1 and 4 atm and heat fluxes of 100 and 400 W/cm² [385]. A triple quadrupole mass spectrometer and micro-thermocouples were applied for measurements of temporal species evolution and temperature profiles. Flame behavior was observed using a high-magnification, high-speed video system. At 400 W/cm², the sequence of flame and species evolution was the same for each material at the two pressure conditions; however, mol fractions of some major species measured were different. In tests at different pressures, the ignition delay of HAN increased with increasing pressure, while the ignition delay of TEAN and XM46 decreased. Additional measurements of species and temperature were made for liquid HAN solution and XM46 droplets to obtain the condensed-phase temperature and species evolution during laser-assisted pyrolysis. Droplets with diameters of 500–800 μm were suspended from type K thermocouples in argon at sea-level pressure and were heated by a CO₂ laser at 50 W/cm². For HAN, the temperature of the droplet experienced two plateaus at ~440 K and ~540 K during the evaporation of H₂O and the decomposition of HAN, respectively. Although no visible flame was observed during the HAN pyrolysis, a brown gas evolved, and the surface of the droplet pulsed. During the HAN decomposition, evolution of NO₂, N₂O, NO, N₂, and H₂O was consistently measured, with HONO only at very small amounts and no O₂ or HNO₃ detected.

In addition to thermally or catalytically induced decomposition of the HAN-based propellants, HAN decomposition by electrolysis has been suggested as a viable alternative for applications in micro-scale thrusters, since thermal management for HAN decomposition would be very difficult to control in small propulsion devices. The other potential benefits of electrolytically induced decomposition of HAN-based

liquid propellants would be low ignition temperature, reduced power requirement, enhanced system durability and reliability, and reduced cost. Extensive studies on electric and electrolytic ignition of XM46 propellant is described in *Encyclopedia of Monopropellants*. Investigators wanted to avoid interference by the fuel component in HAN-based monopropellants, and therefore examined the electrolytic ignition of HAN solutions without fuels.

Electric-current-stimulated ignition of aqueous HAN solutions has been studied experimentally, and electrochemical mechanisms pertaining to HAN-water solutions were established and incorporated into an existing chemical kinetics scheme [261]. The ignition process was treated numerically using a constant-pressure, homogeneous reactor model. Prototype micro-fin electrodes consisting of a Teflon screen sandwiched between two stainless steel meshes and attached to a power supply were reexamined to verify the electrolytic ignition concept. Experiments were conducted using these electrodes, and it was found that the solutions can be ignited at elevated pressure. Based on the temperature-rise profile and the evolution of condensed and gas-phase species, the effects of electric current, voltage, volume, initial temperature, and HAN concentration on the ignition delay were determined and fitted into a kinetic model. A set of ten electrochemical and chemical liquid-phase reactions was included in the analysis, involving 12 species, namely HAN, NH_2OH , HNO_3 , HONO , HNO , N_2O , N_2 , NO , NO_2 , H_2O , H_2 , and O_2 . Among them, H_2 and O_2 appear only in the gas phase. While ignition starts in the liquid phase, combustion occurs in the gas phase and was also modeled using CHEMKIN. The gaseous species produced by the condensed-phase reactions subsequently participate in a series of gas-phase reactions, many of them exothermic. A total of 32 species and 151 reactions in gas phase were considered in the gas-phase model. Results indicated that the electric current significantly enhanced HAN decomposition compared with the pure thermal decomposition process. At a constant temperature and a specified initial volume, increasing the total current decreased the ignition time delay of HAN-water solutions (Figure 43).

In similar tests, the ignition of HAN solutions (no fuel added) was examined [292]. The purpose of that study was to identify the various parameters and mechanisms affecting the electrolytic ignition of HAN-based monopropellants. Electrochemical mechanisms were established and incorporated into an existing chemical kinetics scheme. The ignition of HAN-water solution by electrolysis was treated numerically using a constant-pressure, homogeneous reactor model. A stiff ordinary differential equation solver was used in the analysis to handle the highly stiff species conservation and the energy equations. The analysis focused on the temporal evolution and spatial distribution of temperature and condensed and gas-phase species. Parametric studies were conducted to investigate the effect of electric current, voltage, volume, initial temperature, and HAN concentration on the ignition time delay. The ignition time delay was found to decrease with increase in current, temperature, and HAN concentration and to increase with volume.

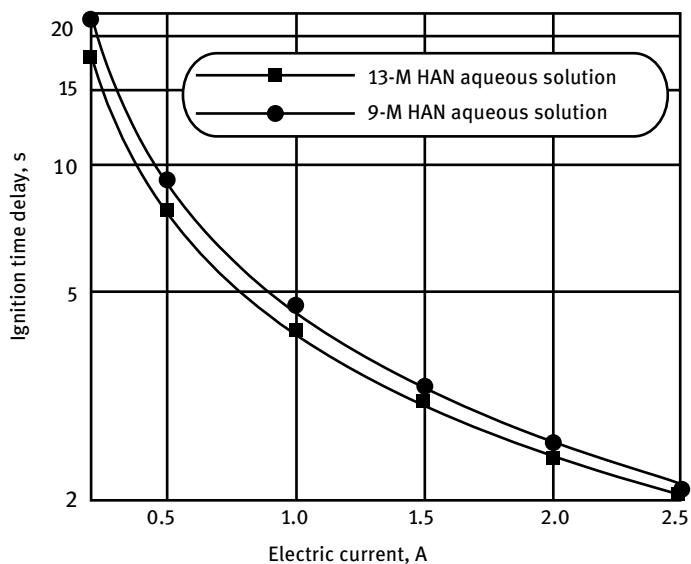


Figure 43: Ignition time delay vs. current at an initial temperature of 300 K and 1 atm pressure. (Reproduced and modified from [261].)

In a study of the thermal and electrolytic decomposition and ignition of aqueous solutions of HAN, experiments were conducted to demonstrate the feasibility of electrolytic ignition of HAN-based monopropellants [386]. Electrolysis of HAN solutions leads to formation of NH_2OH , HNO_3 , HONO , HNO , N_2O , N_2 , NO , NO_2 , H_2O , $\text{H}_2(\text{G})$, and $\text{O}_2(\text{G})$. These species then initiate a series of gas-phase reactions, governed by the H-O-N kinetics scheme, that lead to ignition. Electrochemical mechanisms were incorporated into an existing chemical kinetics scheme for thermal decomposition of HAN/water solutions. The analytical model treated the liquid and gas phases separately and matched their respective processes at the interfacial boundary to determine the overall decomposition and ignition characteristics. Model predictions were compared to experimental data for species evolution in the condensed phase, as well as to laser-induced ignition delay of 13-M HAN/water solutions. The effects of electric current (0–2.5 A), propellant volume (0.1–0.3 mL), initial temperature (300–450 K), and HAN concentration (9–13 M) on the ignition behaviors were investigated systematically. The ignition delay decreased with increasing electric current as a power-law function

$$t_{\text{ign}} = A \times I^{-n}$$

where $A = 3.95$ and $n = 0.95$ for a 0.1-mL 13-M HAN/water solution at an initial condition of 300 K and 1 atm. The exponent n and coefficient A were decreasing functions of the initial temperature. A titanium micro-fin electrode module was used that consisted of

eight evenly spaced parallel fins with dimensions of $9 \times 19 \times 0.25$ mm, separated from each other by 1 mm. The electrode surface area ranged from 1050 to 4200 mm², and the input voltage ranged from 7 to 26 V, similar to conditions described by Risha et al. [387]. Rates of gasification of 15-mL samples of XM46 were measured as a function of electric voltage, current, and electrode geometry. Peak reactivity was achieved after ~0.75 s. Reaction rates and activation energies for eight reaction steps were entered into a kinetic model to derive a global decomposition rate for HAN by itself in aqueous solutions. The electrolytic ignition results were then compared to laser ignition of 13-M HAN by a laser energy flux of 400 W/cm² (120 W into a test sample of 0.3 mL solution with a height of 10 mm). See also [293, 388].

The electrolytic ignition and decomposition of various HAN ternary stoichiometric mixtures prepared according to zero oxygen balance to carbon dioxide showed multiple stages of decomposition depending on the type of fuels added into the HAN solution [389]. While concentrated HAN solution (73 mass-% HAN) had only a single stage of decomposition, the saccharides-based HAN ternary mixtures had three stages of reaction with increased energy release. Based on calorimetric measurements, there was a linear relationship between the electrical resistivity of HAN ternary mixtures and reaction rates in the first stage of reaction, indicating the presence of Joule heating in the process. The influence of electrical resistivity of ternary mixtures became negligible in the second stage of reaction. The release of combined electrical and thermal energy is important in the first-stage decomposition of HAN ternary mixtures.

In a study of the electrolytic decomposition of HAN/water solutions using graphite electrodes, it was noted that the decomposition reaction proceeded in two stages [390]. Electrical energy was consumed for 5 s before the stage-1 reaction ceased. An interesting phenomenon was observed in the stage-2 reaction, in which the decomposition of HAN resumed after the power supply was switched off. A series of spectroscopy and microscopy analyses confirmed that the production of nitric oxide (NO) in the stage-1 reaction caused the formation of nitrous acid (HNO₂), which led to a further autocatalytic reaction. Several reaction mechanisms were proposed and compared with the case of using copper electrodes. Graphite electrodes were identified as more energy efficient in initiating the electrolytic decomposition of HAN/water solution, as lower energy consumption (342 J) was achieved in comparison to the energy required to achieve ignition with copper electrodes (1926 J).

Decreasing the initial volume of the HAN solution also expedited the electrolytic ignition process, indicating that the electrolytically induced HAN ignition should be suitable for applications in small thrusters. It was also seen that at a constant volume and temperature, a more concentrated solution of HAN ignited faster than a less concentrated solution if equal electric current was applied. The same apparatus was later used to study the ignition of XM46 [387].

Hydroxylammonium nitrate solutions as liquid oxidizer for hybrid rockets are easy to handle because they are not toxic, have a low vapor pressure, and are stable at ordinary temperatures and pressures. In studying the decomposition of HAN solution

droplets in a hybrid rocket engine, it was important to observe a single droplet because atomized HAN liquid oxidizer consists of many droplets. HAN concentration affects the ignition characteristics of the HAN droplets. The relationship between HAN concentration and ignition characteristics of the HAN droplets was studied by obtaining the decomposition delay time of the HAN droplets [391].

The electrolytic decomposition of ADN-HAN mixtures in a polymer micropropulsion system was studied as an ignition method for monopropellant or hybrid micro-rockets [392].

3.6 Strand Burning of Solid Hydroxylammonium Nitrate Pellets and Hydroxylammonium Nitrate Solutions

Strand-burning data have been obtained for the burning of HAN by itself as a solid as well as in aqueous solutions in the absence of any combustibles. Nobody was planning on using HAN by itself as a propellant, but since the burning rates of HAN-based monopropellants are determined mostly by the rate of the decomposition of HAN the precedes the combustion, this was important information to have. Also, the major ingredient in all HAN-based monopropellants is HAN itself, usually in concentrations around 60 mass-%, so its decomposition influences the burning rates more than any of the other ingredients do.

It is nearly impossible to obtain solid HAN at room temperature. Therefore, most of the experiments have been done with HAN solutions instead of with the pure compound.

In a study at Sandia National Labs in Albuquerque, New Mexico, HAN solutions and HAN-based propellants were burned in a back-lit strand burner inside a windowed pressure vessel at pressures up to 34 MPa (5000 psi) [237, 393–395]. High-speed cine shadowgraphy was used to capture the decomposition phenomenon. The sample-holder capillary tubes were 5.2–9.1 mm in internal diameter, and the samples were 40 mm long. Later samples were burned in a rectangular cell that was 1.8×1 mm wide. The imaging system was capable of operating at a framing rate of 60 frames/s. Ignition was achieved by an electric discharge. In looking at the burning-rate results, it was noted that there is a decrease in the average volumetric turbulent burning rate of HAN solutions as well as XM46 when the pressure is increased from 6.7 to 34 MPa (1000 to 5000 psi). This “negative pressure exponent” was at first unexplained, but it was later attributed to changes in the stability of the liquid–gas interface with pressure. At the lower pressure, there are more interfacial instabilities, and small droplets get thrown out of the burning meniscus into the flame front. At low pressure, the apparent decomposition rate was approximately proportional to $1/P$ due to hydrodynamic instabilities, which become less noticeable at higher pressures. A “density ratio” parameter was introduced to obtain better correlation of the results. Low-density ratios are associated with

meniscus decomposition fronts, and high-density ratios give flatter flame fronts. At higher pressure, the apparent decomposition rate was proportional to the HAN concentration. The lowest concentration at which HAN decomposition could be sustained was between 3 and 5-M HAN. Water that formed during the decomposition of 5 to 9-M solutions was mostly in the liquid phase (wet steam). The solution concentration has to be at least 11 to 13-M to obtain dry steam. The experimental results confirmed the strong positive influence of the effective diameter of the tube and the negative influence of pressure on the burning rate of water solutions of HAN. It was found that 3.12-M HAN could not sustain decomposition, even when initiated with an electric discharge of as much as 10 J. For solutions of 5.20, 7.02, and 9.10-M HAN, the mass decomposition rate first decreased until reaching about 13 MPa, and then it became independent of pressure. The abnormal behavior of burning rates at $p < 13$ MPa was explained by introducing an “apparent mass decomposition rate.” At low pressures, the interface has a large meniscus with small corrugations. A larger meniscus corresponds to a larger decomposition area and hence a larger apparent mass decomposition rate. As the pressure was increased, the meniscus became less pronounced, becoming indiscernible at pressures above 13 MPa, and at that point the apparent decomposition rate decreased. The apparent decomposition rate for 11.05 and 13-M HAN solutions showed a different trend because it decreased monotonically with pressure. The unusual apparent burning-rate dependence on pressure is the result of a pressure-independent burning rate and hydrodynamic instabilities, which play a lesser role at higher pressures (smaller bubbles).

Combustion studies were conducted on solid crystalline HAN and its water solutions in a constant-pressure bomb within a pressure range of 0.1 to 36 MPa with sample diameters of 7 mm [396]. The test results indicated that solid crystalline HAN was not capable of self-sustained burning at atmospheric pressure. When ignited using a hot Nichrome wire, a slow layer-by-layer decomposition (“fizzing”) was followed by an abundant foam evolution. Above 0.3 MPa the decomposition was found to be self-sustaining, but the velocity was unusually low, only about 50 $\mu\text{m/s}$. The burning-rate equation (Robert de Vieille’s law) of a pellet of burning solid HAN (density 1.78 g/cm^3) had an abnormally high pressure exponent, similar to that of a 9-M HAN solution. For pressures below 10 MPa, the pressure exponent was 1.5 to 2.6 (Figure 44).

It was also found that in contrast to aqueous solutions of HAN and HAN-based liquid propellants, the burning rate of the solid substance increased in a controlled fashion up to 20 MPa, after which it increased even more rapidly with pressure. For pressures >20 MPa, the transitions from slow to extremely fast burning were observed immediately after ignition, and burning rates could not be measured. The pressure exponent was 1.6 up to 1.1 MPa, became as high as 2.6 at $1.1 < p < 2.1$ MPa, and decreased to 1.5 between 2.1 and 2.3 MPa. HAN solutions burning in the turbulent regime showed a sharp decrease in the pressure exponent once the pressure exceeded 10 MPa. In some instances, the burning rate of HAN solutions even decreased with increasing pressure. Solid HAN combustion in the 1.5-L windowed pressure chamber was non-luminescent,

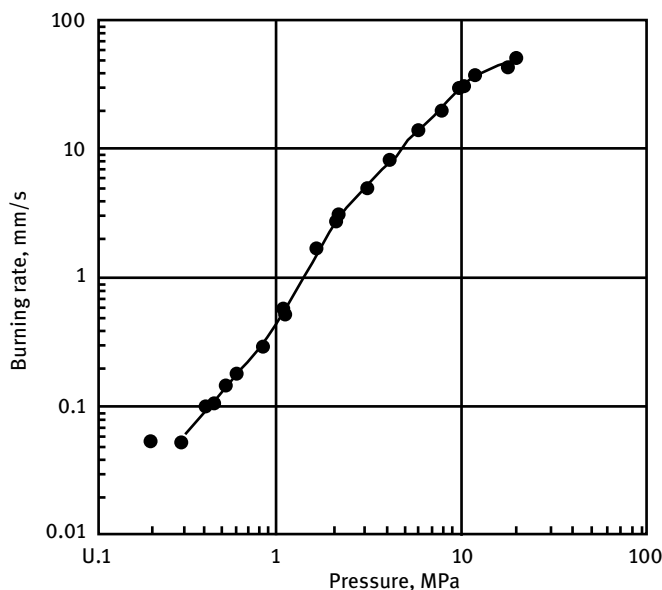


Figure 44: Strand burning rate of solid HAN. (Republished and modified from [396], with permission of Springer Nature BV © 2000; permission conveyed through Copyright Clearance Center Inc.)

such that the high-speed slit camera had to use backlighting or front illumination. When the logarithm of the burning rate of solid HAN vs. $1/T$ was plotted, straight lines with three slightly different slopes were obtained, depending on the pressure regime (<1.1 , 1.1 – 2.1 , and 2.1 – 20 MPa).

Although the main objective of the following work was to optimize burning rates of HAN solutions with methanol and AN, one initial series of strand burning-rate tests was conducted with HAN solutions of five different concentrations from 50 to 95 mass-% HAN without addition of any fuels [397]. The measurement of linear burning rates was done in glass tubes, and the progression of the flame front was recorded with a medium-speed video camera. Burning rates were measured as function of HAN concentration and pressure. As shown in Figure 45, the burning rate peaked at 80 mass-% HAN. The burning rate of 80-% HAN solutions was not very dependent on pressure.

Surprisingly, the burning rates of 85 and 95% solutions were less than that of the 80% solution. The burning rate of a 95 mass-% solution was similar to that of HAN crystals. Figure 46 is a comparison of the solution burning-rate data with data on HAN crystals obtained by Kondrikov et al. [396], also in comparison to solution data obtained by Matsuda [397].

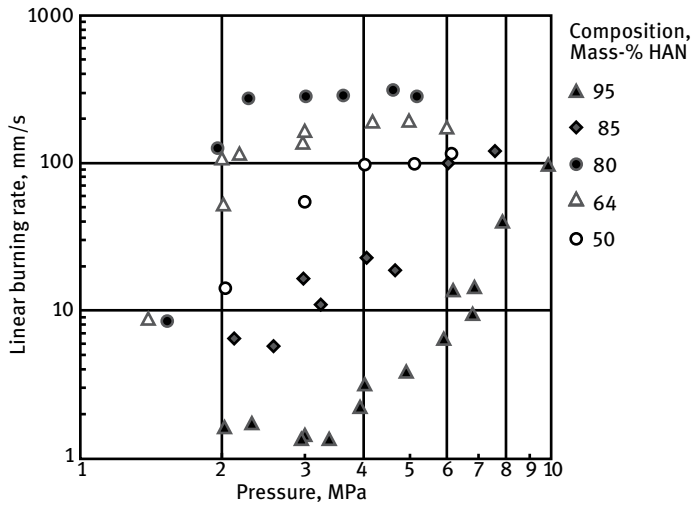


Figure 45: Burning rates of HAN/water solutions. (Reproduced and modified from [397] with permission from Keiichi Hori 11-Feb-2021.)

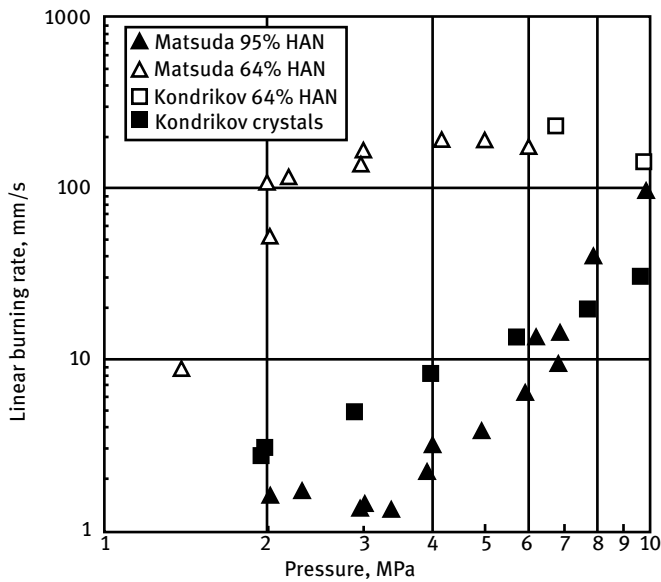


Figure 46: Comparison of burning rates of HAN solutions and HAN crystals. (Reproduced and modified from [397] with permission from Keiichi Hori 11-Feb-2021.)

Note: Kondrikov in Figure 46 is Kondrikov et al. [396]

The combustion modes of 64 and 50 mass-% solutions were the same as that of the 80 mass-% solution. Solutions containing 85 and 80 mass-% HAN had two burning modes: a mixed mode and a high-burning-rate mode. This may indicate that HAN concentration changes the structure of the combustion wave, and the structure character governs the burning rate. The Matsuda et al. [397] work is remarkable for the high-quality color images taken of the HAN decomposition flame front. This vividly illustrates the decomposition at the interface between the liquid and the combustion zone.

Seven aqueous solutions with 95, 85, 82.5, 80, 77.5, 64, and 50 mass-% HAN were prepared in order to measure the effects of HAN concentration on burning rate [398]. For HAN solutions, 95 mass-% HAN is the maximum concentration that can be prepared at room temperature. The sample solutions were placed in glass tubes and burned in a strand burner purged with nitrogen gas at 1–10 MPa. The initial temperature of the sample solutions was set at 297 K (24 °C). The combustion wave of HAN aqueous solutions in the glass tubes was observed with a medium-speed video camera at 500 frames per second. The linear burning rate had a peak at approximately 80 mass-% HAN in water. It is very strange that in the range 80–95% HAN, the burning rate decreased with increasing HAN concentration, and the curvature of the burning rate vs. pressure curve changed from convex to concave (Figure 47).

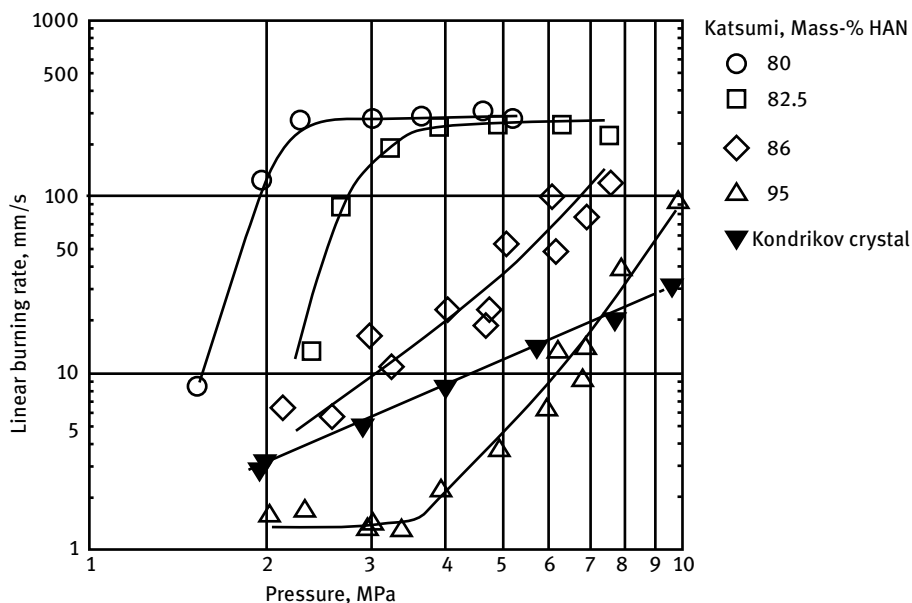


Figure 47: Linear strand burning rates of 80–95% HAN solutions. (Republished and modified from [398], with permission of © 2010 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

This phenomenon has been explained as a hydrodynamic instability in which droplets of liquid are ejected into the flame zone. The burning rate of a 95% solution was very similar to that of an anhydrous HAN crystal. The burning rates of 50–80% solutions increased with increasing HAN concentration, and the curvature of the lines in the $r_b = f(p)$ graph remained the same. The burning rate of a 95 HAN/5 AN/8 H₂O oxidizer solution increased abruptly at 3.5 MPa. A monopropellant of 100 parts of this oxidizer with 8 parts methanol showed a similar behavior at the same pressure, but a monopropellant of this oxidizer with 21 parts methanol had a steady and linear burn rate curve, as one would want to have for a well-behaved monopropellant.

The combustion characteristics of HAN aqueous solutions in the absence of fuels were studied, and it was found that the role of the two-phase region is very important and that the intense boiling of water by superheating and bursting of bubbles is responsible for the high burning rate [399]. The evaluated bubble nucleation rate coincided with burning rate at very high pressure. Hydrodynamic instabilities accelerate the burning rate. The pressure dependency of hydrodynamic instabilities was estimated, and it supported the observed phenomena. It was found that the instability was strongly affected by the Markstein number.

Additional burning-rate results are summarized in *Encyclopedia of Monopropellants* for HAN-based monopropellants in which HAN is not decomposed by itself but in combination with various water-soluble fuels.

It seems that many less-energetic hydroxylammonium salts (less energetic than HAN), although they have negative enthalpies of formation, are also capable of burning in a strand burner. That includes hydroxylammonium chloride and hydroxylammonium sulfate, which are not suitable as rocket propellants, but they have been examined for their safety properties [400]. The critical diameter and the linear burning rate of solid hydrazinium and hydroxylammonium chloride and sulfate were determined in 36-, 39-, and 45-mm-diameter tubes at atmospheric pressure. Hydroxylammonium chloride burned stably at 0.1 mm/s in 44-mm tubes but was quenched in 40-mm tubes. Addition of Cu₂Cl₂ increased the burning rate to 0.25 mm/s. Hydroxylammonium sulfate burned in all three tube diameters at rates of 0.16, 0.10, and 0.07 mm/s in tubes with diameters of 45, 39, and 36 mm, respectively. See also [401].

OXSOL is a name for oxidizer solutions containing HAN and other oxidizers (e.g., 70 mass-% HAN, 15% AN, and 15% H₂O). The strand burning rates of OXSOL-2 were measured in transparent test tubes in a windowed liquid-propellant strand burner [402–404]. The burn rate of OXSOL was deduced from the regression history of the liquid surface as seen in film recordings of the event. The burn rate was found to be a function of test tube diameter and ranged from 40 to 550 mm/s for the pressure range of 2.5–20 MPa. The tests were conducted in tubes with three different diameters. In all diameters, OXSOL exhibited two slope breaks, with a pressure exponent of 2.87 from

2.5 to 5 MPa, 0.42 from 5 to 9 MPa, and -0.78 above 9 MPa (see Figure 48). The burning rate in the low-pressure region below 5 MPa can be expressed by the equation

$$r_b = ap^{2.87}$$

with

$$a = 3.69\exp[0.07(D - 8.3)].$$

where r_b is the burning rate in mm/s, p is the pressure in MPa, and D is the tube diameter in mm. The burning rate in the medium-pressure region from 5 to 9 MPa can be expressed by the equation

$$r_b = ap^{0.41}$$

with

$$a = 184\exp[0.06(D - 8.3)]$$

The burning rate in the high-pressure region above 9 MPa can be expressed by the equation

$$r_b = ap^{-0.78}$$

with

$$a = 2416\exp[0.04(D - 8.3)]$$

The format of burning-rate data representation in Figure 48 is exemplary, and we wish that all burning-rate data by other investigators and in other publications would be

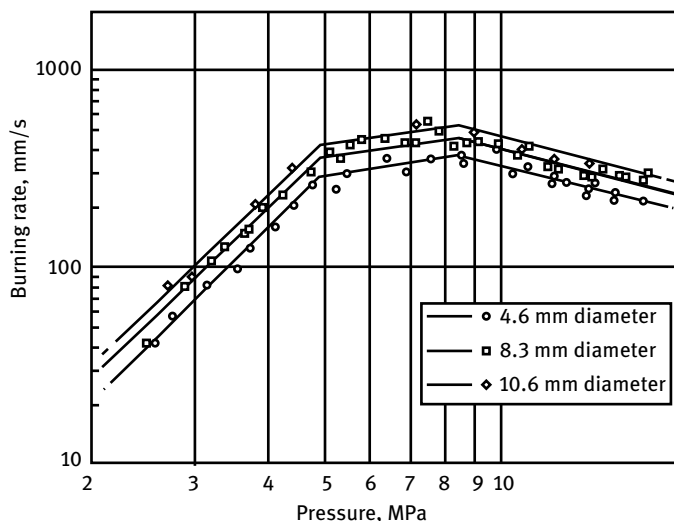


Figure 48: Burning rate of OXSOL-2 as a function of pressure. (Reproduced and modified from [404].)

presented in this format. Some other publications don't even state the strand diameter used. The dependence of the burning rate on strand diameter is clearly evident, although the cutoff pressure below which no further propagation takes place is not clearly marked. The effect of tube diameter on the burning rate of OXSOL is due to hydrodynamic instability of the burning surface, based on the simulation of surface ripples with a vibrating membrane model. The burning-rate slope break at 5 MPa was found to be very close to the slope break at 5.5 MPa in the plot of the ratio of heat of vaporization to the boiling point of water vs. pressure. This implies the involvement of the water-vaporization process in the low-pressure combustion of OXSOL.

The linear burning rates of aqueous HAN solutions and solutions containing methanol and nanoscale fumed silica were observed in a strand burner at pressures between 3 and 22 MPa in a constant volume bomb with pressure (non-optical) measurement [405, 406].

The addition of activated charcoal to HAN solutions lowers the onset temperature of thermal decomposition and increases the burning rate. The large surface area of activated carbon initially acts as a catalyst, but at later stages of the reaction, the carbon is consumed as a fuel and burned to carbon dioxide. The following several references are discussed here for their dealing with the catalytic activity of activated carbon and are also discussed in *Encyclopedia of Monopropellants*, where the addition of active carbon to concentrated HAN solutions provides a recipe for a monopropellant.

The combustion 95 mass-% HAN/water solutions in the presence of highly specific surface-area-activated carbons was investigated in a constant-pressure bomb within the pressure range of 1–6 MPa [407, 408]. The linear burning rates increased for the HAN solution mixed with activated carbons compared to those of HAN solution by itself. The thermal decomposition of 95 mass-% HAN/water solutions spiked with activated carbons was measured using DTA-TGA. The addition of activated carbon decreased the onset of decomposition temperature from 458 to 359 K (185 to 86 °C). The volatile products formed in the course of thermal decomposition of HAN spiked with activated carbons were characterized by electron ionization mass spectrometry analysis. Primary products of HAN decomposition were at $m/z = 33$ (NH_2OH) and $m/z = 63$ (HNO_3), which decomposed to form secondary products such as N_2O , NO , HNO_2 , NO_2 , and O_2 . The concentration of NO_x emissions during thermal decomposition of 95 mass-% HAN/water solutions was reduced by ~30% in the presence of activated carbons.

The burning rate of HAN doped with activated carbon increased to 400 mm/s at a combustion bomb pressure of 6 MPa [409].

The increase in burning rate as the result of using different carbons with different BET surface areas and porosities was most pronounced at 6 MPa and was barely noticeable at 1 MPa [410]. The burning rate as a function of the amount of carbon added increased almost linearly with the carbon concentration (at 4 MPa bomb pressure), from 100 to 210 mm/s at 5 vol-% carbon.

In *Encyclopedia of Monopropellants*, the chapter “Hydroxylammonium Nitrate-Based Monopropellants” contains a much more detailed summary of strand burning rate experiments of HAN solutions with various fuels and burning-rate catalysts added.

3.7 Thermal Stability of Hydroxylammonium Nitrate Solutions

Because HAN is rarely stored in the solid state, the summary provided here deals only with the thermal and storage stability of HAN solutions. This is the section on thermal stability as opposed to storage stability. The two properties are closely related to each other, and it is difficult to divide this subject. The section on storage stability follows later. Until 1992, HAN solutions were available only as 24% solutions, and a shipping classification for this material was in place for a long time. The shipping permit for more concentrated 81% solutions was obtained only in 1993.

Prediction of thermal stability requires the knowledge of both the thermodynamics and the kinetics for the given system.

During the investigation following an accident with HAN solutions at Hanford, Washington [411], the thermal stability of 24 mass-% HAN was tested in the Reactive System Screening Tool (RSST) [263, 412]. The RSST is a calorimeter equipped with temperature and pressure probes as well as a heater that can heat a liquid sample at a preprogrammed rate; it is used for rapid measurement of reaction thermal behavior at temperatures up to 673 K (400 °C) and pressures up to 3.44 MPa (500 psig). A 10-mL sample cell typically made of glass or quartz is placed inside a pressure vessel (400 mL) that can withstand pressures up to 3.44 MPa (500 psig). The RSST can be used not only for screening the reactive chemicals but also for designing emergency-relief devices. A fixed heating rate of 1 °C/min was used for temperatures up to 673 K (400 °C). The shutdown pressure limit was 3.1 MPa (450 psig). Initial nitrogen-pad pressures of 1.72 MPa (250 psig) were used to reduce material loss (water evaporation) from the sample cell. Once the temperature in the sample reached 453 K (180 °C), the pressure and sample temperature increased dramatically. Quite often, the glass sample cells were broken into pieces due to the violence of the reaction.

Thermal stability tests were conducted with a nitric acid/HAN/potassium fluoride solution typically used for plutonium dissolution in nuclear reactor fuel element reprocessing [413]. Tests were carried out in the RSST. In most cases, the calorimeter was pressurized with nitrogen to reduce evaporation of the liquid sample during heating. For the HNO₃/HAN/KF solution, an autocatalytic exothermic reaction occurred between 386 and 404 K (113 and 131 °C) with 2.06 or 0.34 MPa (300 or 50 psig) nitrogen inside the RSST vapor space. At ambient pressure, the solution boiled at about 383 K (110 °C). After extensive boiling, the concentrations of HNO₃ and HAN increased, and the autocatalytic reaction occurred suddenly. Tests were also conducted with 1000 ppm Fe as a contaminant present in the solution. The Fe

addition reduced the range of the autocatalytic reaction initiation temperature to 378–393.5 K (105–120.5 °C). With iron at ambient pressure, the autocatalytic reaction occurred at 381–382 K (108–109 °C). Under actual Purex operating conditions, the dissolving temperature is more like 323–333 K (50–60 °C). Increasing the nitric acid concentration to 3M decreased the reaction initiation temperature to 375–376 K (102–103 °C). Increasing the HAN concentration increased the exothermic temperature rise ΔT of the reaction from 10–30 °C to greater than 40 °C. Increasing both reactants to 3M nitric acid and 0.9M-HAN yielded a reaction initiation temperature of 364 K (91 °C) (with or without iron), the lowest observed in this study.

Another method used to study decomposition of HAN solutions involved an automatic pressure-tracking adiabatic calorimeter (APTAC), [414] which is similar to an accelerating rate calorimeter (ARC). This instrument provided more accurate data than the RSST or ARC. Adiabatic calorimetry is an extremely useful tool to assess thermal hazards of reactive chemicals. It can minimize heat losses by keeping the temperature of the sample surroundings close to the temperature of the sample. The APTAC can be operated in a variety of test modes, such as heat-wait-search heat ramp, and isothermal aging, with temperatures up to 500 °C and pressures ranging from vacuum to 13.76 MPa (2000 psia), and it can track exotherms at heat-rise rates from 0.04 to 400°/min.

The APTAC can use a pressure-compensating technique in which the pressure outside the sample cell is controlled to match the pressure inside the sample cell. This allows use of a thin-wall sample cell that, when combined with the usual charge volume, can produce low thermal inertia data. For the 24% HAN examination, the measurements were conducted in glass sample cells of nominal 100-mL volume, which provided a metal-free environment for the reactions, and also in titanium and stainless steel sample cells of nominal 130 and 50-mL volumes, respectively, to test the effect of metals on the thermal decomposition of HAN.

Teflon-coated thermocouples were used to prevent the contact of HAN solution with the metal thermocouple sheath. The APTAC cannot measure heat of reaction directly, but the system consisting of sample and sample cell was kept nearly adiabatic during runaway reactions. Part of the heat of reaction was absorbed by the sample cell, and the remainder was used to increase the temperature of the sample and vaporize volatile materials.

Two operating modes were used with the APTAC: a heat-wait-search (HWS) mode and a heat-soak-search (HSS) mode. In the HWS mode, the sample was heated at 2°C/min to a selected starting temperature, and the temperature was allowed to stabilize for 25 min, following which the APTAC searched for exothermic behavior. During the search period, the temperature of the containment vessel gas was adjusted to match that of the sample. If the self-heating rate of the sample was greater than a preset threshold (0.05 °C/min), the apparatus tracked the reaction adiabatically until the reaction ended or one of the shutdown criteria was met. If no exotherm was detected, the apparatus heated the sample to the next step-up search temperature,

and the steps repeated until one of the shutdown criteria was met. The onset temperature was defined as the temperature at which an exotherm is detected, and it is usually the lowest temperature at which the sample self-heating rate surpasses the preset threshold (0.05 °C/min) in the search or adiabatic mode.

The APTAC HSS mode was also used. The sample was heated to a specified soaking temperature and held adiabatically. Every 60 min, or when the sample temperature rose 1 °C above the soaking temperature, the self-heating rate would be polled and compared with a pre-defined sensitivity threshold. If the self-heating rate exceeded the threshold, a runaway reaction was detected, and the sample was kept adiabatically. If the self-heating rate was less than the threshold, the sample would be cooled back to the soaking temperature. The steps were then continued for a defined period. If the system failed to detect self-heating at the end of the soaking period, it would proceed with a standard HWS mode. The HSS method is generally used to test the effectiveness of inhibitors added to the reactants.

The HWS mode was employed to determine the overall decomposition behavior of 24 mass-% HAN solutions, such as onset temperature (T_0), maximum temperature ($T_{\max}$), and maximum pressure ($P_{\max}$). The onset temperature in glass was 444 K (171 °C), in titanium it was 423 K (150 °C), and in stainless steel it was lowered substantially to 412 K (139 °C). The heat release was 23–43 kcal/mol and varied with the sample-container material used for the test.

The temperature curve of 24 mass-% HAN decomposition in the APTAC appears to consist of two stages: a slow initiation stage followed by a fast explosion stage. These two stages form a sharp discontinuity at the transition point. In contrast, for the decomposition of hydroxylamine free base, the temperature increase started immediately at the onset temperature and smoothly curved up to the maximum temperature. From comparison of the decomposition temperature curves, it was concluded that HAN decomposition is an autocatalytic reaction [415].

However, the autocatalytic decomposition behavior of HAN under runaway conditions has not been fully described by mathematical kinetic models because of its highly exothermic and rapid decomposition behavior. Additional work [414] focused on extracting HAN autocatalytic kinetics and analyzing HAN critical behavior from adiabatic calorimetry measurements. The heat of reaction of HAN measured by the APTAC was about 118 ± 20 kJ/mol, and the apparent activation energy was 82 ± 0.4 kJ/mol. The apparent activation energy of HAN decomposition depends on the aqueous solution concentration. Other authors [338] reported that the activation energies for 0.92 to 1.52-M HAN and for 1.58 to 1.74-M HAN solutions are 129 and 66 kJ/mol, respectively. A lumped autocatalytic kinetic model for HAN and associated model parameters were developed to describe rapid decomposition events. Critical conditions of diluted HAN solutions without the presence of catalytically active metal contaminants were bracketed. It would be interesting to repeat these tests for 81% HAN solutions, which are of primary interest for rocket propellants.

HAN solution isothermal decomposition measurements were performed in the temperature range of 353–433 K (80–160 °C) using an isothermal calorimeter equipped with a pressure-resistant glass reactor and an APTAC employing glass and titanium cells [98]. Reaction products were identified via UV, HPLC, and ion chromatography. An unidentified intermediate product was observed that is likely to be responsible for the observed autocatalytic behavior. This product was suspected to be an ammonia-related compound, such as NH_2^- or NH_2^- . Dilute aqueous solutions of HAN (<18% NH_3OHNO_3) were kept at constant temperature for different lengths of time in closed glass cells in an APTAC at 403, 413, and 423 K (130, 140, and 150 °C) and in a closed titanium cell at 433 K (160 °C). No evidence of HAN decomposition was observed at any temperature in the glass cells for the duration of the experiment, a period of approximately 1400 min. However, after approximately 800 min at 433 K (160 °C), the substrate in the titanium cell reacted in a very violent autocatalytic form to raise the pressure and the temperature of the system abruptly.

The addition of AN or HN to HAN improves its thermal stability. Such solutions are used as oxidizers (OXSOL-1, OXSOL-2, and S-HAN5). See also [287].

3.7.1 Storage Stability of Hydroxylammonium Nitrate Solutions

Storage stability deals with the thermal stability at room temperature. The chemical changes occur at a much slower rate than in an accelerated thermal stability test in DTA or DSC and are more difficult to measure. Fresh 24 mass-% HAN solutions without metal contamination can be safely stored and used at room temperature. However, under adverse conditions, HAN solutions can decompose at room temperature when the heat is not conducted away, and the reaction rate escalates to a runaway condition.

Following various incidents, extensive research included aging tests and adiabatic calorimetry of HAN solutions. Inverse-based fitting methods were combined to elucidate the aging and storage stability of HAN. Aqueous solutions of 18 mass-% HAN were subjected to aging tests and adiabatic decomposition tests at temperatures in the range of 303 to 433 K (30 to 160 °C), which covers the normal storage operation temperature and the onset temperatures under typical experimental conditions [416]. Furthermore, the influence of pressure, impurities, and temperature history profile were also examined. The liquid residue was analyzed at different stages of aging tests using HPLC. The experimental data were used to elucidate and deduce the mass-loss kinetics parameters. These data could be used to monitor the storage behavior of HAN.

The transportation hazard classification of 13-M HAN was based on the results of an instrumented dual-sample storage test with 50-g samples of 13-M HAN heated to 348 K (75 °C) for 48 h [417]. The test was later repeated with 100-g samples of 13-M HAN heated in an oven to 348 K (75 °C) for 48 h, which did not result in any noticeable changes of the material [418].

3.7.1.1 Effects of Contaminants on Storage Stability of Hydroxylammonium Nitrate Solutions

Many trace contaminants have a pronounced effect on the storability and thermal stability of HAN solutions (and HA free base). The most common contaminant is iron in the form of iron ions, which can be leached from processing equipment. In the case of reaction of HA and its salts with iron ions, Fe^{3+} was found to trigger an exothermic reaction [100]. Complexed iron in the form of $[\text{Fe}(\text{CN})_6]^{3-}$ was less reactive than free $\text{Fe}(\text{III})$ and $\text{Fe}(\text{EDTA})$.

The thermal decomposition behavior of HAN is influenced by starting materials and by-product metal salts or excess nitric acid that could get carried over into the final product during synthesis and purification [419, 420]. Comparing the thermal stability of HAN solution samples prepared by three different routes, it was observed that carryover of metal ions such as barium and calcium ions from the reactants and the by-products into HAN solution during preparation could influence the thermal and catalytic decomposition behavior of HAN as measured by DSC, TGA, and spot-plate tests. The decomposition mechanism of HAN was altered in the presence of barium and calcium ion impurities. Traces of nitric acid can lead to autodecomposition behavior of HAN during storage.

3.7.1.2 Stabilizers for Hydroxylammonium Nitrate Solutions

Stabilizers are typically complexing, chelating, and sequestering agents that inactivate transition metal ions that act as catalysts for HAN decomposition. Stabilizers for HAN solutions can be inorganic or organic compounds. For later use of the HAN as an oxidizer in monopropellants, organic additives would be preferred because they combust without leaving any residues. Some inorganic stabilizers (e.g., phosphates) leave undesirable residues that foul the catalysts. The use of stabilizers is of interest not only for the storage and transport of HAN solutions but also for the storage and transport of liquid propellants formulated with this oxidizer. Stabilizers for HAN-based monopropellants must work equally well regardless of the fuel contained in the mixture. In *Encyclopedia of Monopropellants*, chapter “Hydroxylammonium Nitrate-Based Monopropellants,” we summarize stabilizers tested with HAN-based monopropellants. More stabilizer studies have been done for HAN/TEAN/ H_2O mixtures than for any other propellant.

Several stabilizers patented for hydroxylamine free base would work just as well for HAN, including the trisodium salt of *N*-hydroxyethyl-ethylenediaminetriacetic acid, the tetrasodium salt of ethylenediaminetetraacetic acid, polyvinylpyrrolidone, and poly-*N*-vinyl-5-ethyl-oxalidinone [3].

Stabilizers tested at BRL include cupferron, ethylenediaminetetraacetic acid (EDTA), 1,2-diaminocyclohexanetetraacetic acid monohydrate (DCTA), 2,2'-dipyridyl, and tributylphosphate [421]. BRL researchers also tried removing contaminating transition-metal ions by adsorbing them onto ion exchange resins.

Stabilizers for HAN include pyridinium or pyridone salts, diphosphonates or methylenephosphonate salts, or their parent acids [422]. One of the stabilizers tested was the sodium salt of 2-hydroxypyridine-*N*-oxide. The effect of deliberate iron contamination (50 ppm Fe) and stabilizer addition (0.1%) on excess acid formation during storage of XM46 at 338 K (65 °C) is shown in Figure 49 (NaHPNO = sodium salt of 2-hydroxypyridine-*N*-oxide; NaMPNO = sodium salt of 2-mercaptopyridine-*N*-oxide). In addition to reduction of excess acid formation during storage, the onset of exotherms in DSC or ARC tests was also shifted to higher temperatures as the result of stabilizer addition. Other stabilizers proposed in this patent include diphosphonate or methylenephosphonate salts of the type aminotri(methylenephosphonic acid) and its corresponding pentasodium salt, which are commercially available from Monsanto under the trade names Dequest 2000 and Dequest 2006, respectively. Also patented was diethylenetriaminepenta(methylenephosphonic acid) and its corresponding hexasodium salt, commercially available from Monsanto under the trade names Dequest 2060 and Dequest 2066, respectively.

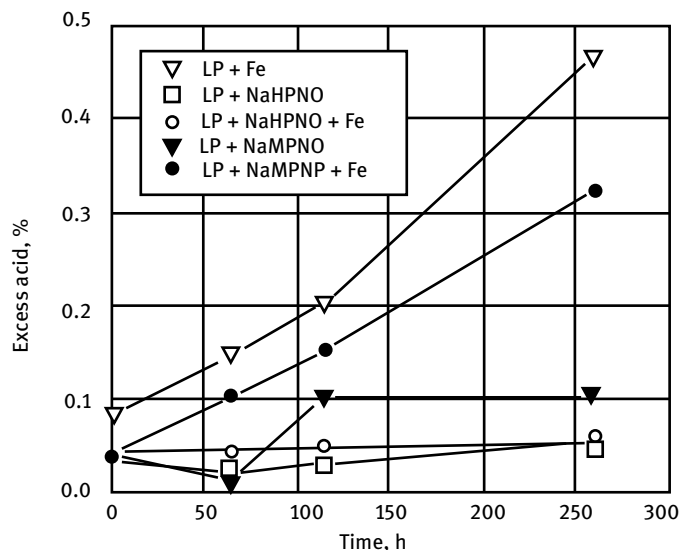


Figure 49: Effect of 50-ppm iron contamination and 0.1% stabilizers on excess acid formation of XM46 during storage at 338 K (65 °C). (Reproduced and modified from [422].)

The sodium salt of 2-hydroxypyridine-*N*-oxide in concentrations from about 10 ppm to about 1000 ppm in either pure HAN solutions or formulated propellants containing HAN and fuels has been patented as stabilizer [123]. Instead of sodium, it may be better to use the ammonium salts, lower alkylamine salts, or alkanolamine salts. Other stabilizers in this category are 2-hydroxy-4-methoxy-pyridine-*N*-oxide, 1,2-dimethyl-3-hydroxy-pyridine-4-one, 4-methyl-pyridine-*N*-oxide, 6-methyl-pyri-

dine-*N*-oxide, and 1-methyl-3-hydroxy-pyridine-2-one. After the effectiveness of this stabilizer was demonstrated for HAN by itself, it was also tested with XM46 [423].

The complexing agents cupferron, EDTA, DCTA, 2,2'-dipyridyl, and tributylphosphate were evaluated as stabilizers for HAN-based propellants [424, 425]. Other patents cover the use of hydroxylurea or hydroxythiourea derivatives as stabilizers for HAN solutions [426]. Suggested stabilizers for PERHAN were EDTA and cyclohexanediaminetetraacetic acid and their sodium salts [230]. Recommended stabilizers for HAN include diamine derivatives, ammonia derivatives, pyridine, and methylene phosphonic acid derivatives [427].

Insufficient storage stability for long service life in orbit is one of the problems with HAN monopropellants, and it is caused mostly by metal ions such as Fe^{3+} . Material compatibility tests showed that some metal ions get leached from the surface of propellant tanks and tubing. The decomposition of HAN is due to redox reactions between HAN and transition metal ions. Three chelating agents, hydroxyethylidene diphosphonic acid, diethylene triamine pentaacetic acid, and *N*-(2-hydroxyethyl)iminodiacetic acid, were selected and added to samples of 93% HAN solutions deliberately doped with Fe^{3+} ions in order to sequester the contaminant ions [428]. Three different molar ratios of chelating agent to Fe^{3+} were tested. When the solutions were examined using DTA-TGA before and after the addition of chelating agents to 93% HAN, the onset of thermal decomposition was shifted from 416 K (143 °C) to 438–444 K (165–171 °C). The burning rates of solutions before and after the addition of chelating agents were not much different, but addition of Fe^{3+} to HAN increased the burning rate. The chelating efficiency of different chelating agents strongly depended on the initial concentration of HAN solutions and was more effective in dilute solutions. Diethylene triamine pentaacetic acid had the best chelating capacity of the three agents tested.

3.8 Materials Compatibility with Hydroxylammonium Nitrate Solutions

There are two concerns about the compatibility of materials of construction with liquid-propellant ingredients. The first is the effect of the corrosive medium on the material, causing possible loss of structural integrity. The second is the effect of contaminants leached from the material of construction on the storage stability of the propellant. Much of the materials compatibility work was done during the RLPG effort for XM46 itself, but early tests often used only 60% HAN solutions as a substitute [429]. The argument was that the presence of fuels (regardless of which fuel is being used) does not significantly alter the corrosive behavior of the HAN/ H_2O system. The results of the materials compatibility tests with live XM46 or AF-M315E instead of HAN solution surrogates are discussed in *Encyclopedia of Monopropellants*, chapter “Hydroxylammonium Nitrate-Based Monopropellants.”

3.8.1 Compatibility of HAN Solutions with Metals

HAN solutions attack metals in two ways: first through the acidity of hydrolyzing salts of a weak base with a strong acid, and second by complexing the metal ions, thus continuously removing them from the galvanic equilibrium potential at the metal surface. Galvanic corrosion of dissimilar metals in contact with each other is the worst case; it might even qualify certain metal galvanic couples as a composition for a battery for generating electricity.

Fifty-one materials specimens (metals, polymers, and coated metals) were exposed to 61.7% HAN solution for 30 d at 298 K (25°C), and after three of them were eliminated, 48 specimens were exposed to 61.7% HAN solution for 30 d at 338 K (65°C) [430]. The samples were sealed under an argon atmosphere in a 50-mL glass ampoule connected to a mercury U-tube pressure gauge. A rubber septum allowed the withdrawal of gas samples for gas analysis and also allowed manual pressure-relief if the end of the mercury gauge pressure-measuring range was approached. The apparatus was immersed in a constant temperature bath such that only the rubber septums stayed above the oil level. The pressure was read daily. The test was continued for 30 d, or it was discontinued earlier if the rate of gas evolution exceeded 30 mm Hg/d. The pressure reading was converted to gas volume under standard (298 K, 1 atm) conditions. Typical coupon size was $5 \times 5 \times 1$ mm. The test coupons were weighed before and after the test, and weight changes were recorded as an indication of incompatibility. The iron, nickel, and copper samples had dissolved. At room temperature, only the samples listed in the upper part of Table 29 showed a measurable rate of gas evolution. Copper and iron were eliminated from high-temperature testing because their rate of gas evolution was unacceptable, even at room temperature. Table 29 lists the materials in the order of increasing gas-evolution rate (decreasing compatibility). Nitrogen and nitrous oxide were the only gases found by gas chromatography.

The compatibility of various materials of construction, including metals, alloys, plastics, and lubricants, with 60% HAN was determined by immersion tests at 298 K (25°C) and 338 K (65°C) under inert gas (argon) at Rocket Research Company, Redmond, WA (RRC) [429]. One hundred tests were performed on 48 government-furnished materials and two controls (HAN without any additive). Pressure rise during the 30-d tests was monitored daily as an indication of compatibility (or incompatibility). Post-test samples were examined for signs of corrosion, and some of the off-loaded propellant was analyzed for leached metals. At the end of the tests, the gas space above the samples was analyzed for chemical composition of the gases formed by drawing a gas sample with a hypodermic syringe needle inserted through a rubber-septum-sealed port at the top of the apparatus. This gas composition information can be useful for interpreting the mechanism of HAN decomposition due to incompatibility. The tests were conducted under argon instead of air so that all evolved gases (including oxygen, nitrogen, and hydrogen) could be analyzed by gas chromatography. Another reason for excluding air from the tests was that oxygen might have interacted with HAN and any corrosion processes in progress. An attempt to conduct the tests under

Table 29: Materials compatibility test results.

Material	Days in test	Volume of gas produced, cm ³			Gas evolution rate
	d	N ₂	N ₂ O	Total	cm ³ (STP)/d
Test temperature 298 K (25 °C)					
Nickel	30	0.39	0.46	0.85	0.028
Al-7075	30	0.54	0.54	1.08	0.036
AlSI 303	30	2.47	0.80	3.27	0.109
Kennametal K801	30	0.21	0.38	0.59	0.197
Metco 505 Mo	30	7.25	17.62	24.87	0.829
Iron	9	4.09	11.53	15.62	1.736
Metco 309N5-3	2			4.13	2.065
Copper	9	4.98	14.52	19.5	2.167
Test temperature 338 K (65 °C)					
Haynes 718	30	0.78	0.20	0.98	0.033
17-4PH	30	0.84	0.25	1.09	0.036
Nitronic 50	30	0.95	0.22	1.17	0.039
Nickel	30	1.01	0.36	1.37	0.046
AlSI 303	30	2.59	1.37	3.96	0.132
AlSI 316	12	2.91	2.83	5.74	0.478
Kennametal K801	15	3.75	9.80	13.56	0.904
Al-7075	6	2.20	5.50	7.70	1.283
Metco 505 Mo	1	6.07	14.73	20.80	20.80

Data source: [430]

helium instead of argon failed because the permeation rate of helium through the rubber septums was too high. The samples were totally immersed in 60% HAN in borosilicate glass ampoules connected to an open-ended mercury-filled U-gauge manometer open to the atmosphere and immersed in a constant temperature bath. The most significant weight loss was with Al-6061, which lost 1.57% at 298 K and 2.1% at 338 K. Silver solder had a weight loss of 9.6% at 298 K. The fastest rate of gas evolution was with Al-6061 (0.3 cm³/d at 298 K and 19.8 cm³/d at 338 K), silver solder, and Aeroshell 17 grease. The gas evolved from the Al-6061 sample contained up to 14% hydrogen. Hydrogen evolution during metals compatibility tests with HAN solutions had not been previously reported in the literature. The other surprise was the high carbon dioxide concentration when testing lubricants with HAN solutions. The highest carbon dioxide concentration, 75.6%, was observed with Aeroshell 14. The second highest carbon dioxide concentration, 57.6%, was found in a sample with 10W-30 motor oil. HAN appears to be a strong oxidizer comparable to concentrated nitric acid and can effectively destroy hydrocarbon bonds in oils and greases. It may be difficult to find a lubricant that is not affected, and additional work in this area may be required. In two of the oil samples, the mercury in the U-gauge turned black, and the presence of hydrogen sulfide in the gas space above the samples was proved by reaction with moist lead

acetate paper. Most of the samples tested (metallic and non-metallic) showed some reaction, and only a few materials emerged as compatible from this preliminary test. True compatibility would have to be proven by conducting tests extending beyond 30 d. The RRC report in the appendix contained the most complete database on HAN materials compatibility assembled to that date. This database was so complete that it was accepted in its entirety into the *JPL Liquid Propellant XM46 Handbook* [431].

It appears that the metal materials compatibility of HAN does not change significantly by adding TEAN or other fuels to the oxidizer solution. The relative ranking of metals tested in 13-M HAN or XM46 remained the same.

13-M HAN was used as a substitute for actual propellant mixtures in a series of materials compatibility tests at the NASA Glenn Research Center [432]. It was felt that because the majority of HAN-based propellants are 13-M HAN, and because the fuels (TEAN, glycine, or methanol) do not alter the results, this was a valid test method. In addition to 13-M, some testing was conducted with propellant blends called XM46, HAN204GLY, and HAN269MEO.

3.8.2 Compatibility of HAN Solutions with Elastomers

Several dozen polymer materials specimens were exposed to 61.7% HAN solution for 30 d at 298 K (25 °C) and 338 K (65 °C) [430]. Nylasint MA, Teflon 05-002, Rynite SST35, and Fluorocarbon 33 showed abnormally high rates of gas evolution and had to be eliminated from further testing.

3.8.3 Compatibility of HAN Solutions with Lubricants

The RLPG had many moving parts that needed to be lubricated to ensure operation without galling and metal particle abrasion. Under the fast and highly turbulent flow conditions, it was likely that some of the lubricants would be entrained into the flowing XM46 propellant. For rocket propulsion applications, there are only a few places that need lubrication that might come into contact with propellants. O-rings are often greased prior to installation to prevent damage during compression in the joint.

3.9 Safe Handling of Hydroxylammonium Nitrate Solutions

The recommended methods for the safe handling of HAN not only are of interest for the oxidizer solution itself for its production, storage, and shipping, but they apply equally to all propellants formulated with HAN.

3.9.1 Protective Clothing

The protective clothing to be worn when handling HAN solutions and HAN-based propellants is the same that would be worn when handling non-volatile acids such as sulfuric acids in lead-acid automotive batteries. Recommended protective clothing includes gloves, apron, face shield, and rubber boots.

After several candidate materials were evaluated in a permeability test apparatus, a polyurethane-coated polyester fabric was chosen to be the main material of the protective suit and hooded mask for HAN-based propellants [433]. Butyl rubber with a thickness of 0.40 mm was chosen as the material for protective gloves.

3.9.2 Fire Fighting

In separate tests, a 5-gallon and a 30-gallon polyethylene drum containing 13-M HAN were subjected to a bonfire test in accordance with U.S. Department of Transportation regulations as part of a test protocol to obtain a shipping permit. The test did not result in any explosions, and nothing was propelled from the burn pile.

3.9.3 Accident Investigations Involving Hydroxylammonium Nitrate

Since the 1970s, HAN has been involved in several incidents at several government facilities. On 14 May 1997, an incident occurred in the chemical preparation room of the Plutonium Reclamation Facility at the U.S. Department of Energy's Hanford Site Plutonium Finishing Plant near Richland, Washington [434]. HAN/HNO₃ solution had been stored in a steel tank (A-109) in the otherwise inactive facility for several years prior to the accident. The reaction created a rapid release of gases that built up pressure inside the tank. The pressure blew the lid off the tank, cut a fire-suppression water line, and damaged the roof and adjacent walls and doors. Water and spilled unreacted solution flooded the area and leaked into adjacent rooms. Residual plutonium leaked from the building as wastewater. The radioactive contamination outside the building was the result of acidic water flowing across contaminated walls and floors and extracting the radioactive salts. During the investigation, it was determined that the root causes of the incident were inadequate hazard evaluation, inadequate auditing of safety management systems, and inadequate training of personnel on reactive hazards [411]. A better understanding of materials compatibility of HAN solutions with tank materials would have prevented the accident.

A systematic approach was proposed to evaluate reactive chemical hazards. The first step of hazard evaluation is to use simple screening tools. For reactivity screening, the Molecular Orbital Package (MOPAC) and the ASTM Chemical Engineering Thermodynamics and Hazard Evaluation (CHETAH) have proven to be reliable and practical tools based on the analysis of 167 incidents reported by the Chemical Safety and Hazard Investigation Board. Until the Hanford incident, it was common practice to add concentrated nitric acid to dilute HAN solutions and store the solutions for some time for later use in nuclear fuel element reprocessing. Thermal stability and mixing tests in a calorimeter with 0.1, 0.25, and 0.5-M HNO₃ and 0, 0.05, 0.1, 0.2, 0.4, 0.7-M, and 1M-HAN showed that the heat release (41.7 cal/g HNO₃ at the highest concentrations tested) in these dilute solutions was solely due to heat of mixing and not to decomposition of HAN [435].

An autocatalytic reaction of HAN in HNO_3 solutions was studied by DTA methods to evaluate safety limits for the handling of HAN/ HNO_3 solutions as a plutonium reductant during the reprocessing of nuclear reactor fuel elements [436]. The initiation temperatures, onset of the autocatalytic reactions, were remarkably lowered with increasing HNO_3 and Fe^{3+} concentrations. By aging the solution, the threshold temperatures were further lowered because of an accumulation of HNO_3 produced from slow decomposition of HAN during storage.

3.10 Safety Properties of Hydroxylammonium Nitrate

The safety properties of 13-M HAN solutions were thoroughly investigated as part of obtaining a hazard classification and a shipping permit in the United States for this material [437]. The less concentrated solutions (24% HAN) had been shipped for several decades without any incidents before the more concentrated (13-M = 81% HAN) solutions became commercially available and required a new shipping permit.

3.10.1 Shock Sensitivity of Hydroxylammonium Nitrate Solutions

The shock sensitivity (cap sensitivity) of 13-M HAN was measured as part of its transportation hazard classification. The shock sensitivity of HAN solutions and other energetic materials depends on the energy density of the stimulus. The stimulus can be either a blasting cap (electric detonator) or it can come from a booster charge such as those employed in card-gap tests.

In addition to binary HAN solutions, two ternary solutions containing HAN, water, and AN or HN were also tested for impact sensitivity, cap sensitivity, card-gap sensitivity, and bullet-impact sensitivity, but no explosions were observed [438]. For both oxidizers, the drop-weight sensitivity was negative at 100 kg-cm, the cap sensitivity was negative with a J2 blasting cap, and the card-gap sensitivity was negative at zero cards. The bullet-impact sensitivity of OXSOL-1 was negative, but OXSOL-2 was susceptible to bullet impact in a steel tube of 2-in diameter.

3.10.2 Adiabatic Compression Sensitivity of Hydroxylammonium Nitrate Solutions

Unconfirmed reports indicate that 13-M HAN solutions gave a reaction when tested in the U-tube adiabatic compression test apparatus at 401 K (128 °C), while tests at 328, 348, and 373 K (55, 75, and 100 °C) were negative [439].

3.10.3 Cook-off Hazards of Hydroxylammonium Nitrate Solutions

The onset of exothermic reactions in HAN solutions was discussed extensively in Section 3.4.2. The direct consequence of this thermal instability is the cook-off hazard when storing and transporting HAN solutions. There have been several cook-off incidents,

although not all of these have been published. Section 3.9.3 is a summary of accident investigations of cook-off and spills with HAN solutions. A bonfire test with 13-M HAN was conducted as part of the hazardous material shipping classification [440, 441].

3.11 Toxicity of Hydroxylammonium Nitrate

Because one of the main motivations for developing HAN-based rocket propellants was the replacement of more toxic oxidizers and fuels with a “green,” environmentally friendly, non-toxic chemical, the toxicity of HAN and the fuels it was potentially combined with received a good amount of attention. People who were advocating the switch from hydrazine to green propellants wanted to make sure that there were no hidden hazards with HAN. Previous toxicity work was motivated by the proposed use of HAN-based propellants in torpedoes and liquid-propellant guns.

Because the main concern about current-technology hypergolic bipropellants (NTO/MMH) and monopropellants (N_2H_4 monopropellant) was the inhalation toxicity, it was welcome news when propellant chemists examined HAN solutions and noticed that this oxidizer has no measurable vapor pressure at all, and that whatever little vapor pressure is measurable is only that of innocuous water.

Hydroxylammonium nitrate is moderately toxic and mildly acidic. Toxicity studies include the potential oral ingestion, aerosol respiratory inhalation, and dermal resorption of propellant splashed on the skin. There are no reports (yet) of actual poisonings or propellant-handling accidents involving humans. All of the HAN toxicity information we have was obtained from animal tests. HAN can cause severe damage to skin, eyes, and red blood cells (RBCs) of the hematologic system. Significant signs of HAN poisoning include hemolytic anemia, methemoglobinemia, splenomegaly, erythrocyte destruction, and Heinz body formation [442]. Another HAN effect is brain ischemia, which is insufficient blood flow to the brain. Brain tissue samples of cerebral cortex, hippocampus, and cerebellum taken from Wistar rats injected with HAN solutions showed brain cell ischemia, unbalanced heme oxygenase, and induction of anoxia [443].

3.11.1 Acute Toxicity of HAN

The standard method of determining LD_{50} is by administering HAN in drinking water or in more concentrated doses by intraperitoneal injection (Table 30).

HAN was administered to male ICR mice at a dose of 120 mg/kg (below the LD_{50}) by intraperitoneal injection. The mice were killed on day 7 after intoxication, and the main organs were removed for pathologic examination [447]. Lung and liver tissues were severely injured. There was widespread pulmonary hemorrhage and severe lung tissue degeneration. Diffuse edema or ballooning degeneration occurred in the liver cells.

Table 30: Summary of LD₅₀ determinations of hydroxylammonium nitrate.

Test animal	Concentration	Mode of administration	LD ₅₀ , mg/kg body weight	References
Rat	13-M	Oral	325	[245]
Male ICR mice		Intraperitoneal	149.6	[444]
Male mice		Celiac artery	183–186	[445]
Wistar rats		Intraperitoneal	139.3	[446]

Both the acute and chronic (sub-chronic) toxicity and the response of main target organs to exposure to HAN were measured in a series of thorough animal-exposure tests [446]. In the acute-toxicity study, rats were administered different doses of HAN only once by intraperitoneal injection, and toxic signs and morbidity within 14 days were observed. In the sub-chronic study, rats were administered different daily doses of HAN (7, 14, or 28 mg/kg) or 0.9% saline for 13 weeks. After the last exposure, three-quarters of the rats were sacrificed. After the recovery and observation period, the remaining animals were sacrificed, and the main toxic target organs of sub-chronic exposure to HAN were evaluated. In the acute-toxicity study, the LD₅₀ of HAN in rats was 139.3 mg/kg, with a 95% confidence interval of 132.3–146.7 mg/kg. In the sub-chronic study, the body weight did not significantly change, but the spleen weights in all HAN-treated groups were significantly higher than those in the control group. Histopathologic observation showed that significant lesions mainly occurred in lung, liver, spleen, and kidney. HAN also caused a large amount of deposit of hemosiderin, especially in the liver, spleen, and kidney.

3.11.2 Inhalation Toxicity

HAN does not have a vapor pressure, thus there is no direct inhalation toxicity hazard. It would be very unlikely that personnel would be exposed to HAN aerosols. The main hazard would be the nitrous oxide and nitric acid fumes emanating from a HAN cook-off situation.

In order to evaluate the inhalation toxicity of XM46 and similar propellants, the inhalation toxicity of HAN solutions by themselves were also evaluated [448]. Rats and dogs were exposed to aerosolized HAN for 90 d at concentrations of 300, 100, or 33 mg/m³. Dose-related effects occurred in both species and documented themselves in rats by weight loss and spleen and liver enlargement. In dogs, respiratory irritation and blood dyscrasia were the major toxic effects observed. Minimal effects were observed at the low concentration, 33 mg/m³.

Personnel should be protected against all routes of HAN exposure since the systemic effects are additive. An airborne concentration of HAN of 3 mg/m³ was suggested as a basis for the development of a maximum allowable workplace atmosphere concentration.

Because HAN solutions do not have a measurable vapor pressure, the worst-case scenario was simulated by creating a HAN aerosol with a sprayer. For a sub-chronic toxicity study, groups of ten rats were exposed to 13.2-M HAN aerosols at three different concentrations (100, 300, or 600 mg/m³) for 6 h/day for 5 and 10 d [449]. At necropsy following the fifth day of exposure, both male and female rats exposed at 300 and 600 mg/m³ had enlarged spleens. Heinz body formation in erythrocytes was seen in both groups at the two highest doses tested. After 10 d, spleen weight to body weight ratios were increased, and liver ratios were decreased. RBC count, hematocrit, and hemoglobin levels were depressed after ten HAN exposures. The degree of severity of splenic hematopoiesis increased in the two high-treatment groups. Heinz body formation in RBCs is considered a valid index of systemic toxicity if workers at HAN factories or rocket test sites should become exposed to HAN aerosols.

When studying the inhalation toxicity of HAN solutions, one must make sure that the pH of the solution remains below 6. Above a pH of 8, there may be vapors of free hydroxylamine base in the vapor phase.

3.11.3 Blood Effects

HAN has adverse effects not only on RBCs already in circulation but also on the bone marrow where RBCs are generated and on reticulocytes that are about to become RBCs.

The effect of HAN exposure on micronucleus frequency of polychromatic erythrocytes from Wistar rats bone marrow was studied by administering different doses of HAN, 6.97, 13.93, or 27.86 mg/kg, to three treated groups by intraperitoneal injection, whereas a control group was treated only with 0.9% NaCl [450]. The treatment was performed every other day and continued for 90 d. After the last treatment on day 90, two-thirds of the rats were sacrificed, and after a 30-d observation period the remaining animals were sacrificed. The micronucleus frequency of bone marrow cells of Wistar rats treated by HAN was not significantly different from that of the control group, except for the highest dose group. After 30 d of recovery, the micronucleus frequency of HAN-treated animals was not significantly different from that of the control group.

The effect of HAN toxicity on the blood system in rats was studied by injecting Wistar rats with 75, 100, or 125 mg/kg, and blood samples were collected after 6 h, 1, 3, 7, 14, 28 d, 2, and 3 months [451]. Blood cell counts, erythrocyte fragility, Heinz body formation, and Howell-Jolly body formation were measured using a blood cell analyzer. The results showed that 6 h to 7 days after HAN injection, erythrocyte fragility, Heinz body formation, and Howell-Jolly body formation increased. RBC count, hematocrit (HCT), and hemoglobin (HGB) decreased, and mean corpuscular volume, mean corpuscular HGB, mean corpuscular HGB concentration, and RBC volume distribution width increased in a dose-dependent manner. The injection of HAN can obviously change the cell count and the structure and function of blood cells, especially for erythrocytes, and these changes are dose dependent.

Acute and sub-acute intraperitoneal administration of HAN solutions to Wistar rats resulted in decreased RBC counts and HGB levels and increased white blood cells (WBCs) at the end of the administration [452, 453]. A total of 160 rats were randomly divided into three HAN-treated groups and one control group. Each group included 40 rats. Different doses of HAN at 6.97, 13.93, or 27.86 mg/kg were administered to the three treated groups by intraperitoneal injection. The control group was injected with 0.9% saline. The treatment was continued every other day for 13 weeks. After the last treatment, 30 rats in each group were sacrificed, and the rest were kept another 4 weeks for observation. Hematologic parameters and reticulocyte and marrow cells were measured. For hematologic parameters, the main changes were decreases in RBC count and HGB level and an increase in WBCs at the end of the administration ($P < 0.05$). The reticulocyte values were obviously increased along with the increasing HAN dosage compared with those of the control group ($P < 0.01$). HAN has definite toxic effects on the blood system in rats for long term exposures.

The effects of HAN on superoxide dismutase (SOD), malondialdehyde (MDA), tumor necrosis factor- α (TNF- α), and interleukin-6 (IL-6) in rat serum were measured by administering different doses of HAN at 50, 75, or 100 mg/kg to three treated groups by intraperitoneal injection [454]. In parallel, a control group was treated only with 0.9% NaCl saline. After 24 h, a sample of blood was collected to measure the activity of SOD and the concentration of MDA, TNF- α , and IL-6. Reactive oxygen species (free radicals) degrade polyunsaturated lipids, forming MDA, which is a marker for oxidative stress. The activity of SOD fell with increasing dose size of HAN, and MDA concentration increased. Compared with the control group, each dose group was significantly different regarding the content of MDA. The groups dosed at 75 or 100 mg/kg were significantly different in SOD activity, and only the group exposed to a dose of 100 mg/kg exhibited a significant increase in TNF- α concentration ($P < 0.01$ and $P < 0.05$, respectively). The IL-6 concentration increased somewhat, but was not significantly different from that of the control group. The oxidative damage to serum enzymes might be one of the primary mechanisms of HAN toxicity. See also [455, 456].

The change of protein profiles in the serum of HAN-intoxicated mice was measured in order to obtain basic data to further explain the mechanism of HAN intoxication [457]. The animals in the HAN-intoxicated group were injected intraperitoneally with HAN ($LD_{20} = 158$ mg/kg), and the control group was injected with 0.9% saline. Serum samples from both groups were analyzed using surface-enhanced laser desorption/ionization time-of-flight mass spectrometry and protein chip technology. Adverse effects in mice in the HAN-intoxicated group included irritation of the respiratory tract and eyes, drooling, cyanosis, dyspnea, restlessness, and muscular shivering. Four different proteins were found in the serum of HAN-intoxicated mice group, which may be tell-tale signs of HAN intoxication.

3.11.4 Skin Effects

Application of HAN solutions to rabbit skin for 3 weeks induced a high incidence of chronic and ulcerative dermatitis in all treatment groups, including the group receiving the lowest dose tested, 0.7 mg/kg [458]. Higher doses (1.5–12 mg/kg) caused Heinz body formation and RBC destruction. It was recommended to avoid contact of HAN solutions with the skin and to wear gloves and splash-proof goggles when handling this material.

Hydroxylammonium sulfate is not used in rocket propellants, but because the toxic element in the salt is the hydroxylammonium ion and not the sulfate ion, information on its skin toxicity is included here. The acute toxicity of hydroxylammonium sulfate was tested in rabbits and rats following a single 24-h dermal exposure [459]. The test materials were applied topically and were occluded under a plastic or gauze cover or were injected subcutaneously. Hydroxylammonium sulfate produced hematotoxic effects similar to those of phenylhydrazine, consisting of methemoglobin formation, anemia, and reticulocytosis. It proved to be more toxic to rabbits than to rats, although both chemicals produced similar hematologic effects at equivalent dose-levels within the same species. Both were lethal to rabbits, but no deaths occurred among the rats. See also [460–462].

3.11.5 Mutagenic Effects

Many countries have invested a substantial amount of research efforts in the development of HAN-based propellants as replacements for more toxic propellants. The fear of inadvertently or unknowingly replacing one carcinogen with another led to a thorough examination of both the mutagenic and carcinogenic properties of hydroxylamine and its salts. Depending on the pH of the substrate, which was often buffered to maintain a constant pH, the tests may have included some free base or not. In discussing the mutagenicity of hydroxylamine and its salts, in particular HAN, there is some overlap between an earlier section (Section 1.8.2) and the current section.

The mutagenic potential of hydroxylammonium chloride NH_3OHCl was assessed in the Ames Salmonella/mammalian microsome mutagenicity test [463]. Tester strains TA97, TA98, TA100, TA102, TA1535, TA1537, and TA1538 were exposed to doses ranging from 0.2 mg/plate to 8.2×10^{-4} mg/plate. In this test, hydroxylammonium chloride produced a relatively high reversion rate at 2.5×10^{-3} mg/plate and 8.2×10^{-4} mg/plate in tester strain TA97, compared with the control (spontaneous revertant) plates. NH_3OHCl also produced a relatively high reversion rate at 0.2 mg/plate in tester strain TA1535. No mutagenic responses were observed for strains TA98, TA100, TA102, TA1537, or TA1538.

The effects of HAN on the *tk* gene of mouse lymphoma L5178Y cells were studied by treatment with HAN at different concentrations [464]. The cell-plating efficiency, relative suspension growth, and mutation frequency were determined. The results showed that HAN (50–500 $\mu\text{g/mL}$) induced *tk* gene mutation with mutation frequencies up to 19 times higher than that of the spontaneous mutation frequency of L5178Y cells.

After single celiac artery administration of HAN in mice, the mortality, chromosome aberration, micronuclei frequency, and physiologic changes of bone marrow cells were examined [445]. The LD₅₀ of HAN in male mice after 1 and 14 d was 186 mg/kg (185–187 mg/kg) and 183 mg/kg (182–184 mg/kg), respectively. No pathologic changes of the other organs were observed. There were significant changes in chromosome aberration and micronuclei rates in experimental groups compared with those of control group ($P < 0.05$). HAN is only a moderate mutagen, but it can induce some genetic damage of bone marrow cells.

3.11.6 Teratogenic Effects

The embryotoxicity of HAN and its teratogenic characteristics were studied by measuring the body weight, the death rate of fetuses, and the rate of absorbed embryos in exposed mice and a control group [465]. The external appearances, internal organs, and skeletons of the mouse embryos were observed. After the mice were given different doses of HAN, their weight, the number of living embryos, the number of absorbed embryos, and the number of dead embryos did not obviously change. The weight of the embryos did not change. There were no malformations in the skeletons of the mouse embryos, their exterior appearance, or their internal organs.

Testicular germ cell micronucleus tests, sperm deformity assay, and flow cytometry were used in order to study potential reproductive damage of testicular germ cells and sperm deformity induced by HAN in mice [466, 467]. It was shown that the percentage of deformities in sperm markedly increased as the dose increased ($P < 0.05$), and the percentage of micronuclei significantly decreased as the dose increased ($P < 0.05$). The damage to sperm could be correlated with the toxic exposure to HAN. The data suggest that HAN causes reproductive damage to testicular germ cells and sperm in mice.

3.11.7 Prophylaxis and Protection Against Accidental HAN Poisonings

People have asked whether there are any antidotes to accidental HAN poisoning; this was discussed as part of a survey on HAN toxicity and handling safety [468]. Prophylactic agents evaluated as antitoxins include squalene [469]. Squalene, an unsaturated hydrocarbon found in shark liver oil, may be a chemopreventive substance against cancer. Male mice were exposed to half the LD₅₀ of HAN by intraperitoneal infusion once per day for 3 d. The animals were divided into three groups: a normal control group, a HAN-treated group, and a HAN and squalene treatment group that was given 130 mg/kg squalene via gastric tube once per day for 7 d after the HAN poisoning. Squalene suppressed the HAN-induced reticulocyte and spleen hemosiderin increases and should be considered as an antidote to HAN poisoning.

Another potential therapy is treatment with methylthioninium chloride (methylene blue) [444]. Male ICR mice were poisoned by different concentrations of HAN. From this set of data, the LD₅₀ of HAN in mice was determined as a baseline

experiment and found to be 149.6 mg/kg body weight. Following HAN injection, methylthioninium chloride 9 mg/kg was injected intraperitoneally in one group of animals. The adverse effects and survival rates of the mice were observed continually for 7 d after injection. At the dosage of LD₅₀, the survival rate of the methylthioninium chloride therapeutic group was 56.5%, which indicates that methylthioninium chloride can antagonize HAN intoxication.

Another therapeutic treatment tested the antioxidant polyphenols from tea leaves (much touted as a cure-all for all ills that may have befallen modern society) [470]. An allotment of male ICR mice were divided into several groups: a control group, a HAN-poisoned group, an experimental group administered tea polyphenols before poisoning by HAN, and an experimental group administered tea polyphenols after poisoning by HAN. Peripheral hemocytology and serum biochemical parameters were measured, and it was shown that although HAN will increase WBCs; decrease RBCs, HGB, and platelet count; and cause serum biochemical parameters to deviate, tea polyphenols can help restore these abnormal values.

3.12 Environmental Effects of Hydroxylammonium Nitrate

Unlike PCB transformer oils or perchlorate ions, hydroxylamine and its salts do not constitute a chronic environmental hazard if spilled accidentally. They deteriorate quickly under the action of air, inorganic oxidants, and bacterial oxidation. Some bacteria even thrive on hydroxylamine, similar to ammonia as a nutrient. As discussed in detail in Section 1, hydroxylamine is an intermediate in the oxidation of ammonia to nitrite and in the reduction of nitrite to ammonia, and it occurs naturally in larger quantities than will ever be used as rocket propellant.

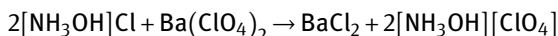
4 Hydroxylammonium Perchlorate

Hydroxylammonium perchlorate [NH₃OH][ClO₄], HAP, CAS RN [15588-62-2] is less water-soluble than the more frequently used HAN. A saturated solution of HAP in water at room temperature contains only 92% HAP, whereas a saturated solution of HAN in water contains 96% HAN. HAP contains 48.3% oxygen. HAP contains more oxygen than HAN, and the chlorine atom also will bind one hydrogen atom. This makes this oxidizer useful for applications in which the exhaust gases must be water soluble, such as in torpedo propellants (*Encyclopedia of Monopropellants*, chapter “Hydroxylammonium Nitrate-Based Monopropellants”).

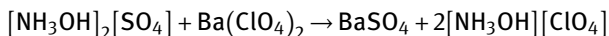
Concentrated solutions of HAP can also be used as liquid oxidizers in bipropellant engines and hybrid rockets.

4.1 Preparation of Hydroxylammonium Perchlorate

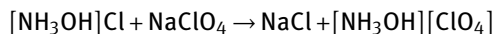
Early investigators studied and patented the reaction of hydroxylammonium chloride with barium perchlorate in anhydrous ethanol. After removal of the barium chloride, the alcoholic solution was evaporated to dryness on a steam bath, extracted with diethyl ether (in which HAP is soluble), and the salt precipitated by addition of benzene [471, 472]:



However, barium chloride is not totally insoluble in ethanol, and the product is likely to contain barium. Precipitating barium sulfate instead of barium chloride would allow a more complete metathetical reaction by metathetical reaction of barium perchlorate and hydroxylammonium sulfate solutions, precipitating insoluble barium sulfate instead of barium chloride: [473]



The hydroxylammonium sulfate should be introduced in a slight excess, which can be removed with barium carbonate. The disadvantage is that the barium sulfate precipitates in very small particles with a high surface area that adsorbs a portion of the desired product. Preparing HAP by the metathetical reaction



in methanol solution would not be successful because sodium perchlorate and HAP are equally well soluble in methanol, and the reaction is an equilibrium that does not go to completion. The equilibrium can be shifted in the desired direction by gradually adding solvents in which sodium chloride is less soluble, followed by stepwise precipitating and removing the undesired NaCl. One such sequence adds n-butanol, removes the NaCl, drives off the methanol at low pressure, adds tert-butanol and isopropyl ether, removes the NaCl, drives off the solvents at low pressure, and finally adds methylene chloride to precipitate the HAP [474]. The NaCl salt cake can be washed with methanol to recover some of the HAP still adhering to the crystals. Another method described in the same patent uses a suspension of finely ground $[\text{NH}_3\text{OH}]_2[\text{SO}_4]$ in methanol, liberates the free hydroxylamine base by the addition of sodium hydroxide, removes the precipitated Na_2SO_4 , and neutralizes the free amine solution with 71% perchloric acid. The HAP is then separated from the methanol solution by the same solvent addition sequence as described for the process starting with the chloride instead of the sulfate.

Instead of using sodium hydroxide to liberate the free base from a suspension of finely ground $[\text{NH}_3\text{OH}]_2[\text{SO}_4]$ in methanol or ethanol, one can also use ammonia [160] to liberate hydroxylamine free base in an alcoholic solution and then neutralize it with perchloric acid or nitric acid to obtain HAP or HAN.

Cation-exchange reactions can use either cation-exchange resins or anion-exchange resins for the production of HAP [475]. If an anion-exchange resin is used, it could be loaded with hydroxyl ions from a caustic solution, a solution of hydroxylammonium chloride passed through the column to liberate the free hydroxylamine base, and the eluent neutralized with perchloric acid.

Another method is to load a cation-exchange resin with hydroxylammonium cations and then elute it with a solution of a perchlorate, preferably in a countercurrent flow arrangement [476].

Electrolytic reduction of nitric acid in perchloric acid solution can lead to HAP in a one-pot synthesis. HAP crystals are extremely hygroscopic, and it is difficult to crystallize them from aqueous solutions. In air at 18% relative humidity, crystals absorb enough water within 18 min to almost dissolve themselves in a deliquescent mess.

Improved packing densities can be achieved if the oxidizer for solid propellants is in spherical form and has a bimodal particle-size distribution. HAP and many other low-melting oxidizers can be prepared in spherical form by pouring a thin stream of the molten material (melting point $368\text{ K} = 95^\circ\text{C}$) into a cooling bath of an inert, high-boiling fluid, such as tetrachloroethylene [477]. The bath has a temperature gradient from top to bottom. The droplets assume spherical shapes by surface tension and solidify while they sink in the liquid.

It was also attempted to avoid the use of water as a solvent by heating a mixture of solid hydroxylammonium chloride with perchloric acid dihydrate, but premature decomposition occurred at the temperature required to drive off the hydrogen chloride [473].

A method suitable for preparation of research quantities of high-purity HAP in a reasonably short time consisted of reacting stoichiometric amounts of $\text{Ba}(\text{ClO}_4)_2$ and HONH_2Cl dissolved in absolute ethanol [478]. BaCl_2 precipitated and was filtered out, and the ethanol was removed in a flash evaporator. The solid HAP was dissolved in anhydrous diethyl ether; any residue filtered out, and the ether was then evaporated. This purification was repeated until no residue could be detected, at which point the HAP was precipitated from the solution with benzene. This material was dried in a glass dead-end tube for approximately 1 h at 343 K (70°C) and 6.7 Pa (0.05 mm Hg), at which point it usually assayed as $>97\%$ pure. Further purification by redissolving in ether and then reprecipitating with benzene and drying for 1 h at 343 K (70°C) and 6.7 Pa (0.05 mm Hg) gave a pure material well in excess of 99% purity, and the drying time was cut by a factor of 12 over that required formerly. Spot tests for Cl^- contamination were regularly negative.

The curing of PBAN binders in HAP-based solid propellants was prevented by premature interaction between the oxidizer and epoxy curing agents, such as Epon H-825. It was attempted to prevent oxidizer–binder interactions by coating HAP with phenylglycidyl ether or inerting HAP with toluene diisocyanate [479]. Substituting some of the HAP with AP also improved the curing of the binder.

4.2 Physical Properties of Hydroxylammonium Perchlorate

Solid HAP exists in three different phases [480]. The high-temperature form (phase B) melts at about 362–364 K (89–91 °C). A third phase (phase C) melts at about 331 K (58 °C) at atmospheric pressure. The HAP phase A crystals at 298 K (25 °C) have a density of 2.02 g/cm³, and the calculated X-ray density is 2.13 g/cm³ at 298 K (25 °C). Other sources have reported a density of 1.96 g/cm³. Physical properties of HAP are summarized in Table 31.

Table 31: Physical properties of hydroxylammonium perchlorate.

Property	SI units	Other units	References
Molecular mass	132.5 g/mol		
Melting point	358.1	85 °C	[481]
	361.1	88 °C	
	360.6–362.1	87.5–89 °C	[471]
Melting point, phase B	362–364 K	89–91 °C	[480]
Density, pycnometric	2.06 g/cm ³		[481]
Density, pycnometric, phase A	2.02 g/cm ³ at 298 K		[480]
Density (calculated from XRD), phase A	2.13 g/cm ³ at 298 K		[480]
Density, pycnometric (at 293 K)	1.77 g/cm ³ ^a		[473]
Enthalpy of formation	–276.5 ± 4.1 kJ/mol	–66.1 ± 1 kcal/mol	[482]
	–276.8 ± 2.7 kJ/mol	–66.16 ± 0.65 kcal/mol	[483]
Heat of vaporization at 95–160 °C	135.1 or 140.2 kJ/mol	32.3 or 33.5 kcal/mol	[484]

^aThe number reported by Zinovev and Zakharova [473] is much too low.

A near-saturated solution of HAP in water that was considered for torpedo applications contains 92 mass-% HAP. It is said to be used in underwater propulsion applications by the British Navy. It has a density of 1.71 g/cm³, a viscosity of 15 cPs, and a heat capacity of 1.84 J g^{–1} K^{–1}. The viscosity is almost double that of 13-M HAN solutions.

The freezing-point properties of HAP solutions are listed in a patent that describes the use of concentrated HAP solutions as liquid oxidizers in non-hypergolic bipropellant combinations to be used in rockets or underwater torpedoes (Table 32) [485].

The densities of 80–85 mass-% aqueous HAP solutions were determined, and the results are listed in Table 33.

A thermal stability test was performed on an 80%-by-weight aqueous HAP solution at 353 K (80 °C) for 30 d. The results indicated no pressure buildup, and the change in concentration of any of the components was negligible. DTA showed that exothermic decomposition of this oxidizer occurs above 483 K (210 °C). The sensitivity characteristics of 82.5 mass-% HAP solutions were investigated by several methods, and the

Table 32: Freezing points of aqueous HAP solutions.

Composition, mass-%		Freezing point	
HAP	H ₂ O	K	°C
10	90	272	−1
20	80	268	−5
39	61	258	−15
49	51	247	−26
59	41	236	−37
64	36	222	−51
79	21	247	−26
85	15	262	−11
90	10	277	+4

Data source: [485]

Table 33: Density of aqueous HAP solutions.

HAP Mass-%	Density g/cm ³
80.0	1.655
82.5	1.715
85.0	1.754

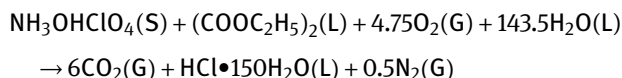
Data source: [485]

solutions were negative in the card-gap test at zero cards with the sample preheated to 298, 323, or 348 K (25, 50, or 75 °C).

4.2.1 Thermodynamic Properties of Hydroxylammonium Perchlorate

Data on the enthalpy of formation of HAP are in [85, 86]. The activation energy of the phase transition that occurs between 330 and 335 K (57 and 62 °C) is 241.4 kJ/mol (57.7 kcal/mol) [486].

In order to determine the enthalpy of formation of HAP, the combustion of HAP was carried out in an oxygen atmosphere using diethyl oxalate as the fuel [483]. The idealized reaction equation from which the heat of formation was calculated is as follows:



The energy of reaction at constant pressure and 25 °C is −788.88 kcal/mol. From that number the enthalpy of formation for crystalline HAP was derived as −276.8 ±

2.7 kJ/mol (-66.16 ± 0.65 kcal/mol). Other sources listed an enthalpy of formation of -278.2 kJ/mol.

4.2.2 Optical Properties of Hydroxylammonium Perchlorate

Infrared spectra of the solid chloride, bromide, iodide, nitrate, sulfate, and perchlorate of hydroxylamine were measured and compared to those of the deuterated salt analogs [282]. The iodide was less stable and could not be deuterated. All bands with the exception of the ν NO band and those of the anions are affected by deuteration (Table 34).

Table 34: Infrared absorption-band assignments for HAP spectra.

Wavenumber		Assignment
Hydrogen	Deuterium	
3145(f)	2350	ν OH
3045(f), 2995(f)	2240	ν NH ₃ ⁺ antisymmetrical oscillations
2900(f)		ν NH ₃ ⁺ symmetrical oscillations
2655(m), 2050, 1895(F)	1970, 1527, 1385	Combinations
1575(F), 1555(f)		δ NH ₃ ⁺ degenerate vibrations
1502, 1480, 1470(F)		δ NH ₃ ⁺ symmetrical oscillations
1194(F)	903	Rotational oscillations NH ₃ ⁺
1157(F)	857	δ OH
997(F)	990	ν NO
543	—	Torsional vibrations OH
1105–1087(F), 932(f), 626(F)		ClO ₄ [−]

Data source: [282]. Absorption band strength legend: (F) very strong, (f) strong, (m) medium.

4.2.3 Molecular Structure of Hydroxylammonium Perchlorate

Solid HAP exists in three different phases, and phase transformations are accompanied by distinct changes in heat capacity and in cracking of previously well-crystallized large crystals. Some of the phase changes are not reversible. The crystal structure of the room-temperature form (phase A) has been determined, but in order to prevent phase changes, it was kept at 123.15 K (-150°C) during the experiment [487]. The high-temperature form (phase B), melting at about 362–364 K (89 – 91°C), was examined at 344 K (70°C). A third phase (phase C), which melts at about 331 K (58°C) at atmospheric pressure, was identified by heat-capacity measurements. Based on XRD, the HAP phase A crystals at 298 K (25°C) were found to be orthorhombic, with the cell dimensions $a = 7.52 \pm 0.02$ Å, $b = 7.14 \pm 0.01$ Å, $c = 15.99 \pm 0.02$ Å, and space group $P2_1cn$ or $Pmcn$. The structure consists of chains of perchlorate ion tetrahedra held together

by hydrogen bonding from parallel chains of NH_3OH^+ ions. The NH_3OH^+ ions may rotate around the N—O axis.

Based on neutron diffraction data, HAP crystallizes in the space group $P2_1cn$, and the cell parameters are $a = 7.52 \text{ \AA}$, $b = 7.14 \text{ \AA}$, $c = 15.99 \text{ \AA}$, and $Z = 8$ [488], in good agreement with XRD data. There is only hindered rotation of the $-\text{NH}_3$ group around the axis defined by the N—O bond.

High-pressure techniques were used to investigate polymorphism in energetic materials, and new high-pressure phases of HAP were structurally characterized using single-crystal X-ray and powder neutron diffraction [489]. Hydroxylammonium perchlorate has been investigated using high-temperature single-crystal X-ray diffraction and powder neutron diffraction, and a high-temperature phase has been fully structurally characterized for the first time. High-pressure studies of HAP indicated the presence of two new polymorphs.

4.3 Chemical Properties of Hydroxylammonium Perchlorate

Hydroxylammonium perchlorate forms solvate complexes with both one and two hydroxylamine molecules, $[\text{NH}_3\text{OH}][\text{ClO}_4] \cdot 2\text{NH}_2\text{OH}$ and $[\text{NH}_3\text{OH}][\text{ClO}_4] \cdot \text{NH}_2\text{OH}$, while the nitrate forms only a monoligand complex with one mol of hydroxylamine in its solvate sphere $[\text{NH}_3\text{OH}][\text{NO}_3] \cdot \text{NH}_2\text{OH}$ [295]. With the strong hydrogen bonding in the free base and in many of its salts, it is not surprising that the free base will attach itself as a solvate to some of its salts. Here is one example: 4.85 g (0.0365 mol) of $[\text{NH}_3\text{OH}][\text{ClO}_4]$ was dissolved in 300 mL of diethyl ether, and 20 mL of ethanol containing 1.21 g (0.0366 mol) of NH_2OH was added with stirring. The precipitate was filtered and dried to give a quantitative yield of the monohydroxylamine complex. These complexes are in general less hygroscopic than the salt itself. For instance, while the HAP gained 11.7 mass-% in 60 h at ambient conditions, its complexes showed no such weight gain. However, the dihydroxylamine complex was not stable, and when the recrystallized material was exposed to the atmosphere at room temperature, the dihydroxylamine complex lost one mol of hydroxylamine over a period of about 14 d, and the mono complex was obtained. The hydroxylammonium perchlorate monohydroxylamine was kept with no sign of moisture absorption or further decomposition at room temperature. The densities and DTA results of some of these complexes are summarized in Table 35.

Similar sparsely soluble complexes were obtained with LiClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$, and $\text{Ba}(\text{ClO}_4)_2$.

Regardless of the anion present, hydroxylammonium forms complexes with a number of transition metal salts, even in strongly acidic solutions. These complex salts include those with iron(II) [490] and vanadium(V) [491, 492]. The ligand in these complexes is free hydroxylamine in spite of the fact that the equilibrium concentration of the free base in strongly acidic solutions is only very small.

Table 35: Properties of complexes with hydroxylamine as the solvate.

Compound	Density, g/cm ³	Endotherms, start at °C	Exotherms, start at °C
[NH ₃ OH][ClO ₄]	2.06	55, 88	180
[NH ₃ OH][ClO ₄]•NH ₂ OH	1.93	75, 100	120
[NH ₃ OH][ClO ₄]•2NH ₂ OH	1.78	85	110
[NH ₃ OH][NO ₃]•NH ₂ OH	1.70	67	75
LiNO ₃ •NH ₂ OH	1.75	95, 140	170

DTA: Heating rate 10 °C/min

4.4 Thermal Stability and Decomposition of Hydroxylammonium Perchlorate

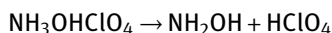
Hydroxylammonium perchlorate has not found any applications in the solid state. Thermal decomposition studies have been performed for both solid crystals and aqueous solutions of this oxidizer.

The DTA thermogram of HAP showed exotherms at 451–493 K (178–220 °C) and 586–643 K (313–370 °C) and an endotherm starting at 793 K (520 °C) [473]. It is assumed that AP is an intermediate in the HAP decomposition.

Over the course of 6 years from 1962 through 1967 and under the sponsorship of the U.S. Air Force Office of Scientific Research with two consecutive contracts, Atlantic Research Corporation conducted a detailed investigation on the deflagration of high-energy solid oxidizers containing the perchlorate anion [493, 494], including ammonium perchlorate, hydrazinium(2+) diperchlorate, and HAP [481]. A similar program at Thiokol Reaction Motors Division studied hydrazinium(1+) perchlorate and HAP [478, 495]. Preliminary studies on the thermal decomposition of HAP indicated lower thermal stability than expected on the basis of literature reports. The autocatalytic nature of the reaction is apparent in the P vs. t plots at 403 and 413 K (130 and 140 °C). Mass spectrometric analyses of the gaseous products indicated 80% N₂O and 20% HCl. No other gaseous products were detected. Physical characteristics of the residue led to the suspicion that it may be hydrazinium perchlorate. Thermal decomposition rate experiments have been performed in the range from 393 to 433 K (120 to 160 °C), and the activation energy of the uncatalyzed reaction was found to be 185 kJ/mol (44.3 kcal/mol) [478]. In contrast to the HONH₃Cl decomposition reaction, no evidence of competing reactions was found. The volatile decomposition products have been identified as N₂O, HCl, and Cl₂. ClO₄[−], HONH₂, and NH₃ have been found in the highly acidic condensed residue, which is suspected to be a mixture of HAP, AP, and aqueous HClO₄. The thermal decomposition reactions of HAP were studied between 393 and 423 K (120 and 150 °C) in a sealed system and at 453 K (180 °C) in an open system [496]. For comparison, the thermal decomposition reactions of HONH₃Cl were studied in the temperature range 403–433 K (130–160 °C) to obtain an understanding of the decomposition reactions of hydroxylammonium ion free from external oxidants. The chloride was found to decompose by two mechanisms, and the reaction of the

perchlorate was found to undergo similar initiating steps, but the presence of excess oxidant increased the reaction rate and led to a different stoichiometry.

Mass spectroscopic analysis of decomposition products during slow ramp-up thermal analysis was used to study the thermal decomposition of hydroxylammonium and methoxyammonium perchlorates [486, 497]. The first step in the thermal decomposition of these salts is the proton transfer from the substituted ammonium ion to the perchlorate anion to form the free substituted amine and perchloric acid. An activation energy of $241 \pm 29 \text{ kJ/mol}$ ($57.7 \pm 7 \text{ kcal/mol}$) was calculated for the transition from the slope of the line below 273 K (0 °C). Once the crystalline phase transition is complete, dissociation of the solid HAP continues smoothly to its melting point at 353 K (80 °C). Slow dissociation (proton transfer) begins below and continues to its melting point at 353 K (80 °C). The activation energy of the dissociation process



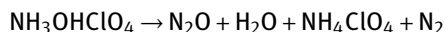
is 86.6 kJ/mol (20.7 kcal/mol) when based on NH_2OH measurements, but it is 194 kJ/mol (46.4 kcal/mol) when the calculation is based on the ClO_3^- concentration measured with the mass spectrometer in the gas space above the sample. The latter number is similar to breaking the $\text{HO}-\text{ClO}_3$ bond energy in HClO_4 , which is 188 kJ/mol (45 kcal/mol). In comparison, the O-methylhydroxylammonium perchlorate has no phase transitions in the solid state between 326 and 350 K (53 and 77 °C). The activation energy calculated from the slope of the free H_3CONH_2 base is 125 kJ/mol ($30 \pm 2 \text{ kcal/mol}$) and that from the slope of the ClO_3^- ion is 185 kJ/mol ($44.2 \pm 2 \text{ kcal/mol}$), similar to the $\text{NH}_3\text{OHClO}_4$ value. H_3CONH_2 is a stronger base than HONH_2 .

An examination of the compatibility and stability characteristics of HAP and hydrazinium(2+) diperchlorate (HP-2) and the inherent reactivities of the oxidizers with several types of organic substances showed that both are relatively weak oxidizers, with HP-2 being slightly more reactive than HAP and both being more reactive than AP [498]. Both oxidizers react prematurely with candidate binders in solid propellants, in particular with isocyanates, which complicates the preparation of solid propellants with these oxidizers.

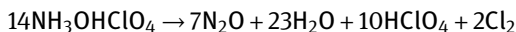
The vapor species evolved from subliming HAP at 383–393 K (110–120 °C) were trapped in a frozen matrix and analyzed by IR absorption spectrometry [499]. The sublimation and decomposition of HAP in comparison to AP, methylammonium perchlorate, and hydrazinium(1+) perchlorate examined by a cold matrix isolation–infrared spectroscopic technique was shown to vaporize by dissociation. IR spectra of the frozen matrix showed individual free hydroxylamine and perchloric acid. This observation supports the proton transfer theory as the initiating step of HAP decomposition. Other species observed were water and nitrous oxide. In a comparison of the vaporization temperatures of HAP, AP, HP, and methylammonium perchlorate, the relative vaporization temperatures could be correlated with the pK values of the bases in aqueous solution. The spectrum of the vapor species from HAP at 393 K (120 °C) clearly showed perchloric acid, and the bands at 3640, 1604, 1364, 1132, and

893 cm^{-1} agreed well with the hydroxylamine free base gas-phase bands of Giguere and Liu 1952 [38] at 3656 , 1605 , 1125 , 1115 , and 896 cm^{-1} if small matrix shifts are permitted.

One of the possible decomposition reactions is



but this reaction has not yet been balanced for stoichiometry. The residue of partially decomposed samples contains AP. Samples that have completely decomposed satisfy the stoichiometry of equation



The products of the decomposition of HAP include NH_4ClO_4 , N_2O , H_2O , HClO_4 , Cl_2 , HCl , O_2 , and unidentified oxides of chlorine [500]. The rate of decomposition is quite slow below the melting point.

A reversible $10.46\text{--}12.55\text{ J/g}$ ($2.5\text{--}3.0\text{ cal/g}$) endotherm was observed with HAP at $\sim 333\text{ K}$ ($\sim 60^\circ\text{C}$) and considered to be a phase transformation [501]. The $<0.2\%$ mass loss associated with the transformation was explained by a release of volatiles through crystal relaxation. The possibility that the endotherm resulted from impurity melting was considered as well, but the absence of any associated freezing exotherm and the time delay in recovery when the sample was cooled were more consistent with a crystal phase change. The melting endotherm reappeared upon successive heating at 368 K ($\sim 95^\circ\text{C}$). When the molten material was cooled, a sharp freezing exotherm was visible as either a large single peak or two smaller peaks between 329 and 336 K (56 and 63°C). The water that was detected in the mass spectra of HAP probably came from adsorbed moisture due to the hygroscopic nature of HAP.

At low degrees of conversion, the rate of gas evolution from decomposing HAP decreases until it reaches a constant value [502]. Addition of hydroxylammonium sulfate slows down the decomposition. Addition of sequestering agents capable of complexing transition metal cations improves the stability of HAP by one order of magnitude.

HAP forms an adduct with free hydroxylamine $\text{HONH}_3\text{ClO}_4 \bullet \text{NH}_2\text{OH}$, CAS RN [25417-72-5] [503–505]. The effect of the addition of guanidine or HAP and of dilution with H_2O , MeOH , or EtOH on the burning rate was also investigated. The decomposition of the adduct involves monomolecular dissociation, and a decomposition of the HAP and free NH_2OH base thus formed. The decomposition products contain ammonia, which displaces NH_2OH from the adduct.

4.5 Reactions of Hydroxylammonium Perchlorate

Studies of the stability of HAP and its compatibility with binders and curing agents showed that HAP was less reactive than HP-2 but more reactive than AP [506]. Binders investigated included hydroxyl- and carboxy-terminated polybutadiene and

polyisobutylene prepolymers, as well as poly-1,2-bis(difluoroamino)-2,3-propylene oxide (P-BEP). Binder prepolymers studied were hydroxyl terminated polyisobutylene (UTREZ-diol), carboxyl terminated UTREZ, hydroxyl terminated polybutadiene (R-45-M), carboxyl terminated polybutadiene (Telagen CT), saturated hydroxyl terminated Telagen, a carboxyl terminated polyisobutylene (EMD-590), and two ethyl acrylate–acrylic acid copolymers. The curing agents studied included isocyanates, an aziridine (MAPS), and an epoxide (ERLA-4221). Parallel studies of hydrazinium(2+) diperchlorate (HP-2) and AP were included to provide a baseline for comparing the relative merits of the more energetic oxidizers. Later in the program, and after HP-2 was essentially eliminated as a candidate oxidizer, the compatibility of HAP with two NF plasticizers, 1,2,3-tris[1,2-bis(difluoroamino)]ethoxy propane (TVOPA) and 2,3-bis(difluoroamino)-propyl-2,2-dinitropropylcarbonate (P-722), and with aluminum hydride (LMH-1) were studied. HAP, which was slightly more attractive from a compatibility viewpoint than HP-2, was carried along as a candidate advanced oxidizer.

4.5.1 Reaction of HAP and HClO_4

HAP does not form an adduct with excess perchloric acid [507]. To 0.267 g (2mmol) of HAP at -196°C , approximately 2mL of anhydrous HClO_4 was added. The reaction mixture was allowed to warm to room temperature. After 15 min of stirring at ambient temperatures, the excess HClO_4 was slowly removed in a vacuum. The $\text{NH}_3\text{OHClO}_4$ was found to be unchanged on the basis of XRD analysis.

4.5.2 Reaction of HAP and Nitrate Esters

HAP solutions have been considered as oxidizers to be injected into Otto Fuel II exhaust gases in torpedoes to increase the performance, remove soot, and reduce the non-condensable gases in the wake of the torpedo. It has been considered to store the two immiscible fluids in the same propellant tank, but they are not compatible and cannot be stored in contact with each other. Headspace gas analysis has shown that nitrous oxide is the principal gas evolved during contact between Otto Fuel II and 82 mass-% aqueous HAP solution at temperatures close to ambient [508–510]. The gas was produced mainly from the 82% HAP layer and was generated in significant amounts only after the Otto Fuel II had already become blackened as a result of extreme degradation. The pH of the HAP solution fell during contact with Otto Fuel II, and the Otto Fuel II blackening point was the same for each of three storage temperatures investigated, indicating that the production of N_2O may depend upon the attainment of a specific HAP solution acidity. It was suggested that the propylene glycol dinitrate (PGDN) component in Otto Fuel II undergoes acid hydrolysis at the liquid/liquid interface and that the nitric acid produced leads to the decrease in HAP solution pH and to stabilizer depletion in Otto Fuel II. Experiments involving contact between 82% HAP and the other components of Otto Fuel II confirm the key role of PGDN: In its

absence there was no change in HAP solution acidity, no gas evolution, and no violent reaction between the two liquids.

Gas chromatography with a flame ionization detector was used to determine changes in the concentrations of the components of Otto Fuel II in contact with 82% aqueous solution of HAP in sealed glass vials at 31.7°C during the period leading up to autoignition of the two incompatible liquids [511]. The concentration of hydroxylamine in HAP was monitored over the same period using a titration method. It was found that 2-nitrodiphenylamine (2-NDPA), the stabilizer in Otto Fuel II, was completely consumed after about 65–70 h and that the concentration of hydroxylamine began to fall at this point. 1,2-propanediol dinitrate (propylene glycol dinitrate, PGDN), the energetic component in Otto Fuel II, was not depleted significantly until after about 90 h. The evolution of nitrous oxide (N_2O) between 65 and 90 h is attributed to the reaction of the hydroxylammonium ion with nitrous acids produced by PGDN decomposition at the liquid–liquid interface.

4.6 Strand Burning Rates of Hydroxylammonium Perchlorate

The strand burning behavior of HAP and other perchlorate salts was studied in a series of research contracts at Atlantic Research Corporation under the sponsorship of the U.S. Air Force [481, 512, 513]. HAP powder was either gently tamped into Pyrex tubes (bulk density $\rho = 1.10 \text{ g/cm}^3$) or pressed into pellets ($\rho = 2.05 \text{ g/cm}^3$). The combustion was somewhat luminous and formed a foamy molten layer on the surface. The lower pressure limit for stable deflagration was at 13.6 MPa (135 atm) for HAP tamped into 8-mm diameter tubes. There was a lot of scatter in the burning-rate data at pressures below 20.2 MPa (200 atm). Burning rates at 15.15 MPa (150 atm) varied from 2 to 4 cm/s. Due to the data scatter, a burning-rate coefficient could not be obtained for pressures below 20.2 MPa (200 atm). At higher pressures, the burning rate coefficient was 0.52. Results of tests with HAP in different diameter tubes suggested that HAP will not sustain combustion below 10.1 MPa (100 atm), even with very large samples. The burning rate of HAP increased with tube diameters ranging from 3.8 to 8 mm.

The deflagration of solid HAP has been studied at pressures of 21–6900 kPa (3–1000 psia) and compared to that of AP and HNF. HAP exhibited a low-pressure deflagration limit of 14.75 MPa (146 atm), analogous to the 2.02 MPa (20 atm) limit of AP [514]. This high value was obtained in spite of a flame temperature for HAP that is 100° higher than that of AP, and despite the fact that at pressures at which HAP does burn, it burns two to three times more rapidly than AP does. A comparison of results for several oxidizers suggested that AP should be regarded as exhibiting an unusually low low-pressure limit.

The pressure dependence of the strand burning rate of HAP as well as of HAP/AP mixtures and non-stoichiometric HAP/free HA and HAP/ HClO_4 adducts was deter-

mined in 7-mm ID tubes at 0.1 to 13.1 MPa (1 to 130 atm) [515]. HAP by itself burned unstably and had a discontinuity in the $r_b = f(p)$ curve in the range of 3–10.1 MPa (30–100 atm). In the intermediate range, combustion is either impossible or is troubled by quenching and pressure pulsations. Small (0.1%) HClO_4 additions inhibited HAP over a wide range, but larger (0.4 and 0.6% HClO_4) additions increased the burning rate by a factor of 1.5 over a wide range of pressures and lifted it out of the discontinuity shown by pure HAP. At least 10% AP addition was required to get HAP/AP mixtures to burn over the entire range of pressures tested. The HAP/HA adduct burned stably at pressures from 100 mm Hg to 130 atm. It burned much faster than HAP by itself. The pressure dependence of the temperature coefficient was also measured for all samples.

4.7 Handling and Safety Properties of Hydroxylammonium Perchlorate

Dry HAP is very sensitive to impact in the drop-weight test with a 2-kg weight in the U.S. Bureau of Mines apparatus (50% point at 15 cm [471]).

4.8 Detonability of Hydroxylammonium Perchlorate Solutions

The detonability of aqueous solutions/suspensions of organic amine perchlorates and HAP was studied in steel and glass ampoules with an electric detonator with or without an intermediate hexogen booster. The isochoric detonation temperature of aqueous solutions of HAP was 680–860 K, and the upper concentration limit of H_2O below which the solutions retained their detonation capacity was 20–25% H_2O [516].

Hydroxylammonium perchlorate solutions have been proposed as a liquid explosive [517], as well as in mixtures with ethanolammonium perchlorate (monoethanolammonium perchlorate, MEAP). Solutions of HAP were found to have an especially high tendency to propagate detonation by low-velocity detonation (LVD) [518, 519]. Explosives that are sensitive to LVD are not very safe to handle, since a minor shock may cause them to explode, particularly in the presence of gas bubbles. Both HAP and MEAP are quite soluble in water. It is thus possible to create fairly concentrated detonable solutions without any suspended solids. The tests were done in moderate confinement (glass tubes) and heavy confinement (steel pipes). High-velocity detonation could be achieved only for larger diameters and with heavy confinement. Two mixtures with different HAP:MEAP molar ratios were studied in more detail: a mixture with a HAP:MEAP molar ratio of 4:1 and one with a ratio of 4:5. The mixtures have a very small critical diameter, below which detonation does not propagate. The critical diameter of two HAP/MEAP mixtures is shown in Figure 50 as a function of the amount of water diluent. The critical diameter of the more energetic mixture (4:5 molar ratio) may be as small as 2 mm.

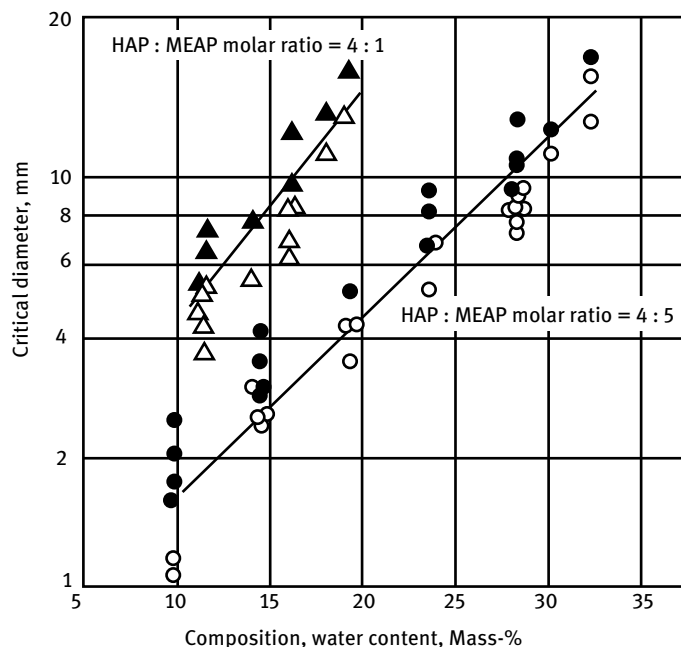


Figure 50: Critical diameter of HAP/MEAP explosives as a function of water content. (Republished and modified from [518], with permission of Springer Nature BV © 1988; permission conveyed through Copyright Clearance Center Inc.)

Circles: 4:5 mixture. Triangles = 4:1 mixture. Solid symbols: Detonation positive. Open symbols: Detonation failed.

The critical diameter as a function of the O:F mixture ratio goes through a minimum at 1.4 mm for the most energetic 4:5 mixture (Figure 51). Additional tests were conducted in which the explosive was gelled and aerated such that small bubbles were trapped. Such bubbles form hot spots when suddenly compressed. The detonation velocity was dependent on pipe diameter but was not very dependent on the degree of aeration or the charge density. The highest detonation velocity measured in steel pipes was 6200 m/s. For tests in glass tubes, the detonation velocity dropped sharply below a certain concentration of air bubbles.

In the NOL Large Scale Gap Test, HAP packed to a density of 0.97 g/cm^3 had a sensitivity of 363 cards (50% point), corresponding to an attenuated shock pressure of 6 kbar [520].

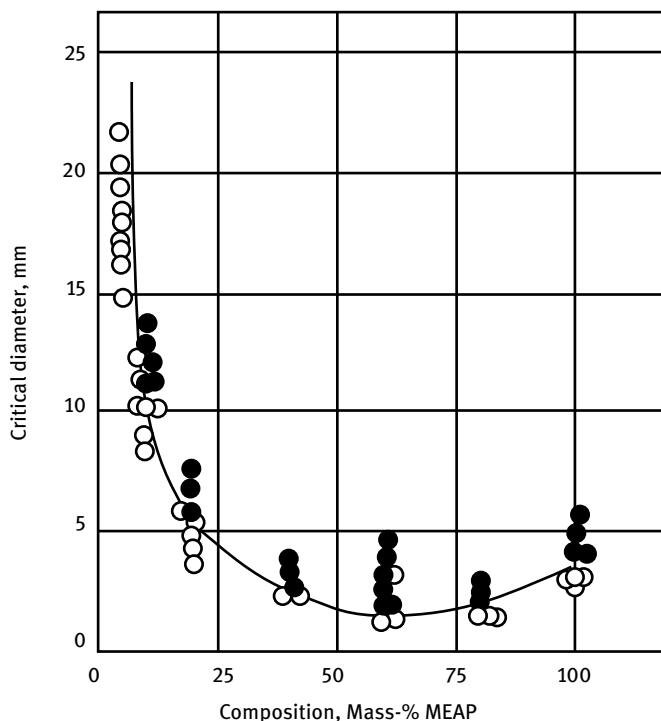


Figure 51: Critical diameter of HAP/MEAP explosives with 9–12% water as a function of mixture ratio. (Republished and modified from [518], with permission of Springer Nature BV © 1988; permission conveyed through Copyright Clearance Center Inc.)

Solid symbols: Detonation positive. Open circles: Detonation failed.

4.9 Applications of Hydroxylammonium Perchlorate

Hydroxylammonium perchlorate has been evaluated as an oxidizer in solid-propellant formulations. Thiokol developed HAP-based solid propellants in the 1960s, but the work was discontinued after interest waned [521].

The burning rate of AP/polysulfide solid propellants can be increased significantly by adding as little as 5% HAP [472]. Similar results were obtained with hydrazinium(1+) perchlorate and semicarbazide perchlorate.

HAP has been evaluated as an oxidizer in solid-propellant formulations with various binders. Efforts to prepare HAP/P-BPE (a domino binder)/AlH₃ propellants were not successful [522].

Composite solid propellants containing HAP, also in the form of AP/HAP mixtures and with a variety of conventional binders, including isocyanate-cured HTPB with or without the addition of aluminum powder, have been patented [521].

Water-soluble polymers (polyvinyl alcohol, polyvinyl pyrrolidone) are also soluble in molten HAP or molten HAN, forming a castable solid propellant that is actually a solid solution [523]. Instead of mixing the binder into the molten oxidizer, both oxidizer and binder can be first dissolved in methanol, mixed, and the solvent evaporated. Increased specific impulse can be achieved by incorporating up to 20% aluminum powder in the formulation. High-temperature safety tests indicated that the dry molten HAP process for preparing the solid solution was not suitable for scaling up to pound-size batches in larger mixers.

The performance of Otto Fuel II in torpedo drives can be increased by 40% on a mass basis and 66% on a volume basis by injecting a HAP solution into the hot exhaust [524]. The injection of HAP solutions into Otto Fuel II exhaust not only increases the performance but also cleans up the exhaust and burns up all the soot. It has been considered to store the two immiscible fluids in the same container, but they are not compatible and cannot be stored in contact with each other (Section 4.5.2). HAP solutions have also been proposed as an oxidizer for bipropellant-powered torpedoes [525] and in monopropellants with dioxane or glycerol as the fuel [526].

5 Other Hydroxylammonium Salts

5.1 Hydroxylammonium Dinitramide

Hydroxylammonium dinitramide, $[\text{NH}_3\text{OH}][\text{N}(\text{NO}_2)_2]$, HADN, if it existed in the pure state, would have a better oxygen balance at +34.27% than ADN, with +25.79%. It contains 2.14 g-atom oxygen/100 g of salt. It appears that the only compound known with a structure similar to HADN is an adduct that contains a mol of free hydroxylamine as a solvate, which has an oxygen balance of only +23.11%.

5.1.1 Preparation of Hydroxylammonium Dinitramide

Hydroxylammonium dinitramide was prepared by ion exchange from a column loaded with dinitramide ions.

5.1.2 Physical Properties of Hydroxylammonium Dinitramide

5.1.2.1 Melting Point and Phase Diagrams of Hydroxylammonium Dinitramide

Hydroxylammonium dinitramide does not crystallize readily at room temperature. In one literature reference, HADN is described as a liquid. In another reference, a melting point is given as 291–296 K (18–23 °C) [527, 528]. It is not certain that these investigators had a pure substance. In both cases, HADN appears to be a room-temperature ionic liquid.

5.1.2.2 Density and Partial Molar Volumes of Hydroxylammonium Dinitramide

The X-ray density of HADN is $\rho_c = 1.859 \text{ g/cm}^3$ [529]. Pycnometric density measurements indicated a lower density of 1.733 g/cm^3 at 293 K.

5.1.2.3 Thermodynamic Properties and Thermal Properties of Hydroxylammonium Dinitramide

The predicted enthalpy of formation of HADN is $-144.3 \text{ kJ/mol} = -34.5 \text{ kcal/mol}$.

5.1.2.4 Molecular Properties of Hydroxylammonium Dinitramide

Hydroxylammonium dinitramide crystallizes in the orthorhombic space group *Pcab* (non-standard setting of *Pbca*) with cell dimensions $a = 6.439(2)$, $b = 12.470(4)$, $c = 30.816(14) \text{ \AA}$, $Z = 8$, and $\rho_c = 1.859 \text{ g/cm}^3$ [529]. In HADN there are both neutral and zwitterionic hydroxylamine moieties involved in the hydrogen-bonding scheme. The complete formula unit is $[\text{NH}_3^+\text{OH}]_2[\text{N}_3\text{O}_4^-]_2 \cdot (\text{NH}_2\text{OH}) \cdot (\text{NH}_3^+\text{O}^-)$, and in this structure the hydroxylamine exists in three possible forms: protonated, neutral, and zwitterionic. In these structures, the conformations adopted by the dinitramine anions can be related to the types of hydrogen bonds formed with the surrounding amine cations. Atomic coordinates, bond lengths and angles, and equivalent isotropic displacement parameters for the salts have been calculated and tabulated. These cations provide a constrained local environment for the dinitramide anions due to extensive hydrogen bonding.

5.1.3 Chemistry of Hydroxylammonium Dinitramide

Hydroxylammonium dinitramide is miscible with acetonitrile, dimethylformamide, nitromethane, and methanol.

5.1.3.1 Thermal Stability of Hydroxylammonium Dinitramide

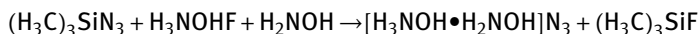
In DSC, HADN begins to decompose at 407 K (134°C), compared to an onset of exotherm of 413 K (140°C) for ADN. The activation energy of HADN decomposition is 117 kJ/mol (28 kcal/mol).

5.1.4 Explosive and Fire Hazards of Hydroxylammonium Dinitramide

A compound described as SRI-14 is a hydroxylammonium dinitramide containing some free hydroxylamine as a solvate with a gross formula of $\text{N}_5\text{H}_7\text{O}_6$. It is a solid that melts at 357 K (84°C) and is less soluble in water (42%) than ADN (70%), both saturated at 273 K (0°C). The impact sensitivity of SRI-14 was found to be approximately 3–4 J (16–20 cm with a 2-kg weight), which is in the same range as that of ADN [530].

5.2 Hydroxylammonium Azide

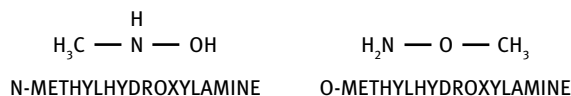
Hydroxylammonium azide solvated with an extra mol of hydroxylamine free base can be prepared by reaction of trimethylsilyl azide with ammonium fluoride in methanol: [531]



The same method can also be used for preparation of hydrazinium(1+) azide or ammonium azide. It melts at 337 K (64 °C) and begins to decompose exothermically, with a peak at 387 K (114 °C). The theoretical density calculated from XRD data is 1.611 g/cm³.

6 Alkylhydroxylammonium Salts

One, two, or three hydrogen atoms on hydroxylamine can be substituted by alkyl groups on either the N-atom or the O-atom or both. When writing the name “alkylhydroxylamine,” one must always indicate the location where the alkyl substitution has taken place. Both types of substituted derivatives and their salts are known [532]. The most frequently used substituent is the methyl group, leading to the isomers *O*-methylhydroxylamine and *N*-methylhydroxylamine:



Both groups of compounds are potential rocket propellants, either in the form of the free base or in the form of their salts with oxidizing acids, such as nitrates and perchlorates.

The length of the alkyl group will rarely exceed two carbon atoms, so the energy contributed by the —NHOH group is not too diluted. Methyl substituted hydroxylamines are the ones examined most frequently as potential rocket propellants. They have a combustible alkyl group and an oxygen-carrying group in the same molecule and would make potential monopropellants.

In trying to decide whether the *O*-alkylhydroxylamines or *N*-alkylhydroxylamines should be discussed first, it was arbitrarily decided to do the *O*-alkyl hydroxylamine compounds first and the *N*-alkyl compounds last.

6.1 *O*-Methylhydroxylamine

O-methylhydroxylamine, hydroxylamine, *O*-methyl-; methoxyamine, $\text{H}_3\text{C}-\text{O}-\text{NH}_2$, $\text{C}_1\text{H}_5\text{N}_1\text{O}_1$, CAS RN [67-62-9], is sometimes also called methoxyamine. It forms stable salts with many acids, including nitric acid and perchloric acid. The free base and the chloride salt are commercially available, although the prices seem unreasonable. Isomers of *O*-methyl hydroxylamine are *N*-methyl hydroxylamine and aminomethanol $\text{H}_2\text{NCH}_2\text{OH}$.

6.1.1 Preparation of *O*-Methylhydroxylamine

O-alkylhydroxylamines can be prepared by reaction of chloramine with sodium alcoholate of the alcohol intended as the alkyl rest [533].

O-methylhydroxylammonium chloride can be prepared by alkylating potassium hydroxylaminedisulfonate with dimethyl sulfate or by reaction of sulfamic acid $\text{NH}_2\text{OSO}_3\text{H}$ with sodium alcoholates in alcohols containing a polar aprotic solvent [534]. Thus, 3.0 mol NaOMe in 378 g MeOH was added over 30 min at $<283\text{ K}$ ($<10^\circ\text{C}$) to a suspension of 1.0 mol $\text{NH}_2\text{OSO}_3\text{H}$ in 1200 g MeCN, and the mixture was stirred 3 h at 293 K (20°). NH_2OMe was distilled off at 313 K (40°C) and 20 kPa (200 mbar) and treated with acids to make the desired salt.

Another process obtains *O*-methylhydroxylamine by reacting an alkali metal salt of hydroxylaminedisulfonic acid with an alkyl chloride to form an alkali metal salt of an *O*-substituted hydroxylaminedisulfonic acid, which will then be hydrolyzed [535]. Thus, methyl chloride was added to a mixture of hydroxylaminedisulfonic acid disodium salt and 50% NaOH in a pressure vessel, and the resulting mixture was stirred at 323 K (50°C) for 2 h to give a product containing *O*-methylhydroxylaminedisulfonic acid disodium salt, which was hydrolyzed with sulfuric acid and then neutralized with aqueous NaOH to give *O*-methylhydroxylamine by distillation with a boiling point of 322 K (49°C) in 80% yield.

O-methylhydroxylamine in mixtures with other fuels has been proposed as a rocket fuel [536].

6.1.2 Physical Properties of *O*-Methylhydroxylamine

The boiling point of *O*-methylhydroxylamine is 322.6 K (49.5°C). The density of *O*-methylhydroxylamine at 293 K is 0.9069 g/cm^3 [537]. *O*-methylhydroxylamine has a melting point of 186.7 K (-86.4°C), a boiling point of 321.2 K (48.1°C), a heat of evaporation of 32.2 kJ/mol (7.71 kcal/mol), and a Trouton constant of 24.0 [538]. The vapor pressure of *O*-methylhydroxylamine can be calculated from

$$\log P = -2433.7/T + 23.9284 - 5.3746 \log T$$

where P is the pressure in mmHg and T is the temperature in kelvin. The basicity constant pK_b of *O*-methylhydroxylamine at infinite dilution is $pK_b = 9.25 \pm 0.02$; this compares to 8.04 ± 0.02 for the *N*-methylhydroxylamine isomer.

The IR spectra of CH_3ONH_2 , CH_3OND_2 , $\text{CH}_3\text{ONH}_3\text{Cl}$, and $\text{CH}_3\text{OND}_3\text{Cl}$ were obtained in the region $4000\text{--}400\text{ cm}^{-1}$ with the samples in the form of thin crystalline films at liquid nitrogen temperature [539]. With the exception of the CH_3 and NH_3^+ torsions, all the fundamentals for methoxyamine and methoxyammonium ion have been observed and assigned. The assignments for $\text{CH}_3\text{ONH}_3^+$ ion were readily correlated with those for CH_3ONH_2 , and for both species the assignments for the A' vibrations were consistent with the product rule.

The liquid state IR spectra of the *O*-alkylhydroxylamines $n - \text{C}_n\text{H}_{2n+1}\text{ONH}_2$, $n = 1, 2, 4, 6, 8$, or 10 in the range $3650\text{--}375\text{ cm}^{-1}$ and the Raman spectra of the compounds $n = 1, 6, 8$, or 10 were measured and compared for assignment of the absorption bands to molecular vibrations [540].

6.1.3 Chemical Properties of *O*-Methylhydroxylamine

O-methylhydroxylamine H_3CONH_2 , with a pK_a of 4.66 ± 0.70 , is a stronger base than hydroxylamine HONH_2 . The positive induction effect of alkyl groups causes a higher basicity of aliphatic amines with respect to ammonia, but the alkylation of hydroxylamine brings about a decrease in the pK_a values of alkylhydroxylamines in comparison with hydroxylamine. This effect was described in earlier literature but remained without explanation until it was examined again in 1975 [541]. *N*-alkylated hydroxylamines were stronger bases than *O*-alkylated hydroxylamines due to hydrogen-bonding effects.

6.1.3.1 *O*-Substituted Hydroxylammonium Salts

The melting point of *O*-methylhydroxylammonium chloride is $422\text{--}423\text{ K}$ ($149\text{--}150^\circ\text{C}$). The melting point of *O*-ethylhydroxylammonium chloride is $398\text{--}399\text{ K}$ ($125\text{--}126^\circ\text{C}$). The boiling point of the *O*-ethylhydroxylamine free base is 342 K (69°C).

6.1.3.2 *O*-Methylhydroxylammonium Nitrate

O-methylhydroxylammonium nitrate, MAN, $\text{H}_3\text{CON}^+\text{H}_3\text{ NO}_3^-$, $\text{C}_1\text{H}_6\text{N}_2\text{O}_4$, with a molecular mass of 110.069 g/mol and an oxygen balance of -14.5% , is a candidate ingredient for water-soluble monopropellants.

The salts of methoxyamine were evaluated as additives to hydrazine to produce low-freezing storable monopropellants. Further investigation of these salts as propellant constituents was done in ternary systems, adding H_2O as an additional freezing point depressant so that the salt content could be kept at a safer level.

6.1.3.3 Toxicity of *O*-Methylhydroxylammonium Nitrate

In vitro rat hepatocyte toxicity and bacteria (*Salmonella*) genotoxicity assays were performed on 13 high-energy chemicals that are candidates for potential replacement monopropellants for hydrazine [542]. The chemicals were mostly hydrazine derivatives and amino compounds in the form of their nitrate salts. The results in hepatocytes showed a dose-dependent decrease in mitochondrial activity, an increase in lactate dehydrogenase leakage, and depletion of GSH levels. *O*-methylhydroxylammonium nitrate displayed medium toxicity (HDN > EAN > MAN). Results of genotoxicity tests (Ames assay) indicated that *O*-methylhydroxylammonium nitrate is mutagenic.

6.1.3.4 *O*-Methylhydroxylammonium Perchlorate

O-Methylhydroxylammonium perchlorate, methoxyammonium perchlorate, MAP, $\text{H}_3\text{CON}^+\text{H}_3\text{ClO}_4^-$, $\text{C}_1\text{H}_6\text{N}_1\text{O}_4\text{Cl}$, with a molecular mass of 147.51 g/mol, was a candidate ingredient for monopropellants, but its shock sensitivity prevented further work on the pure compound. Mass spectroscopic analysis of decomposition products during slow ramp-up thermal analysis was used to study the thermal decomposition of methoxyammonium perchlorate [486]. The activation energy for the dissociation of methoxyammonium perchlorate was 125 kJ/mol between 326 and 350 K (30 kcal/mol, 53 to 77 °C).

6.2 Methylenedioxyamine

Not just one but two hydrogens on methane can be replaced by oxyamino groups, leading to $\text{H}_2\text{N}-\text{O}-\text{CH}_2-\text{O}-\text{NH}_2$, methylenedioxyamine, which forms stable salts with strong acids.

Other authors have called this compound methylene**b**isoxamine, but it is our understanding of chemical nomenclature that bis and tris and tetrakis as prefixes are to be used only if the rest of the name already contains di or tri or tetra to indicate the presence of two, three, or four substituents or in the word tridecyl or tetradecyl. The International Union of Pure and Applied Chemistry (IUPAC) nomenclature rules state, “However, the multiplying prefixes ‘bis-’, ‘tris-’, etc., are used instead of ‘di-’, ‘tri-’, etc., when the use of the latter would result in a potential ambiguity.” *Chemical Abstracts* uses a two-part nomenclature that may be systematic but is not very convenient, e.g., hydroxylamine, *O,O'*-methylenebis-. Such nomenclature is suitable for an index but not for running text. If conducting a literature search, one will have to search under both names, methylenedioxyamine and methylenebisoxamine. The name may also have been split into two words: methylene bisoxamine or ethylene bisoxamine. The location of the bonds between the heteroatoms and the carbon skeleton is not always indicated, but it could be *O,O'* or *N,N'*.

O,O'-methylenedioxyamine, also known as *O,O'*-methylenedioxamine, *O,O'*-methylenebisoxamine, MBO; hydroxylamine, *O,O'*-methylenebis-; $\text{H}_2\text{N}-\text{O}-\text{CH}_2-\text{O}-\text{NH}_2$, $\text{C}_1\text{H}_6\text{N}_2\text{O}_2$, CAS RN [40770-44-3], is not very stable as the free base, but it is stable enough to be distilled under vacuum. It can be prepared by hydrolysis of methylene-*O,O'*-di(ethylacethydroximate) with hydrochloric acid in diglyme as the solvent, isolation as the hydrochloride, followed by hydrolysis of the chloride salt solution and liberation of the free base by reaction with alcoholic sodium hydroxide [543]. The preparation of the methylenedioxyamine precursor is described in [544]. The free base is a colorless oil with a freezing point of 265 to 264 K (−8 to −9°C) and a boiling point of 340 K (67°C) at 3 mm Hg. The free base can be distilled under vacuum at 340 K/0.4 kPa (67°C/3 mm Hg). Methylenedioxyamine is a slightly viscous liquid with a refractive index $n_D = 1.4625$, which is thermally stable when pure to 443 K (170°C). At temperatures above 443 K (170°C), detonation can occur. Its melting point is approximately 273 K (0°C); however, it tends to form a viscous liquid or glass when cooled below that temperature. The heat of formation is −92 kJ/mol (−22 kcal/mol), and the drop-weight sensitivity is $H_{50} = 60$ kg-cm.

6.2.1 *O*-Methylenedioxyamine Salts

Normally, if an $-\text{NH}_2$ group is protonated to become a cation, the new compound is an ammonium salt, called methylammonium nitrate and not methylamine nitrate. In the case of methoxyamines, this nomenclature rule has not always been followed, and the name of the unprotonated hydroxylamine has been kept in several publications. Several methylenedioxyamine salts have been prepared and proposed as potential rocket propellants [545]. The salts described in the patent literature [546] include the methylenedioxyamine diperchlorate, with a melting point of 388 K (115°C).

The monoprotonated and diprotonated salts of methylene dioxyamine with nitric acid, perchloric acid, trinitromethane, and dinitramidic acid have been prepared as crystalline materials and characterized by DSC, IR, Raman, NMR, and elemental analysis [547–549]. The methylene dioxyamine mononitrate was obtained as colorless crystals with a melting point of 385 K (112°C) and the dinitrate with a melting point of 403 K (130°C). Methylene dioxyamine monoperchlorate was obtained as colorless crystals with a melting point of 404 K (131°C), and the diperchlorate melted at 400 K (127°C). With nitroform, only the monoprotonated salt could be formed. Methylene dioxyamine mononitroformate was obtained as bright yellow crystals with a melting point of 380 K (107°C). The colorless crystals of methylene dioxyamine monodinitramide melted at 369 K (96°C), and the methylene dioxyamine bisdinitramide melted at 358–368 K (85–95°C). The drop-weight sensitivity of the methylene dioxyamine bisdinitramide was less than 5 kg-cm, indicating that this is a very sensitive compound. Friction sensitivity of the monoperchlorate and the monodinitramide salt was less than 0.45 kg_f, indicating that these are indeed extremely sensitive compounds that should not be scaled up to larger-scale preparation.

6.2.2 Methylenedioxyamine Diperchlorate (DOAP)

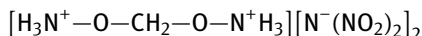
If the hydrolysis of methylene-*O,O'*-di(ethylacethydroximate) is conducted with perchloric acid instead of hydrochloric acid, one obtains the diperchlorate salt, which has a density of 2.0 g/cm³ and a drop-weight sensitivity of $H_{50} = 110$ kg-cm and melts at 391 K (118 °C) [546]. The enthalpy of formation of the diperchlorate salt is -431 kJ/mol (-103 kcal/mol) [550].

Methylenedioxyamine diperchlorate $[\text{H}_3\text{N}^+ - \text{O} - \text{CH}_2 - \text{O} - \text{N}^+\text{H}_3][\text{ClO}_4^-]_2$, $\text{C}_4\text{H}_{10}\text{N}_2\text{O}_4\text{Cl}_2$, has been prepared and its thermal stability studied by thermal analysis (DTA/TGA), with simultaneous identification of the off-gassing by mass spectrometry [551]. The initial step in the thermal decomposition of DOAP occurred at 333 K (60 °C) with the loss of a perchloric acid group to form the monoperchlorate salt as an intermediate. As the temperature increased, the latter underwent a concerted cyclization-cleavage reaction leading to formamide and HAP. The existence of each of the postulated intermediates in the reaction was verified by separate experiments.

A sample of the vacuum-dried DOAP liquefied in the dry box after standing at ambient temperature for 2 weeks [506]. The thermal stability of DOAP was studied at 298, 313, 333, and 353 K (25, 40, 60, and 80 °C). While both HAP and HP-2 showed only trace amounts of gaseous decomposition products after 72 d at 343 K (70 °C), DOAP liberated 2–3 mL of gas per gram at 333 K (60 °C) in 32 d and 13–20 mL at 333 K (60 °C) in 90 d. The gaseous product consisted mainly of CO and lesser amounts of N₂, CO₂, and N₂O.

6.2.3 Other Methylenedioxyamine Salts

Other methylenedioxyamine salts claimed but not characterized included the dinitrate, the dinitroformate, and the dipicrate. Combining this energetic amine with energetic anions from acids like dinitramide



led to an interesting high-energy material, O-methylene dioxammonium(2+) bis-dinitramide, which has not yet found any applications [545]. It was reported to be a colorless oil at room temperature with a melting point of 293 K (20 °C). Repeated studies preparing the salt via cation exchange and neutralization of the free base obtained a purer product in the form of white crystals melting at 368 K (95 °C). The product was very shock sensitive (<5 kg-cm in the drop-weight tester, detonating with a light hammer blow) and had an onset of exotherm at 376 K (103 °C) in DSC [545]. The researchers also synthesized the monodinitramide salt, which had similar properties, melting at 359 K (96 °C), having a drop-weight sensitivity of 12 kg-cm, and showing the onset of an exotherm at 392 K (119 °C).

6.3 *O,O'*-Ethylenedioxyamine

Homologs of the compound *O*-methylenedioxyamine described in the preceding section are *O,O'*-ethylenedioxyamine, also known as *O,O'*-ethylenebisoxamine, ethylene di(oxyamine), 1,2-di(oxyamino)ethane; hydroxylamine, *O*-[2-(aminooxy)ethyl]-; $\text{H}_2\text{NOCH}_2\text{CH}_2\text{ONH}_2$, $\text{C}_2\text{H}_8\text{N}_2\text{O}_2$, CAS RN [5627-11-2] and *O,O'*-propylenedioxyamine, also known as *O,O'*-propylenebisoxamine, 1,3-di(oxyamino)propane; hydroxylamine, *O,O'*-1,3-propanediylbis-; $\text{H}_2\text{NOCH}_2\text{CH}_2\text{CH}_2\text{ONH}_2$, $\text{C}_3\text{H}_{10}\text{N}_2\text{O}_2$, CAS RN [98627-69-1], obtained by adding one or two more $-\text{CH}_2-$ groups.

1,2-di(oxyamino)ethane free base is a solid at room temperature that melts at 398–407 K (125–134 °C) and decomposes at 407 K (134 °C). 1,2-di(oxyamino)ethane-based energetic ionic liquids (EILs) belong to a group of salts that fail to meet the IL designation.

The synthesis, characterization, theoretical performance calculations, and safety properties of energetic salts based on 1,2-di(oxyamino)ethane, ($\text{H}_2\text{NOCH}_2\text{CH}_2\text{ONH}_2$), were investigated, and the salts were characterized by IR, Raman, multi-nuclear (^1H , ^{13}C) NMR, DSC, and elemental analysis, as well as by impact and friction-sensitivity testing [552, 553]. The crystal structures of the monoperchlorate and the double-nitrate salts were identified by single-crystal XRD (Table 36).

The salts with nitrate, perchlorate, trinitroformate, and dinitramidate as the anion behave as ionic liquids and are extremely shock sensitive [554]. In almost all cases, ethylene di(oxyamine) salts were extremely sensitive to impact and friction, often with quite spectacular results being observed, including loud responses and the shearing of the entire steel-pin apparatus on both the drop-weight tester and the friction tester.

1,3-di(oxyamino)propane is a relatively stable liquid with a boiling point of 338–343 K (65–70 °C) at 0.3 mmHg and a glass point of 233 K (–40 °C). The monoprotonated and diprotonated nitrate, perchlorate, and dinitramidate salts of *O,O'*-ethylenebisoxamine were prepared and characterized [555]. Ethylene di(oxyamine) bis(dinitramide) did not crystallize. After workup under vacuum, a viscous straw-colored ionic liquid had been evacuated to a constant weight. The dinitrate salt was a crystalline solid with acceptable properties, but the diperchlorate was very sensitive. The properties of these salts are summarized in Table 36, 37, and 38.

O,O'-ethylenedi(oxyamine) bisdinitramidate melts below 273 K, qualifying it as a room-temperature ionic liquid. Its decomposition temperature is $T_{\text{dec}} = 388 - 393 = 115 - 120$ °C, the impact sensitivity is 20 kg-cm, and the friction sensitivity is $< 4.4 \text{ N} = < 0.45 \text{ kg}_f$. However, this compound proved to be very sensitive, having a highly explosive response and completely destroying the scratcher from the Julius Peters-style friction tester.

The most stable ionic liquid was *O,O'*-ethylenedi(oxyamine) mononitrate, $[\text{H}_2\text{NOCH}_2\text{CH}_2\text{ONH}_3][\text{NO}_3]$, $\text{C}_2\text{H}_9\text{N}_3\text{O}_5$, with a melting point of $T_{\text{melt}} = 346 - 349 = 73 - 76$ °C, a decomposition onset of $T_{\text{dec}} = 353 \pm 80$ °C, impact sensitivity of 94 kg-cm,

Table 36: Properties of energetic salts of *O,O'*-ethylene di(oxyamine).

	Mononitrate	Dinitrate	Monoperchlorate	Diperchlorate	Monodinitramide	Bisdinitramide
Gross formula	C ₂ H ₉ N ₃ O ₅	C ₂ H ₁₀ N ₄ O ₈	C ₂ H ₉ N ₂ O ₆ Cl	C ₂ H ₁₀ N ₂ O ₁₀ Cl ₂	C ₂ H ₉ N ₅ O ₆	C ₂ H ₁₀ N ₈ O ₁₀
Oxygen balance, %	-36.1	-7.1			-20.1	+5.2
Molecular mass	155.110	218.123	192.556	293.014	199.123	306.148
Melting point, °C	73-76	135	134-137 (dec.)	123 or 137	59	<0
Melting point, K	346-349	408	407-410 (dec.)	396 or 410	332	<273
Density ρ _{XRD} , g/cm ³		1.751	1.808			
Crystal structure		Monoclinic	Orthorhombic			
Space group		C2/c	Pbca			
Onset of exotherm, °C	100	165	137	185	75-80	120
Onset of exotherm, K	373	438	410	458	349-353	393
Impact sensitivity, 2-kg, cm	94 kg cm					20 kg cm
Friction sensitivity, N	224 N = 22.8 kg _f					<4.4 N = 0.45 kg _f

Data sources: [553, 555, 556]

Table 37: Melting points and decomposition onset temperatures of ethylene di(oxyamine) salts.

Compound	Melting point		Decomposition onset temperature	
	K	°C	K	°C
[H ₂ NOCH ₂ CH ₂ ONH ₃][NO ₃]	346–349	73–76	353	80
[H ₂ NOCH ₂ CH ₂ ONH ₃][ClO ₄]	407–410	134–137	410	137
[H ₂ NOCH ₂ CH ₂ ONH ₃][N(NO ₂) ₂]	330–332	57–59	348–353	75–80
[H ₃ NOCH ₂ CH ₂ ONH ₃][NO ₃] ₂	403–408	130–135	423	150
[H ₃ NOCH ₂ CH ₂ ONH ₃][ClO ₄] ₂	395–400	122–127	463	190
[H ₃ NOCH ₂ CH ₂ ONH ₃][N(NO ₂) ₂] ₂	<273	<0	388–393	115–120
For comparison: H ₂ NOCH ₂ CH ₂ ONH ₂ free base	398–407	125–134	407	134

Data source: [553]

Table 38: Safety test results for ethylene di(oxyamine) salts.

Compound	Drop height	Friction force	
	kg-cm	kg _f	N
[H ₂ NOCH ₂ CH ₂ ONH ₃][NO ₃]	94	22.8	224
[H ₂ NOCH ₂ CH ₂ ONH ₃][ClO ₄]	<20*	<0.45*	<4.4*
[H ₂ NOCH ₂ CH ₂ ONH ₃][N(NO ₂) ₂]	28	1.5	14.7
[H ₃ NOCH ₂ CH ₂ ONH ₃][NO ₃] ₂	<20	Not tested	Not tested
[H ₃ NOCH ₂ CH ₂ ONH ₃][ClO ₄] ₂	10*	<0.45*	<4.4*
[H ₃ NOCH ₂ CH ₂ ONH ₃][N(NO ₂) ₂] ₂	20	<0.45*	<4.4*

Note: Values with * had a highly explosive response, destroying the striker or scratcher completely.

Data source: [553]

and a friction sensitivity of 224 N = 22.8 kg_f; showing less impact sensitivity (in the Olin Matheson–style drop-weight tester with a 2-kg mass) than the HMX standard (impact sensitivity 34 kg-cm).

6.4 1,3-Propylene-*O,O'*-dihydroxylamine

1,3-propylene-*O,O'*-dihydroxylamine, also known as 1,3-bis(oxyamine)propane; 1,3-propanediamine, *O,O'*-dihydroxy-; hydroxylamine, *O,O'*-1,3-propanediylbis-; H₂N–O–CH₂–CH₂–CH₂–O–NH₂, C₃H₁₀N₂O₂, CAS RN [98627-69-1], is a reactant for preparation of energetic salts. The free base 1,3-di(oxyamine)propane boils at 338–343 K (65–70 °C) at 0.3 mm Hg and solidifies to a glass at 233 K (–40 °C).

The nitrate, perchlorate, trinitromethide, and dinitramidate salts of this compound have very low melting points, which classify them as ionic liquids.

They are extremely shock sensitive and could not be used as rocket propellants [554]. This compound forms complexes with metal ions and has been evaluated for pharmaceutical purposes.

6.5 *N*-Methylhydroxylamine

N-methylhydroxylamine; also known as hydroxylamine, *N*-methyl; *N*-hydroxymethanamine, methylhydroxylamine, *N*-hydroxymethylamine, *N*-methylhydroxylamine, H_3CNHOH , $\text{C}_1\text{H}_5\text{N}_1\text{O}_1$, CAS RN [593-77-1], is an isomer of *O*-methylhydroxylamine and aminomethanol $\text{H}_2\text{NCH}_2\text{OH}$. *N*-methylhydroxylamine can be used as an oxygen scavenger in boiler feedwater treatment as a replacement for hydrazine hydrate.

6.5.1 Preparation of *N*-Methylhydroxylamine

N-methylhydroxylamine can be prepared by hydrogenation of nitromethane in 3.5- N H_2SO_4 at 35–40° in the presence of poisoned Pt/C catalysts [557], in the presence of a palladium catalyst, [558] or by electrolytic reduction of nitromethane in aqueous solution. Synthesis of *N*-methylhydroxylamine by electroreduction of nitromethane can be carried out in aqueous acidic medium with Monel, nickel, stainless steel, or lead cathodes and anodes separated by a cation-exchange membrane [559]. The electroreduction of nitromethane can also be carried out on mercury cathodes [560], on gold electrodes [561], or on Cu and Cu/Hg as the cathode [562].

6.5.2 Physical Properties of *N*-Methylhydroxylamine

N-methylhydroxylamine has a melting point of 311.6 K (38.5°C), a boiling point of 388 K (115.0°C), a heat of evaporation of 49.7 kJ/mol (11.88 kcal/mol), and a Trouton constant of 30.6 [538]. The vapor pressure of solid *N*-methylhydroxylamine can be calculated from

$$\log P = \frac{13.7}{T} - 4.261 + 5.63 \times 10^{-5} T$$

and the vapor pressure of molten *N*-methylhydroxylamine can be calculated from

$$\log P = -\frac{2597}{T} + 9.570$$

where P is the pressure in mmHg and T is the temperature in kelvin. The $\text{p}K_{\text{b}}$ of *N*-methylhydroxylamine at infinite dilution is 8.04 ± 0.02 ; this compares to $\text{p}K_{\text{b}} = 9.25 \pm 0.02$ for the *O*-methylhydroxylamine isomer.

6.5.3 Molecular Structures of *N*-Methylhydroxylamine and Isomers

Alkylation of the NH_2 group in hydroxylamine changes the proton-transfer barriers. The physical properties of HAN solutions are determined by hydrogen bonding and proton transfer between neutral molecules and ion clusters in the ionic liquid structure. The effects of alkyl (CH_3 or C_2H_5) substitutions for hydrogen on the proton-transfer barriers in ammonium nitrate and HAN were studied using *ab initio* electronic structure calculations [563]. The optimized hydrogen-bonded neutral-pair structures and the ion-pair transition states for proton transfer were calculated. Zero-point energies, basis-set superposition corrections, and single-point MP2 calculations on the optimized structures were applied to obtain binding energies for these hydrogen-bonded molecules. The alkyl substituents strengthen the hydrogen bonding in both the neutral-pair and ion-pair complexes, but the ion-pair forms are stabilized to a greater extent, which results in an effective decrease in the barrier to proton transfer and exchange. The energy barrier to proton transfer in AN is 33.89 kJ/mol (8.1 kcal/mol), whereas in methylammonium, ethylammonium, and dimethylammonium nitrate, this barrier decreases to 17.15, 15.48, and 5.86 kJ/mol (4.1, 3.7, and 1.4 kcal/mol), respectively. Alkyl substitution reduces the proton-transfer barrier, and dialkyl substitution reduces it even further. A similar trend holds for HAN and *N*-methylhydroxylammonium nitrate: The barrier to proton transfer from the most stable neutral-pair HAN to the lowest-energy ion-pair configuration is 56.9 kJ/mol (13.6 kcal/mol), whereas this barrier decreases to 39.75 kJ/mol (9.5 kcal/mol) in the corresponding MeHAN complex.

Computer calculations were performed to predict the heat capacity, enthalpy, entropy, bond lengths, and bond angles of MeONH_2 , HONHMe , and HONMe_2 [564].

Electron-diffraction studies showed that MeNHOR and R_2NOMe ($\text{R} = \text{H}, \text{Me}$) exist in two conformations differing by a 180° rotation about the $\text{N}-\text{O}$ bond, as previously predicted by MO calculations, but with a much smaller free-energy difference (~ 2.5 kJ/mol = ~ 0.6 kcal/mol) than that predicted by calculations (~ 29 – 46 kJ/mol = ~ 7 – 11 kcal/mol) [565].

Gas-phase He(I) photoelectron spectra were measured for H_2NOH and the five methylhydroxylamines [566]. To study the interactions of the $n(\text{N})$ and $n(\text{O})$ orbitals, MINDO/2 calculations were performed for various conformations of the hydroxylamines. The *trans* forms are the most stable conformations, but *cis* conformers cannot be excluded.

The MNDO/H approximation has been used to calculate bond lengths, effective atomic charges and bond orders, and some physicochemical properties of methyl derivatives of hydroxylamine [567].

Molecular orbital calculations showed that hydroxylamine and methylated hydroxylamines exist in two conformations that are 11.7–26.3 kJ/mol (2.8–6.3 kcal/mol) apart in energy and that the length of the $\text{N}-\text{O}$ bond does not change upon methylation [568].

6.5.4 *N*-Methylhydroxylammonium Salts

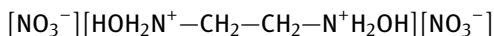
N-methylhydroxylamine can be imagined as *N*-methylation of NH_2OH or by replacing a hydrogen in methane CH_4 by an $-\text{NHOH}$ group. In carrying the synthesis of energetic salts by replacing hydrogen on methane by hydroxylamino groups one step further, not just one but two hydrogens on methane can be replaced by hydroxylamino groups, and the resulting methylene dihydroxylamine can form useful oxidizer salts with perchloric acid.

6.5.5 Methylene dioxyammonium Salts

Instead of substituting only one hydrogen atom in methane with an NHOH group, up to two hydrogen atoms in methane can be substituted with hydroxylamine groups, and the di(hydroxylamino)methane can be reacted with diluted perchloric acid, making an even better oxidizer than *O*-methylhydroxylammonium perchlorate. *N,N'*-methylene dihydroxylamine, also known as methylene bishydroxylamine, di(oxyamine)methane; methanediamine, *N,N'*-dihydroxy-; $\text{HO}-\text{NH}-\text{CH}_2-\text{NH}-\text{OH}$, $\text{C}_1\text{H}_6\text{N}_2\text{O}_2$, CAS RN [4410-93-9], is not very stable as the free base, but the free base and several of its salts have been prepared and evaluated as propellant ingredients [569, 570]. The heat of formation of methylene dioxyamine diperchlorate dissolved in ethylene glycol was determined by oxygen bomb calorimetry as -437 kJ/mol (-104.4 kcal/mol) [571]. The heats of formation of methylene dioxyamine and methylene dioxyamine diperchlorate were derived from oxygen bomb combustion calorimetry and solution calorimetry [572]. Selected best values for the two compounds were -94.6 kJ/mol (-22.6 kcal/mol) for liquid methylene dioxyamine and -431 kJ/mol (-103.0 kcal/mol) for crystalline methylene dioxyamine diperchlorate.

6.6 1,2-Ethane di(*N*-hydroxylammonium) Nitrate

Similar to the methylenedioxyamine, hydroxylamino groups can be introduced in both the 1-position and the 2-position of ethane to form 1,2-ethanedioxyamine; 1,2-ethanediamine, *N,N'*-dihydroxy-; $\text{HO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{OH}$, $\text{C}_2\text{H}_8\text{N}_2\text{O}_2$, CAS RN [30718-86-6], also called 1,2-ethylenedioxyamine. The parent free base is not very stable, but its salts have been prepared and characterized. The melting point of 1,2-ethane di(*N*-hydroxylammonium) nitrate



is below room temperature, and it is difficult to get it to crystallize. It is a perfect ionic liquid, except its thermal stability and shock sensitivity are less than optimal. The density of the melt is 1.93 g/cm^3 . Its oxygen balance is -29.3% .

For the preparation of ethylene dihydroxylamine, 1,2-ethylene-*N,N'*-dihydroxylamine, 1,2-di(hydroxylamino)ethane, $\text{HO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{OH}$,

the intermediate 1,2-bis(phthalimidooxy)ethane was first prepared via the treatment of 1,2-dibromoethane with *N*-hydroxyphthalimide, and then hydrazinolysis gave the ethylene dihydroxylamine [573].

The nitrate, perchlorate, trinitromethide, and dinitramide salts of this compound have very low melting points, which classifies them as ionic liquids. They are extremely shock sensitive and could not be used as rocket propellants [554]. The most stable ionic liquid in this group was 1,2-ethylene-*N,N'*-bis(hydroxylammonium) mononitrate, with T_m 346–349 K (73–76 °C), T_{dec} 353 K (80 °C), impact sensitivity 94 kg-cm, friction sensitivity 22.8 kg, and showing less impact sensitivity (Olin Matheson-style drop-weight tester with 2-kg mass) than the HMX standard (34 kg cm). Its melting and decomposition temperatures, however, fell short of the desirable values. On the whole, ethylene bis(oxyammonium) salts were extremely sensitive to impact and friction, possessed fairly narrow liquid ranges that were followed by rapid and highly exothermic decompositions, and were unstable (exhibiting visible changes) even when stored under inert atmospheres. See also [556].

6.7 1,3-Propylene-*N,N'*-Dihydroxylamine

1,3-propylene-*N,N'*-dihydroxylamine, 1,3-bis(oxyamine)propane; 1,3-propanediamine, *N,N'*-dihydroxy-; $\text{HO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{OH}$, $\text{C}_3\text{H}_{10}\text{N}_2\text{O}_2$, CAS RN [337905-76-7] is a reactant for the preparation of energetic salts.

6.8 *N,N*-Dialkylhydroxylamines

N,N-dimethylhydroxylamine (DMHA) has been used in the separation of uranium from plutonium and neptunium in the reprocessing of spent fuel rods from nuclear power plants. *N,N*-dimethylhydroxylamine has a melting point of 290.7 K (17.6 °C), a boiling point of 373.7 K (100.6 °C), a heat of evaporation of 40.4 kJ/mol (9.670 kcal/mol), and a Trouton constant of 25.9 [538]. The molecular structure, bond lengths, bond angles, electron density, and lone-electron pair interactions of *N,N*-dimethylhydroxylamine have been computed in comparison to other hydroxylamine derivatives [574].

N,N-diethylhydroxylamine in the form of its nitrate salt has been used in HAN-based liquid gun propellants (*Encyclopedia of Monopropellants*, chapter “Hydroxylammonium Nitrate-Based Monopropellants”). The enthalpy of formation of *N,N*-diethylhydroxylamine is -174.8 ± 7 kJ/mol in the liquid state and -121.8 ± 7 kJ/mol in the vapor state.

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Mixed Nitric Acid

Nitric Acids

Although chemically speaking there is only one nitric acid with the formula HNO_3 , we have subdivided this chapter into three subchapters in *Encyclopedia of Oxidizers*, dealing with four technical grades of nitric acids of different chemical composition: **white fuming nitric acid** (WFNA), **red fuming nitric acid** (RFNA), and **mixed acid** (MA). There are two variants of RFNA, **inhibited red fuming nitric acid** (IRFNA) and **high-density acid** (HDA).

1 Mixed Acid

The addition of concentrated sulfuric acid or its anhydride to nitric acid (WFNA) shortens the ignition delay with various organic amines. This mixture is called mixed acid, MA. It may also be called mixed nitric acid. Typical MAs contain 88% WFNA and about 12% fuming sulfuric acid (oleum). Organic preparative chemistry has used the addition of sulfuric acid to nitric acid as a means to introduce the nitro or nitrate group into organic compounds for several centuries. This used to be called nitrating acid. Both the improved ignition delay and the increased yield of nitro compounds in organic syntheses are caused by the formation of nitronium ions NO_2^+ in mixtures.

MA is a mixture of about 88 mass-% WFNA and 12 mass-% fuming sulfuric acid with an SO_3 content of 20 mass-%. Fuming sulfuric acid is often described by its traditional name, oleum. The composition of MA is similar but different from nitric acid/sulfuric acid mixtures used in preparative organic chemistry for the nitration of aromatic compounds or alkanols to produce nitro and nitrate ester compounds.

Though MA has no advantages over WFNA or RFNA as far as specific impulse (Isp) performance is concerned, the opposite may be true. MAs were used during World War II because the addition of oleum enhanced the hypergolic ignition of WFNA/hypergolic fuel mixtures with aromatic amines, vinyl ethers, and TONKA amines. Similar mixtures were prepared from nitric acid with perchloric acid replacing some or all of the sulfuric acid, but they have not found flight applications [1].

1.1 Physical Properties of Mixed Acid

The physical properties listed here are of interest for the use of MA as a nitrating acid (still widely used in production of nitrated explosives and nitrocellulose for double-base propellants) and not so much as a rocket propellant oxidizer (because it is no longer used as such).

1.1.1 Freezing Point of Mixed Acid

The freezing points and heat of mixing in the ternary system $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ were examined over a wide range of compositions [2]. The freezing point of MA is only 10 °C lower than that of pure nitric acid. Mixing nitric acid and sulfuric acid or even nitric acid and oleum will result in the dehydration of nitric acid, with partial conversion to its anhydride, dinitrogen pentoxide.

1.1.2 Vapor Pressure of Mixed Acid

The vapor pressure of MA is only slightly lower than that of WFNA.

1.1.3 Thermodynamic Properties of Mixed Acid

Mixing WFNA and concentrated sulfuric acid or oleum is an exothermic process. The enthalpies of this mixing process can be read from a nomogram [3].

When preparing MA from concentrated nitric acid and concentrated sulfuric acid or even oleum with an excess of free SO_3 , the mixing heat is exothermic. The integral heats of solutions of HNO_3 in three different grades of H_2SO_4 (different levels of free SO_3 or H_2O) were measured calorimetrically at 298 K, but only for low initial HNO_3 concentrations [4–6]. One of the species formed in MA is $\text{NO}_2^+ \text{HSO}_4^-$. In oleum containing 2.58–4.93% of free SO_3 and with HNO_3 concentrations of 0.1 mol/L, the heat of solution value was $-85.4 \pm 0.8 \text{ kJ/mol}$ ($-20.42 \pm 0.2 \text{ kcal/mol}$).

1.2 Chemical Properties of Mixed Acid

MA does not have a higher specific impulse than WFNA, but the density-specific impulse may be improved slightly due to the higher density of sulfuric acid.

The main reason for the introduction of MA during World War II was that prior to the invention of alkylhydrazines, the ignition delays with various organic amines (aniline, xylidine, triethylamine) could be improved by the addition of sulfuric acid to nitric acid.

The early versions of the Agena upper stage used MA with unsymmetrical dimethylhydrazine (UDMH). MA was used in the early Agena upper stages, but MA is no longer used in the United States.

1.2.1 Analysis Methods for Mixed Acid

The purpose of analyzing MA is to verify the H_2SO_4^- , HNO_3^- , H_2O^- , NOHSO_3^- , and NO_2^- content of a mixture. Several different analysis methods are described in the literature [7, 8].

Extended storage of MA can result in the precipitation of insoluble corrosion products (metal sulfates and metal nitrates), which can clog filters and injector orifices [9].

The sludge must be filtered before conducting an analysis of the liquid, and the precipitate must be analyzed separately.

1.3 Materials of Construction for Mixed Acid

Basically, the same construction materials that are used for WFNA or RFNA can also be used for MA [10].

2 Other Mixtures with Nitric Acid

Attempts were made to lower both the freezing point and the vapor pressure of WFNA by adding other chemicals (other than water or dinitrogen tetroxide). These additives should not worsen the rocket performance of nitric acid as an oxidizer. The additives in this category are mostly nitrates, i.e., salts of nitric acid with various metals or organic bases.

2.1 Solutions of Nitrates in Nitric Acid

2.1.1 Ammonium Nitrate Solutions in Nitric Acid

Solutions of ammonium nitrate in diluted nitric acid have been proposed as high-density oxidizers [11]. They are less corrosive than WFNA or RFNA, which they were intended to replace.

2.1.1.1 Density of Solutions of Ammonium Nitrate in Nitric Acid

The densities of solutions of ammonium nitrate in nitric acid were measured for a wide range of compositions and over two temperature ranges from about 278 to 298 K (5 to 25 °C) and from 269 to 248 K (−4 to −25 °C) in comparison with the densities of solutions of tetramethylammonium nitrate [11–13]. The partial molar volumes of both solutes went through a minimum near 1-molal concentrations. Density-temperature data were obtained for each solute up to concentrations of about 22 mass-%. The density of nitric acid increases with the addition of ammonium nitrate and decreases with the addition of tetramethylammonium nitrate. The data were fitted to straight lines in the form of the equation

$$\rho = \rho_0 - \alpha t$$

where ρ is the density at temperature t in g/cm³, ρ_0 is the density at 0 °C, α is the slope (density coefficient) of the linear function, and t is the temperature in °C. The results are summarized in Table 1 and illustrated in Figure 1.

Table 1: Density coefficients of solutions of ammonium nitrate in nitric acid.

Molality	ρ_0 , g/cm ³	– (negative) α
Ammonium nitrate/nitric acid ratio		
0.02754	1.5491	0.001766
0.05778	1.5500	0.001782
0.2759	1.5511	0.001716
0.5145	1.5548	0.001642
0.8484	1.5625	0.001553
1.125	1.5699	0.001502
1.416	1.5751	0.001443
1.721	1.5795	0.001408
1.876	1.5825	0.001386
2.260	1.5874	0.001344
2.695	1.5922	0.001309
3.331	1.5969	0.001235

Data source: [12]

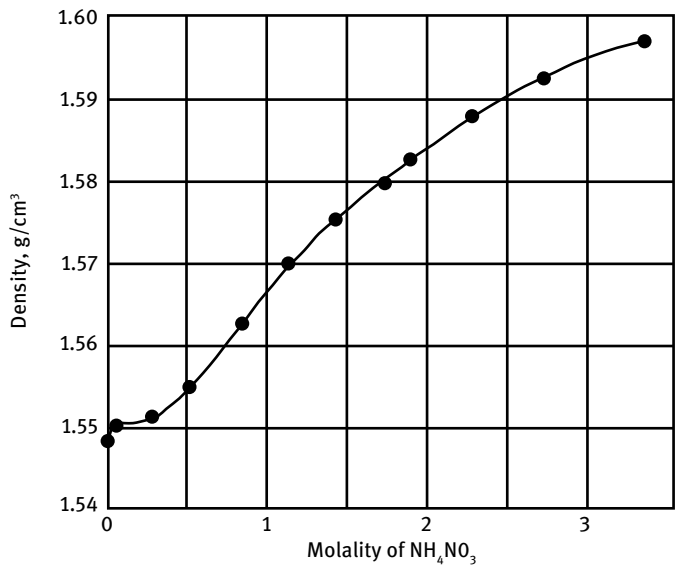


Figure 1: Density of ammonium nitrate solutions in nitric acid at 273 K. (Reproduced and modified from [12].)

2.1.2 Alkylammonium Nitrate Solutions in Nitric Acid

Alkylammonium nitrate solutions in nitric acid were studied mostly as monopropellants, not so much as methods to lower the freezing point or vapor pressure of WFNA as an oxidizer. Monopropellants made of alkylammonium nitrate solutions in nitric acid were called “CAVEA”.

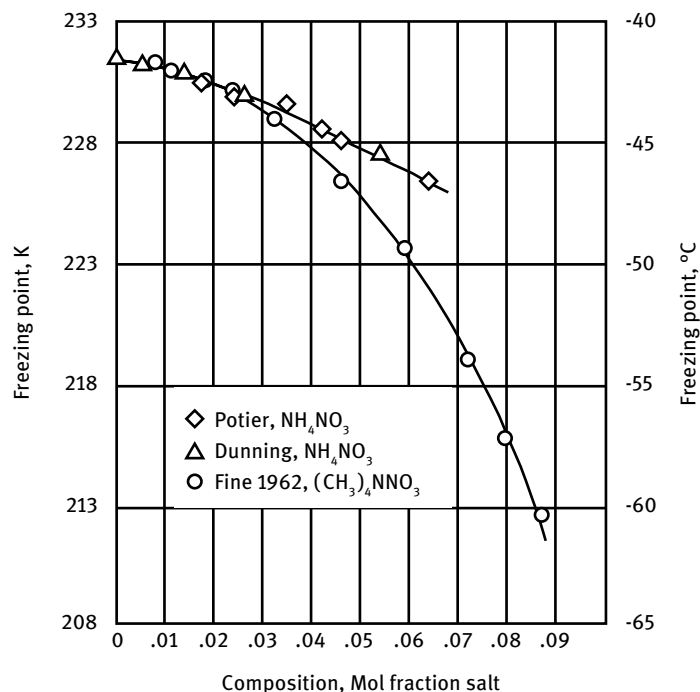


Figure 2: Comparison of freezing point depression in nitric acid caused by ammonium nitrate or tetramethylammonium nitrate. (Reproduced and modified from [13].)

2.1.2.1 Freezing Points of Alkylammonium Nitrate Solutions in Nitric Acid

On a molar concentration scale, tetramethylammonium nitrate is a more effective freezing point depressant than ammonium nitrate, as shown by a comparison of Figures 1 and 2.

The phase diagram of tetramethylammonium nitrate $[(\text{CH}_3)_4\text{N}]\text{NO}_3$ solutions in nitric acid was measured over a temperature range from 199 to 325 K (-74 to $+52^\circ\text{C}$), covering a range of salt concentrations up to about 50 mass-% [14, 15]. The results are illustrated in Figure 3.

The compositions at the two shallow maxima (shoulders) correspond closely to acid:salt mol ratios of 6:1 and 3:1. Such 6:1 and 3:1 complexes represent a much higher degree of solvation than the 2:1 complexes reported for NO_2 , KNO_3 , and NH_4NO_3 with nitric acid. This is because the tetraalkylammonium ion is a larger ion than K^+ or NH_4^+ ions.

Such solutions of organic amine nitrates in nitric acid are not only usable as oxidizers but may also react as monopropellants (“Cavea” propellants, see *Encyclopedia of Monopropellants*, in the chapter “Nitric Acid or Perchloric Acid-Based Monopropellants”).

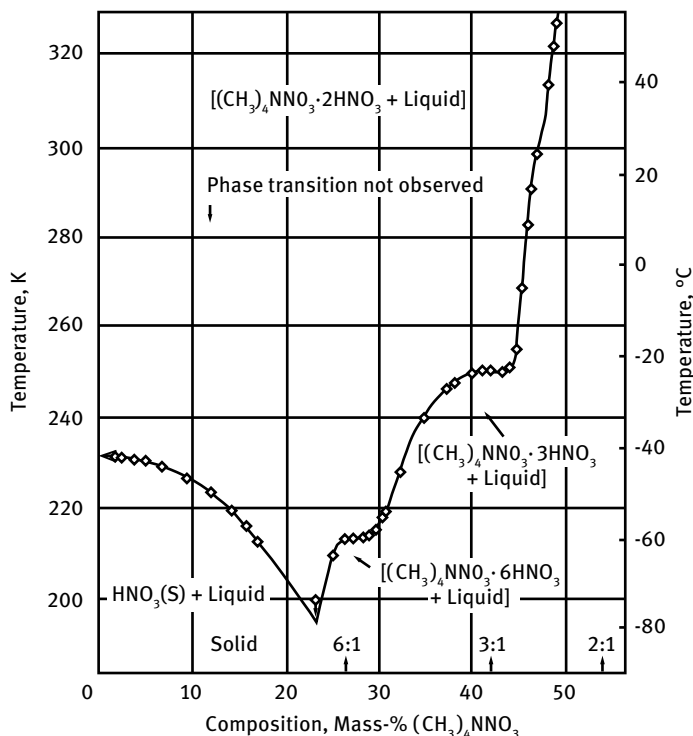


Figure 3: Melting point diagram of tetramethylammonium nitrate/nitric acid system. (Reproduced and modified from [13].)

2.1.2.2 Densities of Alkylammonium Nitrate Solutions in Nitric Acid

The densities of solutions of tetramethylammonium nitrate in nitric acid were measured for a wide range of compositions and over two temperature ranges from about 278 to 298 K (5 to 25 °C) and from 269 to 248 K (−4 to −25 °C) in comparison to the density of solutions of ammonium nitrate [12]. The partial molar volumes of both solutes went through a minimum near 1-molal concentrations. Density-temperature data were obtained for each solute up to concentrations of about 22 mass-%. The density of nitric acid increases with the addition of ammonium nitrate and decreases with the addition of tetramethylammonium nitrate. The data were fitted to straight lines in the form of the equation

$$\rho = \rho_0 - \alpha t$$

where ρ is the density at temperature t in g/cm^3 , ρ_0 is the density at 0 °C, α is the slope (density coefficient) of the linear function, and t is the temperature in °C. The results are summarized in Table 2 and illustrated in Figure 4.

Table 2: Density coefficients of solutions of tetramethylammonium nitrate in nitric acid.

Molality	ρ_0 , g/cm ³	– (negative) α
Tetramethylammonium nitrate/nitric acid		
0.05875	1.5443	0.001797
0.1293	1.5392	0.001741
0.2207	1.5289	0.001707
0.4000	1.5144	0.001634
0.4138	1.5116	0.001690
0.5877	1.4998	0.001549
0.6458	1.4965	0.001587
0.6713	1.4942	0.001585
0.8453	1.4837	0.001481
1.039	1.4720	0.001426
1.330	1.4564	0.001364
1.635	1.4419	0.001349
0.761	1.4350	0.001251
2.072	1.4188	0.001201

Data source: [12]

2.1.3 Alkali Metal Nitrate Solutions in Nitric Acid

NaNO_3 and KNO_3 dissolve in 100% HNO_3 with the formation of ions, which is shown by the Raman spectrum. The heat effect is 4184 J (1000 cal) evolved per mol of salt dissolved in a large excess of HNO_3 . The vapor pressure of the solution decreased rapidly with increasing salt concentration [16]. This indicates complex formation between the HNO_3 and NO_3^- . In 80% aqueous HNO_3 the degree of ionization is approximately 2%, and the HNO_3 molecules are in large part hydrated. The vapor pressure of water from this solution is only 266 Pa (2 mm Hg) at 303 K (30 °C). The addition of NaNO_3 or KNO_3 to this solution decreased the HNO_3 vapor pressure and increased the water vapor pressure. This indicated that NO_3^- is a stronger base than water. When a mol of water was added to a large excess of HNO_3 of varying concentrations, the heat evolved increased up to a sharp maximum of approx. 16.7 kJ (4 kcal) for 97% HNO_3 and then decreased very rapidly.

In the IR spectrum, a band at 3400 cm^{-1} characteristic of pure HNO_3 disappeared when the composition was $1\text{ KNO}_3 + 2\text{ HNO}_3$ [17]. At the same time, three new bands appeared at 3150, 2950, and 2700 cm^{-1} .

2.2 Mixtures of Nitric Acid with Other Oxidizers

2.2.1 Mixtures of Nitric Acid and Dinitrogen Pentoxide

Mixtures of nitric acid and dinitrogen pentoxide were investigated extensively as an environmentally more friendly nitrating acid, replacing $\text{HNO}_3/\text{H}_2\text{SO}_4$ nitrating acid

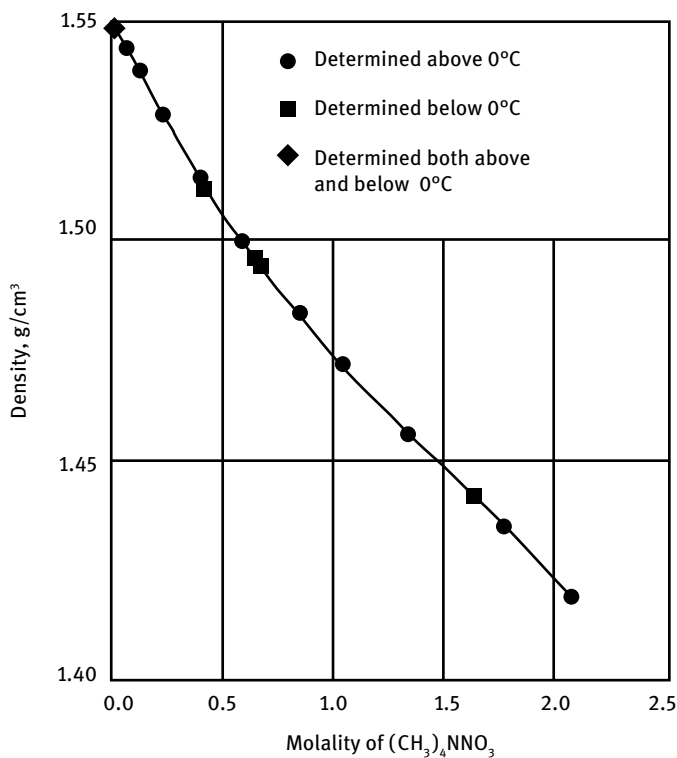


Figure 4: Density of solutions of tetramethylammonium nitrate in nitric acid. (Reproduced and modified from [12].)

and avoiding some of the problems with the disposal of spent nitrating acids in the production of organic nitro compounds, predominantly explosives and toluene diisocyanate precursors. In addition, mixtures of nitric acid and dinitrogen pentoxide would make a good rocket propellant, but only limited testing has been done with this oxidizer so far. The properties of dinitrogen pentoxide are described in *Encyclopedia of Oxidizers*, in the chapter “Dinitrogen Pentoxide.”

The vapor-pressure curve for mixtures of N_2O_5 and HNO_3 at 273 K (0 °C) showed additive behavior, and total pressure equaled the sum of the component vapor pressures [18].

N_2O_5 is best made through the electrolysis of WFNA, but the interim product that is retrieved from the anode space of a diaphragm cell consists of HNO_3 , N_2O_5 , and N_2O_4 . One method of obtaining pure N_2O_5 from this mixture is by extraction with N_2O_4 , in which it is soluble. The phase diagram of the ternary system $\text{HNO}_3/\text{N}_2\text{O}_5/\text{N}_2\text{O}_4$ was investigated by the cloud point method at four different temperatures in support of pure N_2O_5 production [19]. The triangular diagram (Figure 5) can be subdivided into

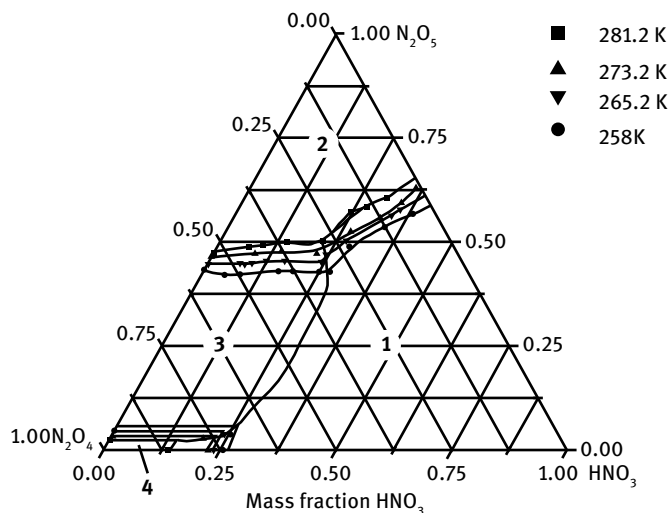


Figure 5: Phase diagram of $\text{HNO}_3/\text{N}_2\text{O}_5/\text{N}_2\text{O}_4$ system. (Reprinted and modified from [19] with permission from © 2009 American Chemical Society; permission conveyed through RightsLink.)

four phase zones: **(1)** the $\text{N}_2\text{O}_5(\text{S}) + \text{HNO}_3(\text{L}) + \text{N}_2\text{O}_4(\text{L})$ region, **(2)** the $\text{HNO}_3(\text{L})$ region, **(3)** the $\text{HNO}_3(\text{L}) + \text{N}_2\text{O}_4(\text{L})$ region, and **(4)** the $\text{N}_2\text{O}_4(\text{L})$ region. The intersection of the liquid-solid lines and liquid-liquid lines constituted the critical points. At these points, the mass fraction of N_2O_5 was 24.74, 26.57, 24.62, and 19.24% at 258.2, 265.2, 273.2, and 281.2 K, respectively. With an increase in temperature, the two-phase region shrank, and the solubilities of dinitrogen pentoxide in dinitrogen tetroxide and nitric acid, dinitrogen tetroxide in nitric acid, and nitric acid in dinitrogen tetroxide increased correspondingly.

2.2.2 Mixtures of Nitric Acid and Hydrogen Peroxide

Peroxynitric acid, HOONO_2 , plays an important role in atmospheric chemistry in polluted atmospheres, but it is very unstable and not suitable as a rocket propellant. Hundreds of publications deal with the decomposition, mostly by photolysis, of peroxynitric acid, but very few describe how the material can be made in the laboratory. In the stratosphere it forms by recombination of $\text{HOO}^\bullet$ and $^\bullet\text{NO}_2$ free radicals.

Attempts to prepare pure HNO_4 were unsuccessful. Dilute reaction mixtures of HNO_4 were prepared by reacting 50% H_2O_2 with 100% HNO_3 or with N_2O_3 , but the use of 100% H_2O_2 always led to explosions [20]. The highest concentration of HNO_4 in aqueous solutions reached was about 7%. Attempts to prepare salts of HNO_4 were unsuccessful.

2.2.3 Mixtures of Nitric Acid and Perchloric Acid

Low-freezing-point mixtures were obtained by the addition of perchloric acid to nitric acid [1].

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Nitrate Esters

1 Alkyl Nitrates

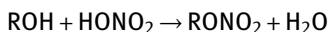
A parallel chapter of *Encyclopedia of Oxidizers* dealt with nitro compounds, which should not be confused with alkyl nitrates. This section and the next several sections deal with alkyl nitrates, which are the esters of nitric acid. This group of compounds is occasionally also referred to as “nitrate esters”, a term that is less specific because it might also include aromatic and heterocyclic rings with nitrato groups attached. The —O—NO_2 nitrate group attached to an organic skeleton is sometimes also called a nitroxy or nitroxyl or nitrato group. Occasionally the R—O—NO_2 compounds have been called “nitro ethers” because there is an oxygen in the middle, but that is a very uncommon designation. The “ether” designation should be reserved for the R—O—R type of compounds.

The current chapter deals mostly with liquid alkyl nitrates. Some solid nitrate esters, such as cellulose nitrate (nitrocellulose) will be included in future chapters on energetic materials in solid propellants. In alkyl nitrates, there may be one or more nitrato groups —O—NO_2 attached to a carbon atom or carbon skeleton. The number of nitrato groups that can be attached is limited by the number of hydrogen atoms that can be replaced by steric hindrance and by the degrading thermal stability of polynitrato molecules with an increasing number of nitroxy groups in the molecule.

The following introductory sections deal with alkyl nitrates as a group and compare their properties. This is followed by sections on specific alkyl nitrates of interest as rocket propellants.

1.1 Preparation of Alkyl Esters of Nitric Acid (Alkyl Nitrates)

Preparation of alkyl nitrates is fairly straightforward by the reaction of alcohols or polyols with nitrating acid (a mixture of anhydrous nitric acid and concentrated sulfuric acid)



The sulfuric acid serves to increase the concentration of nitronium ions and to absorb the water formed in the reaction, thereby shifting the equilibrium toward the right in the direction of ester formation. Because mixtures of alcohols and nitric acid are potentially explosive and may autoignite (even before they start reacting to form alkyl nitrates), the production of alkyl nitrates requires special safety precautions. This is particularly true of the large-scale production of propanetriol trinitrate, glycerol trinitrate (GTN), also erroneously called **nitroglycerin** (NG). Some alkanols can be nitrated by reaction with anhydrous nitric acid alone in the absence of sulfuric acid, making

the product recovery and cleanup a lot easier. Tertiary butyl nitrate can be made in 60% yield by the addition of >98% nitric acid to a cold (243 K = -30°C) solution of the alcohol in methylene chloride.

An excellent summary of the chemistry of alkyl nitrates is Chap. 3 in the book by Agrawal and Hodgson, *Synthetic Routes to Nitrate Esters*, pp. 85–123 [1]. It lists a wide array of methods for the preparation of alkyl nitrate esters. The most common is the O-nitration of alcohols with nitric acid and sulfuric acid. The presence of nitrous acid during the preparation of alkyl nitrates is highly undesirable because the contaminants jeopardize the thermal stability of the nitrate esters. Unwanted nitrite ester formation can be avoided by adding a small amount of urea to the nitrating batch that acts as a nitrite and NO_x scavenger. Methylene chloride is often used as a process solvent for polyol nitrations to allow better temperature control and avoid runaway reactions. Another common nitrating agent is fuming nitric acid in acetic acid anhydride (which is a potentially explosive mixture even before adding the reactant to be nitrated). Dinitrogen tetroxide and dinitrogen pentoxide also have been used as the nitrating agents for the preparation of alkyl nitrates. Nitration is a fundamental chemical process by which less reactive hydrocarbons or alkanols are converted to energetic compounds. Nitration is an important chemical reaction not only for production of rocket propellants and explosives, but also for the chemical process industry in general, producing many intermediates that eventually are converted to dyes, pharmaceuticals, polymers, or pesticides. There are several summary books on the kinetics and industrial applications of nitration reactions [2–5].

The addition of nitric acid to alkenes also leads to the formation of nitrate esters. Isobutylene reacts with fuming nitric acid to form *tert*-butyl nitrate. Other reaction products of alkenes with nitric acid are 2-nitroalkyl nitrates, *vic* dinitrate esters, or nitroalkenes. Metathetical reactions between alkyl halogenides (bromides and iodides) and silver nitrate, preferably in acetonitrile as the solvent, lead to alkyl nitrates with the precipitation of insoluble silver halogenide. Other methods of synthesis of nitrate esters are reviewed in [6]. The synthesis of unsaturated nitrate esters and dinitrate esters in a single step by the use of NO_2BF_4 in diethyl ether at 195 K (-78°C) is a nitration route relatively free from side reactions [7].

The 1963 Proceedings of the International Symposium on Nitro Compounds contains many contributions to the synthesis and applications of alkyl nitrates and nitro compounds [8].

1.2 Natural Occurrence of Alkyl Nitrates

With various alkanes and alkenes floating around in the atmosphere, in particular in the vicinity of petroleum recovery and refining operations, and with NO_2 , ozone, and HNO_3 present in the upper layers of the atmosphere, traces of various alkyl nitrates and alkyl peroxy nitrates are formed and can be detected in the atmosphere and in the

oceans [9]. Alkyl nitrates and alkyl peroxy nitrates participate in the nitrogen cycle in the atmosphere, and as much as 10% of all NO_x may be in the form of alkyl nitrates. Alkyl nitrates form in the atmosphere primarily as a result of the reaction between $\text{RO}^\bullet$ and NO , which competes with the oxidation of NO to NO_2 . In the atmosphere, once formed, alkyl nitrates are photolyzed by sunlight and establish a dynamic equilibrium concentration between the rate of formation and the rate of destruction.

1.3 Properties of Alkyl Nitrates

The lower alkyl nitrates are colorless, low-viscosity liquids whose boiling point is slightly higher than that of the corresponding alcohols. They possess pleasant, sweetish odors, some quite similar to those of the parent alcohols. The nitrates are somewhat denser than the alcohols and have slightly higher refractive indices. Nitrate esters are quite insoluble in water but are miscible with alcohols and ethers.

Summaries of the properties of alkyl nitrates are published in a very useful book on nitrate esters [10].

1.3.1 Mechanical Physical Properties of Alkyl Esters of Nitric Acid (Alkyl Nitrates)

Physical properties of alkyl nitrates are summarized in Table 1.

Table 1: Physical properties of alkyl mononitrates.

Compound	Boiling point		Density	Refractive index
	K	°C	g/cm^3	n_{20}^D
Methyl nitrate	337.7	64.6	1.205	1.3748
Ethyl nitrate	360.8	87.7	1.12	1.3857
<i>n</i> -Propyl nitrate	383	110	1.06	1.3980
<i>iso</i> -Propyl nitrate	375	102	1.05	1.3913
<i>n</i> -Butyl nitrate	406	133	1.03	1.4069
<i>iso</i> -Butyl nitrate	396	123	1.02	1.4026

Data source: [11]

1.3.1.1 Melting Points and Boiling Points of Alkyl Nitrates

Melting points and boiling points of lower alkyl mononitrates are summarized in Table 2.

Table 2: Physical properties of several alkyl nitrates.

Compound	Melting point		Boiling point*	
	K	°C	K	°C
Methyl nitrate	191	−82	338	65
Ethyl nitrate	179	−94	361	88
<i>n</i> -Propyl nitrate	—	—	384	111
<i>iso</i> -Propyl nitrate	191	−82	375	102
<i>n</i> -Butyl nitrate	370	97	409	136
<i>sec</i> -Butyl nitrate	—	—	397	124
<i>iso</i> -Butyl nitrate	—	—	396	123
<i>tert</i> -Butyl nitrate	—	—	294 (0.6 kPa)	21 (5 mm Hg)
Ethylene glycol mononitrate	<253	<−20	364 (2.7 kPa)	91 (20 mm Hg)
Ethylene glycol dinitrate	250.2	−22.8	472 dec.	199 dec.
1-Glyceryl nitrate	327	54	428	155
2-Glyceryl nitrate	331	58	428	155
1,2-Propylene glycol dinitrate	231	−42	365 (1.3 kPa)	92 (10 mm Hg)
1,3-Propylene glycol dinitrate	235	−38	381 (1.3 kPa)	108 (10 mm Hg)
1,2-Glyceryl dinitrate	—	—	419 (2 kPa)	146 (15 mm Hg)
1,3-Glyceryl dinitrate	299	26	419 (2 kPa)	146 (15 mm Hg)
Glycerol trinitrate	286.6	13.5	418 dec.	145 dec.

* Unless otherwise noted, boiling point data are at atmospheric pressure.

1.3.1.2 Vapor Pressures of Alkyl Nitrates

The vapor pressures of alkyl mononitrates can be calculated from the Antoine equation

$$\log p = A - B/(t + D)$$

where p is the decadic logarithm of the vapor pressure in mm Hg, t is the temperature in °C, and A, B, and D are constants. The constants of the Antoine equations that best fit all the available vapor-pressure and normal-boiling-point (NBP) data are listed in Table 3.

Table 3: Antoine equation constants for vapor pressure of alkyl nitrates.

Compound	A	B	D
Ethyl nitrate	7.146	1329	224.0
<i>n</i> -Propyl nitrate	7.246	1444	220.8
<i>iso</i> -Propyl nitrate	7.303	1467	227.5
<i>n</i> -Butyl nitrate	7.607	1742	236.6
<i>iso</i> -Butyl nitrate	7.424	1697	228.6

Data source: [11]

Methyl nitrate was not included in the above table. For methyl nitrate the alternative equation

$$\log p = 26.6767 - 6.3431 \log T - 2620.1139/T$$

has been fitted successfully to the experimental data, where p is the vapor pressure in mm Hg and T is the temperature in kelvin.

1.3.1.3 Physical Properties of Aliphatic Compounds with Two or More Nitroxy Groups

Table 4 is a summary of freezing or melting points and heat of fusion data of aliphatic compounds with two or three nitroxy groups in the molecule. The 1,2,5-trinitroxypentane could not be made to freeze.

Table 4: Freezing or melting points and heat of fusion data of aliphatic compounds with two or three nitroxy groups in molecule.

Compound	Freezing/melting point		Nitrogen content	Heat of fusion			
	K	°C		J/g	cal/g	kJ/mol	kcal/mol
1,3-Dinitroxypentane	243.61	-29.49	16.87	—	—	—	—
1,2,3-Trinitroxypentane (mixed acid nitration)	285.93	12.83	18.51	105	25	23.8	5.68
1,2,3-Trinitroxypentane (straight HNO ₃ nitration)	285.96	12.86	18.51	118	28.1	26.6	6.36
1,3-Dinitroxybutane	285.4	12.3	15.55	93	22.2	16.7	4
1,4-Dinitroxybutane	253.32	-19.78	15.55	148	35.4	26.7	6.38
1,2,4-Trinitroxybutane	261.76	-11.34	17.43	—	—	—	—
1,5-Dinitroxypentane	256.51	-16.59	14.43	80	19.1	15.5	3.7
2,4-Dinitroxypentane	254.62	-18.48	14.43	125	29.8	24.2	5.79
2,5-Dinitroxyhexane	323.47	50.37	13.46	265	63.4	55.2	13.2

Data source: [12]

A method has been developed to predict the melting/freezing points of aliphatic nitrate ester compounds from the molecular mass and molecular structure [13]. The list of examples where predicted freezing/melting points were compared to measured data included nine alkyl nitrates. The average deviation of predicted temperature from measured temperatures was 5.4%. See also [14]. These methods are based on the elemental composition of energetic compounds and the contributions of some specific polar groups/structural moieties as additive and non-additive functions, respectively.

Table 5 is a summary of vapor pressure and heat of evaporation data of aliphatic compounds with two or three nitroxy groups in the molecule.

Table 5: Vapor pressure and heat of evaporation of aliphatic dinitroxy and trinitroxy compounds.

Compound	Vapor pressure, Pa			Vapor pressure, $\mu\text{m Hg}$			Heat of evaporation	
	Temperature, K			Temperature, $^{\circ}\text{C}$			kJ/mol	kcal/mol
	293	303	313	20	30	40		
1,3-Dinitroxypropane	2.26	5.4	15.4	17	41	116	75 ± 5	17.9 ± 1.1
1,2,3-Trinitroxypropane I	0.03	0.11	0.4	0.21	0.82	3.2	105 ± 6	25.1 ± 1.4
1,2,3-Trinitroxypropane II	0.03	0.15	0.5	0.2	1.1	3.5	109 ± 11	26 ± 2.7
1,3-Dinitroxybutane	2.9	6.8	18.9	22	51	142	72 ± 7	17.2 ± 1.7
1,4-Dinitroxybutane	1.21	2.7	5.4	9.1	20	41	57 ± 0.8	13.7 ± 0.2
1,2,4-Trinitroxybutane	0.15	0.33	0.7	1.1	2.5	5.3	60 ± 11	14.4 ± 2.7
1,5-Dinitroxy pentane	0.62	1.8	4.9	4.7	13.6	36.5	79 ± 6	18.8 ± 1.4
2,4-Dinitroxy pentane	3.7	9.6	18.3	28	72	138	61 ± 6	14.5 ± 1.4
1,2,5-Trinitroxy pentane	0.02	0.04	0.1	0.16	0.29	0.48	42 ± 2	10 ± 0.5
2,5-Dinitroxyhexane	0.16	1.0	3.5	1.2	7.2	26	110 ± 16	$26.2 \pm 3.8^*$

* Heat of evaporation computed by subtracting heat of fusion.

Data source: [12]

Table 6 lists the vapor pressures of GTN in comparison to those of other alkyl polynitrates. Samples of the following esters were prepared in a high state of purity and vapor pressures determined over a temperature range of 288 to 328 K (15 to 55 $^{\circ}\text{C}$): GTN, ethylene glycol dinitrate (EGDN), diethylene glycol dinitrate (DEGDN), propylene glycol dinitrate (PGDN), and trimethylene glycol dinitrate [15]. The data presented in Table 6 are also illustrated in Figure 1.

The vapor pressures of methyl nitrate, ethyl nitrate, *iso*-propyl nitrate (IPN), butyl nitrate, and isoamyl nitrate were measured at 263, 273, and 283 K (−10, 0 and +10 $^{\circ}\text{C}$) by a static method [16].

Table 6: Vapor pressure of GTN and other alkyl polynitrates.

Temperature, K	288	288	298	298	308	308	318	318	328	328
	15	15	25	25	35	35	45	45	55	55
Vapor pressure	Pa	mm Hg	Pa	mm Hg	Pa	mm Hg	Pa	mm Hg	Pa	mm Hg
Glycerol trinitrate	0.17	0.0013	0.24	0.0018	0.61	0.0046	1.72	0.0129	4.8	0.0359
Ethylene glycol dinitrate	3.11	0.0233	9.41	0.0706	29.2	0.2189	59	0.4425	128	0.9619
Diethylene glycol dinitrate	0.29	0.0022	0.79	0.0059	1.97	0.0148	3.8	0.0284	12	0.0867
1,2-Propylene glycol dinitrate	5.15	0.0386	13.1	0.0984	33.8	0.2532	66.1	0.4955	133	0.9951
Trimethylene glycol dinitrate	1.55	0.0116	5.31	0.0398	8.28	0.0621	19.5	0.1466	43	0.3222

Data source: [15]

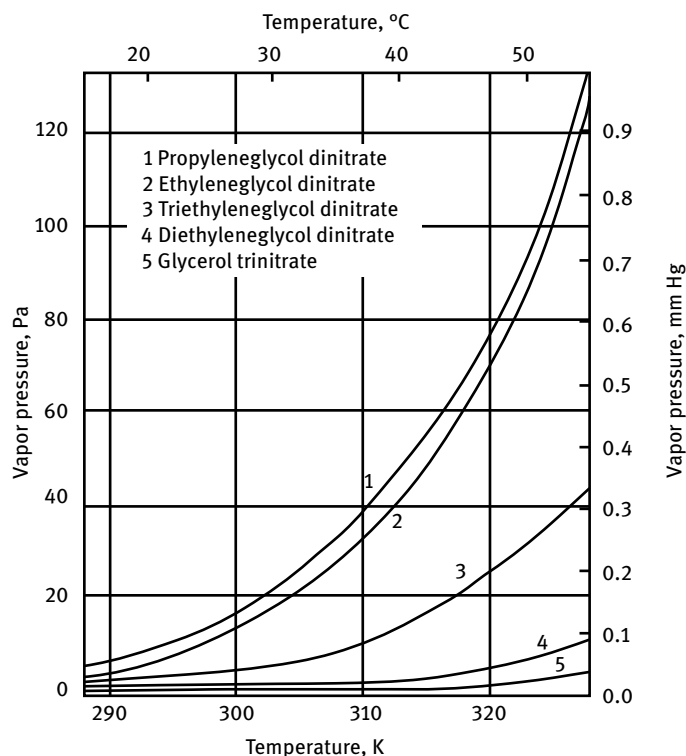


Figure 1: Vapor pressure of alkyl polynitrates. (Reproduced and modified from [15], with permission from © 1929 American Chemical Society; permission conveyed through RightsLink.)

1.3.1.4 Densities of Alkyl Nitrates

The densities of a few alkyl mononitrates were already presented in Table 1. For some applications of alkyl nitrates, such as in explosives, density is an important performance parameter. The densities of alkyl nitrates can be determined experimentally, and several measured data for individual compounds are listed later on or can be predicted theoretically. One of the first predictive methods was based on the group additivity method [17], comparing predictions for 173 energetic compounds with experimental results.

Correlations to predict crystal density based on two different models were introduced for 82 different energetic compounds, including 9 nitrate esters whose molecules contained functional groups common to CHNO explosives [18–20]. Additional work expanded the list of energetic materials to 172 compounds [21]. Root mean square (RMS) deviations for acyclic and cyclic nitramines were worse than for nitrate esters and nitroaliphatic explosives. This method is a simple procedure for predicting the crystal densities of energetic compounds, and it gave good results compared

to group additivity methods for estimating the density of organic explosives. The predictions are less accurate for liquid alkyl nitrates. See also [22].

1.3.2 Optical Properties of Alkyl Nitrates

1.3.2.1 Infrared Spectra of Alkyl Nitrates

This section contains information on the IR spectra of alkyl nitrates as a group, often providing a discussion of the differences in absorption spectra with increasing length or branching of the alkyl rest. IR spectra of selective alkyl nitrates are in subsequent individual sections on specific alkyl nitrates. IR spectra can be used to identify the type of carbon atom to which the —O—NO_2 group is attached. The spectra of primary, secondary, and tertiary alkyl nitrates are different. If the —O—NO_2 group is close to other bulky groups, the asymmetric and symmetric bands of —O—NO_2 will be blue shifted.

A vibrational analysis of the IR spectra of several alkyl mononitrates was the foundation of an investigation of the applicability of force constants from one alkyl nitrate to another alkyl nitrate [23]. IR spectra and analyses were reported for methyl, ethyl, *n*-propyl, isopropyl, and propylene nitrates.

1.3.2.2 Raman Spectra of Alkyl Nitrates

The Raman spectra of methyl, ethyl, propyl, butyl, amyl, hexyl, or heptyl nitrates were measured and compared to each other [24]. New lines were found, and others were shown to belong together as doublets. The frequency due to the NO_3^- ion did not occur in methanol solutions of methyl nitrate. The frequencies 1295 and 1679 cm^{-1} in 99.8% HNO_3 corresponded to internal vibrations, comparatively little influenced by the alkyl rest R, of the —NO_2 groups, while the frequency 612 cm^{-1} related to the angle subtended by the two oxygen atoms, and it decreased to 570 cm^{-1} when R was larger than methyl. The differences between the corresponding frequencies of the alkyl carbon chain decreased as the length of the chain increased.

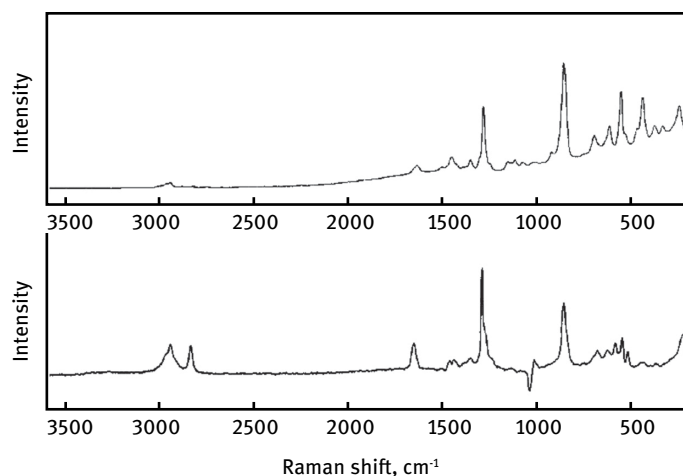
The Raman spectra of 8 alkyl nitrates and 24 other explosives were recorded for use in an explosive detection device [25, 26]. The samples were excited with the 1064-nm line from a diode-pumped Nd:YAG laser. The spectra showed the typical bands for the —O—NO_2 nitrate ester group for ν_s at $1300\text{--}1270\text{ cm}^{-1}$ and ν_{as} at $1660\text{--}1610\text{ cm}^{-1}$ (Figure 2). The typical nitrate ester Raman features are as follows:

1. Broad and intense aliphatic CH stretching vibrations
2. Anti-symmetric NO_2 stretching vibration observed as a broad feature in the majority of covalent nitrate spectra between 1670 and 1630 cm^{-1}
3. Symmetric stretching vibration of the nitro groups observed at approximately 1280 cm^{-1} and varies by up to $\pm 14\text{ cm}^{-1}$.
4. Intense broad band observed at approximately 860 cm^{-1} (Figure 2); this band is tentatively assigned to the O—N stretching mode. The measured frequencies are summarized in Table 7.

Table 7: Observed wavenumbers of symmetric and anti-symmetric $\nu(\text{NO}_2)$ Raman band.

Compound	Acronym	Wave number of $\nu_s(\text{NO}_2)$ band cm^{-1}	Wavenumber of $\nu_{as}(\text{NO}_2)$ band cm^{-1}
Glycerol trinitrate	GTN	1294	1656
Pentaerythritol tetranitrate	PETN	1288	1658
Trimethylolethane trinitrate	TMETN	1287	1647
Nitrocellulose	NC	1287	1667
Propylene glycol dinitrate	PGDN	1286	1639
Mononitroglycerol	MNG	1282	1638
Diethylene glycol dinitrate	DEGDN	1281	1636
Triethylene glycol dinitrate	TEGDN	1280	1634

Data source: [26]

**Figure 2:** Raman spectra of PGDN (top) and GTN (bottom). (Republished and modified from [25], with permission of © 1995 Elsevier; Permission conveyed through RightsLink.)

1.3.2.3 NMR Spectra of Alkyl Nitrates

The nuclear magnetic resonance (NMR) spectra of alkyl nitrates are useful to identify explosive residues from accident scenes and to identify contaminants in propellants that may be responsible for the inferior quality of a product. The ^1H NMR spectra of 21 alkyl nitrates and alkylene dinitrates and a few trinitrates were recorded and compared [27]. A complete analysis of the ^1H NMR spectra was not possible because the spectra were more complex than those of the corresponding fluorides, which gave deceptively simple spectra. In others the resolution was not sufficient to allow all the NMR parameters to be evaluated. It would be difficult to use NMR in the analysis of

nitrate ester mixtures. As an example, Figure 3 shows a trace of ethyl nitrate (b) as a contaminant in IPN (a).

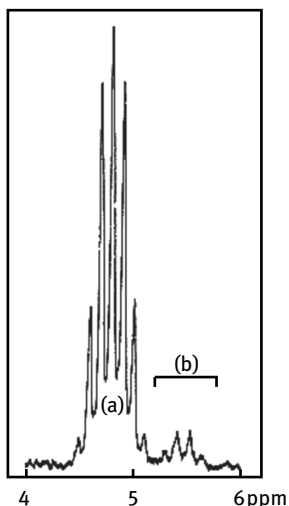
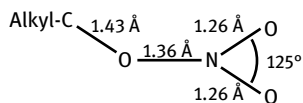


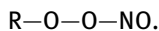
Figure 3: NMR spectrum of ethyl nitrate (b) as a contaminant in IPN (a). (Reproduced and modified from [27].)

1.3.3 Molecular Structure of Alkyl Nitrates

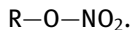
The generally recognized structure of the nitrate group $-\text{NO}_3$ in nitrate esters is a symmetrical structure:



The bond lengths and bond angles of nitrate esters are similar to those of nitro compounds. Because nitrate esters are so much more reactive than nitro compounds, it has been speculated that one of the more reactive species in alkyl nitrates might be a hyperoxide group



However, the hyperoxide structure was not found in nitrate esters after multiple chemical structure analysis techniques. The only structure of nitrate esters is



The structure of nitrate esters was further characterized by Raman spectroscopy, IR spectroscopy, electron diffraction, dipole moment, and X-ray diffraction (XRD). The results supported the finding of no hyperoxide structure in nitrate esters.

Three density-functional methods were used to investigate the O—NO₂ bond lengths, frontier orbital energies, and O—NO₂ bond dissociation energies (BDEs) of IPN, *n*-propyl nitrate (NPN), 2-ethylhexyl nitrate (EHN), tetraethylene glycol dinitrate (Tetra-EGDN), and TEGDN [28]. It was found that the O—NO₂ bond lengthens (destabilizes) in the aforementioned order. From the data of frontier orbital energies and energy gaps, the relative thermal stabilities of the five nitrates and their corresponding radicals was estimated, and the predicted BDEs of O—NO₂ bonds in IPN, NPN, EHN, Tetra-EGDN, and TEGDN were 174.5, 176.6, 168.1, 159.3, and 156.1 kJ/mol, respectively. Based on the finding that the results of BDEs were in agreement with experimental results of apparent activation energies from the literature, it was suggested that the experimental thermolysis of these five nitrates is only unimolecular homolytical cleavage of the O—NO₂ bonds.

1.3.4 Thermodynamic Properties of Alkyl Esters of Nitric Acid (Alkyl Nitrates)

The vapor pressures of *n*- and *iso*-propyl and *n*- and *iso*-butyl nitrate were measured from 273 to 344 K (0 to 70 °C), and their NBPs were remeasured [11]. From these numbers accurate values could be derived for the latent heats of evaporation of the nitrates at 298 K (25 °C) and at their boiling points by means of the Clausius-Clapeyron equation. In Table 8 the corrected and the uncorrected latent heats of evaporation of the six alkyl nitrates are listed, for evaporation at 298 K (25 °C), and at the NBPs at atmospheric pressure.

Table 8: Corrected enthalpy of evaporation of alkyl nitrates.

Compound	ΔH_{vap} at 298 K		ΔH_{vap} at NBP		ΔS_{vap}	
	kJ/mol	cal/mol	kJ/mol	cal/mol	J K ⁻¹ mol ⁻¹	cal °C ⁻¹ mol ⁻¹
Methyl nitrate	34.1	8150	31.5	7540	93.3	22.3
Ethyl nitrate	36.3	8670	33.1	7920	91.6	21.9
<i>n</i> -Propyl nitrate	40.6	9700	35.9	8580	93.3	22.3
<i>iso</i> -Propyl nitrate	38.8	9270	34.9	8350	92.9	22.2
<i>n</i> -Butyl nitrate	43.6	10420	39.1	9340	96.7	23.1
<i>iso</i> -Butyl nitrate	42.2	10080	37.3	8920	95.0	22.7

Data source: [11]

All the Trouton constants were about $22.5 \pm 0.5 \text{ cal } ^\circ\text{C}^{-1} \text{ mol}^{-1}$, an indication that no association of molecules took place in the vapor phase. The variation of latent heat with temperature indicated that at room temperature fewer than half the possible vibrational modes are active in gaseous nitrates.

The heats of combustion of liquid ethyl nitrate, NPN, and IPN were measured using a bomb calorimeter of conventional design from which the heats of formation were derived [29]. The results obtained are shown in Table 9. See also [30, 31].

Table 9: Heat of combustion and heat of formation of liquid alkyl nitrates.

Compound	ΔH_c°		ΔH_f°	
	kJ/mol	kcal/mol	kJ/mol	kcal/mol
EtNO ₃	-1311 ± 0.96	-313.39 ± 0.23	-190.4 ± 1.04	-45.51 ± 0.25
<i>n</i> -PrNO ₃	-1966 ± 1.2	-470.00 ± 0.3	-214.5 ± 1.2	-51.27 ± 0.3
<i>iso</i> -PrNO ₃	-1951 ± 1.2	-466.35 ± 0.3	-229.8 ± 1.2	-54.92 ± 0.3

Data source: [29]

1.3.4.1 Computational Prediction of Thermodynamic Properties of Alkyl Nitrates

Heats of formation for several nitramines and alkyl nitrates were calculated with two semiempirical molecular orbital theory methods [32]. Both methods can estimate heats of formation ΔH_f° accurately. By combining heats of evaporation and sublimation obtained by the additivity rule with ΔH_f° in the gas phase obtained by this predictive method, heats of formation ΔH_f° in condensed phases can be estimated accurately enough for energetic accident hazards predictions.

The ideal gas (**not** condensed phase!) thermodynamic properties of 29 nitro and alkyl nitrate compounds, including NPN and GTN, were predicted from spectroscopic data and compared to calorimetric results reported in the literature [33, 34]. The fundamental vibrations, bond lengths, and moments of inertia of all the molecules were calculated using semiempirical methods. The resulting thermodynamic properties were represented in a polynomial form, ready for use in rocket propulsion I_{sp} calculations. The format used was the OLD NASA CEC polynomial format and consisted of two sets of polynomial coefficients for each species. The first set of seven coefficients represented the properties above 1000 K and the second from 200 to 1000 K. Both polynomials gave the same values at 1000 K for the properties. The 15th (last) coefficient represented the enthalpy of formation $\Delta H_f(298)/R$. The results are summarized in Table 10.

Table 10: Ideal gas thermodynamic properties of alkyl nitrate compounds.

Gaseous (vapor) compound name	Formula	ΔH_f^{298} kJ/mol	S^{298} JK ⁻¹ mol ⁻¹	C_p^{300} JK ⁻¹ mol ⁻¹
Methyl nitrate	CH ₃ ONO ₂	-122.01	305.79	76.88
Nitroxymethyl free radical	•CH ₂ ONO ₂	98.95	312.17	77.05
Ethyl nitrate	C ₂ H ₅ ONO ₂	-154.98	928.86	95.54
<i>n</i> -Propyl nitrate	C ₃ H ₇ ONO ₂	-174.05	362.60	123.79
Glycerol trinitrate	C ₃ H ₅ (ONO ₂) ₃	-279.07	545.87	235.12
Pentaerithrytol tetranitrate	C ₅ H ₈ N ₄ O ₁₂	-387.02	614.71	296.08

Data source: [34]

The N—O BDEs and the heats of formation of alkyl nitrate and alkyl nitrite compounds in the gas phase at 298 K were theoretically calculated using a density functional theory (DFT) method [35]. The DFT and the *ab initio* method can both yield good results with respect to the experimental heats of formation with a deviation of less than 8.1 kJ/mol (2.0 kcal/mol). As the number of methylene groups increased, the heats of formation of alkyl nitrate and nitrite compounds increased with the number of carbon atoms.

Comparative quantum chemical calculations have been carried out for five nitrate esters: ethyl nitrate, NPN, IPN, EHN, and tetraethylene glycol dinitrate (Tetra-EGDN) [36]. The relative thermal stability ordering of the five nitrates was estimated on the basis of the frontier orbital energy and the energy gap. The heats of formation of the five alkyl nitrates ethyl nitrate, NPN, IPN, EHN, and Tetra-EGDN in the vapor state calculated from isodesmic reactions were -156, -175, -191, -272, and -791 kJ/mol, respectively.

The heats of formation of 24 nitrate esters in the vapor state were computed by quantum chemical calculations and compared to experimental data for only 5 nitrate esters available from the literature [37]. The calculated heats of formation of the five compounds were very close to measured data for ethyl nitrate, NPN, IPN, EGDN, and GTN. The heats of formation of 19 other nitro ester energetic compounds were tabulated. The computed heat of formation decreased when the number of methylene (CH₂) groups increased for normal alkane chain nitrate ester compounds.

The molecular structure and bond energies of aliphatic polynitrates of polyols were studied using a DFT method [38]. The IR spectra of a few samples were measured and used to compute the thermodynamic properties based on the absorption band frequencies and principles of statistic thermodynamics. The reliability of this theoretical method was tested by comparing the theoretical densities with the experimental ones. Detonation properties were predicted using modified Kamlet-Jacobs equations based on the calculated densities and heats of formation. The energetic properties of other polyol nitrates, e.g., xylitol pentanitrate (XPN) or mannitol hexanitrate (MHN), were examined as well.

1.3.4.2 Computational Prediction of Density of Alkyl Nitrates

Correlations to predict densities based on two different models were introduced for 82 different energetic compounds, including nitrate esters and nitroaliphatic compounds whose molecules contained functional groups common to CHNO explosives [18–20]. The RMS deviations for acyclic and cyclic nitramines were worse than for nitrate esters and nitroaliphatic explosives. This method is a simple procedure for calculating the density of energetic compounds and gave good results compared to group additivity methods for estimating the density of organic explosives.

1.4 Chemical Properties of Alkyl Nitrates

1.4.1 Reactions of Alkyl Nitrates

Unwanted reactions of alkyl nitrates during their synthesis may reduce the yield or lead to unwanted byproducts that are difficult to remove and may worsen the sensitivity of the compounds, making them more hazardous.

Controlled reactions of alkyl nitrates that we want to learn more about are the thermal or catalytic decomposition taking place in rocket engines, which will be discussed in *Encyclopedia of Monopropellants*. Alkyl nitrates have been extensively examined as additives to diesel fuels to improve the cetane number and facilitate ignition under arctic conditions. The initial reactions in the decomposition of alkyl nitrates taking place in diesel fuel droplets during the compression stroke are similar to those during startup in a monopropellant rocket engine.

At the end of their useful lifetime, alkyl nitrates may have to be disposed of as part of a demilitarization of outdated weaponry or to clean up a spill. Many different reactions can convert hazardous alkyl nitrates to innocuous products that can be safely burned or landfilled. The disposal of alkyl nitrates is discussed in Section 9.3.1.1.7 and 9.4.6.

The lifetime of alkyl nitrates that exist in the atmosphere either naturally or as the result of anthropogenic pollution is limited by photolysis in bright sunlight. The photolysis of alkyl nitrates is discussed in Section 1.4.3.

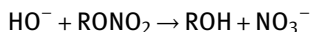
All esters are eventually susceptible to hydrolysis, converting them back to alcohols and acids. The hydrolysis of alkyl nitrates is very undesirable and may limit their useful lifetime in moist environments or if they were not perfectly dried following production and prior to sending them into storage. Nitric acid formed during hydrolysis would be very corrosive to shipping containers.

A historical and very detailed summary of the reactions of alkyl nitrate esters is found in [6]. This work contains sections on synthesis, physical properties, chemical reactions, physiological properties, and hazards involved in handling alkyl nitrates, along with 188 literature references to now mostly antiquated earlier publications.

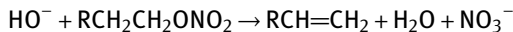
1.4.1.1 Hydrolysis of Alkyl Nitrates

It is surprising that hydrolysis of nitrate esters involves the occurrence of other reactions besides the normal ester hydrolysis to alcohol and nitrate ion or nitric acid. Considerable confusion has existed, especially in the older literature, regarding these side reactions, with some investigators believing that they arise from a subsequent oxidation reduction between the alcohol and nitric acid, while others regarded the side reactions as proceeding simultaneously with, and independently of, the normal hydrolysis reaction. The hydrolysis of nitrate esters may actually take place by a combination of three distinct reactions:

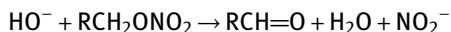
(1) Nucleophilic substitution:



(2) Elimination of β -hydrogen:



(3) Elimination of α -hydrogen:



Reaction (1) predominates in both alkaline and neutral hydrolysis of primary and secondary alkyl nitrate esters. Besides alcohols and nitrate in reversal of the formation reaction, the hydrolysis of alkyl nitrates may create aldehydes, ketones, carboxylic acids, and unsaturated hydrocarbons as byproducts [39, there p. 187–190]. Reactions are sought for the disposal of unwanted alkyl nitrates. In addition to the hydrolysis of alkyl nitrates, reactions with sodium hydrogen sulfide have been extensively investigated.

The hydrolysis of alkyl nitrates precedes several analysis methods. Several hydrolysis methods have been tested to make sure none of the volatile nitrate is lost during the procedure. One of the hydrolysis procedures uses metallic calcium in a solution of potassium methanolate in methanol [40]. Hydrolysis would be a preferred way for the disposal and inerting of alkyl nitrates.

1.4.1.2 Acidity of Alkyl Nitrates

Similar to the acidity of the α -hydrogen in nitroalkanes, the α -hydrogen in alkyl nitrates is acidic and can also form salts. The salts are more sensitive than the parent alkyl nitrate.

1.4.1.3 Alkyl Nitrates as Nitrating Agents

Alkyl nitrates can serve as the source of $-\text{NO}_3$ or $-\text{NO}_2$ in the preparation of other nitrate and nitro compounds. In concentrated sulfuric acid, nitrate esters undergo a complex ionization, yielding nitronium ion NO_2^+ , which is the main nitrating agent.

1.4.2 Thermal Decomposition of Alkyl Nitrates

Alkyl nitrates have good storage stability and can be stored in the dry state for a long time without decomposition; however, some contaminants will decrease storage stability and lower the autodecomposition temperature. Alkyl nitrates, nitramines, and nitro compounds have in common that they possess a $-\text{NO}_2$ group. The thermal stability of these three groups of energetic chemicals differs significantly, depending on how the $-\text{NO}_2$ group is linked to the hydrocarbon skeleton. The best thermal stability

is achieved by direct linkage of the $-\text{NO}_2$ group to a carbon atom. The intermediate $-\text{N}-$ or even $-\text{O}-$ atom will make the chemical more reactive and less stable. On the other hand, thermally less stable compounds are easier to ignite in a monopropellant rocket engine. The thermal stability of alkyl nitrates is inferior to that of nitramines. All alkyl nitrates will autodecompose exothermally above a certain autodecomposition temperature. Compounds that autodecompose below their boiling point at normal pressure must be distilled (with adequate precautions) under reduced pressure. Studies on the inflammation of alkyl nitrate vapors have demonstrated the existence of three modes of thermal decomposition: chemiluminescence, explosion, and decomposition without glow. The luminescent mode, as obtained at low pressures in the case of methyl nitrate, was attributed to the methoxyl radical and, as such, was substantiation of the primary reaction being the fission of the alkoxyl-nitrogen bond.

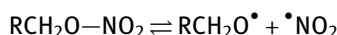
This chapter is primarily concerned with the decomposition of alkyl nitrates in the absence of additional oxidizers or catalysts. Many studies have looked at vapor decomposition flames and flames stabilized on stationary burners, usually at low pressure or with inert gas diluents, but without the addition of oxygen. However, a few studies have also looked at flames burning in oxidizing environments (ambient air), and we have included these here as well, since they help to understand the monopropellant burning mechanism. Decomposition data on specific alkyl nitrates will be presented in subsequent sections. This section discusses general aspects on the decomposition of alkyl nitrates as a family of compounds, often comparing the properties of different alkyl nitrates that are either structural isomers or homolog, and looking for a correlation between molecular structure and thermal decomposition, in particular trying to find the weakest link in the molecule.

1.4.2.1 Slow Thermal Decomposition of Alkyl Nitrates

The thermal decomposition of four different alkyl nitrates was measured and compared in view of the different structures of these molecules. The four alkyl nitrates tested were IPN, *sec*-butyl nitrate, *n*-butyl nitrate, and ethylene glycol mononitrate (EGMN) [41].

The decomposition of alkyl nitrates often leads to alkyl nitrites, which in turn will decompose on further heating and are much less stable than the nitrates from which they are derived [42]. The alkyl nitrites are also the isomers of the nitro compounds with the same gross chemical formula and were at one time suspected to be intermediates in the decomposition of nitro compounds. One example alkyl nitrite is isopropyl nitrite which will be discussed further down in the chapter on IPN.

The thermal decomposition of ethyl nitrate was already examined by a number of researchers [43, 44], and it was proposed that the first, and rate-determining, step was the reversible loss of NO_2 :



Rates of thermal decomposition and solvent rate effects were measured for a series of nitrate esters. The alkoxy radicals formed by homolysis together with some of their further degradation products have been stabilized by hydrogen donation. Internal and external return of nitrogen dioxide has been demonstrated by solvent cage effects and isotope exchange. Radical stabilizing substituents favor β -scission. Dinitrates in a 1,5 relationship behave as isolated mononitrates. Dinitrates in a 1,3 or 1,4 relationship exhibit intramolecular reactions. Tertiary nitrate esters in diethyl ether undergo elimination rather than homolysis.

Summaries of the reactions in the pyrolysis of alkyl nitrates, alkyl nitrites, and nitro compounds are published in [45] and [46]. The culprit in the autocatalytic acceleration of alkyl nitrate decomposition may not be NO_2 , as was widely assumed, but actually it may be formaldehyde [47].

The thermal decomposition rates were measured and mechanisms proposed for the following primary, secondary, and tertiary mononitrates: *n*-pentyl nitrate, 3-buten-1-yl nitrate, ethyl nitrate, neopentyl nitrate, 2-phenylethyl nitrate, 2-propyl nitrate, cyclohexyl nitrate, 2-methyl-2-propyl nitrate, and 2-methyl-2-butyl nitrate [48]. In addition, the mechanisms of thermolysis of the multiple nitrates 1,4-butanediol dinitrate, 1,5-pentanediol dinitrate, 2,2-dimethyl-1,3-propanediol dinitrate, nitropentaglycerin [1,1,1-tris(hydroxymethyl)ethane trinitrate], and pentaerythritol tetranitrate (PETN) have been studied.

A relationship was found between activation energies E_a of low-temperature non-autocatalyzed thermolysis of nitric acid esters on the one hand and their oxygen balances on the other [49]. By this relationship is evidenced a molecular-structural dependence of values E_a , and at the same time existence is signalized of a direct relationship between the values E_a and the impact sensitivity of nitro esters. Similar relationships exist between other sensitivity parameters and molecular structure of polynitro compounds [50, 51].

The primary processes of nitrate ester thermal decomposition, such as homolytic O—N bond scission, the effect of molecular structure, and the reversible elimination of NO_2 were reviewed in an effort to develop thermally more stable energetic materials [52].

In addition to experimental measurement of the decomposition of alkyl nitrates, computational models for thermal decomposition of organic compounds were developed. Based on an analysis of the experimental data on the mechanisms of thermal decomposition, empirical rules were developed for simulating possible thermal decomposition reactions of the major classes of energetic compounds. The proposed approach made it possible to describe the complete spectrum of reactions occurring in the course of thermal decomposition. The approach was exemplified by the simulation of the thermal decomposition of methyl, ethyl, and isopropyl nitrates [53]. All stages of the mechanisms (some of which have been reported in the literature) were

reproduced, and a number of new decomposition reactions, which had not yet been studied experimentally, were suggested.

Measurements of the rate constants for the thermal, unimolecular decomposition of organic nitrates confirmed that the rate-determining step is the homolytic cleavage of the weak O—N bond to form alkoxy radical and NO₂, but the rate constants reported previously were found to be incorrect [54]. The alkoxy radical and NO₂ engage in secondary reactions that ultimately generate stable products such as carbonyl and nitro compounds. IR and gas chromatography-mass spectrometry (GC/MS) were used to monitor the time-dependent loss of organic nitrates and to characterize the products of the thermal reactions. Past research indicated that oxygen slowed the rate of homolytic O—N bond cleavage to form radicals, but now it was found that the rates are the same in nitrogen as they are in air. Unhindered, linear alkyl nitrates have lower reaction rate constants than sterically hindered organic nitrates. Activation energies were found to be lower for sterically hindered organic nitrates. The steric strain present in the hindered organic nitrates may account for the weaker O—N bonds and faster thermal reaction rates. Reaction rates for thermal decomposition under nitrogen were found to decrease as the viscosity of the solvent increased.

If the influence of chemical structure on the thermal stability of nitric acid esters were fully understood, one could design nitric acid esters with improved thermal stability. In trying to establish a correlation between molecular structure and thermal stability, the thermal stability and decomposition mechanism functions of 10 nitric acid esters, including glycerol trinitrate (NG), PETN, trimethylolethane trinitrate (TMETN), dipentaerythritol hexanitrate (DiPEHN), trimethylolpropane trinitrate (TMPTN), erythritol tetranitrate (ETN), XPN, sorbitol hexanitrate (SHN), MHN, and nitroisobutylglycerol trinitrate (NIBGT) were determined by non-isothermal thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) [55]. It was found that the mean activation energies for most nitric acid esters were comparable at a constant heating rate (around 145 kJ/mol), indicating that their main decomposition pathways might be the same. Based on the critical temperature of thermal decomposition, the order of molecular stability for nitric esters was MHN XPN TMPTN SHN NIBGT ETN PETN DiPEHN. The introduction of functional groups to the tertiary carbon may increase thermal stability due to an increase of symmetry and rigidity of the molecule. Two types of decomposition kinetic behavior were observed, and most nitrate esters followed typical decomposition kinetics close to the first-order reaction.

The thermal stability of 10 different nitric acid esters was evaluated in an effort to explain the relationship between molecular structure and thermal stability [56]. The thermal stability and decomposition kinetics of 10 nitric acid esters, including NG, PETN, TMETN, TMPTN, XPN, SHN, ETN, mannitol hexanitrate, and NIBGT, were investigated by non-isothermal TGA and DSC. It was shown that the mass loss processes of NG, TMETN, and TMPTN are more dependent on the heating rate, and the simultaneous evaporation makes the initial temperatures for their mass loss lower than those

of the other nitric esters. Based on the correlations among their thermal stability, activation energy, detonation velocity, and heat of combustion, it was concluded that the oxygen coefficient (α) plays a positive role in the decomposition heat release efficiency (η_d) when it is less than one, whereas when the α is greater than or equal to one, the fuel elements, such as C and H contents, would play a decisive role in η_d . It was shown that the order of contribution rate of function groups on the tertiary carbon to the detonation velocity could be $-\text{CH}_3 > -\text{NO}_2 > -\text{C}_2\text{H}_5 > \text{ONO}_2$. The introduction of functional groups to the tertiary carbon facilitates increasing the thermal stability of nitric acid esters due to an increase in symmetry and rigidity of their molecules. The ratio numbers (C_s) of the methylene group ($-\text{CH}_2-$) to tertiary carbon or quaternary carbon will also, to some extent, determine the thermal stability of the nitric acid esters.

1.4.2.2 Rapid Thermal Decomposition of Alkyl Nitrates

T-Jump/Fourier transform infrared (FTIR) and T-jump/Raman spectroscopies were used to analyze the gaseous products from six nitrate esters, which were rapidly heated (2000 °C/s nominal) to preset temperatures in the 523 to 773 K (250 to 500 °C) range while maintaining a pressure of 0.5 MPa (5 atm) Ar [57]. The compounds studied were GTN, PETN, butanetriol trinitrate (BTTN), TMETN, triethyleneglycol dinitrate (TEGDN), and bis(nitratomethyl) oxetane (BNMO). With few exceptions, the oxygen balance of the nitrate esters correlated with the thermal stability of the products, the CO_2/CO ratio, the NO/CO ratio, and the amounts of H_2O and total hydrocarbon liberated. The amounts of NO_2 and CH_2O scaled with the number of $-\text{NO}_2$ groups and $-\text{CH}_2\text{O}-$ units in the parent molecule. The relation between the composition of the parent nitrate ester and the gaseous products from pyrolysis was the most straightforward of the various classes of oxidizing energetic functional groups studied by that group to date. Some degree of evaporation of the undecomposed parent nitrate ester was observed upon flash heating and identified by IR. The IR-active modes of GTN and BTTN in the gaseous phase were assigned by calculation of their frequencies by DFT in the energy-minimized structure. The pyrolysis of alkyl nitrates and alkyl nitrites is described in [58].

1.4.3 Photolysis of Alkyl Nitrates

The photolysis of alkyl nitrates is discussed in this chapter because it is a method for controlled and repeated ignition of a decomposition reaction in rocket engines by laser photolysis. Photolysis determines the rate of decay of spilled propellants in surface waters under the influence of sunlight. UV-photolysis is a useful method for decontaminating wastewaters from propellant production facilities.

The discovery of naturally occurring alkyl nitrates in the atmosphere and in the ocean has prompted a large number of investigations in the photolysis of alkyl nitrates and alkyl nitrites in order to see what equilibrium concentrations one must expect un-

der conditions of sunlight illumination. For the use of alkyl nitrates as rocket propellants, photolysis would only be of interest as a means of ignition in a rocket engine or as a means of wastewater treatment from propellant production plants. The use of alkyl nitrates as rocket propellants does not contribute to atmospheric contamination.

Organic nitrates produced in the atmosphere through photochemical reactions involving hydrocarbons and oxides of nitrogen may constitute a significant fraction of reactive nitrogen oxide NO_x . UV absorption cross sections of methyl, ethyl, 1- and 2-propyl, 1-, 2-, and *tert*-butyl, cyclopentyl nitrate, and (nitrooxy)ethanol were measured to provide estimates of atmospheric removal rates [59]. The spectra were very similar in the range of atmospheric interest (290 nm), and UV absorption cross sections decreased from $\sigma = 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ to $10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$ above 330 nm. An increasing trend in σ was observed with length and degree of substitution of the alkyl substituent.

The UV absorption cross sections of methyl, ethyl, and IPN between 233 and 340 nm have been measured using a diode array spectrometer in the temperature range 240–360 K [60]. The absorption cross sections of these alkyl nitrates decreased with increasing wavelength and decreased with decreasing temperature for $\lambda \geq 280 \text{ nm}$. The photodissociation quantum yield for CH_3ONO_2 to produce NO_2 and CH_3O was essentially unity at 248 nm using transient UV absorption methods. Production of O and H atoms in the photodissociation of methyl nitrate at 248 and 308 nm was negligible using resonance fluorescence detection of the atoms. High quantum yields for O atoms were measured following 193-nm photolysis of methyl nitrate. The OH radical was a photoproduct with a very small quantum yield. Using OH rate coefficients, UV absorption cross sections, and photodissociation quantum yields, the first-order rate constants for atmospheric loss of methyl, ethyl, and IPN were calculated. Photolysis was found to be the dominant atmospheric loss process for the three alkyl nitrates.

1.4.4 Analysis of Alkyl Nitrates

Analytical methods for alkyl nitrates are needed for quality control of the propellant ingredients and for monitoring workroom air where personnel may be exposed to physiologically active vapors. Because of the strong effect of alkyl nitrate vapors on blood pressure, air monitoring in the workplace is extremely important. Vaporizing energetic plasticizers are a main aging mechanism, limiting the storage and service life of double-base propellants, and therefore vapor concentrations of plasticizers in propellant or assembled munitions storage areas need to be measured periodically. Another area where sensitive analytical methods are needed is the detection of explosive vapors in aircraft luggage, suspected terrorists, and buried land mines, a category often described as improvised explosive devices (IEDs).

Because of the low thermal stability of nitro and nitrate compounds, the operating temperature of gas liquid chromatography (GLC) columns for the GC analysis of these compounds is limited. Oven temperature, column material, and column length must be chosen to achieve good separation without losing any of the analyte in the process [61]. To prevent accumulation of less volatile compounds on columns, it was recommended to wash columns with acetone after every 50th injection.

GTN, EGDN, and dinitrotoluene can be detected by optoacoustic spectroscopy techniques at 6, 9, and 11 μm [62]. The effect of interference by normal atmospheric pollutants needs to be accounted for, and it was found that of those wavelengths proposed for use, the 9- and 11- μm spectral regions, using a CO_2 laser as radiation source, were the most promising for use in explosive detection.

Nitrate esters show characteristic absorption bands in the IR near 6.1, 7.8, and 11.8 μm , and the last band has been used for the quantitative estimation of ethyl nitrate in complex gaseous mixtures.

The characteristics of the mass spectra of C_1 – C_5 alkyl nitrates (RONO_2) were systematically examined with a proton transfer reaction time-of-flight mass spectrometer operating at different field strengths, E/N , of the drift tube [63]. Although protonated alkyl nitrates were detected for C_1 – C_4 alkyl nitrates, their signal intensities were, at most, only a few percent of the total ion signals. The major product ions were several fragment ions, including NO_2^+ , RO^+ , R^+ , and $\text{ROH}\cdot\text{H}^+$, whose abundances and relative intensities depended on the E/N ratio. The intensity of NO_2^+ ions increased with increasing E/N ratio, whereas the intensities of organic fragments, such as R^+ and RO^+ ions, relative to the total product ions, decreased with increasing E/N ratio. NO_2^+ fragment ions were detected regardless of the speciation of alkyl nitrates, which suggested that the detection of C_1 – C_2 alkyl nitrates by this technique was not selective, but the abundant fragment ion signals of R^+ ions could be useful for the identification of C_3 – C_5 alkyl nitrates.

The structures of organic components in an alkyl nitrate-based propellant (probably similar to Otto Fuel II) were identified by NMR and validated by GC/IR [64]. The organic energetic oxidant (alkylene dinitrate), stabilizer, and phlegmatizer (a sebacate) content of the propellant was quantified. The NMR result was consistent with that obtained by high-performance liquid chromatography (HPLC). The relative standard deviations (RSD) were 0.21% for the organic energetic oxidant, 0.32% for stabilizing agent, and 0.11% for phlegmatizer.

1.5 Handling Safety of Alkyl Nitrates

1.5.1 Toxicity of Alkyl Nitrates

Alkyl nitrates are readily absorbed into the body by inhalation and skin permeation, in addition to accidental ingestion. The most characteristic symptoms of poisoning

by nitrate esters (particularly that due to GTN) are severe headache and a feeling of pressure on the front and back of the head. The dilation of the peripheral blood vessels results in a shift of blood to the splanchnic area and may cause a decreased supply of blood to the brain (despite cerebral vasodilation), resulting in vertigo or fainting. Continued routine exposure to GTN may build up some tolerance against low levels of this compound.

Although alkyl nitrates and alkyl nitrites have several features in common (nitrogen–oxygen grouping, explosiveness, methemoglobin formation), there are significant differences in their toxic effects. Some of their attributes were summarized in a review paper [65]. The esters of nitric and nitrous acids, whose nitrogen is linked to carbon through oxygen, are very similar in their pharmacological effects. Both produce methemoglobinemia and vascular dilatation with hypotension and headache. These effects are transient. None of the compound series has appreciable irritant properties that would warn of their presence in the air in the workplace. Pathological changes occur in animals only after high levels of exposure and are generally non-specific and reversible.

Medicinal uses of alkyl nitrates are for controlled lowering of the blood pressure in hypertensive human patients with high blood pressure. The toxicity of alkyl nitrates is due mainly to their vasodilating effects on the blood and the circulatory system. Alkyl nitrates oxidize hemoglobin to methemoglobin and, by depression of the muscles in the vascular walls, cause a peripheral vasodilation, resulting in lowered systolic blood pressure and increased pulse and respiratory rates. Owing to this vasodilator action, several of the nitrate esters, including amyl nitrate and GTN, are widely used therapeutically for the relief of high blood pressure [66].

1.5.2 Impact Sensitivity of Alkyl Nitrates

GTN is notoriously sensitive to impact and other stimuli. Many industrial accidents have been caused by the impact sensitivity of alkyl nitrates. A method for predicting the impact sensitivity of alkyl nitrates was based on some structural parameters of $C_aH_bN_cO_d$ explosives [67]. Three essential parameters would be needed in this scheme. The results were compared with experimental data and some empirical correlations. Predicted impact sensitivities for 58 explosives had a RMS of deviation from experiment of 27 cm, which was considered good agreement with respect to less accurate values obtained with previous empirical models.

Drop weight impact sensitivities of 58 liquid explosives and melts of high explosives were summarized in [68]. Compounds that were solids at room temperature were heated to just above their melting points. That publication contained data on 12 alkyl nitrate esters, 8 azidonitro compounds, 5 fluoronitro compounds, and 14 nitramines. The data for individual alkyl nitrates were extracted from that paper and inserted in the hazard property tables of individual compounds (Table 11). The compound numbers in the first column of the table are the same as those used in Figure 4. As shown

Table 11: Physical properties and impact sensitivities of alkyl nitrates.

No.	Compound	H50, cm	T, K	T, °C	ΔH_f° , kJ/mol	ΔH_f° , kcal/mol	ρ , g/cm ³	$Q_{\max}$, kcal/g	$\rho Q_{\max}$, kcal/cm ³
1	C(CH ₂ ONO ₂) ₆	2.7	415	142	-558	-133.3	1.6	1.633	2.61
2	O ₂ NOCH ₂ CN(ON(→O)CCH ₂ ONO ₂) ^a	4.5	293	20	-43	-10.3	1.64	1.73	2.84
3	O ₂ NOCH ₂ CH(ONO ₂)CH ₂ ONO ₂	5.6	293	20	-372	-89	1.6	1.603	2.56
4	O ₂ NOCH ₂ CN(ONCCH ₂ ONO ₂) ^a	7.5	293	20	-48	-11.4	1.58	1.638	2.58
5	O ₂ NOCH ₂ CH ₂ ONO ₂	17	293	20	-251	-59.9	1.49	1.742	2.6
7	O ₂ NOCH ₂ CH ₂ OCH ₂ CH ₂ ONO ₂	32	293	20	-367	-87.6	1.39	1.667	2.32
14	CH ₃ CH ₂ ONO ₂	160	293	20	-190	-45.5	1.11	1.635	1.815
19	O ₂ NO(CH ₂) ₄ ONO ₂	67	293	20	-347	-83	1.32	1.58	2.08
26	O ₂ NOCH ₂ CH(ONO ₂)CH ₂ CH ₂ ONO ₂	25.5	293	20	-435	-103.9	1.46	1.628	2.38
28	O ₂ NO(CH ₂) ₆ ONO ₂	160	293	20	-402	-96	1.23	1.509	1.85
32	O ₂ NCNONCCNOC(CH ₂ ONO ₂)N ^a	25	293	20	130	31	1.64	1.479	2.41

^a This is a heterocyclic ring compound
Data source: [68]

in Figure 4, a linear correlation between impact sensitivity and their maximum volumetric heats of explosion $\rho Q_{\max}$ could be established, similar to one already shown for nitroalkanes in section “Nitroaliphatic Compounds”, see also [69].

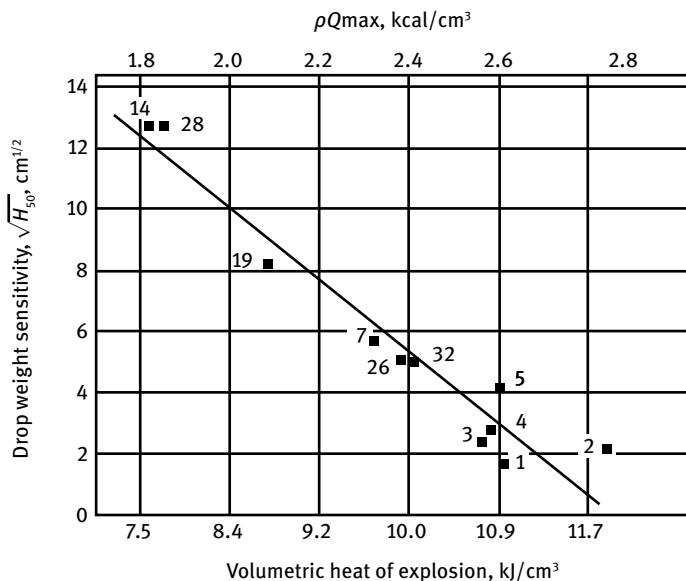


Figure 4: Correlation between the sensitivity of nitrates not containing azide and nitramine groups and their maximum volumetric heats of explosion. (Republished and modified from [68], with permission of © 2010 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

1.6 Detonation Performance of Alkyl Nitrates

Many alkyl nitrates are used as explosives instead of rocket propellants [70]. Detonability of alkyl nitrates intended as rocket propellants is more of a disadvantage, and often desensitizing (phlegmatizing) additives are required before alkyl nitrates can be used as rocket propellants, gas generants, torpedo propellants, or liquid gun propellants. The boosted detonation properties of some alkyl nitrates and alkyl nitrites with a charge diameter of 10 mm in steel tubes are summarized in Table 12.

Table 12: Detonation properties of alkyl nitrates and alkyl nitrites.

Compound	Density	Heat of explosion		Detonation velocity
	g/cm ³	kJ/kg	kcal/kg	km/s
Ethylene glycol dinitrite	1.22	5188	1240	6.45–6.50
1,4-Butylene glycol dinitrite	1.17	3598	860	5.19–5.21
2,3-Butylene glycol dinitrite	1.07	3598	860	—
Ethyl nitrate	0.90	2887	690	4.2–4.5
Nitroethane	1.05	3012	720	—
1,4-Butylene glycol dinitrate	1.315	4519	1080	6.25
2,3-Butylene glycol dinitrate	1.30	4519	1080	6.0–6.19

Data source: [71]

1.7 Applications of Alkyl Nitrates

The list of industrial applications of alkyl nitrates is very long, too long to include in this book. We list here only a few summaries of the uses of alkyl nitrates as energetic materials in propellants and explosives.

A recent book on liquid explosives contains a chapter on the properties and applications of alkyl nitrates as liquid explosives [70]. Some of this information is also useful in evaluating alkyl nitrates as rocket propellants.

The following sections discuss properties and applications of individual alkyl nitrates in detail, starting with mononitrates and then moving on to compounds with more than one nitrate (nitroxy) group in the molecule.

2 Methyl Nitrate

Methyl nitrate, H_3CONO_2 , CH_3NO_3 , $M = 77.0394 \text{ g/mol}$, CAS RN [598-58-3], is an unwanted byproduct in the synthesis of RDX and HMX, and it must be continuously removed during the process. There are few other good uses for this waste material. Theoretically, it could be used as a monopropellant, but it may be too sensitive for that purpose.

Methyl nitrate can be prepared by dissolving methanol in sulfuric acid and slowly adding this solution to a mixture of sulfuric acid and nitric acid with some urea added to prevent formation of nitrites. Both batch and continuous methods were reported to give yields up to 90% [72]. Another synthesis method obtains the product as a 60% solution in methanol, thereby preventing explosions during the nitration.

Methyl nitrate is too sensitive to be used as a rocket propellant by itself and without a diluent. It is mostly used as a simple model substance to study the kinetics of de-

composition in comparison to reactions of higher, more complex alkyl nitrates. Methyl nitrate can be used as a mild nitrating agent. Methyl nitrate and other alkyl nitrates exist as pollutants in the atmosphere and participate in photochemical reactions that lead to smog formation.

2.1 Physical Properties of Methyl Nitrate

The physical properties of methyl nitrate have been thoroughly investigated because it often serves as a model compound for more complex nitrate esters with greater importance. The physical properties of methyl nitrate are summarized in Table 13.

Table 13: Physical properties of methyl nitrate.

Property	SI units		Other units		References
Molecular mass	77.0394 g/mol	12.98 mol/kg			[73]
Freezing point	190.6 K		−82.5 °C		
Boiling point	338 K		65 °C	149 °F	[74]
	338.15 K		65 °C		[75]
Density	1.217 g/cm ³		1.217 g/cm ³		[74]
Triple point	190.2 K		−82.9 °C		[76]
Heat capacity	157.19 J mol ^{−1} K ^{−1}		276.6 cal mol ^{−1} °C ^{−1}		[76]
Enthalpy of formation, liquid	−155.8 kJ/mol	−2023.6 kJ/kg	−37.24 kcal/mol	−483.6 cal/g	[74]
Enthalpy of formation, vapor	−122 ± 1 kJ/mol	−1583 ± 13 kJ/kg	−29.16 kcal/mol	−378.5 cal/g	[73]
Heat of evaporation	34.8 kJ/mol	451.7 kJ/kg	8.3 kcal/mol	107.9 cal/g	[11]
	34.10 kJ/mol	442.6 kJ/kg	8.15 kcal/mol	105.8 cal/g	
Heat of fusion	8.242 kJ/mol	107 kJ/kg	1.97 kcal/mol	25.6 cal/g	

The vapor pressure of methyl nitrate can be calculated from the equation

$$\log p = 26.6767 - 6.3431 \log T - 2620.1139/T$$

where p is the vapor pressure in mm Hg and T is the temperature in kelvin [11]. Additional properties of methyl nitrate and other alkyl nitrates are discussed in [77, 78].

2.1.1 Infrared Absorption Spectra of Methyl Nitrate

Along with publications on the IR spectra of methyl nitrate, there is a large number of publications on the absorption spectra of methyl nitrite that were not included in the current section. Methyl nitrite is only of interest as an atmospheric pollutant and as an isomer to nitromethane (NM), but would not be used as a rocket propellant.

Methyl nitrate is a relatively simple and symmetric molecule but the IR spectrum is nevertheless complex with many absorption bands. The two halves of the molecule rotate freely around the C–N axis. In the IR spectrum of methyl nitrate, the stretching vibrations of the C–H bond appeared in the 3020–2800 region. Three calculated frequencies (3011, 2959, and 2853 cm^{-1}) corresponded to three measured bands in this region [79].

The IR spectrum of methyl nitrate has been reinvestigated [80]. A few errors in previous assignments were corrected (notably the CH stretching modes that are now assigned as $\nu_1 = 3034.1 \text{ cm}^{-1}$, $\nu_2 = 2961.5 \text{ cm}^{-1}$, and $\nu_{13} = 3014.5 \text{ cm}^{-1}$ and the methyl deformation ν_{15} , assigned to 1155.7 cm^{-1}).

A typical IR spectrum of methyl nitrate is shown in Figure 5. Near 3000 cm^{-1} , three peaks occurred in the IR absorption of the liquid but only two peaks were observed in the vapor spectrum [81].

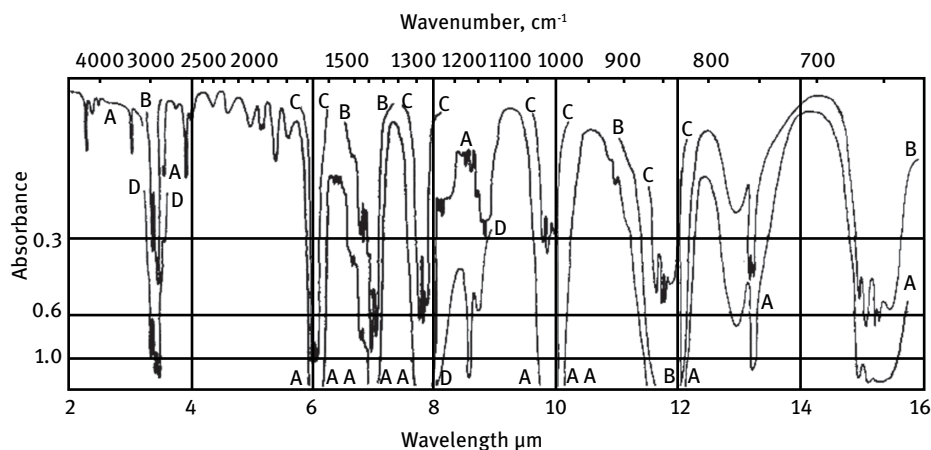


Figure 5: Infrared absorption spectrum of methyl nitrate. (Reprinted [adapted] from [81], with permission from © 1955 American Chemical Society; permission conveyed through RightsLink.)
 Legend: A, 150 mm; B, 40 mm; C, 5 mm vapor in 10-cm cell; D, liquid in 0.1-mm cell

2.1.2 Microwave Spectra of Methyl Nitrate

Microwave spectra of methyl nitrate help to identify the structure of this molecule and complement measurements in other ranges of the electromagnetic spectrum in the IR range. The ground-state rotational constants of methyl nitrate measured by microwave absorption showed that the five heavy nuclei of the molecule lie in the same plane [82,

83]. The hydrogen atoms of the methyl group are found to be staggered with respect to the nearest oxygen of the —NO_2 group. Stark effect measurements gave a dipole moment of 3.10 ± 0.05 D. Data seemed to indicate a significant amount of double-bond character in the CO—N bond. The barrier to internal rotation of the methyl group, as determined from torsional satellite splittings, was 2321 cal/mol. A large discrepancy existed between the experimental and statistical entropies, the reason for which was not clear. Interpretation of this requires inclusion of the —NO_2 group torsion.

The microwave spectra of the normal species and seven isotopic species of methyl nitrate gave data for a detailed structure of the molecule, which has a planar heavy-atom skeleton, with the methyl group staggered with respect to the *cis* oxygen atom [84, 85]. The molecular structure is $\text{C—O}' = 1.437$ Å, $\text{N—O}' = 1.402$ Å, $\text{N—O}(\text{cis}) = 1.205$ Å, $\text{N—O}(\text{trans}) = 1.208$ Å, C—H (in plane) = 1.088 Å, C—H (out-of-plane) = 1.095 Å, $\angle \text{O}'\text{CHi} = 103.4^\circ$, $\angle \text{O}'\text{CHO} = 110.4^\circ$, $\angle \text{HOCHO} = 109.8^\circ$, $\angle \text{CO}'\text{N} = 112.72^\circ$, $\angle \text{O}'\text{NO}(\text{cis}) = 118.10^\circ$, $\angle \text{O}'\text{NO}(\text{trans}) = 129.52^\circ$. The methyl and nitro groups are tilted away from each other; the former is inclined at 4.8° to the $\text{C—O}'$ bond direction, and the latter at 2.9° to the $\text{N—O}'$ direction. The components of the dipole moment determined from Stark effect measurements were $\mu_a = 3.07$ D, $\mu_b = 0.235$ D, $\mu_t = 3.08$ D, and similar measurements on the *trans*- ^{18}O species have shown that the dipole moment in the normal species is oriented at 39.6° to the bridging $\text{N—O}'$ bond. The structure and bonding of methyl nitrate relates to nitric acid as methyl formiate does to formic acid.

2.1.3 Molecular Structure of Methyl Nitrate

The molecular structure of methyl nitrate has been derived from Raman spectra and electron diffraction experiments and discussed in terms of the adjacent charge rule in comparison to methyl azide and nitroxyl fluoride [86]. The molecular structure of methyl nitrate is shown in Figure 6.

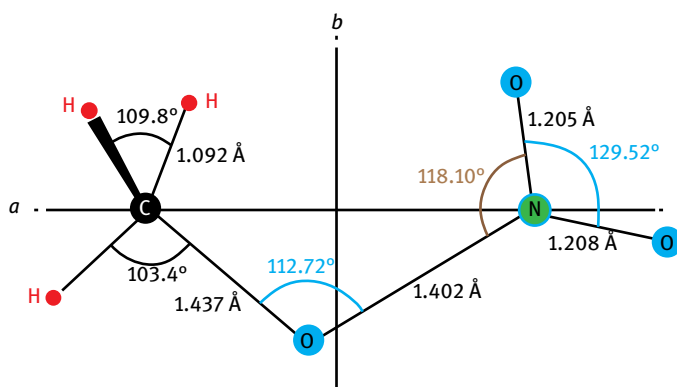
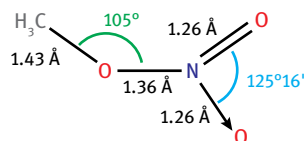


Figure 6: Molecular structure of methyl nitrate

A comparison of measured Raman frequencies with those calculated from various molecular models indicated that the methyl nitrate molecule is not plane but it has a coplanar plane of symmetry (symmetry group C_s) [87]. The atoms O—NO₂ are in one plane and the C atom is in a plane perpendicular to this; the latter plane is the plane of symmetry of the molecule. The C—O—N angle is approximately 116°. The NO₂ group in methyl nitrate has the same structure as in HNO₃.

Electron diffraction studies led to the following structure for methyl nitrate, similar to that shown above [75]:



Based on an *ab initio* study on the intermolecular interaction and thermodynamic properties of methyl nitrate in the vapor phase, methyl nitrate may associate to dimers [88]. The thermodynamic properties of methyl nitrate and its dimers have been calculated based on vibrational analysis and statistical thermodynamics.

Ab initio calculations of the structure and harmonic force field of methyl nitrate have been computed and assignments of the experimental frequencies of CH₃ONO₂ and CD₃ONO₂ were made using quantum-mechanical force constants, which suggested a reassignment of the $\delta(\text{NO}_2)$ and $\rho r(\text{NO}_2)$ vibrations of CD₃ONO₂ [89]. Taking into account these new vibrational assignments, a refined harmonic force field for methyl nitrate was computed using a least-squares technique. See also [79].

2.1.4 Solubility and Miscibility of Methyl Nitrate

Methyl nitrate is slightly soluble in water and miscible with methanol, ethanol, or diethyl ether. Methyl nitrate and methanol form an azeotrope with a composition of 75% methyl nitrate and 25% methanol. This mixture has a boiling point of 330.6 K (57.5 °C). The advantage for the safety of such a mixture is that on evaporation it does not leave the sensitive 100% methyl nitrate behind.

Methyl nitrate in mixture with 20–25% methanol was tested as a monopropellant in rocket engines (*Encyclopedia of Monopropellants*). This mixture became known under the code name *Myrol*.

2.1.5 Thermodynamic Properties of Methyl Nitrate

The heat of formation of methyl nitrate vapor is $\Delta H_f^\circ \text{gas} = -122 \pm 1 \text{ kJ/mol}$ [90]. The entropy of liquid methyl nitrate is $S^\circ_{\text{liquid}} = 216.98 \text{ J mol}^{-1} \text{ K}^{-1}$ [76]. The heat capacity of liquid methyl nitrate at 298 K is $157.19 \text{ J mol}^{-1} \text{ K}^{-1}$. The heat of evaporation of methyl

nitrate at its NBP is $\Delta H^\circ_{\text{vap}} = 31.5 \text{ kJ/mol}$ [11] (Table 14). The enthalpy of fusion at 190.2 K is 8.242 kJ/mol, and the entropy of fusion at 190.2 K is $43.33 \text{ J mol}^{-1} \text{ K}^{-1}$, see [76].

Table 14: Corrected enthalpy of evaporation of methyl nitrate.

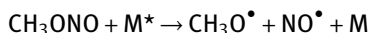
	ΔH_{vap} at 298 K		ΔH_{vap} at NBP		ΔS_{vap}	
	kJ/mol	cal/mol	kJ/mol	cal/mol	$\text{J K}^{-1} \text{ mol}^{-1}$	$\text{cal } ^\circ\text{C}^{-1} \text{ mol}^{-1}$
Methyl nitrate	34.1	8150	31.5	7540	93.3	22.3

2.2 Chemical Properties of Methyl Nitrate

Methyl nitrate has an oxygen balance of -10.4% and thus requires only little oxidizer to make a stoichiometric mixture. However, for optimum rocket performance it is not necessary to operate with stoichiometric mixtures. A slight fuel excess will usually result in better rocket performance. Methyl nitrate has found application as an ingredient in rocket propellants only once.

2.2.1 Rapid Decomposition of Methyl Nitrate

Although our primary interest is in methyl nitrate, a few papers dealing with methyl nitrite are interspersed here for comparison. Methyl nitrite is an intermediate product of methyl nitrate decomposition. Methyl nitrite is an isomer of NM. The thermal decomposition of methyl nitrite in excess argon was studied behind both incident and reflected shock waves [91]. Kinetic data were obtained in the temperature range 715–1118 K and total pressure range 0.8–5 atm. The reaction



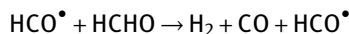
was found to be unimolecular in nature and occurring in the low-pressure region, with a rate constant expression

$$k = 10^{16.36 \pm 0.22} \exp(-30400 \pm 850/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

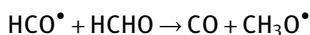
giving the best least-squares fit to the data.

The decomposition of methyl nitrate (0.25–1.75% in argon at 880–1250 K and 2.8–18.6 atm) behind incident shock waves was measured by monitoring visible and UV absorptions in the reacting gas was observed to occur in two distinct stages. The initial dissociation and subsequent fast reactions of the methoxy radical occurred almost instantaneously at the shock front [92]. This was then followed by a much slower reaction involving decomposition of formaldehyde in the presence of nitrogen oxides. The kinetics of this second reaction showed a total order of slightly less than 2.0 and

an apparent activation energy of about 100 kJ/mol (24 kcal/mol). Second-stage rates for ethyl nitrate (1.0% in argon) were virtually identical to those for methyl nitrate, even though much less NO₂ is present in the case of ethyl nitrate. Second-stage reactions did not occur below about 800 K. Modeling calculations showed that at these temperatures, methoxy radicals will dissociate in the first reaction stage, rather than disproportionate as at lower temperatures. In the second stage of reaction, NO₂ interrupts the normal chain decomposition of formaldehyde to produce OH radicals, which then propagate the chain by hydrogen abstraction from formaldehyde. It is proposed that direct attack of formyl radicals on formaldehyde, i.e.,



or



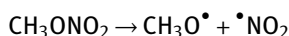
may be the dominant pathway for formaldehyde decomposition (in the absence of NO₂) for temperatures too low for fast unimolecular dissociation of HCO.

The rapid decomposition of methyl nitrate and other alkyl nitrates in shock waves is a good method to obtain kinetic rate data for fast decomposition rates for relatively simple reactions [93, 94].

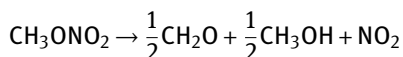
2.2.1.1 Methyl Nitrate Decomposition Mechanisms

Methyl nitrate, the lowest member in the family of alkyl nitrates, is often used as a model substance to study the decomposition mechanisms of more complex alkyl nitrates. These studies have only academic value because methyl nitrate has not seen any application in rocket engines.

The proposed first step for the thermal decomposition of methyl nitrate is the homolysis of the N–O bond:



At 483–513 K (210–240 °C) and 666–2000 Pa (5–15 mm Hg), the thermal decomposition of methyl nitrate is unimolecular and the chemical equation is

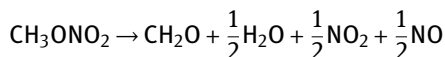


The rate constant for thermal decomposition of methyl nitrate in the temperature range 483–516 K is [95, 96]

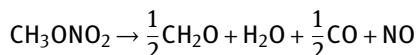
$$k = 2.50 \times 10^{14} \exp(-165000/RT)$$

where k is the rate constant in s⁻¹, R is 8.314472 J mol⁻¹ K⁻¹, and T is the temperature in kelvin. The activation energy is 165 kJ/mol. Above 513 K (240 °C) more complete decom-

position takes place, and between 529 and 597 K (256 and 324 °C) an explosion with an induction period follows the equations

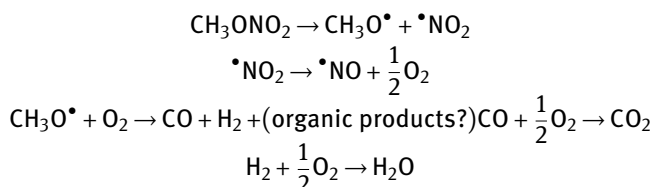


and



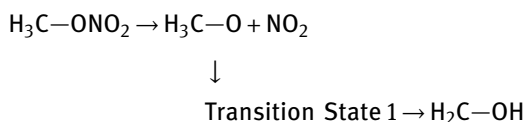
From the change in the induction period as a function of pressure and temperature, surface area/volume ratio and the effect of addition of inhibitors such as NO_2 , it was concluded that the explosion is a thermal explosion.

The following decomposition mechanism was proposed for methyl nitrate:

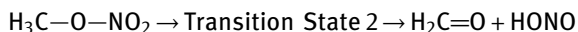


To decide which of these mechanisms is rate determining, one must use isotope labeling, identify short-lived intermediates spectroscopically, or use a computer-based prediction method.

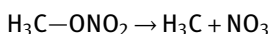
Two DFT computational methods were used to predict some possible decomposition pathways for methyl nitrate [97]. Two likely routes were found to be (a) loss of NO_2 , followed by eventual rearrangement to $\text{H}_2\text{C}-\text{OH}$,



or (b) formation of $\text{H}_2\text{C}=\text{O}$ and HONO :



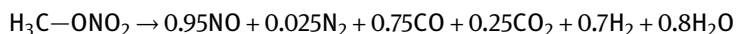
The initial energy requirement for each process was about 167 kJ/mol (40 kcal/mol), and the second was exothermic, $\Delta H = -67$ kJ/mol = -16 kcal/mol of $\text{H}_3\text{CO}-\text{NO}_2$. The computation was found to underestimate the $\text{H}_3\text{CO}-\text{NO}_2$ and $\text{H}_3\text{C}-\text{ONO}_2$ dissociation energies by about 29.3 kJ/mol (7 kcal/mol). A third, less likely, route would split the C—O bond directly



The thermal decomposition of methyl nitrate vapor can transition to a detonation [98, 99]. See also [100].

2.2.2 Autoignition of Methyl Nitrate Vapor

The P - T_{autoign} ignition boundary of the thermal decomposition of methyl nitrate at low pressures in a closed vessel and the resultant self-heating leading to ignition in a spherical, Pyrex-glass reaction vessel ($V = 1088 \text{ cm}^3$, $r = 6.4 \text{ cm}$) over a wide temperature range (510–650 K) has been measured [101]. Explosion at the highest pressures studied (4 kPa) was made more difficult by convection. In all circumstances ignition did not occur instantly on gas entry. An induction time was observed and several pre-reactions may take place simultaneously during the delay. The overall activation energy for the fast reaction varied, and it corresponded to an overall activation energy of $142 \pm 8 \text{ kJ/mol}$. The half-life for methyl nitrate decomposition decreased 1000-fold over the whole temperature range. Whereas at low temperatures ignition instability appeared to be controlled by the rate of O–N bond fission, at high temperatures secondary reactions of the molecular products of decomposition become more important. In comparison, the activation energy of the slow, isothermal decomposition of methyl nitrate is only $E_{\text{act}} = 151 \pm 3 \text{ kJ/mol}$ [102], which is appreciably lower than that obtained by Appin, Khariton, and Todes [95] from slow-decomposition studies ($E_{\text{act}} = 165 \text{ kJ/mol}$). The decomposition of methyl nitrate vapor, when it ignites spontaneously at 573 K (300 °C), follows the equation



2.2.3 Computations of Methyl Nitrate Hydrolysis and Decomposition

The high-temperature decomposition of methyl nitrate was modeled by a kinetic model, assuming activation energies obtained from other sources [103] and rate-of-decomposition data obtained from decomposition of methyl nitrate in shock waves [94].

A semiempirical molecular orbital computational method has been employed to investigate the mechanism of the alkaline SN_2 hydrolysis of methyl nitrate and the influence of solvents on the hydrolysis reaction [104, 105]. The activation energy calculated was 50.6 kJ/mol for hydrolysis in the gas phase; however, when the solvent effect was taken into account, it increased to 89.6 kJ/mol, in agreement with the experimental result (82.4 kJ/mol). It was shown that the solvation energy is an important segment of the activation energy.

Although methyl nitrate and ethyl nitrate are not (normally) found in standard minimum-smoke rocket propellant formulations, they are the simplest organic nitrate esters and suitable for modeling the decomposition of alkyl nitrates as a family. Various measurements of their decomposition and combustion have been published. A computational method was developed to characterize postulated (unimolecular) thermal decomposition pathways for the decomposition of methyl nitrate or ethyl nitrate [106]. Thermochemical properties and reaction path parameters were estimated on the basis of results from *ab initio* and DFT-based quantum chemistry models. Those data were then utilized in conjunction with (1) the principles of thermochemical kinetics, (2) transition state theory/variational transition state

theory, and (3) quantum theory with master equation analysis to develop rate expressions for elementary reactions. Combined with a set of rate expressions for small-molecule reactions that were developed for modeling other systems, a detailed mechanism for the pair was assembled.

2.2.4 Photolysis of Methyl Nitrate

All studies of the photolysis of methyl nitrate have been conducted with highly diluted samples simulating the processes taking place in a polluted atmosphere. For us it would be interesting to study the laser ignition of methyl nitrate if it was to be used as a rocket propellant (again).

Atmospheric photodissociation rate coefficients and photodissociation lifetimes for NM, methyl nitrite, and methyl nitrate were calculated as a function of altitude from their measured visible and near-UV photoabsorption cross sections at 298 K [107]. The lifetime of methyl nitrite is nearly independent of altitude and is approximately 2 min. From 0 to 50 km the lifetime of NM varies from 10 to 0.5 h, while that of methyl nitrate changes from 5.3 to 0.09 d, respectively.

The photodissociation dynamics of methyl nitrate has been investigated at 193 nm by examining the products from the primary dissociation channel, namely $\text{CH}_3\text{O}^\bullet$ and $^\bullet\text{NO}_2$ [108]. The $\text{CH}_3\text{O}^\bullet$ photoproducts were probed by laser-induced fluorescence under both nascent and jet-cooled conditions. The NO_2 fragment is produced electronically excited with internal energies extending to the $\text{NO} + \text{O}$ dissociation limit.

Quantum yields were measured for the NO_2 formation channel ($\text{RO}^\bullet + ^\bullet\text{NO}_2$) following photodissociation of methyl nitrate or IPN at the tropospherically relevant wavelengths of 308–320 nm [109]. Measurements were made using UV laser absorption and cavity ring-down spectroscopy detection of the NO_2 photoproducts. Photodissociation quantum yields were measured to be unity for both methyl nitrate and IPN at wavelengths of 308, 315, and 320 nm in the presence of N_2 bath gas at pressures of up to 700 Torr and at a temperature of 294 K.

A laboratory study of the gas-phase photolysis and $^\bullet\text{OH}$ -initiated reactions of methyl nitrate and ethyl nitrate with a focus on elucidating the detailed photochemical reaction mechanisms of alkyl nitrates in the atmosphere gave unexpectedly high yields of HNO_3 and peroxyacyl nitrates such as $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ [110]. The results implied that alkyl nitrates could potentially serve as a sink for reactive nitrogen in the atmosphere. An attempt was made to estimate the production of HNO_3 and peroxyacyl nitrates derived from NO_x by alkyl nitrates as intermediates in the atmosphere.

2.3 Handling and Safety Properties of Methyl Nitrate

2.3.1 Toxicity of Methyl Nitrate

The physiological action of methyl nitrate is similar to that of GTN and other alkyl nitrates. If inhaled accidentally, it causes headaches, but the headaches subside more quickly than those caused by GTN.

2.3.2 Explosive Properties of Methyl Nitrate

Methyl nitrate and its mixtures with methanol, nitrobenzene, or benzene were used in Germany toward the end of World War II (WWII) as explosives in war heads, mines, torpedoes, and grenades. Several Myrol manufacturing plants were built in Germany toward the latter half of WWII and the nominal capacity was reported to have been near 20000 tons per month. A single installation could produce as much as 400 tons per month.

For use as a plastic explosive, methyl nitrate or Myrol was gelled with a few percent of nitrocellulose. Adding as much as 25% nitrocellulose would form a hard gel.

2.3.2.1 Shock Sensitivity of Methyl Nitrate

In the Bundesanstalt für Materialforschung und -prüfung (BAM) impact sensitivity test apparatus the impact sensitivity of methyl nitrate was 0.2 N·m. In another drop weight sensitivity test apparatus with a 2-kg mass, methyl nitrate exploded at 40 cm (for comparison: GTN 4 cm). In the BAM friction sensitivity test apparatus methyl nitrate showed no reaction at piston loads up to 353 N.

2.3.2.2 Adiabatic Compression Sensitivity of Methyl Nitrate

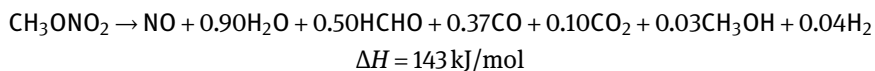
In a U-tube apparatus with variable, preselected push pressure and constant bubble size, the push pressure required to explode methyl nitrate was the lowest in a group of 20 energetic liquids tested [111]. Only methyl nitrate and allyl nitrate were more sensitive than GTN. The adiabatic compression sensitivity of these compounds depends on the degree of dissolved gas saturation.

2.3.2.3 Autodecomposition Temperature and Diluent Effects of Methyl Nitrate

The decomposition of methyl nitrate, air, and water vapor mixtures heated to 473 K (200 °C) and ignition by hot wire at 373 K (100 °C) was studied for methyl nitrate concentrations from 15 to 35%, air from 15 to 45%, and steam from 20 to 65% [112]. Ignition with explosion was observed for 24% methyl nitrate, 29% air, and 47% H₂O, and for 30% methyl nitrate, 15% air, and 55% H₂O. Combustion without explosion on ignition was observed for other mixtures. Air saturated with H₂O and methyl nitrate over liquid methyl nitrate was ignited in a lead block and produced sympathetic detonation of the liquid below. With a protective layer of H₂O covering the methyl nitrate, a detonation

of the liquid did not occur. Heating to 473 K (200 °C) (no hot wire) caused only slow decomposition and no explosions.

The spontaneously explosive decomposition of methyl nitrate vapor over the temperature range 523–589 K was measured using fine thermocouples and fast-response recorders [113]. Product analysis gave the stoichiometry and thermochemistry of the subcritical decomposition of methyl nitrate as



Indirect tests for a thermal explosion were applied to the spontaneous ignition of methyl nitrate, and critical initial reactant pressures could be correlated on the basis of thermal theory. A prediction that the critical partial pressure of diluted reactant should be directly proportional to the thermal conductivity of the mixture was only approximately satisfied. Self-heating was always observed, and ignition could not occur without it. The maximum subcritical rises measured in a cylindrical vessel were about 18 K, and in a spherical vessel they were about 40 K.

2.4 Explosive Performance of Methyl Nitrate

In the lead block test, detonation of methyl nitrate caused an increase of the cavity volume by 610 cm³/10 g, which is a very respectable number. The brisance in the lead block test was 132% of that of GTN. Other sources reported 102.5% of that of GTN for a 10-g sample with water tamping. The detonation velocity of methyl nitrate confined in a steel tube is 6300 m/s = 20700 ft/s at $\rho = 1.217 \text{ g/cm}^3$.

Methyl nitrate confined in a glass tube can detonate in three different ways, depending on sample diameter and method of initiation [114]. In a 10-mm glass tube it can detonate with high velocity detonation (HVD) at 6704 m/s, stable low velocity detonation (LVD) at 2540 m/s in a similar glass tube, and unstable LVD in a 5-mm glass tube at 2140 m/s.

In similar tests, when confined in glass or metal tubes of small diameter (3 to 5 mm), the detonation velocity was low, ranging from 1890 to 2482 m/s, vs. 1500 m/s for GTN. When confined in a glass tube with 20-mm diameter and 1-mm wall thickness, the detonation velocity was 6600 m/s. According to some authors, values up to 8000 m/s should be obtainable in tubes with a diameter of 30–40 mm.

3 Ethyl Nitrate

3.1 Physical Properties of Ethyl Nitrate

Ethyl nitrate, $\text{C}_2\text{H}_5\text{NO}_3$, CAS RN [625-58-1], is a colorless, volatile, highly flammable liquid. It is used in organic synthesis and as an intermediate in the preparation of some drugs, dyes, and perfumes. It is unlikely that ethyl nitrate will be used as a rocket propellant, but it has been used in mixtures with propyl nitrate as a gas generant for auxiliary power units, and it can serve as a model substance for the study of the entire family of alkyl nitrates, some of which have been used as gas generants. Physical properties of ethyl nitrate are summarized in Table 15.

Table 15: Physical properties of ethyl nitrate.

Property	SI units	Other units	References
Molecular mass	91.0660 g/mol	10.98 mol/kg	[73]
Freezing point	171 K	$-102^\circ\text{C} = -151.6^\circ\text{F}$	[115]
Melting point	178.6 K	-94.5°C	[116]
Boiling point	361.8 K	$88.7^\circ\text{C} = 191.7^\circ\text{F}$	[115]
Boiling point	362 K	89°C	[116]
Density (at 22°C)		1.105 g/cm^3	[115]
Index of refraction $n_D^{21.5}$	1.38484		
Enthalpy of formation, liquid	$-190.4 \text{ kJ/mol} =$ -2091 kJ/kg	$-45.49 \text{ kcal/mol} =$ -499.5 cal/g	[74]
Enthalpy of formation, vapor	-155.0 kJ/mol	-37.05 kcal/mol	[117]
Enthalpy of formation, liquid	-190.4 kJ/mol	-45.5 kcal/mol	[118]
Enthalpy of formation, vapor	-154.0 kJ/mol	-36.80 kcal/mol	[118]

The vapor pressure of ethyl nitrate can be represented by an Antoine equation,

$$\log_{10} p = 7.145 - 1329/(t + 224.0)$$

where p is the vapor pressure in mm Hg and t is the temperature in $^\circ\text{C}$ [119]. From the vapor pressure curve a heat of evaporation can be calculated, and it is $36.4 \text{ kJ/mol} = 8.7 \text{ kcal/mol}$ at $298 \text{ K} = 25^\circ\text{C}$ and $33.9 \text{ kJ/mol} = 8.1 \text{ kcal/mol}$ at the NBP at $360.8 \text{ K} = 87.7^\circ\text{C}$. The Trouton constant is $92 \text{ J K}^{-1} \text{ mol}^{-1} = 22 \text{ cal } ^\circ\text{C}^{-1} \text{ mol}^{-1}$. The enthalpy of formation of ethyl nitrate vapor at $298 \text{ K} = 25^\circ\text{C}$ is $-155 \text{ kJ/mol} = -37.0 \text{ kcal/mol}$. See also [120, 121].

3.1.1 Optical Properties of Ethyl Nitrate

3.1.1.1 Infrared Spectra of Ethyl Nitrate

The far-IR spectra of gaseous and solid ethyl nitrate have been recorded from 500 to 50 cm^{-1} to determine the relative proportions of *gauche* and *trans* conformers and the energy barriers for transitions from one form to the other [122]. The results of a variable-temperature Raman study indicated that the *trans* conformer is more stable than the *gauche* conformer by $328 \pm 96\text{ cm}^{-1}$ ($938 \pm 275\text{ cal/mol}$).

A vibrational assignment for the normal vibrational modes of gaseous, liquid, and solid ethyl nitrate was proposed based on Raman spectra ($4000\text{--}10\text{ cm}^{-1}$), depolarization values, group frequencies, and normal coordinate calculations [123]. The structures for the *trans* and *gauche* conformers were determined from *ab initio* Hartree-Fock gradient calculations. The energy difference between the more stable *trans* conformer and the higher-energy *gauche* conformers was found to be 474 cm^{-1} (1.36 kcal/mol). The *trans* to *gauche* and *gauche* to *gauche* barriers were 990 cm^{-1} (2.83 kcal/mol) and 3152 cm^{-1} (9.01 kcal/mol), respectively. Barriers to internal rotation for the CH_3 and NO_2 groups were also obtained from *ab initio* calculations. For the *trans* conformer the values were 1304 cm^{-1} (3.73 kcal/mol) and 2702 cm^{-1} (7.73 kcal/mol), and for the *gauche* conformer they were 1161 cm^{-1} (3.32 kcal/mol) and 2758 cm^{-1} (7.89 kcal/mol) for the CH_3 and NO_2 rotational barriers, respectively. The IR spectrum of ethyl nitrate is shown in Figure 7.

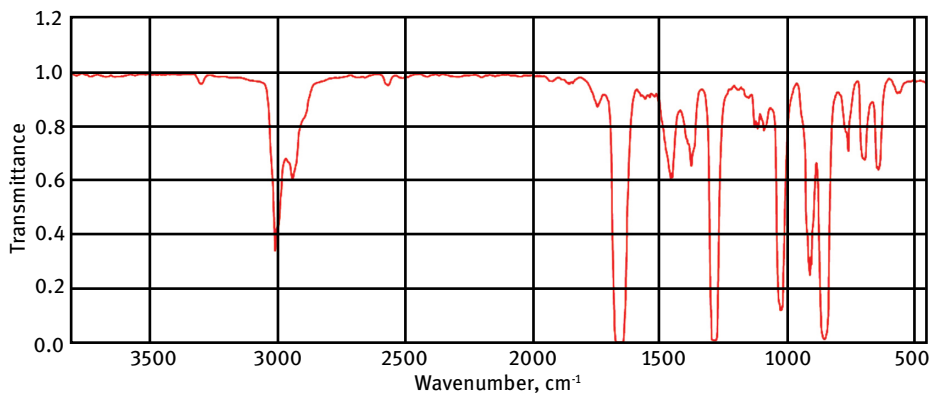


Figure 7: IR Spectrum of ethyl nitrate. (Reproduced and modified with permission from [124])

3.1.1.2 Ultraviolet Spectra of Ethyl Nitrate

The photoabsorption spectra of gaseous ethyl nitrate, NPN, 2-propyl nitrate, and *n*-butyl nitrate were measured in the laboratory at room temperature for $\lambda \geq 185$ nm [125]. The spectra were continuous and exhibited low- and high-intensity absorption bands. The maximum for the high-intensity band occurred at 188 ± 2 nm. Atmospheric photodissociation rate coefficients for alkyl nitrates were estimated in the range 0–50 km and were found to have a strong dependence on altitude. Photodissociation lifetimes were on the order of days and hours for the troposphere and stratosphere, respectively. Compared with the reaction with $\cdot\text{OH}$, photodissociation is the dominant removal process for alkyl nitrates throughout the atmosphere.

3.1.2 Thermodynamic Properties of Ethyl Nitrate

The standard enthalpy of formation at 298 K (25 °C) of liquid ethyl nitrate, -191 kJ/mol (-45.7 kcal/mol), and of gaseous ethyl nitrate, -155 kJ/mol (-37.0 kcal/mol), derived from vapor pressure measurements and IR spectra, was later substantiated from the heat of combustion which resulted in a standard enthalpy of formation of liquid ethyl nitrate of -190.4 ± 1.0 kJ/mol (-45.51 ± 0.25 kcal/mol) [126].

The recommended enthalpy of formation of liquid ethyl nitrate is $\Delta H_f^{298} = -191.6 \pm 3.3$ kJ/mol = -45.8 ± 0.8 kcal/mol, and the entropy of formation is $\Delta S_f^{298} 494 \text{ J K}^{-1} \text{ mol}^{-1} = 118.1 \text{ cal } ^\circ\text{C}^{-1} \text{ mol}^{-1}$ [116].

3.1.3 Molecular Structure of Ethyl Nitrate

The existence of two rotational isomers (“rotamers”) of ethyl nitrate has been confirmed by gas phase microwave spectroscopy [127]. The isomers were designated *trans* and *gauche* to indicate the relative positions of the $-\text{CH}_3$ and $-\text{NO}_2$ groups. The rotamers of ethyl nitrate are illustrated in Figure 8.

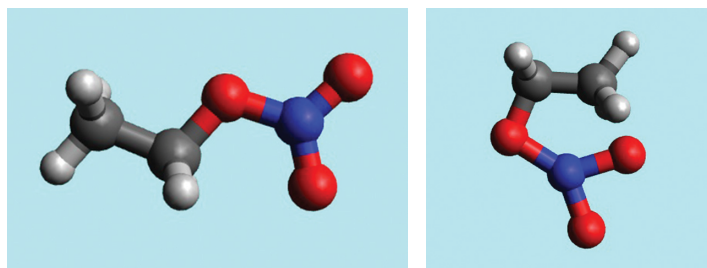


Figure 8: Conformations of *trans* and *gauche* rotamers of ethyl nitrate.

In the *trans* form all the heavy atoms lie in a plane. The *gauche* form differs from the *trans* by a rotation about the C–O bond of 95° and by an opening of the $\angle \text{CON}$ angle

by $\approx 3^\circ$. Both changes appear to indicate considerable non-bonded interaction of the $-\text{CH}_3$ and $-\text{NO}_2$ groups. Stark effect measurements determined the dipole moments to be: $\mu_{\text{trans}} = 3.39 \text{ D}$ and $\mu_{\text{gauche}} = 3.23 \text{ D}$. The *gauche* form is less stable by $143 \pm 70 \text{ cm}^{-1}$. The bond distances and angles in Figure 9 are color coded.

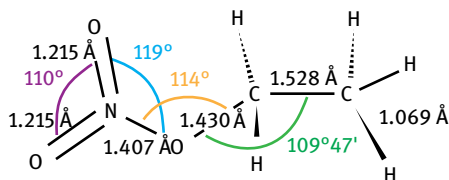


Figure 9: Molecular structure of ethyl nitrate (*gauche* configuration).

The molecular geometry of ethyl nitrate has been determined by gas-phase electron diffraction and *ab initio* molecular orbital calculations [128]. There was reasonable agreement between the experimental and computed structures and also with the rotational constants from a previous microwave study. Both *anti* and *gauche* forms were present at 310 K with the *anti* form prevailing. The following bond lengths and bond angles were obtained for the *anti* form: $\text{C}-\text{O} 1.444 \pm 0.004 \text{ \AA}$, $\text{N}-\text{O} 1.406 \pm 0.004 \text{ \AA}$, $\text{C}-\text{C} 1.520 \pm 0.004 \text{ \AA}$, $\text{N}-\text{O}(\text{mean}) 1.208 \pm 0.003 \text{ \AA}$, $\angle \text{CON} 113.0 \pm 0.6^\circ$, $\angle \text{ONO}(\text{anti}) 112.2 \pm 1.0^\circ$, $\angle \text{ONO}(\text{syn}) 118.2 \pm 0.7^\circ$, $\angle \text{CCO} 106.0 \pm 1.0^\circ$. The angles of torsion are $\varphi_{\text{anti}} 5.4 \pm 3.0^\circ$ and $\varphi_{\text{gauche}} 104 \pm 8^\circ$; an angle of 0° corresponds to the *anti* form. The nitrogen bond configurations were similar in ethyl nitrate, methyl nitrate and nitric acid. The most important *anti/gauche* parameter difference appears in the $\angle \text{CCO}$ bond angle; this angle being some 7° smaller in the *anti* form than in the *gauche* form.

The geometries, total energies, and electronic structures of ethyl nitrate and its dimers have been calculated by using an *ab initio* method [129]. All the binding energies have been corrected by the basis set superposition error and zero point energy. The greatest corrected dimer binding energy was 11.46 kJ/mol . Charge transfer between two subsystems was small. Based on vibrational analysis, the changes of thermodynamic properties from monomer to dimer have been calculated using a statistical thermodynamic method. See also: [130, 131].

3.2 Chemical Properties of Ethyl Nitrate

Ethyl nitrate has an oxygen balance of -61.5% and thus would require a substantial amount of oxidizer to be mixed in to make a decent near-stoichiometric monopropellant.

At one time the US Department of Defense had a military specification for an ethyl nitrate/propyl nitrate mixture MIL-E-26603 – Ethyl Nitrate-Propyl Nitrate Mixture, Pro-

pellant but it has been canceled and is no longer maintained. This indicates that there must have been an application for this propellant mixture, most likely as a gas generator for jet engine starters, but no documents about its use have survived.

3.2.1 Slow Thermal Decomposition of Ethyl Nitrate

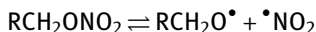
Because ethyl nitrate is readily available, it has been often used (similar to methyl nitrate) as the model compound for studies of the thermal decomposition of nitrate esters, although it has never seen practical applications as a monopropellant by itself like the homologue propyl nitrates.

A stream of dry, oxygen-free nitrogen at atmospheric pressure was bubbled through ethyl nitrate to load it with a partial pressure of 2.4 kPa (18 mm Hg) of ethyl nitrate vapor and passed through an electrically heated glass tube at 473–523 K (200–250 °C) and the decomposition products were analyzed [132]. The dwell times were 8–38 s. The decomposition of ethyl nitrate is a first-order reaction. Incomplete decomposition showed ethanol and acetaldehyde as intermediate products. The reaction zone emitted a faint, uniform light that was visible only in a darkened room.

The thermal decomposition of gaseous ethyl nitrate has been studied at 434–474 K (161–201 °C) at pressures of a few cm Hg to below 20 cm Hg in a static test in glass bulbs [133–135]. An analytical technique was developed using the absorption spectra in the IR and visible regions that made it possible to follow the disappearance of ethyl nitrate directly. It was found that ethyl nitrite is a major product of the reaction and that methyl nitrite and NM were formed in minor amounts. Nitrogen dioxide and nitric oxide were also observed. The variations with time of ethyl nitrate, ethyl nitrite, and nitrogen dioxide have been followed quantitatively to serve as input for kinetic rate calculations. The effects of nitrogen dioxide, ethyl nitrite, and mercury on the reaction have been studied. The activation energy was initially 164.4 kJ/mol (39.3 kcal/mol) and later dropped to 153.1 kJ/mol (36.6 kcal/mol). The mechanism for nitrate ester decomposition was reexamined in light of these results, and some revisions had to be suggested. See also [136].

The effects of nitrogen dioxide, oxygen, nitric oxide, acetaldehyde, and diethyl peroxide on the thermal decomposition of ethyl nitrate at 454 K (181 °C) were studied, and the progress of the reaction was monitored by IR [137, 138]. The results of these studies have been examined in light of a mechanism proposed in an earlier paper and gave it strong support. On the basis of the proposed mechanism, it has been possible to carry out the thermal decomposition of ethyl nitrate under conditions such that the kinetics were truly first order and the activation energy and frequency factor could be properly related to the step wherein the N–O bond was broken. Addition of NO₂ lowered the rate of nitroethane decomposition to half the rate that would have been required in the absence of added NO₂. Ethyl nitrite did not affect the rate of decomposition of ethyl nitrate. Nitric oxide addition resulted in a sharp rate increase, but it was not proportional to the amount of NO added.

The primary step in the decomposition of alkyl nitrates is considered to be the breaking of the N—O bond. It was shown that such decompositions are retarded by initially added nitrogen dioxide, and it was suggested that this primary step is an equilibrium reaction [139]:



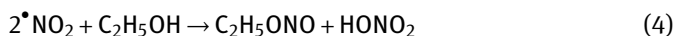
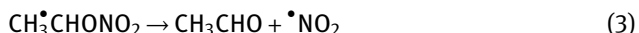
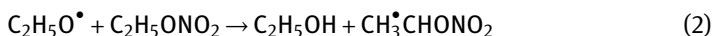
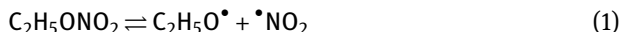
Nitric oxide, NO, is often added as a free radical getter. Reactions that can be impeded by NO addition usually involve free radicals in some of the rate-determining steps of the reactions. It has been customary to assume that NO inhibits reactions in the gas phase by the removal of active free radicals with the formation of compounds of the type RNO, where R is the radical. However, inhibition by nitric oxide may not necessarily indicate a free radical mechanism [140].

The kinetics of the thermal decomposition of ethyl nitrate in the gas phase have been studied in the temperature range 448–482 K (175–209 °C) [141, 142]. The initial rate of pressure rise has been used to deduce the first-order rate equation

$$k = 10^{14.74} \exp(-38000 \pm 380)/RTs^{-1}$$

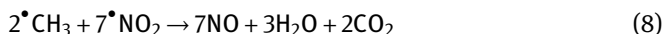
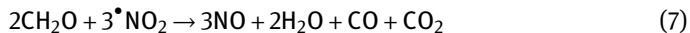
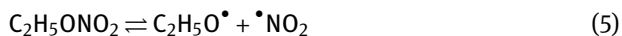
Additional information was obtained from photometric measurements of the nitrogen dioxide concentration throughout the reaction. Ethyl nitrite has been detected in the products of the ethyl nitrate + nitric oxide reaction at 463 K (190 °C) by UV spectrophotometry, and ethyl nitrate has been detected in the products of the ethyl nitrite + nitrogen dioxide reaction at 463 K (190 °C) by GC. Standard analytical techniques showed that the final gaseous products are CO₂, CO, NO, N₂O, and N₂, with possibly a trace of hydrogen.

The principal product of ethyl nitrate decomposition is ethyl nitrite, with NM and methyl nitrite being minor products. On the basis of outdated kinetic studies that relied solely on manometric data, the following (incorrect) mechanism was proposed at one time:

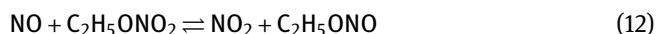


Later work with improved instruments showed that ethyl nitrite is the principal product formed in the early stages of reaction, with NM and methyl nitrite occurring in minor quantities. The outdated mechanism would set an upper limit of 50% on the yield of ethyl nitrite, based on the ethyl nitrate decomposed, whereas yields as high as 75% were found. Reactions (3) and (4) can likewise be rejected since acetaldehyde, which should be a major product if the proposed mechanism were valid, is present in

the products in only very small amounts. A more complex mechanism was proposed later:



The observed lowering of the rate by the addition of nitrogen dioxide can be explained by the fact that the nitrogen dioxide accelerates the reverse of step (5). At one time, an exchange reaction between nitric oxide and ethyl nitrate was proposed:



If reaction (12) were to occur, there should be a continual increase in the rate with addition of nitric oxide, contrary to what was observed.

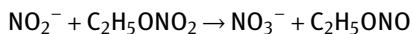
The reaction kinetics of ethyl nitrate decomposition by pyrolysis in a temperature range of 515–533 K (242–260 °C) were examined in a flow reactor in a stream of ethyl nitrate vapor in helium carrier gas and found to be of one-half order with respect to the reactant [143, 144]. A major portion of the organic product was a polyether, probably formed from formaldehyde. The activation energy and frequency factor were determined to be 46.8 kcal/mol and $10^{18.2} (\text{mmol/L})^{1/2} \text{s}^{-1}$, respectively. These data were consistent with a radical chain mechanism in which termination occurs through the interaction of two of the monomolecularly decomposing chain-carrying species, which is the ethoxide radical.

The fact that a decrease in volume: surface ratio and coating the interior of glass vessels with KCl will move the explosive limits up is an indication that the decomposition of ethyl nitrate is a radical mechanism. In a plain, uncoated Pyrex vessel, the kinetic rate equation was

$$k_1 = 10^{14.7} \exp(-38.3/RT) \text{s}^{-1}$$

The presence of a copper surface accelerated the thermal decomposition of ethyl nitrate [145]. Under these conditions the rate-controlling step appeared to involve the NO_2 molecule. The presence of a lead oxide surface in the glass vessel retarded the thermal decomposition of ethyl nitrate in the temperature range studied (453–493 K = 180–220 °C). It was suggested that this was due to the destruction of radicals through which the reaction normally proceeds under these conditions.

High-pressure mass spectrometric measurements were carried out to examine the mechanism of gaseous NO_3^- ion formation in pure ethyl nitrate vapor and its binary mixtures with various diluent gases [146]. An ion exchange reaction



occurring with an activation energy was reported, and evidence for collisional deactivation of the intermediate complex $\text{NO}_2 \bullet \text{C}_2\text{H}_5\text{ONO}_2$ was obtained.

Although ethyl nitrate is not (normally) found in standard minimum-smoke rocket propellant formulations, it is one of the simplest organic nitrate esters and suitable for modeling the decomposition of alkyl nitrates as a family. Various measurements of ethyl nitrate decomposition and combustion have been published. A computational method was developed to characterize postulated (unimolecular) thermal decomposition pathways for the decomposition of ethyl nitrate [106]. Thermochemical properties and reaction path parameters were estimated on the basis of results from *ab initio* and DFT-based quantum chemistry models. Those data were then utilized in conjunction with (1) the principles of thermochemical kinetics, (2) transition state theory/variational transition state theory, and (3) quantum theory with master equation analysis to develop rate expressions for elementary reactions. Combined with a set of rate expressions for small-molecule reactions that were developed for modeling other systems, a detailed mechanism for ethyl nitrate was assembled. Incorporated into a one-dimensional, two-phase burn-rate model, this mechanism yielded predictions for the rate of decomposition of ethyl nitrate at pressures from 0.1 to 6.8 MPa (1 to 68 atm) that were in reasonable agreement with measured data. See also [6].

3.2.2 Rapid Thermal Decomposition of Ethyl Nitrate

The rapid thermal decomposition of ethyl nitrate and other nitrate esters is typically examined in shock tubes, where the sample can be heated almost instantly to the desired test temperature without spending too much time at intermediate temperatures while it is warming up. The decay of the reactant and the rate of formation of intermediate and final products can usually be monitored by spectroscopic or mass spectrometric methods.

The decomposition of alkyl nitrates (0.25–1.75% in argon at 880–1250 K and 2.8–18.6 atm) behind incident shock waves as measured by monitoring visible and UV absorptions in the reacting gas was observed to occur in two distinct stages. The initial dissociation occurred almost instantaneously at the shock front [92]. This was then followed by a much slower second reaction. Second-stage rates for ethyl nitrate (1.0% in argon) were virtually identical to those for methyl nitrate, even though much less NO_2 is present in the case of ethyl nitrate. Second-stage reactions did not occur below about 800 K.

The rapid decomposition of ethyl nitrate and other alkyl nitrates in shock waves is a good method of obtaining kinetic rate data for fast decomposition rates for relatively simple reactions [94].

3.2.3 Temperature Threshold of Autodecomposition of Ethyl Nitrate

Ethyl nitrate and many other alkyl nitrates and nitroalkane vapors will autoignite once they are heated beyond a threshold temperature where autodecomposition will result in a runaway reaction, leading to ignition. The threshold temperature depends on the sample pressure, eventual diluents or inhibitors, and the surface condition of the reaction vessel.

The inflammation of methyl nitrate, ethyl nitrate, or NG vapors and the influence of different diluents on the threshold temperature were investigated over a temperature range of 513 to 773 K (240 to 500 °C) [99, 147]. The explosion of methyl nitrate is facilitated by both argon and nitrogen. With oxygen as diluent, explosive combustion occurs. The results showed that the explosion is not thermal, but due to chain branching. A glow region has been observed with MeNO_3 , EtNO_3 , or NG at below-explosion-limit marginal pressures and temperatures. These nitrates will emit a glow on admission to a hot quartz vessel, even when diluted from a thousand to a million times with inert gases. It was suggested that the glow is associated with the production of excited formaldehyde molecules. The explosion of MeNO_3 was aided over the whole temperature range by dilution with argon or nitrogen. This showed that self heating is of secondary importance and that the explosion developed by a branching-chain mechanism. The effect of surface-to-volume ratio on the explosion limit is in accord with this view if the radicals causing branching are lost principally by diffusion to the walls.

The reaction in a closed vessel would just cause a single puff. The continuing decomposition of alkyl nitrate vapors in a stationary, stabilized flame or propagation of a flame front through a shock tube will be discussed in *Encyclopedia of Monopropellants*.

3.2.4 Photolysis of Ethyl Nitrate

Ethyl nitrate and other alkyl nitrates have been found in the atmosphere and in some ocean waters. They may occur naturally or form as a result of artificial atmospheric pollution. There is a stationary equilibrium between the formation of ethyl nitrate and the photolysis of ethyl nitrate under the influence of sunlight. Most of the photolysis in alkyl nitrate studies were done for atmospheric chemistry research. None relate to its use in rocket propellants. For us it would be interesting to study the laser ignition of ethyl nitrate only if it was to be used as a rocket propellant.

Photolysis of ethyl nitrate yields a variety of products [148]. If ethyl nitrate vapor is photolyzed at 368 K (95 °C) with 2537 Å UV light, the following compounds can be found among the products: nitrogen dioxide, nitric oxide, nitrous oxide, nitrogen, NM, hydrogen, carbon monoxide, carbon dioxide, formaldehyde, and acetaldehyde. There is evidence that the ethoxy radical can break down in two ways, one forming acetaldehyde and a hydrogen atom and the other formaldehyde and a methyl radical. The methyl radical appeared to react preferentially with NO₂, forming NM.

The photolysis rate coefficient of ethyl nitrate to NO₂ and the ethoxy radical was measured using a luminol chemiluminescence NO₂ detector [149]. The photolysis of ethyl nitrate is slow: at a temperature of 288 K and a zenith angle of 60°, it is $0.45 \times 10^{-6} \text{ s}^{-1}$. At a zenith angle of 0°, it was estimated to be ca. $1.1 \times 10^{-6} \text{ s}^{-1}$. This implies a photolytic lifetime of about 1 month in the planetary boundary layer. Observed photolysis rate coefficients agree with coefficients calculated using absorption cross sections and an assumed quantum yield of unity.

The UV absorption cross sections for ethyl nitrate were measured as a function of temperature between 265 and 340 nm using cavity ring-down spectroscopy [150]. Absorption cross sections increased with temperature between 238 and 298 K. The variation with temperature was greater at longer wavelengths. Photodissociation product channels of ethyl nitrate at 308 nm were determined using an excimer laser and a cavity ring-down spectrometer. C₂H₅O and NO₂ were the sole photofragmentation products with a quantum yield of 1.0 ± 0.1 , independent of temperature.

Absorption cross sections and quantum yields for NO₂ production by photolysis of ethyl nitrate at 294 K in a wavelength range of 240–320 nm were measured [151]. NO₂ quantum yields at photoexcitation wavelengths of 290, 295, and 315 nm were unity within experimental uncertainties for all of the alkyl nitrates studied and were independent of diluent gas (N₂) pressure for total sample pressures in a range of 250–700 mm Hg.

3.2.5 Handling and Safety Properties of Ethyl Nitrate

The flash point of ethyl nitrate is 236 K = –37 °C. The lower limit of flammability of ethyl nitrate vapors in air is 4.0 vol.-% with upward propagation in a 53-mm-diameter tube that is open at the bottom [152]. The upper flammability limit is presumably at 100%. No additional oxygen is needed to sustain a decomposition flame in ethyl nitrate vapor.

3.2.5.1 Explosive Sensitivity of Ethyl Nitrate

In the card gap test with 0.050-in.-thick cardboard cards and a 20-g tetryl booster in a 27-mm-inner-diameter (ID) steel pipe, the probability of 10 failures within 10 tests was 0.458 at 43 cards [153]. In a card gap test with a 1.27-cm diameter, 10.2-cm-long steel tubes with 0.25-cm wall thickness, ethyl nitrate was positive with a 3.17-cm Plexiglas gap and negative with a 3.81-cm Plexiglas gap [154].

Ethyl nitrate and NPN were used to calibrate an adiabatic compression U-tube test apparatus in preparation for additional tests with difluoroamino compounds [155]. The 50% probability points shown in Table 16 were derived from a probit plot using the up-and-down method.

Table 16: U-Tube adiabatic compression sensitivity calibration data.

Calibrating material	Gas bubble pressurant	Initial pressure, atm	50% probability positive driving pressure ratio
Ethyl nitrate	Air	1	7.3
Ethyl nitrate	Air	2	7.9
Ethyl nitrate	Air	3	8.6
Ethyl nitrate	Air	5	8.0
Ethyl nitrate	Nitrogen	3	24
<i>n</i> -Propyl nitrate	Air	1	21
Nitroethane	Air	1	120

Data source: [155]

All tests were conducted at ambient temperature ($\sim 294\text{ K} = \sim 70^\circ\text{F}$). The average driving pressure ratio for ethyl nitrate was 7.81 ± 0.71 . The ambient pressure calibrations with ethyl nitrate were comparable to the results of both Minnesota Mining and Manufacturing Co. [156] and Air Reduction Co.

In a series of tests to study LVD, ethyl nitrate was tested in lead and steel tubes in comparison to 1,2-bis(difluoroamino)propane (1,2-DP) and a NM/tetranitromethane (TNM) mixture. The results differed depending on whether or not a witness plate was at the end of the sample. The results are shown in Table 17. Ethyl nitrate was the least sensitive compound of the three materials tested.

Table 17: LVD Gap sensitivities of ethyl nitrate in comparison to 1,2-DP and a NM/TNM mixture.

Compound	Confinement, steel tubes		LVD gap sensitivity, cm of Plexiglas	
	I. D., cm	Wall thickness, cm	Witness plate	No witness plate
Ethyl nitrate	12.7	0.23	2.54–5.4	3.8–5.1 (probe)
For comparison:				
1,2-DP	12.7	0.63	91–126	61 (camera)
TNM/NM (18.7/81.3 mass-%)	12.7	0.63	8.9–10.2	11.0 (probe)

Data source: [157]

3.2.6 Explosive Performance of Ethyl Nitrate

In the lead block test the enlargement of the cavity was $420 \text{ cm}^3/10 \text{ g}$. The detonation velocity of ethyl nitrate confined in a steel tube was 5800 m/s at a density of 1.1 g/cm^3 .

The shock initiation of ethyl nitrate was tested in comparison to GTN and TMETN [158]. The donor charges were 3.5-cm-diameter Composition B pellets, 10 to 12.5 cm in length. The spacers were 6.5×8.0 -cm square glass plates of varying thicknesses S_1 (3.2–9.3 mm), and the receptor explosive was contained in 4- to 7.5-cm-diameter glass cylinders. The initial wave velocity and delay to detonation were measured with a streak camera and were $4220 \text{ mm}/\mu\text{s}$ and the delays were 0.45–1.8 μs .

3.2.7 Applications of Ethyl Nitrate

We have often wondered why ethyl nitrate has not found the same range of examination as a rocket propellant as the two propyl nitrates described in the following section. Ethyl nitrate has a more favorable oxygen balance (–61.5% vs. –99% for the propyl nitrates) and higher specific impulse (227 vs. 207 s at $p_c = 1000 \text{ psia}$ and shifting equilibrium expansion to 14.68 psia).

4 *n*-Propyl Nitrate

There are two propyl nitrates, NPN with a straight carbon chain and IPN with a branched carbon chain. Both have been tested as rocket propellants and as liquid gas generants. They differ in their chemical reactivity and thermal stability and sensitivity to external stimuli such as impact or rapid compression. NPN is discussed here first, followed by IPN. Some references cited here treat both nitrates and other alkyl nitrates side by side. The oxygen balance of propyl nitrates is substantially fuel-rich, –99% for combustion to CO_2 . With that negative oxygen balance, one must expect that the exhaust from a rocket or gas generator operating on propyl nitrate would be very sooty. The oxygen balance for monopropellants with propyl nitrates can be improved by adding other nitrates (polynitrates) with a better oxygen content.

Either of the two propyl nitrates can be prepared by nitration of the corresponding propanol with mixed acid. The formation of unwanted nitrites is prevented by adding ~3% urea [159, 160]. It would be desirable to perform the nitration without using sulfuric acid since disposal of the spent acid is a difficult task.

Normal propyl nitrate, also known as normal propanol nitrate, 1-propanol nitrate, nitric acid propyl ester, $\text{C}_3\text{H}_7\text{ONO}_2$, NPN, CAS RN [627-13-4] is the isomer of IPN. Both nitrates have been extensively investigated and some have even been used in flight applications as rocket propellants or gas generants. NPN and other alkyl nitrates can be synthesized by the reaction of alkyl halides (iodides or bromides) with silver nitrate.

An improved method for preparation of 1-propanol nitrate from 1-propanol is using a mixture of nitric acid and ammonium-magnesium nitrate as nitrating agent which facilitates waste acid disposal [161]. Nitric acid can be recycled.

4.1 Physical Properties of *n*-Propyl Nitrate

Physical properties of NPN are available in [162] and are summarized in Table 18.

Table 18: Physical properties of NPN.

Property	SI units	Other units	References
Molecular mass	105.0926 g/mol	9.515 mol/kg	[73]
Freezing point	172 K	−101.1 °C	[115]
Boiling point	383.6 K	110.5 °C	[115]
Boiling point	383.7 K	110.6 °C	[73]
Density at 293 K	1.058 kg/L	1.058 g/cm ³	[74]
Density at 293 K	1.0573 kg/L	1.0573 g/cm ³	
Viscosity at 273 K	0.99 μPa s	0.99 cPs	[115]
Surface tension at 22.3 °C	27.02 × 10 ^{−3} N/m	27.02 dyn/cm	[115]
Refractive index n_D^{20}	1.3979		[115]
Refractive index n_D^{25}	1.3949		[163]
Dielectric constant (at 18 °C and 360 MHz)	13.9		[115]
Enthalpy of formation ΔH_{298}^f	−214.5 kJ/mol	−2041 kJ/kg −51.27 kcal/mol −487.8 cal/g	[74]

See also [164–167]. The density of NPN as a function of temperature can be calculated from the equation

$$\rho = 0.55892 - 0.00066 t + 0.77527(307 - t)^{\frac{1}{3}}$$

where ρ is the density in g/cm³ and t is the temperature in °C. The compressibility of NPN and *n*-butyl nitrate is described in [168].

Isolated vapor pressure data are from the literature: p_v at 34.5 °C = 40.2 mm Hg and at 88.1 °C = 378.1 mm Hg. The vapor pressure as a function of temperature can be calculated from the equation

$$\log p_v = 7.3506 - \frac{1520}{t + 230}$$

where p_v is the vapor pressure in mm Hg and t is the temperature in °C. A similar Antoine equation for the vapor pressure of NPN is (from NIST, based on [11] data)

$$\log_{10} p_v = 4.86209 - [1721.723 / (T - 27.66)]$$

where p_v is the vapor pressure in bar and T is the temperature in kelvin. Viscosity and surface tension data for NPN are listed in Table 19 and 20.

Table 19: Viscosity of NPN.

Temperature		Viscosity	
K	°C	μPa s	cPs
194.65	−78.5	8.1	8.1
215.15	−58.0	3.3	3.3
243.15	−30.0	1.9	1.9
273.15	0.0	0.99	0.99
303.15	30.0	0.58	0.58
313.15	40.0	0.50	0.50
333.15	60.0	0.38	0.38

Data source: [115]

Table 20: Surface tension of NPN.

Temperature		Surface tension	
K	°C	N/m	dyn/cm
290.95	17.8	27.45×10^{-3}	27.45
295.45	22.3	27.02×10^{-3}	27.02
314.05	40.9	24.45×10^{-3}	24.45
331.55	58.4	22.53×10^{-3}	22.53

Data source: [115]

4.1.1 Critical Point Data of *n*-Propyl Nitrate

The critical point properties of NPN are listed in [169].

$t_{\text{crit.}}$ about 580 K = 307 °C;

$p_{\text{crit.}}$ 3.95 MPa = 39 at,

$\rho_{\text{crit.}}$ 0.334 g/cm³.

4.1.2 Pressurant Gas Solubility

The sensitivity of nitroalkanes and alkyl nitrates to sudden compression depends on the presence of gas bubbles in the liquid. The presence of gas bubbles depends on the degree of saturation and the pressure history as the propellant flows from a reservoir through the metering and flow control device into the combustion chamber. The degree of saturation depends on the solubility of pressurant gases in the liquid at different temperatures and pressures. For this reason the solubility of gases in alkyl nitrates has been thoroughly investigated [170, 171]. The solubility of air, nitrogen and oxygen in NPN at room temperature and pressures of 0.26 to 1 atm was measured and can be expressed by

$$\begin{aligned}\text{Air} \quad S &= 5.787 \times 10^{-9}P + 4.265 \times 10^{-12}P^2 \\ \text{Nitrogen} \quad S &= 7.371 \times 10^{-9} - 7.277 \times 10^{-13}P^2 \\ \text{Oxygen} \quad S &= 7.515 \times 10^{-9} + 6.012 \times 10^{-12}P^2\end{aligned}$$

where S is the mols of gas absorbed per g of liquid and P is the total pressure in atm minus the vapor pressure of propyl nitrate. The solubility of oxygen was significantly greater than that of nitrogen. A consequence is that bubbles formed by the release of pressure during pumping of air-saturated NPN can be enriched in oxygen and more likely to react.

4.1.3 Optical Properties of *n*-Propyl Nitrate

4.1.3.1 IR Spectra of *n*-Propyl Nitrate

The IR spectrum of NPN is very similar to that of other alkyl nitrates (Figure 10). See also [172].

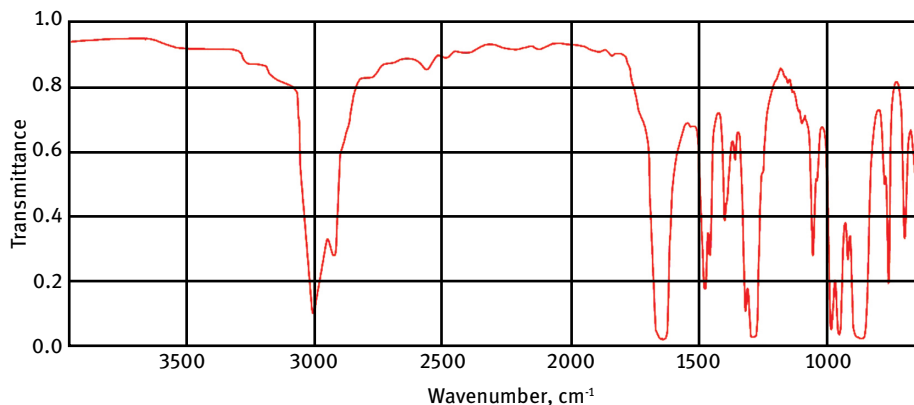


Figure 10: IR spectrum of NPN. (Reproduced and modified with permission from [124].)

4.1.4 Molecular Structure of *n*-Propyl Nitrate

4.1.4.1 Computational Studies of *n*-Propyl Nitrate Molecular Structure

With the increasing power of computers, the molecular orbitals and molecular structure of even more complex (containing 10 or more atoms) molecules can be calculated and used to predict absorption spectra and thermodynamic properties.

A conformational analysis of the propyl nitrate molecule by *ab initio* and DFT methods revealed seven energy minima corresponding to seven different conformers [173]. Both methods predicted that the *gauche* conformer with the $\angle\text{CCCO}$ (t_3) being twisted by about 63° had the lowest energy and was more stable than the planar conformer, but the stability order of different conformers obtained by other methods was somewhat different. The energy differences between various conformers and the barriers to internal rotation are all very low. The standard thermodynamic functions and the equilibrium mole fractions can be derived for various conformers. The calculated thermodynamic properties and heats of formation of propyl nitrate were in reasonable agreement with experimental results.

Similar calculations were performed for the molecular structures, vibrational spectra standard thermodynamic functions, and heats of formation of methyl nitrate, ethyl nitrate, NPN, IPN, butyl nitrate, EGDN, and GTN [174].

DFT methods were used to investigate the equilibrium geometry, frontier orbital energy, and energy gap, as well as BDEs, of NPN and IPN [175]. The thermal stability of the two nitrates and the corresponding radicals were analyzed. The O—NO₂ BDEs of NPN and IPN were close to the experimental values. That the experimental thermolysis of two nitrates is only unimolecular homolytical dissociation of the O—NO₂ bonds is corroborated by the finding that the present results of BDE are well coincident with the experimental results of activation energy from literature data.

4.1.5 Microwave Spectra of *n*-Propyl Nitrate

Microwave spectra of alkyl nitrates help to identify the structure of these molecules and complement measurements in other ranges of the electromagnetic spectrum in the IR range. Low-resolution microwave spectra of *n*-propyl, isopropyl, *n*-butyl, and 2-butyl nitrate revealed mixtures of conformational isomers that have been characterized and correlated with conformations observed in the simpler ethyl nitrate molecule [176]. Conformers of the three primary esters can be assigned to *anti* and *gauche* configurations about the NOCC torsional angle coupled with *gauche* or *anti* configurations about τ_3 (OCCC) and τ_4 (CCCC) for *n*-propyl and *n*-butyl nitrate. IPN was predicted to exist in a *gauche* (τ_2 (NOCH)~ 60°) conformation. For each compound all of the observed conformers were approximately equally stable. The low-resolution microwave spectra were insensitive to orientation about τ_1 (ONOC).

4.1.6 Refractive Index of *n*-Propyl Nitrate

The refractive index of NPN at 298 K (25 °C) is 1.3949 [163].

4.1.7 Magnetic Properties of *n*-Propyl Nitrate

A complete analysis of the ^1H NMR spectra of 21 nitrate esters from *n*-propyl to *n*-decyl nitrate, as well as isopropyl and isobutyl nitrates, several dinitrates, and trinitrates, was not possible [177]. The resolution was not sufficient to allow all the NMR parameters to be evaluated. It would be difficult to use NMR in the analysis of nitrate ester mixtures.

4.1.8 Thermodynamic Properties of *n*-Propyl Nitrate

Thermodynamic properties of NPN are summarized in Table 21.

Table 21: Thermodynamic properties of NPN.

Property	SI units		Other units		References
Heat capacity at 298 K (25 °C)	1.75 J K ⁻¹ g ⁻¹		0.419 cal °C ⁻¹ g ⁻¹		[169]
Enthalpy of formation, liquid ΔH_f^{298}	-214.5 kJ/mol	-2041 kJ/kg	-51.27 kcal/mol	-487.8 cal/g	[74]
	-214.5 kJ/mol	-2041 kJ/kg	-51.27 kcal/mol		[118]
	-215 ± 1 kJ/mol				[29]
Enthalpy of formation, vapor ΔH_f^{298}	-174 kJ/mol		-41.60 kcal/mol		[118]
	-174.1 kJ/mol		-41.60 kcal/mol		[117]
Heat of evaporation at 298 K	40.6 kJ/mol		9.7 kcal/mol		[11]
Heat of evaporation at NBP	36.3 kJ/mol		8.68 kcal/mol		[11]
Heat of combustion	1966 ± 1 kJ/mol				[29]

4.2 Chemical Properties of *n*-Propyl Nitrate

Commercial grades of NPN may contain several percent of other alkyl nitrates, depending on the source of the material. The now obsolete military specification MIL-N-8722A (US Air Force) (Publication Date: Jan 12, 1968) at one time set minimum purity requirements for NPN, but it has since been canceled and is no longer maintained.

NPN is a good solvent. It is miscible with C₁–C₄ alcohols in all mixture ratios but does not dissolve in water. Its solubility in water at 293 K (20 °C) is only 0.3 mass-%.

The oxygen balance of NPN is -99.0%, and the nitrogen content is 13.33 mass-% N.

4.2.1 Reactions of *n*-Propyl Nitrate

Alkyl nitrates are not moisture sensitive, but in alkaline conditions they will hydrolyze. Hydrolysis is a very undesirable reaction because it detracts from the energy available as propellant.

The stability of nitrate esters in 90 vol.-% ethanol containing sodium hydroxide was studied by measuring the rates of hydrolysis [178]. Initial rates of hydrolysis were determined at either 303 or 333 K (30 or 60 °C) in the case of methyl, *n*-propyl, *n*-butyl, *n*-heptyl, *iso*-butyl, and ethylene glycol mononitrates; ethylene glycol, propane 1,3-diol, butane 1,4-diol, pentane 1,5-diol, butane 1,3-diol, butane 2,3-diol, propane 1,2-diol, diethylene glycol, and triethylene glycol dinitrates; glycerol 1- and 2-mono- and 1,3-di- and trinitrates; and metriol trinitrates; and PETN and 2-nitro-ethyl nitrate. Longer alkyl substituents, with retarding inductive effects, stabilized the esters, whereas nitro, nitrate, and hydroxyl substituents in the alkyl groups (with electron-attracting properties) increased the rate of hydrolysis by increasing the ionization of α -hydrogens. The effects fell off rapidly as the distance between groups increased. Ammonium salts decreased reaction rates by combining with hydroxyl ions.

4.2.2 Thermal Decomposition of *n*-Propyl Nitrate

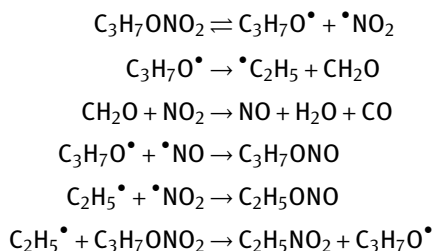
4.2.2.1 Slow Thermal Decomposition of *n*-Propyl Nitrate

The decomposition of NPN has been investigated in the temperature range 438–460 K (165–187 °C) using manometric techniques [179]. The reaction is first order and essentially homogeneous. The rate constant over the temperature interval studied was found to be

$$k = 10^{14.7} \exp(-36860/RT) \text{ s}^{-1}$$

Studying the decomposition of NPN vapor at 454 K (181 °C) as a function of time used the same techniques previously used by the same investigators for the decomposition of ethyl nitrate [180, 181]. The initial pressures of NPN were on the order of 20 mm Hg in a Pyrex bulb. Analyses for NPN, *n*-propyl nitrite, and nitroethane were made using the IR absorption peaks at 11.68, 12.55, and 6.31 μm , respectively. Nitrogen dioxide and nitric oxide were analyzed colorimetrically. The presence of formaldehyde in the products was indicated by its odor and by the deposition of a white deposit on the reaction walls of the glass bulb assumed to be paraformaldehyde. The study revealed that the decomposition of NPN is similar in many respects to the decomposition of ethyl nitrate. The principal products, as revealed by IR and visible region spectra, were *n*-propyl nitrite, nitroethane, nitrogen dioxide, and nitric oxide. The effect of additives upon the reaction appeared to parallel the results observed previously in ethyl nitrate decomposition. Nitrogen dioxide and oxygen inhibited decomposition, and nitric ox-

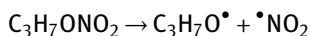
ide had an accelerating effect. The following reaction sequence was proposed:



Alkoxy free radicals play a substantial role in the decomposition of alkyl nitrates [182].

NPN is thermally stable at temperatures up to its NBP. A sample was boiled and refluxed for 10 d, and very little decomposition was noted. Decomposition in the liquid phase may be accelerated by contaminants. Commonly observed contaminants are nitrogen dioxide and acetaldehyde.

The pyrolysis of NPN at very low pressures gave for the reaction



the following high-pressure rate expression at 300 K [183]:

$$\log k_1(\text{s}^{-1}) = 16.5 - 40.0 \text{ kcal/mol} / 2.3RT$$

From various assumptions the derived $\log k$ was $\log k_{-1}(\text{M}^{-1} \cdot \text{s}^{-1})$ (300 K) = 9.5. In contrast, the pyrolysis of methyl nitrite and methyl d3 nitrite afforded NO and HNO and DNO, respectively, in what appeared to be a heterogeneous process.

The BDEs of O—NO₂ bonds in four alkyl nitrates, NPN, IPN, EHN, and TEGDN, were calculated and compared to experimental results of apparent activation energies [184]. The thermal decomposition characteristics of NPN, IPN, EHN, and TEGDN were investigated by DSC and high-pressure DSC, and the kinetic parameters of thermal decomposition were obtained. The results showed that the thermal decomposition of the four nitrates under ambient pressure occurred in the gas phase. When the pressure was increased to 2 MPa, their decomposition processes occurred in the liquid phase. Because the calculated results of O—NO₂ BDEs of the four nitrates were in good agreement with the experimental results of apparent activation energies obtained from DSC, it was concluded that the thermolysis of the four nitrates is by way of unimolecular homolytic cleavage of the O—NO₂ bonds.

The thermal stability and thermal decomposition properties of the four nitrates, that is, NPN, IPN, TEGDN, and DEGDN, were examined by ARC under adiabatic conditions [185]. The onset temperature, the initial temperature rise rate, and the maximum temperature rise rate were recorded, and the apparent activation energy and preexponential factors of the thermal decomposition were calculated. The self-accelerating decomposition temperatures of the four nitrates in three different containers (4.5-L iron drum, 25-L iron drum, and 210-L fiber drum) were calculated. It was concluded that the onset temperatures of the exothermic decomposition of

NPN, IPN, TEGDN, and DEGDN were 422.9, 429.7, 423.7, and 423.7 K (149.8, 156.6, 150.6, and 150.6 °C), respectively, while the maximum temperature rise rates of NPN, IPN, TEGDN, and DEGDN were 18.2, 12.1, 59.7, and 209.8 °C/min, with the apparent activation energy of NPN, IPN, TEGDN, and DEGDN being 214.4, 213.8, 226.4, and 214.5 kJ/mol, respectively. The thermal stability of the four nitrates was ranked (from worst to best) as DEGDN TEGDN NPN IPN.

NPN sometimes is found in the residual acid solutions (spent acid) of industrial nitration processes. Spent acid sometimes undergoes unexpected, violent decomposition reactions, which may result in industrial accidents. A mixture containing 2% NPN in white fuming nitric acid was heated in an open test tube with an immersed thermocouple, and the results were compared to those obtained by DSC with sealed crucibles [186]. Under open-air conditions, an exothermic reaction started at 338 K, and in the sealed DSC the exotherm started at 318 K.

4.2.2.2 Computational Chemistry Treatment of *n*-Propyl Nitrate Decomposition

Three different DFT methods were used to investigate the O—NO₂ bond lengths, frontier orbital energies, and O—NO₂ BDEs of NPN, IPN, EHN, TEGDN, and Tetra-EGDN [28, 187]. It was found that the O—NO₂ bond lengthened (i.e., destabilizes) in the order IPN, NPN, EHN, Tetra-EGDN, and TEGDN. From the data of frontier orbital energies it was estimated that the relative thermal stability ordering of five nitrates as expressed by predicted BDEs of O—NO₂ bonds in NPN, IPN, EHN, TEGDN, and Tetra-EGDN are 176.6, 174.5, 168.1, 156.1, and 159.3 kJ/mol, respectively. Predicted BDEs were in agreement with the experimental results of apparent activation energies from the literature, and the thermolysis of these five alkyl nitrates is predominantly by unimolecular homolytic cleavage of the O—NO₂ bonds.

The following parameters for a molecule must be known before one can predict the energy release and the path of thermal decomposition of an energetic molecule: vibrational frequencies, moments of inertia, collision cross sections, critical energy, and sterical factors. The unimolecular decomposition of NPN was used as an example for testing a new theory [188]. An attempt was made to correlate the vapor-phase decomposition with liquid strand burning rates, but it was concluded that the initial decomposition reaction of nitrate esters could not be the rate-determining step for the observed variation of liquid burning rate with pressure.

4.2.2.3 Rapid Thermal Decomposition of *n*-Propyl Nitrate

The rapid decomposition of alkyl nitrate vapors is often studied in shock tubes with reflected shock waves while monitoring reactant and product concentrations with fast spectrophotometric methods. This makes it possible to study the effects of diluents, inhibitors, and oxidants on the reaction kinetics. From this standpoint it is interesting to compare the different behavior of the isomeric NPN and IPN under these conditions.

The strand burning of liquid NPN and NPN mixtures will be discussed in *Encyclopedia of Monopropellants*.

4.2.3 Photolysis of *n*-Propyl Nitrate

Several alkyl nitrates, including NPN, have been detected in the atmosphere and in the oceans as a result of naturally occurring processes and/or anthropogenic atmospheric pollution. Under the influence of sunlight, vapors are photolyzed and form other pollutants. A dynamic equilibrium is established between the formation and photolysis of propyl nitrate(s).

The photolysis of NPN and other alkyl nitrates is discussed in this chapter because this is a method for controlled ignition of the decomposition reaction in rocket engines by laser photolysis. Photolysis determines the rate of decay of spilled propellants in surface waters under the influence of sunlight. UV photolysis is a useful method for removing wastewater from propellant production facilities.

Absorption cross sections and quantum yields for NO₂ production by the photolysis of methyl, ethyl, *n*-propyl, and isopropyl nitrate at 294 K in a wavelength range of 240–320 nm were measured [151]. NO₂ quantum yields at photoexcitation wavelengths of 290, 295, and 315 nm were unity within experimental uncertainties for all of the alkyl nitrates studied and were independent of diluent gas (N₂) pressure for total sample pressures in a range of 250–700 mm Hg. When averaged over all wavelengths and sample pressures, the values of quantum yields for NO₂ formation were near unity.

4.2.4 Storage Stability of *n*-Propyl Nitrate

4.2.4.1 Liquid-Phase Slow Decomposition

The slow decomposition of NPN during storage, its compatibility with metals, and the solubility of gases in this propellant have been measured in detail [181].

4.2.5 Analytical Methods for *n*-Propyl Nitrate

There were at one time military specifications for propyl nitrates, but they are no longer maintained, and it is difficult to obtain copies of these old, obsolete specifications, such as MIL-E-26603 – Ethyl Nitrate-Propyl Nitrate Mixture, Propellant or MIL-P-8722 – Propellant, *n*-Propyl Nitrate.

Propyl nitrate is not (was not) that widely used as a propellant ingredient or anywhere else that a large working population would be at risk of inhaling the vapors in the air or ingest it by any other means. Nevertheless, a colorimetric method for the analysis of propyl nitrate in blood was developed that was based on the reaction of alkyl nitrates with 3,4-xylenol [189]. Propyl nitrate in the presence of a 10-fold excess of inorganic nitrate and organic and inorganic nitrite was extracted from blood with petroleum ether and subsequently determined by the 3,4-xylenol method. The solvent extraction removed the interference from blood chloride and inorganic nitrate and nitrite. Shaking the extract with an aqueous solution of sulfamic acid removed the interference from organic nitrite. Recoveries averaged 92% of propyl nitrate from a 1-mL sample of blood using sulfamic acid.

4.3 Materials of Construction for *n*-Propyl Nitrate

Pure and dry NPN can be stored in steel drums for several years without any noticeable decomposition [190]. Moist NPN may corrode metal walls, but the liquid remains uncontaminated.

Steel and aluminum are acceptable materials for the construction of NPN storage containers. Copper or bronze will be stained by a green layer of corrosion products when they come into contact with NPN.

Aluminum alloy ST, soft aluminum 28, Monel K, and stainless-steel CRES 303 are well suited for use with NPN [181]. Armco cast iron is less suitable. Wrought steel 1020 is not suitable for NPN service. Polyethylene, Kel-F, Teflon, and melamine resins are NPN resistant. Polyethylene and polyisobutylene and mixtures of the two elastomers have been approved [191, 192]. The lubricants Kel-F oil, graphite, and molybdenum sulfide have been recommended for NPN service.

4.4 Handling Safety and Storage of *n*-Propyl Nitrate

For safety reasons it was recommended to subdivide NPN storage facilities into many smaller tanks, each surrounded by a berm or wall to prevent sympathetic detonations. The UN shipping designation for NPN is UN1865.

4.4.1 Transfer of *n*-Propyl Nitrate

NPN should be kept free of dissolved gases to minimize the risk of accidental explosions by adiabatic compression of bubbles. It is best to degas it by evacuating and preventing the readmission of gases. Transfer of NPN should not be done by pressurization because pressurant gases might dissolve in the liquid and render it more sensitive [170].

At one time General Electric had developed a special pump for gently pumping NPN for transfer between transportation and ground storage tanks.

Accidental explosions can be caused by pressure spikes during the transfer of explosive liquids like propyl nitrate. The pressures commonly referred to as surge pressures are as follows:

- Pressure waves caused by opening a valve between high-pressure and low-pressure domains
- Pressure surges by priming an evacuated line with liquid
- Pressure surges produced by the application of an external static load
- Pressure surges caused by deceleration of moving masses (bumping a railroad tanker car)
- Pressure waves related to pump characteristics commonly referred to as *pump ripple*

- Rapid compression of gas bubbles in contact with liquid force due to mechanical shock in a pump
- Rapid compression of gas bubbles in a pump

4.4.2 Toxicity of *n*-Propyl Nitrate

Most alkyl nitrates are vasodilators, resulting in a rapid drop in blood pressure. For this reason alkyl nitrates (and nitrites) have been used in the treatment of angina pectoris.

In dogs, the 4-h LC₅₀ of NPN vapor is 2000 to 2500 ppm [193].

NPN is of low acute dermal toxicity in rabbits. It is moderately toxic to rats following single or repeated administration by oral and inhalation routes, causing effects on the central nervous system and blood (red blood cell damage and a reduction in oxygen levels). Mice and dogs treated by inhalation also showed central nervous system and blood effects [194].

The NIOSH recommended exposure limit (REL) time-weighted average (TWA) for NPN is 25 ppm with a short-term limit of 40 ppm. The OSHA permissible exposure limit (PEL) is 25 ppm, but the short-term exposure limit (STEL) of 40 ppm was later rescinded. The American Conference of Governmental Industrial Hygienists (ACGIH) recommended threshold limit value (TLV) TWA is 25 ppm. The original Immediately Dangerous to Life or Health Concentration (IDLH) for NPN was 2000 ppm, but this was later lowered to 500 ppm. See also [65, 195].

4.4.3 Safety Properties of *n*-Propyl Nitrate

4.4.3.1 Fire Hazard Properties of *n*-Propyl Nitrate

The ignition properties of NPN in air are summarized in Table 22.

Table 22: Ignition properties of NPN in air.

Property	References
Autoignition temperature (at 1 atm)	466 K = 193 °C
Autoignition temperature	448 K = 175 °C [196]
Flammable limits (in air at 398 K = 125 °C and 101 kPa = 1 atm)	1.8 to 100 vol.-% [196]
Flash point, open cup	299.8 K = 26.7 °C
Flash point, closed cup	293 K = 20.0 °C

For additional information on the safety properties of NPN see [39, 197–200].

In evaluating fire and explosion hazards, it is the lowest temperature at which ignition can accidentally occur that is of interest. The spontaneous ignition temperature, or autoignition temperature (AIT), is determined in a uniformly heated apparatus that is sufficiently large to avoid wall quenching effects. The time from reaching

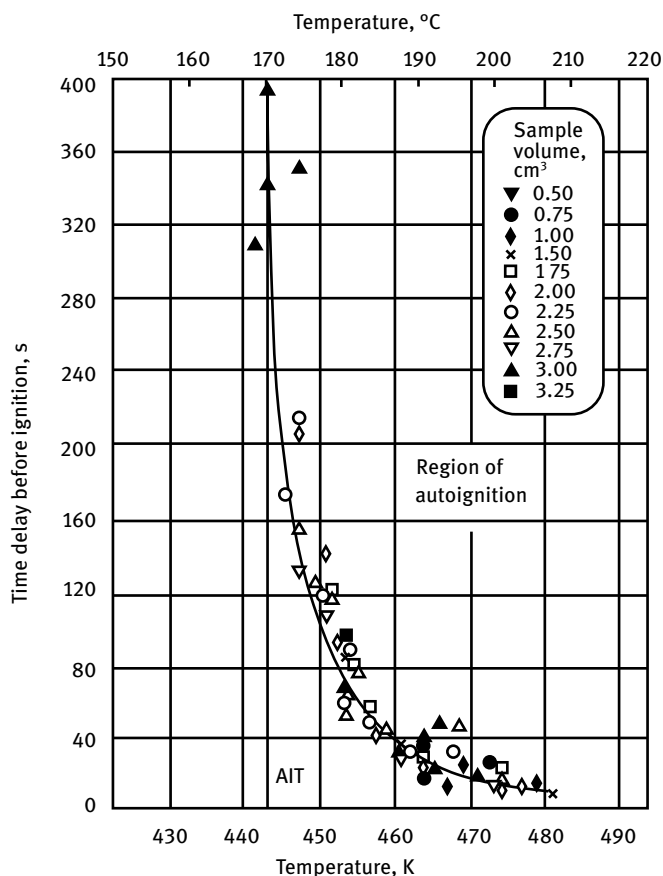


Figure 11: Time delay before autoignition of NPN in air at 6.8 MPa. (Reproduced and modified from [196].)

temperature to the point of ignition is the delay time, and it is temperature and pressure dependent. Figure 11 illustrates typical autoignition-temperature data. In Figure 11 the minimum AIT value for NPN is 443 K (170 °C) at an initial pressure of 6.8 MPa (1000 psig). If one plots the logarithm of the delay time vs. reciprocal absolute temperature, the activation energy can be derived from the slope of the straight line.

Materials like alkyl nitrates that are oxidized or decomposed readily may yield erratic flammability limit data under certain conditions. This effect is illustrated in Figure 12, which summarizes the lower flammability limit (LFL) data with NPN in air at various temperatures and pressures [199]. An increase in temperature from 348 to 398 K (75 to 125 °C) was accompanied by a modest decrease in the lower limit values; a further increase in temperature to 423 K (150 °C) resulted in a further lowering of the lower limit at pressures below 100 psig, but not at the higher pressures. An increase

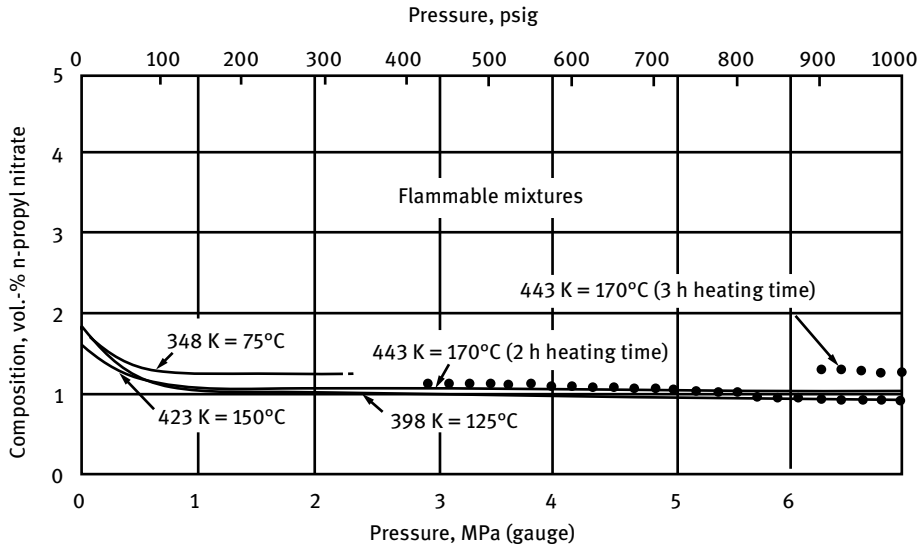


Figure 12: Lower limit of flammability of NPN as a function of pressure. (Reproduced and modified from [196].)

in the temperature to 443 K (170 °C) resulted in an apparent increase in the lower limit value because of the slow oxidation of NPN.

Obviously one would not want to use air to pressurize a propyl nitrate tank, but even using nitrogen instead of air carries some hazards; the temperature boundary of autoignition is shifted upward, as shown in Figure 13, but the nitrogen/NPN va-

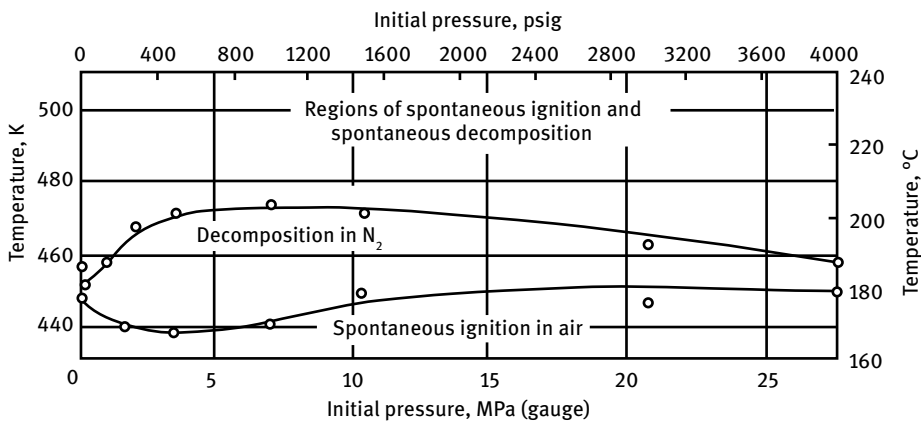


Figure 13: Minimum spontaneous ignition and decomposition temperatures of NPN as a function of pressure. (Reproduced and modified from [196].)

por mixture can still decompose. The data given in this figure exhibit a behavior that is typical of that found with other combustibles at elevated pressures; the minimum spontaneous ignition temperature first decreases with an initial increase in pressure and then increases as the pressure is increased still further.

4.4.3.2 Explosive Sensitivity of *n*-Propyl Nitrate

4.4.3.2.1 Mechanical Shock Sensitivity of *n*-Propyl Nitrate

NPN is shock sensitive and must be handled with the same precautions as a liquid explosive. There are several reports about accidents with NPN. The shock and adiabatic compression sensitivity of both propyl nitrates is dependent on the degree of saturation with dissolved gases. Completely degassed nitrate esters behave differently from those that are saturated with pressurant gas or even air at sea-level pressure.

Both NPN and IPN have often been used as calibration fluids for drop weight impact sensitivity apparatus. Because there are so many different drop weight impact apparatus in use (Picatinny, Olin-Technoproducts, BAM), it helps to display the results from different machines on a common denominator using the same test samples. Both NPN and IPN are easy to obtain, easy to purify, and relatively safe to handle in small quantities.

The addition of 10% by weight of ethylene oxide to NPN or to 2-methoxyethyl nitrate increased the 50% point for positive results in the drop weight sensitivity impact tester from a value of 20–22 cm (8–9 in.) to a value of about 1.27 m (50 in.), which was the upper energy limit of the apparatus [163]. Mixtures of ethylene oxide and NPN were stored for 3 months at 333 K (60 °C), and there were no signs of reaction between the two monopropellants, as indicated by the absence of change in the drop weight sensitivity or refractive index.

Experimental impact sensitivity data were obtained for NPN as the condensed phase with gas bubbles consisting of argon, helium, nitrogen, and Freon-12 by themselves and binary mixed gas systems: (helium/oxygen), (nitrogen/oxygen), (Freon-12/oxygen), and one ternary system: (Freon-12/helium/oxygen) [201, 202]. The experimental program was able to separate the effects of heat capacity ratio, thermal conductivity, and chemical reactivity of the gas bubble on the impact sensitivity. Based on a proposed theoretical model of initiation, the impact sensitivity of NPN was correlated with the thermal diffusivity of the entrapped gas bubble. The correlation correctly predicted that argon, nitrogen, and Freon-12 gas bubbles with high C_p/C_v would require energies above 92 kg-cm for initiation to occur.

4.4.3.2.2 Explosive Shock and Card Gap Sensitivity of *n*-Propyl Nitrate

In the card gap test with 0.050-in.-thick cardboard cards and a 20-g tetryl booster and with the sample confined in a 27-mm-ID steel pipe, the probability of 10 failures within 10 tests in NPN was 0.54 at 16 cards [153].

Determining the safety properties of NPN included tests for flash point, flammability limits in air, and shock sensitivity [39, 203, 204].

The sensitivity of NPN and other sensitive liquids to accidental explosion by shock or adiabatic compression can be reduced by sparging it with a low-gamma gas prior to use [205]. The low-gamma gas should have a gamma (C_p/C_v) value of 1.15 or less. To be effective, the solubility of the gas must be high enough to result in a solution that contains 1–2 mass-% of the gas. Examples of low-gamma gases and vapors are butane, propane, chloroform, diethyl ether, and dimethyl ether.

Ab initio methods were used to model the propyl nitrate molecule and predict its behavior under conditions of shock initiation. Calculations of the molecular structure of propyl nitrate using *ab initio* methods indicated that NO₂ radical concentrations will decay quickly [206]. After completing the computations, the delay time of shock ignition was determined experimentally using a spectrophotometric method, i.e., the earliest emergence of an intermediate product for the loaded propyl nitrate was determined with a spectrometer. The first product to emerge from propyl nitrate after shock ignition was always NO₂. The monochromator was adjusted to the 463-nm wavelength of NO₂ absorption, and the time of arrival for the shock wave was measured by pressure gauges. The delay time determined by the spectrophotometric method was closer than that determined using a photoelectric diode, whose peak wavelength of sensitivity is about 800 nm. The emergence times for O, NO₂, CO, C₂, CH, CO₂, and H₂O fragments and products were obtained after the shock wave entered into the propyl nitrate.

4.4.3.2.3 Bullet Impact Sensitivity of *n*-Propyl Nitrate

Although NPN was rarely ever used in military equipment and was always at risk of bullet impact in a battlefield situation, the bullet impact sensitivity of NPN was tested [207]. Tests were conducted to determine the effects of bullet impact on NPN contained in four- and six-quart thin-wall aluminum canisters and in drums. Seven types of ammunition were used: 30-caliber ball, 50-caliber ball, 20-mm ball, 20-mm armor-piercing incendiary, 20-mm high-explosive incendiary, 7162-mm tracer, and a 20-mm flechette. The review of high-speed film (2000 and 4000 frames per second) indicated that there were no detonations; however, the 20-mm high-explosive incendiary rounds initiated burns.

4.4.3.2.4 Adiabatic Compression Sensitivity of *n*-Propyl Nitrate

The adiabatic compression sensitivity of NPN was tested in an adiabatic compression sensitivity tester developed by Aerojet in comparison to that of NM, methylacetylene, and a mixture of 60% ethyl nitrate/40% propyl nitrate [208]. The apparatus consisted of a pneumatically driven piston rapidly compressing a gas bubble above a liquid propellant sample. In a few cases, the apparatus was also inverted, pushing the liquid upward into the gas (vapor) bubble. The sensitivity was expressed in terms of the piston kinetic energy divided by the size of the gas bubble, which is the slope of a straight line separating the go-no go areas in an x-y chart (Figure 14). The results are summarized in Table 23. NPN was one of the more sensitive samples in this series of tests.

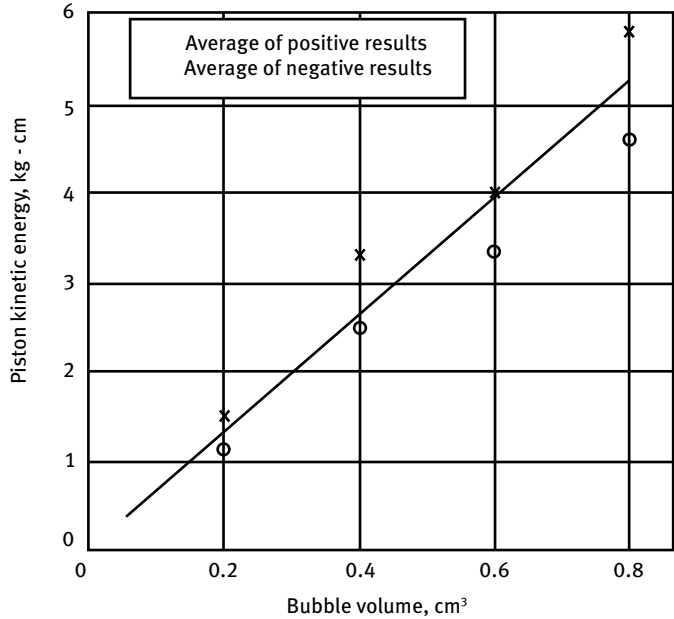


Figure 14: Adiabatic compression sensitivity of NPN. (Republished and modified from [208], with permission from © 1959 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

Table 23: Adiabatic compression sensitivity of NPN in comparison to other monopropellants.

Compound	Adiabatic compression sensitivity, kg-cm mL ⁻¹
Mixture of 60% ethyl nitrate/40% propyl nitrate	4.0 ± 0.8
<i>n</i> -Propyl nitrate	6.7 ± 1.2
Nitromethane	10.4 ± 1.7
Methylacetylene	86 ± 12

Data source: [208]

The compression ignition sensitivity of a 60/40 volume ratio mixture of ethyl and NPN was tested in an apparatus where the compression piston was hydraulically driven, enabling the operator to control the compression ratio and piston travel distance and velocity [209]. The phenomena occurring during compression were observed by high-speed cameras and pressure-time traces. Compression tests at three different piston velocities and different chamber attitudes (orientations) showed that, contrary to expectations, increases in piston velocity did not always lead to lower compression ratios to achieve ignition. Ignition was observed at the lowest

compression ratios for the vertical downward piston travel, even at the slowest of the three piston velocities tested. See also [210].

In another apparatus, a stroke compressor, a volume of gas was rapidly compressed by a piston driven by a larger piston under a predetermined initial pressure. At the end of a stroke the piston was locked in place, thus maintaining essentially constant volume and, hence, constant pressure, except for a pressure drop due to cooling by the walls. Light emission in case of ignition was detected by a photomultiplier tube that “looked” through the window and showed up as a brightening of the pressure trace. The time at which light is emitted can thus be found. At a compression ratio of 17:1, peak pressures in the range 4.8–5.5 MPa (700–800 psia) and peak temperatures 650–800 K and compression rates of 20000 atm/s were obtained, with compression times of 1–4 ms. With different bubble sizes, ignition of NPN occurred in six out of nine tests [211].

The importance of the type of gas present in gas bubbles entrained in alkyl nitrate monopropellants was already pointed out in previously cited references in the section on drop weight impact sensitivity [201, 202].

The results of adiabatic compression sensitivity testing for NM, nitroethane, and a propyl nitrate are shown in Table 24 [212]. The data in Table 24 show that the values of 50% fire point of NM and propyl nitrate are nearly identical to those previously determined at the US Bureau of Mines, marked with an asterisk. Additional calculations were made to determine energy/liquid volume and compression power and are shown in the last columns. Since the pressure rise in the test chamber was very rapid (10000–1000000 psi/s), the compression was nearly adiabatic and rapid temperature rise resulted. NPN was the most sensitive liquid of the three liquids tested, with the least energy required to initiate an explosion in 50% of the tests.

Table 24: Adiabatic compression initiation sensitivity at volume ratio of 25 ($T_{\max} = 1311 \text{ K} = 1900^\circ\text{F}$).

Material	50% fire point h	Impact energy		Energy/time	Energy/time per volume of compression	Energy per volume of compression
	cm	Joule	kg-cm	J/s	$\text{J s}^{-1} \text{ m}^{-3}$	J/m^3
Nitromethane	23 (24.2*)	11.28	1.15	948	524×10^6	6×10^6
Nitroethane	37	18.15	1.85	1925	1006×10^6	10×10^6
<i>n</i> -Propyl nitrate	4 (4*)	1.96	0.2	68	38×10^6	1×10^6

* US Bureau of Mines Data

Data source: [212]

4.4.4 Detonation Performance of *n*-Propyl Nitrate

The detonation velocity of $n\text{-C}_3\text{H}_7\text{ONO}_2$ in the liquid phase is 4700 to 5100 m/s [199, 200].

4.5 Applications of *n*-Propyl Nitrate

In addition to its application as a gas generant in gas generators for aircraft starter motors or torpedo propellant, NPN has been considered as a fuel for air-fuel explosives. NPN dissolves readily in kerosene and other hydrocarbon fuels and can improve their ignition characteristics at low temperatures or high altitudes. It can be added to diesel fuel as a cetane number improver.

5 Isopropyl Nitrate

Isopropyl nitrate, also known as IPN, 2-propyl nitrate, *sec*-propyl nitrate, 2-propanol nitrate, Isonite; nitric acid 1-methylethyl ester; *i*-C₃H₇ONO₂, CAS RN [1712-64-7], is an isomer of NPN and a potential monopropellant of equal or even higher importance.

Similar to the preparation of NPN, IPN is prepared by nitrating isopropanol with mixed acid, but the process is more difficult with secondary alcohols than with primary alcohols. In one process, a mixture of isopropanol and urea was dropwise added to boiling nitric acid [160]. The use of sulfuric acid in the mixed acid can be avoided by nitrating the isopropanol with nitric acid at 373 K (100 °C) in the presence of urea and ammonium nitrate [213]. The yield of IPN thus obtained can be over 85% under the optimum reaction conditions. The purity of IPN can be over 98% based on the analysis of the product by GC. The book by Liu (2015) contains several pages that describe the IPN production process [10].

IPN and other alkyl nitrates can be synthesized by reaction of alkyl halides (iodides or bromides) with silver nitrate, but that is a very expensive process.

IPN and other alkyl nitrates can be dried by passing them through molecular sieves [214].

5.1 Physical Properties of Isopropyl Nitrate

The physical properties of IPN are summarized in Table 25. See also [39, 166, 167, 215].

5.1.1 Density of Isopropyl Nitrate

The density of IPN as a function of temperature in a range of 233 to 303 K (−40 to +30 °C) can be expressed by the equation

$$\rho = 1.065 - 1.25 \times 10^{-3}t$$

where ρ is the density in g/cm³ and t is the temperature in °C [217].

Table 25: Physical properties of IPN.

Property	SI units	Other units	References
Molecular mass	105.0926 g/mol	9.516 mol/kg	[73]
Freezing point	190.6 K	−82.5 °C	
Triple point	190.81	−82.34 °C	[73]
Boiling point	374.85 K	101.7 °C	
	373.7 K	100.6 °C	[73]
Density at 293 K	1.036 g/cm ³	1.036 g/cm ³	[74]
	1.043 g/cm ³	1.043 g/cm ³	[216]
Refractive index n_D^{20}	1.3882		[216]

5.1.2 Compressibility of Isopropyl Nitrate

For data on the compressibility of IPN, see also [168].

5.1.3 Velocity of Sound in Isopropyl Nitrate

The room temperature sound speed was measured as 1.10 mm/μs [218].

5.1.4 Vapor Pressure of Isopropyl Nitrate

The vapor pressure of IPN in the range 273–343 K can be calculated from an Antoine equation:

$$\log_{10} p_p = 3.54496 - [1018.568 / (T - 89.622)]$$

where p_v is the vapor pressure in bar and T is the temperature in kelvin. For a single data point, a vapor pressure of 5.065 kPa at 293 K was reported.

5.1.5 Viscosity of Isopropyl Nitrate

The viscosity of IPN is 0.66 cPs at 293 K. Other sources gave a viscosity of 6.6×10^{-4} Pa s, which is the same number, but in different units; see [219].

5.1.6 Surface Tension of Isopropyl Nitrate

The surface tension of IPN is 29.3×10^{-3} N/m; see [219].

5.1.7 Optical Properties of Isopropyl Nitrate

5.1.7.1 IR Spectra of Isopropyl Nitrate

IR spectra are useful in determining the molecular structure of IPN and to detect trace quantities in the atmosphere and in the air in work spaces at rocket test sites. IR spectra are a useful analytical tool to verify purity of IPN and to measure the rate of decomposition of IPN under various conditions of heating and illumination. Raman and IR spectra of IPN and isobutyl nitrate were used in combination with computational stud-

ies employing DFT to assign the vibrational transitions to their corresponding normal coordinates [220]. Like other alkyl nitrates, the frequency of the NO₂ symmetric stretch remained relatively unchanged while the asymmetric stretch shifted to a lower frequency with increasing α -carbon substitution. The mode assignments involving the photochemically relevant —ONO₂ chromophore agreed well with those from previous IR work. Raman depolarization ratios provided evidence that the condensed-phase, ground-state molecular structure of isobutyl nitrate is of C_s symmetry. In contrast, the minimum energy structure of IPN was predicted to contain a pronounced twist around the C—O bond relative to the C_s-symmetry structure that lies 10.9 kJ/mol (2.6 kcal/mol) higher in energy. The IR intensities of IPN absorption bands were consistent with the twisted geometry, demonstrating that this conformer is most likely favored in solution.

5.1.7.2 Raman Spectra of Isopropyl Nitrate

Absolute resonance Raman scattering cross sections for IPN dissolved in cyclohexane or acetonitrile were measured at excitation wavelengths spanning the strong π – π^* absorption located at ~200 nm [221]. Resonance enhancement was observed for seven vibrational coordinates, all involving the —ONO₂ chromophore, demonstrating that the photoinduced excited-state structural evolution is dominated by structural changes localized to the —ONO₂ group. The absorption and absolute resonance Raman cross sections were modeled using the time-dependent formalism for absorption and Raman scattering. This analysis demonstrated that the photoinitiated excited-state structural-relaxation dynamics were multi-dimensional, and consistent with N—O bond cleavage. This observation is consistent with N—O bond dissociation being the dominant photodissociation pathway for larger (e.g., three or more carbon atoms) alkyl nitrates.

5.1.7.3 Ultraviolet Spectra of Isopropyl Nitrate

Eight simple representative nitrate esters (methyl nitrate, ethyl nitrate, NPN, IPN, *n*-butyl nitrate, *tert*-butyl nitrate, benzyl nitrate, and phenylethyl nitrate) were investigated by the extended Hueckel molecular orbital (MO) method [222]. The UV spectra of this set of compounds were recorded in heptane solution and resolved into a number of component bands as suggested by the MO calculations. The charge distributions of these molecules were calculated by an iterative charge consistency method.

5.1.7.4 Microwave Spectra of Isopropyl Nitrate

Low-resolution microwave spectra of *n*-propyl, allyl, *n*-butyl, isopropyl, and 2-butyl nitrate revealed mixtures of conformational isomers that have been characterized and correlated with conformations observed earlier in ethyl nitrate [176]. Conformers of the three primary esters could be assigned to *anti* and *gauche* configurations about the NOCC torsional angle coupled with *gauche* or *anti* configurations for *n*-propyl and *n*-butyl nitrate. IPN exists in a *gauche* conformation. For each compound all of the observed conformers were approximately equally stable.

5.1.8 Thermodynamic Properties of Isopropyl Nitrate

Thermodynamic properties of IPN are summarized in Table 26. The heat of evaporation of IPN at 298 K is 38.8 kJ/mol = 9.27 kcal/mol, and at the NBP it is 35.0 kJ/mol = 8.36 kcal/mol [11].

Table 26: Thermodynamic properties of IPN.

Property	SI units	Other units	References
Heat capacity at 298 K	191.1 J K ⁻¹ mol ⁻¹	45.67 cal mol ⁻¹ °C ⁻¹	
Enthalpy of formation	-229 kJ/mol	-2184 kJ/kg	[74]
ΔH_{298}^f , liquid	-230 ± 1 kJ/mol	-2189 kJ/kg	[29]
	-229.8 kJ/mol	-54.92 kcal/mol	[118]
Enthalpy of formation	-191.2 kJ/mol	-1819 kJ/kg	
ΔH_{298}^f , vapor	-191.2 kJ/mol	-45.7 kcal/mol	[117]
	-191.0 kJ/mol	-45.65 kcal/mol	[118]
Enthalpy of fusion at 191 K	10.1 kJ/mol	2.41 kcal/mol	
Entropy of fusion	52.43 J K ⁻¹ mol ⁻¹	12.53 cal mol ⁻¹ °C ⁻¹	
Enthalpy of evaporation	35.32 ± 0.62 kJ/mol		
Enthalpy of evaporation at NBP	35.0 kJ/mol	8.36 kcal/mol	[11]
Heat of evaporation at 298 K	38.79 kJ/mol	9.27 kcal/mol	[11]
Heat of evaporation at 288 K	39.7 kJ/mol	9.49 kcal/mol	[73]

5.2 Chemical Properties of Isopropyl Nitrate

5.2.1 Thermal Decomposition of Isopropyl Nitrate

5.2.1.1 Slow Liquid-Phase Decomposition of Isopropyl Nitrate

The rates of decomposition of IPN were compared to those of secondary butyl nitrate, normal butyl nitrate, and EGMN [41].

IPN was decomposed in a closed reactor at temperatures below 500 K and pressures up to 40 kPa [224, 225]. The reaction was first order with respect to IPN, and the main products of the reaction were isopropyl nitrite, methyl nitrite, NM, acetaldehyde, acetone, nitrogen oxides, and carbon dioxide. The addition of nitric oxide to decomposing IPN caused isopropyl nitrite and nitrogen dioxide to form exclusively in the earliest stages of reaction, although it did not alter perceptibly the overall rate and ki-

netics of reaction. The mechanism of decomposition may be rationalized in terms of an initial fission of the O—N bond to yield an isopropoxyl radical and nitrogen dioxide. The isopropoxyl radical is able to decompose to a methyl radical and acetaldehyde. Each of these products then reacts further, in part to convert nitrogen dioxide to nitric oxide and then to form organic derivatives of nitric oxide. The overall behavior of the low-temperature decomposition of IPN resembled that of ethyl and NPNs rather than that of *tert*-butyl nitrate.

In a similar study, IPN was decomposed at pressures greater than 1.4 MPa and at temperatures in the range 1300–1550 K using two types of reactors [226, 227]. Reaction times were extended from a few milliseconds (in a combustion chamber flow reactor) to several minutes (in a closed bomb reactor). The products of decomposition were analyzed by MS and their concentrations compared with those calculated for thermodynamic equilibrium. The main products were H_2 , N_2 , CO , CO_2 , CH_4 , NO , and H_2O . Even at long reaction times not all the measured concentrations corresponded to calculated values; in particular, the experimental concentration of methane was higher and that of hydrogen lower than expected for thermodynamic equilibrium. This very slow approach to overall thermodynamic equilibrium was due to the endothermic decomposition of methane, which is slow at temperatures below 1500 K. Therefore, the burning temperature of IPN is greater than expected, and the solid carbon content of exhaust gases remained low. The usefulness of IPN as a monopropellant would be enhanced by these effects.

Most of the work was done on IPN instead of isopropyl nitrite, but isopropyl nitrite is an intermediate product of IPN decomposition. Therefore, its decomposition was examined in a separate test series, starting with isopropyl nitrite instead of IPN. The rate of decomposition of isopropyl nitrite in dilution with CF_4 was studied in a static system over a temperature range of 403–433 K (130–160 °C) [228]. The addition of large amounts of NO (~0.9 atm) in place of CF_4 almost completely suppressed acetaldehyde formation. In addition to acetaldehyde, acetone and isopropyl alcohol were produced in approximately equal amounts. This test was part of a series of tests that also examined ethyl nitrite and *tert*-butyl nitrite.

The pyrolysis of IPN in the presence of NO was studied in a flow system with a molecular beam mass spectrometer at temperatures up to 700 K and pressures of 200–300 mbar, with residence times in the hot zone of the quartz reactor of ca. 30 ms [229]. This method allowed rapid quenching of the reaction and direct sampling and was designed to optimize detection of intermediates and radicals. Nitric oxide, NO , was added in the reactor at a partial pressure of 5–10 mbar to see whether it would impede the reaction. Isopropyl nitrite was shown to be a stable intermediate up to 490 K. From this molecule, several other species are formed by dissociation or reaction with methyl radicals and NO , and the alkyl nitrate reactions are thus similar to the alkyl nitrite reactions. In previous studies of IPN pyrolysis reactions the products varied strongly with temperature. It was shown that this temperature variation was due to

the existence of thermally labile species like isopropyl nitrite and methyl nitrite. Nitrosomethane, CH_3NO , was found at intermediate temperatures, and HCN was found at temperatures above 600 K.

The reaction path of nitrate ester decomposition is dependent on pressure. Secondary nitrate esters shift their major decomposition pathway from homolysis of the $\text{O}-\text{NO}_2$ bond to elimination of HNO_3 in a pressure range of 0.4 to 0.8 GPa [230]. The elimination reaction resembled carboxylate ester pyrolysis with E_1 character.

The decomposition of IPN was examined by DSC, heat flux calorimetry (HFC), and accelerating rate calorimetry (ARC) measurements [231, 232]. Evaporation precedes decomposition. First, the ASTM DSC method using a hermetic aluminum pan having a lid with a laser-produced pin hole was used to determine the vapor pressure of IPN. Results calculated from an Antoine equation were in substantial agreement with those determined from DSC measurements. From the latter measurements the enthalpy of evaporation was determined to be $35.32 \pm 0.62 \text{ kJ/mol}$. Attempts to determine vapor pressures above about 0.8 MPa resulted in significant decomposition of IPN(G). The enthalpy change for decomposition in sealed glass systems was found to be $-3.43 \pm 0.09 \text{ kJ/g}$ and $-3.85 \pm 0.03 \text{ kJ/g}$, respectively, from DSC and HFC measurements on IPN(L) samples loaded in air. Slightly larger exotherms were observed for the HFC results in air than those in inert gas, suggesting some oxidation occurs. In contrast, no significant difference in the observed onset temperature of about 423 K (150°C) was observed for either the HFC or ARC results. From DSC measurements, an Arrhenius activation energy for decomposition of 1264 kJ/mol was found. These measurements were also conducted in sealed glass systems, and decomposition appeared to proceed primarily from the liquid phase.

The IR spectra of NPN and IPN were measured using FTIR and found to be very similar. The kinetic parameters of the thermal decomposition of the two nitrates obtained by DSC showed that the thermal stability of IPN was slightly lower than that of NPN, according to the rate constants at three different temperatures and the peak temperature of the thermal decomposition [233].

Aluminized IPN may be used as a fuel-air explosive. Two mixtures of IPN and aluminum (mass ratio of IPN:aluminum = 2:1 and 1:13.7) were prepared, and their decomposition behaviors were determined by DSC [234]. The results showed that the most probable decomposition mechanism of the aluminized IPN did not change with a different ratio of components. The peak temperatures of the decomposition processes for the two samples were lower than that of pure IPN, and the apparent activation energy and the preexponential factor were correspondingly smaller. The thermal parameters and decomposition rate of the sample with an IPN:aluminum mass ratio of 1:13.7 were higher than those of the sample with a mass ratio of 2:1 during the whole process. See also [235].

5.2.1.2 Slow Vapor-Phase Decomposition of Isopropyl Nitrate

If IPN vapor is admitted to a heated quartz vessel at low pressures, chemiluminescence, similar to that observed with methyl nitrate, can be seen in a darkened room for less than a second. Depending on the sample pressure, it may precede an explosion of the vapor [236]. An examination of IPN over the temperature range 513–613 K (240–340 °C) and pressure range 13–1732 Pa (0.1–12 mm Hg) in a 350-mL quartz reaction vessel with a surface-to-volume ratio of 1.0 cm⁻¹ showed behavior similar to that of methyl nitrate. There were two modes of reaction: at low temperature and pressure in the aforementioned ranges the reaction was accompanied by an immediate (0.5 s) faint blue-white luminescence, while at higher pressures but the same temperature the luminescence was followed by a short induction period and then explosion. The two decomposition modes were not shown by NPN. Above 553 K (280 °C) and above the critical pressure, decomposition was accompanied by an immediate faint, brief, white glow.

A generalized gradient approximation of DFT was used to investigate the adsorption and dissociation of a single IPN molecule on an Al(111) surface [237]. Computations indicated that the IPN molecule tends to adsorb in a parallel mode with respect to the Al(111) surface. The dissociation behaviors and mechanisms of IPN on a metallic aluminum surface would be different from that on a catalyst like Cr₂O₃ or NiO.

5.2.1.3 Rapid Vapor-Phase Decomposition of Isopropyl Nitrate

The thermal decomposition of IPN vapor was studied in a shock tube in the temperature range 533–635 K [238]. A similar method was previously used for the study of the decomposition of di-*tert*-butyl peroxide. The kinetic rate equation was

$$k = 10^{16.51 \pm 0.55} \exp[-169.5 \pm 6 \text{ kJ/mol}/RT] \text{ s}^{-1}$$

Reactions in the vapor-phase decomposition of IPN as a candidate liquid gun propellant were studied by time-resolved monitoring using IR spectroscopy, identifying intermediates and developing kinetic rate equations for IPN decomposition [239].

The evaporation and chemical decomposition kinetics of single IPN droplets were investigated at 473, 498, and 523 K (200, 225, and 250 °C) by monitoring the gas phase using rapid-scan FTIR spectroscopy [240, 241]. The study used a reaction cell that could withstand pressures up to 10 bar and could be kept at a constant temperature (± 1 °C) in the interval 293–548 K (20–275 °C). The liquid was introduced into the chamber by a septumless injection system. The injected volume was variable between 0.2 and 10 μL . The cell volume was 8.9 cm³ and the optical path length was 5.0 cm. The cell was equipped with IR-transparent CaF₂ windows. For IPN, a nitrate symmetric stretching band centered at 1281 cm⁻¹ was selected and the boundaries for integration were set at 1279 and 1283 cm⁻¹. The temporal resolution used throughout the experiment was 0.25 s at a spectral resolution of 4 cm⁻¹. The droplet diameter was determined by recording the injection process and the formation of the droplet in the gas phase of the

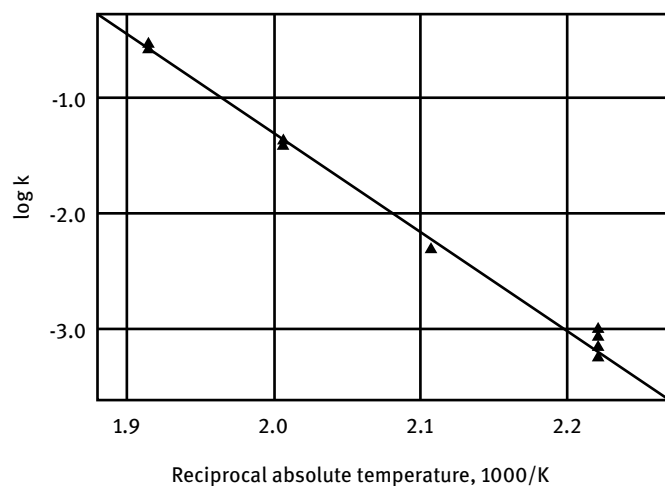


Figure 15: Kinetic rate constants for IPN decomposition. (Republished and modified from [240], with permission of © 1989 Elsevier Science Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

cell using a video, and measured diameters ranged from 1.9 to 0.5 mm, depending on the injected volume. The resultant activation energy determined from the slope of the solid straight line in an Arrhenius graph (Figure 15) was 158 kJ/mol and the frequency factor, $\log z$, was 15.2. These values compared quite well with those obtained by Julien et al. [238] in a shock tube experiment at 533–633 K (260–360 °C) with activation energy being 169.5 kJ/mol and the log of the frequency factor being 16.5. The corresponding values for other nitrate esters having related structures were 154.5 kJ/mol and 14.7 for NPN and 154.5 kJ/mol and 14.7 for ethyl nitrate (from [142]). Evaporation and decomposition rates were determined by a fit of a special model to the experimental absorption-time profiles. The model combined elements of quasi-static theory and simple chemical reaction kinetics.

The rapid decomposition of IPN and other alkyl nitrates in shock waves is a good method to obtain kinetic rate data for fast decomposition rates of alkyl nitrates [94]. The strand burning of liquid IPN and IPN mixtures will be discussed in *Encyclopedia of Monopropellants*.

5.2.2 Electron Bombardment Decomposition of Isopropyl Nitrate

Alkyl nitrates that need to be analyzed by MS need to be ionized by electron bombardment. Electron bombardment also offers clues about the weak links in a molecule where decomposition is likely to start first. The appearance potential is the electron energy level (in eV), where fragments begin to appear in the analyzer.

5.2.3 Photolysis of Isopropyl Nitrate

The photolysis of IPN and other alkyl nitrates is discussed in this chapter because this is a method for controlled ignition of the decomposition reaction in rocket engines by laser photolysis.

A comparison of the unimolecular decomposition behavior of electronically excited nitro-containing molecules with different $X-\text{NO}_2$ ($X = \text{C}, \text{N}, \text{O}$) bond connections is important for the understanding of the reactivity differences between NM, dimethylnitramine (DMNA), and IPN [242]. Illumination by UV lasers at different wavelengths, such as 226, 236, and 193 nm, created the excited states of these molecules. The decomposition products were then detected by resonance-enhanced two-photon ionization (R2PI), laser-induced fluorescence (LIF) techniques, or single-photon ionization at 10.5 eV. NO molecules were observed to be the major decomposition product from electronically excited NM, DMNA, or IPN. The NO products from decomposition of electronically excited (226 and 236 nm) NM and IPN displayed similar rotational (600 K) and vibrational distributions. OH radicals were observed as a minor dissociation product from all three compounds. The major decomposition pathway of electronically excited NM and IPN involved fission of the $X-\text{NO}_2$ bond to form electronically excited NO_2 product, which further dissociated to generate NO.

5.2.4 Analysis of Isopropyl Nitrate

The European NATO specification [243] for IPN, also known under the designation AVPIN, requires the purity properties listed in Table 27. There does not appear to be a US equivalent specification for IPN in the MIL-SPEC or MIL-PRF series.

Table 27: IPN specification NATOS-746AVPIN; Def Stan91-89/1.

UN designation	UN1222
Density at 20 °C	1041–1047 kg/m ³
Acidity, total, as nitric acid, max.	100 mg/L
Nitrite, as nitrous add, max.	25 mg/L
Water, max.	1200 mg/L

IPN and other alkyl nitrates may be used as cetane number improvers in diesel fuels. There are several analytical method for determining IPN in diesel fuels. IPN and other alkyl nitrates may be used as ignition enhancers in hydrocarbon fuels for pulse detonation engines.

5.3 Handling of Isopropyl Nitrate

When military propellant storage magazines in Russia were decommissioned as part of the SALT agreements, it was found that IPN had been used and stored in Russia and USSR member states under the code names OT-155 or Isonite. In one location in Azerbaijan, a stash of 24489 kg of OT-155 was found and had to be neutralized [244].

5.4 Safety Properties of Isopropyl Nitrate

5.4.1 Autoignition Temperature of Isopropyl Nitrate

The AIT of IPN vapor in air is 463 K (190 °C). The pressure-temperature conditions for the spontaneous ignition of IPN vapor were measured at 492–512 K [245]. Ignition was impossible below 492 K, even with increased pressure. Beyond 510 K the critical pressure fell below 0.8 kPa and did not vary much with further increases in temperature. The extent of self-heating preceding ignition (i.e., during the induction period) was limited (ΔT 20 K). The measured temperature excursions during ignition itself did not significantly exceed 200 K. The final products of ignition at 500 K included CH₄, methanol, acetaldehyde, and NM in substantial yield.

5.4.2 Flash Point of Isopropyl Nitrate

The flash point of IPN as measured with the Cleveland open-cup method is 295.3 K (22.2 °C).

5.4.3 Flammable Range of Isopropyl Nitrate in Air

USBM Bulletin 627 [196] and USBM Bulletin 503 [152] do not contain information on the flammable range of IPN (but they do contain data on NPN). One must assume that the upper limit of flammability is at 100% because no additional oxygen is needed to sustain combustion of IPN vapors. See also [246].

5.4.4 Detonation Sensitivity of Isopropyl Nitrate

IPN, like all other alkyl nitrates, is a potential explosive, and detonation can be initiated accidentally or deliberately by a variety of different stimuli. The hazard properties must be known to assign the proper transportation hazard classification for this chemical. The UN Transportation hazard code is UN 1222.

5.4.4.1 Cap Sensitivity of Isopropyl Nitrate

Shock initiation of detonation and critical diameters were investigated for IPN [247]. Both direct initiation of detonation and shock-to-detonation transition via the onset of detonation were observed. The initial shock pressure vs. time of onset of detonation

and catch-up time were measured, and the critical shock initiation pressure was determined to be in the range of 7–8.5 GPa at $0 \pm 5^\circ\text{C}$. The critical diameter for neat IPN was found to exceed 310 mm at 289 K (16°C) when confined in low-impedance PVC tubes. Shock initiation studies of IPN were carried out for four PVC attenuator thicknesses (6.24, 12.48, 18.72, and 25 mm) for a temperature range between 268 and 278 K (-5 and $+5^\circ\text{C}$). The critical gap thickness for shock initiation at $0 \pm 5^\circ\text{C}$ must be in a range of 18.72 to 25 mm. Aluminum particles of 100 nm average size were added to IPN in the belief that the fine aluminum would react within the reaction zone of the IPN detonation. The critical diameter of aluminized IPN indeed was found to lie between 29 mm (no detonation) and 48 mm (detonation) in PVC tubes, meaning it was one order of magnitude smaller than for neat IPN. The critical diameter for IPN detonation in the low-impedance PVC tube was larger than 307 mm. When compared with the critical diameter for NM detonation in a glass tube (20–25 mm), the critical diameter for IPN was one order of magnitude larger than that for NM.

5.4.4.2 Drop Weight Impact Sensitivity of Isopropyl Nitrate

The drop weight impact sensitivity of IPN has been measured by many laboratories. Because IPN is readily available, IPN was often chosen as a reference material when other sensitive materials were tested in the same apparatus.

The drop weight sensitivity of IPN was tested in comparison to NOSET-A and Otto Fuel II [248]. The results from instrumented drop weight tests indicated that ignition occurred at critical pressure ratios of 15 ± 1 for IPN, 124 ± 6 for Otto Fuel II, and 143 ± 6 for NOSET-A. The compressive energies for the ignition were 5, 12.2, and $13.1 \text{ kg cm cm}^{-3}$, respectively. NOSET-A and Otto Fuel II were respectively 2.6 and 2.4 times less sensitive than IPN.

5.4.4.3 Adiabatic Compression Sensitivity of Isopropyl Nitrate

The sensitivity of IPN and other monopropellants to accidental adiabatic compression ignition can be reduced by modifying the composition of the bubble so that the constituent gas in the bubble has a high specific heat and contains no oxygen. Various additives were tested to reduce the sensitivity of IPN to adiabatic compression, a property often called *dieseling*. For a vapor bubble above IPN that is saturated with propane, adiabatic compression ignition did not occur, even at the highest pressure ratios envisaged for any practical application [249]. Ignition has not been observed in any test with propane/IPN bubbles. The effect of dissolved propane on performance is insignificant, and there is no visible soot in the decomposition products. It was recommended that IPN tanks be filled with IPN saturated with propane. If desired, the initial pressure in the tank may be increased by the addition of nitrogen. For tanks that will never be used at above 303 K (30°C), it is sufficient to fill the ullage with nitrogen only.

Rapid compression of IPN vapor by a solid piston in a cylinder, even when it is in more than 50-fold dilution in air, can result in explosions [250, 251]. The

compression ratio ($V_{\text{initial}}/V_{\text{final}}$) was 11.4:1, and the travel duration of the piston was 20 ms. Pressure-time curves were measured and mean gas temperatures calculated from them. Product compositions and extents of reaction were measured by GC following removal of a sample and quenching by a rapid sampling technique. Heating accompanies rapid compression of gases, and its extent depends on the ratio of the specific heats, the adiabatic coefficient. Temperatures achieved at the end of compression in this apparatus by inert gases starting at room temperature fell in the range of ca. 500 K (for CO_2) to ca. 1000 K (for Ar). The temperature began to fall immediately after compression ceased. From starting pressures of about 45 kPa the range of maximum measured pressures attained was approximately 0.5–1.2 MPa. When IPN vapor (1 mol-%) is present in inert atmospheres, pyrolysis will occur and its extent will depend on the temperature achieved. For temperatures greater than 600 K, decomposition of IPN began before piston motion ceased, and more than 90% was consumed within about 5 ms. Even so, not all the IPN decomposed; a small fraction, which had resided in the cool boundary layers, remained in the end gas. Although pyrolysis in inert atmospheres is exothermic, ignition did not occur with inert gas dilution. When IPN vapor was compressed in the presence of oxygen (e.g., in air), the reaction occurring before the end of compression was followed by a second very exothermic stage. The temperature rose sharply, and ignition was achieved. Measured composition-time profiles showed that ignition resulted principally from the oxidation of aldehydes formed in the earlier stages by IPN decomposition and partial oxidation of its initial products.

In a continuation of this work the compression ratio ($V_{\text{initial}}/V_{\text{final}}$) was 10.8:1 and the time for motion of the piston was 20 ms [252]. Pressure-time histories were measured by pressure transducers and gas temperatures derived from them, assuming adiabatic compression. The temperatures reached during compression depended on the ratio of the principal specific heats of the reactant compositions; they fell in a range of around 500 K (in CO_2) to around 1000 K (in Ar). From starting pressures of about 0.5 atm the pressures reached varied between approximately 7 and 16 atm. Spontaneous ignition may be achieved in particular in the presence of oxygen, which was a prerequisite for the ignition of IPN vapor. Overall extents of reaction and product abundances were measured by GC and enthalpies of reaction calculated from these. At all but the lowest temperatures (600 K) virtually all of the IPN reacted (i.e., less than 5% remained), whether or not oxygen was present. But even at very high temperatures (1000 K) very small amounts always remained. This was attributed to the fact that part of the IPN was confined to a cool boundary layer at the combustion chamber wall. Pyrolysis of IPN occurred in inert atmospheres and among the major products at moderate temperatures were aldehydes, NM, methyl nitrite, and methanol. At temperatures above 1000 K, carbon monoxide and methane predominated. When excess oxygen was present, carbon oxides and formaldehyde were the predominant carbon-containing products.

In the adiabatic compression apparatus, temperatures rose to ~ 600 K at the end of the compression stroke. Conditions then remained constant for nearly a hundredth of a second, and 90% of the IPN has been consumed by the end of 8 ms. Dynamic absorption spectra showed that NO_2 was an important intermediate product during this period, although it was wholly consumed [253].

The adiabatic compression sensitivity of IPN, NOSET-A, and Otto Fuel II was measured at ambient temperature (290 ± 5 K = 17 ± 5 °C), also in comparison to drop weight sensitivity measured during the same investigation [248]. The adiabatic compression test apparatus consisted of a 28-mm-ID steel tube with 2.5-mm wall thickness bent in the form of a U at the lower end and containing a known volume of liquid (385 mL). This slug of liquid was accelerated into a closed volume (130 mL) by nitrogen gas pusher suddenly released from a pressurized reservoir of 2.65 L. Bubble and driver pressure were measured by fast-response quartz crystal transducers. The driver pressure was increased incrementally from one test to the next until dieseling was detected in the closed volume. For IPN, dieseling occurred at pressures above 24 bar, for Otto Fuel II dieseling occurred at pressures above 190 bar, and for NOSET-A dieseling occurred at pressures above 230 bar, which was near the measuring range of the pressure transducers. In all cases the reaction propagated into the liquid phase, but only with IPN was there evidence of a gas-phase ignition reaction. The U tubes were shattered into fragments.

5.5 Detonation Performance of Isopropyl Nitrate

5.5.1 Detonation Velocity of Isopropyl Nitrate

The velocity of sound of IPN was measured and used in the universal liquid Hugoniot to produce an estimated Hugoniot curve [218]. The room temperature sound speed for IPN was 1.10 mm/ μ s. Gas-gun-driven projectile impact, multiple-magnetic-gauge detonation pressure measurements were made to measure a Hugoniot state at 6 GPa, which was in good agreement with predictions. Two similar experiments were conducted at higher pressure inputs to study the shock-to-detonation transition in IPN. The high inputs required for initiation necessitated the use of a two-stage gun. One experiment with an input of 9.0 GPa into the IPN produced a run to detonation of about 3 mm, and the *in-situ* particle velocity profiles showed the expected homogeneous initiation behavior of a growing wave behind the shock front that overtook the front and decayed to a steady detonation. The reactive wave in the shocked IPN appeared to have achieved a steady superdetonation in both of the initiation experiments. The waveforms showed that the superdetonation achieved a velocity of about 8 mm/ μ s. After overtake of the initial wave, the overdriven velocity was 6.3 mm/ μ s, which then decreased to a steady 5.34 mm/ μ s. The measured steady-state detonation velocity was 5.34 mm/ μ s = 5340 m/s.

The detonation of liquid IPN depends on the type of confinement not only on the diameter of the tubes and their thickness, but also on the thermomechanical characteristics of the wall, i.e. its acoustical impedance relative to that of the liquid explosive. The detonation velocity of liquid IPN in steel tubes was between 5.3 and 5.4 mm/ μ s, depending on the tube diameter. The critical diameter in steel is about 10 mm radius (20 mm diameter) [254, 255]. Testing was done in 50-cm long tubes with varying wall thickness and internal diameters. Wall thickness was varied from 0.1 to 6 mm and internal diameter was varied from 10 to 42 mm. Initial temperature was varied from 270 to 350 K. The booster was a pellet containing 75% PETN in direct contact with the IPN. In a 27-mm tube, detonation velocity decreased from 5350 to 5100 m/s when the initial sample temperature was increased from 280 to 350 K. The limits of detonation depended strongly on the nature of the confinement. When IPN was contained in a lead tube at initial temperatures ranging between 310 and 325 K, the detonation velocity was found to be non-constant, decreasing roughly from 6000 to 5000 m/s along the length of the tube. However, in Pyrex and PVC tubes no detonation at all could be initiated in the range of experimental conditions, ($T \sim 330$ K, i. d. 42 mm). Experimental results lead to the conclusion that for charge diameters lower than critical diameters, the detonation of IPN is governed by the same physical principles as those governing detonation in gaseous mixtures. In particular, limits of detonation, density effect on the velocity of propagation and detonation pressure agreed both qualitatively and quantitatively with expected results deduced from the theories.

The detonation velocity and pressure of *iso*-PrNO₃ depends on the initial density ρ_1 of the liquid [256]. The detonation pressure increased linearly from $p_2 = 71$ kbar at $\rho_1 = 967$ kg/m³ and an initial temperature of $T_1 = 353$ K to $p_2 = 79$ kbar at $\rho_1 = 1042$ kg/m³ and $T_1 = 293$ K.

Confinement in heavy metal tubes has a pronounced effect on the detonability of IPN, also measured in comparison to that of NM [257]. Even the roughness of the inner surface of the wall can have an important effect on propagation of detonation waves in *iso*-PrNO₃.

Optical pyrometry was used to study initiation and propagation of detonation in homogeneous liquid high explosives (LHE): bis-(2-fluoro-2,2-dinitroethylformal), IPN and 1,6-diazido-2-acetoxylhexane [258]. The brightness temperature profiles were measured at various intensities of the incident shock wave. The observations showed that LHE decomposition progresses monotonically (particularly at low shock pressures) in time, and the intensity of the initial stage of detonation onset depends on the initial shock amplitude. Therefore the selection of the instant when the violent chemical reaction starts and, hence, of the adiabatic explosion delay is somewhat arbitrary.

5.5.2 Vapor Phase Detonation of Air/Isopropyl Nitrate Mixtures

There is interest in the potential use of IPN as a fuel or fuel additive for pulse detonation or rotating detonation propulsion. The detonation velocity of fine droplet/air mixtures is usually approximately 100–200 m/s slower than the calculated Chapman-Jouguet (C-J) velocity. Detonations of gaseous mixtures containing IPN were investigated in a 280 mm diameter, 7.3 m long detonation tube [259]. Measurements were made of detonation pressures, velocities and cell widths for a range of air/IPN mixtures. Cell widths were measured on soot-covered aluminum foil lining the chamber and plotted as a function of chamber pressure and equivalence ratio. Tests were conducted for stoichiometric air/IPN at initial pressures ranging from 10 to 100 kPa, and air/IPN equivalence ratios were varied between 0.3 and 3.0 for a series of tests at 1 bar initial temperature. To ensure full evaporation of the liquid fuel, tests were performed at an initial temperature of 373 K. Preliminary efforts were made to interpret the results using a detailed chemical reaction mechanism based on previous work on nitrated hydrocarbons, including propellants and high explosives. The reaction mechanism was compared with existing shock tube data and applied in a tentative investigation of the reaction zone structure. Measured detonation velocities (▼) did not vary from calculated velocities (solid line) by more than 3% (Figure 16).

Deflagration-to-detonation transition (DDT) in air/IPN mist aerosol sprays showed the formation of a self-sustained detonation wave, as indicated by the existence of a transverse wave and a spinning wave structure [219]. The run-up distance

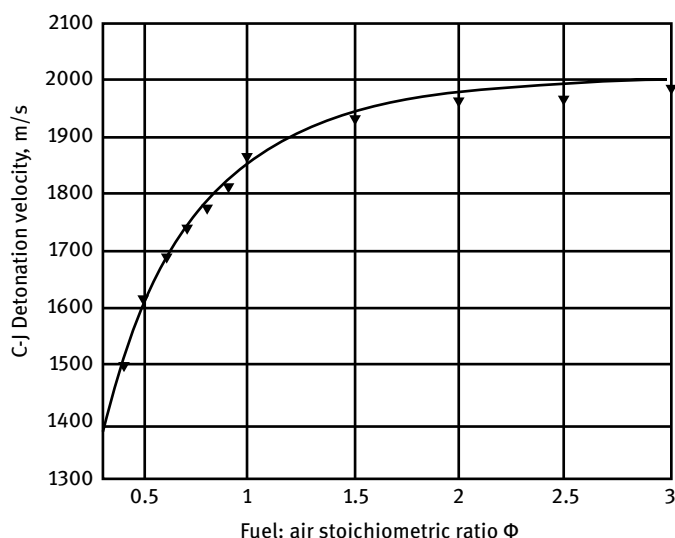


Figure 16: Detonation velocity of IPN vapor as a function of fuel:air stoichiometric ratio. Comparison of measured detonation velocities with computed C-J velocities. (Reproduced and modified from [259], with permission from Dr. Josef E. Shepherd 11-Feb-2021.)

of the DDT process and the pitch size of the self-sustained spinning detonation wave in air/IPN mixtures were analyzed. A detonation wave formed during the DDT. Two propagation modes, a high-speed deflagration mode and a self-sustained detonation mode, of the shock-reaction complex in IPN mist/air mixtures were identified. The influence of the aerosol concentration and droplet size on the detonation propagation mechanism was studied. The minimum IPN concentration for DDT occurrence in air/IPN aerosol mixtures was 450 g/m^3 . The optimum IPN concentration for DDT occurrence was 473 g/m^3 . The propagation velocity and overpressure of the self-sustained detonation wave in air/IPN aerosol mixtures were measured and calculated. Under specific experimental conditions, a DDT process occurred in air/IPN aerosols within a transition distance of 14.35 m. A self-sustained detonation wave formed and propagated with velocities between 1540 and 1660 m/s, with a mean velocity of $\approx 1600 \text{ m/s}$. The overpressure of the detonation wave oscillated between 2.90 and 6.60 MPa, with a mean value of 4.75 MPa.

The explosion pressure, flame temperature, maximum rate of pressure rise, maximum rate of temperature rise, and LFLs were measured for two sets of IPN and mixed IPN/JP-10 in air aerosols at different concentrations and droplet mean diameters of 19 and $34 \mu\text{m}$ [260]. Experiments were performed to study various concentrations at various ignition energies for the IPN/air aerosols and the explosions of binary mixture aerosols with various mass ratios of IPN and JP-10. The results indicated that for the IPN/air and JP-10/air aerosols with a mean droplet diameter of $\sim 34 \mu\text{m}$, the maximum peak pressure and maximum peak temperature of the IPN/air aerosols were greater than those of the JP-10/air aerosols. The maximum rate of pressure rise of the IPN/air aerosols reached a maximum value of 395 MPa/s at a mean droplet diameter of $\sim 34 \mu\text{m}$, and the pressure increased more abruptly in the IPN/air aerosols than in the JP-10/air aerosols. The LFLs of the IPN/air aerosols occurred with a total concentration of 197 g/m^3 at a mean droplet diameter of $19 \mu\text{m}$ and a total concentration of 233 g/m^3 at a mean droplet diameter of $34 \mu\text{m}$.

5.6 Applications of Isopropyl Nitrate

IPN has been extensively investigated as a gas generant in auxiliary power units for jet aircraft [217]. Monopropellant applications of IPN will be discussed in *Encyclopedia of Monopropellants*. It has also been proposed as a power source for underwater vehicles and torpedoes [261].

As part of the Strategic Arms Limitation Talks (SALT) disarmament agreement, stocks of Isonite (IPN) stored in Azerbaijan (a former USSR republic) had to be demilitarized. It is not known what this material was used for and what they eventually did with it to neutralize it [262].

6 Higher Alkyl Mononitrates

Higher ($C_{n \geq 3}$) alkyl mononitrates would be too fuel-rich to be of any value as monopropellants. They may be used as process solvents or plasticizers. Amyl nitrate is used as a cetane number enhancer in diesel fuels.

6.1 *n*-Butyl Nitrate

There are three possible isomers of butyl nitrates, but they are rarely used as propellant ingredients. The physical properties of several butyl nitrates were already summarized earlier in Table 2.

Butyl nitrate, *n*-butyl nitrate, CAS RN [928-45-0], could not be made to explode under the maximum impact load of the apparatus used when tested for impact sensitivity in comparison to GTN, EGDN, and other energetic liquids [263].

The rates of decomposition of *n*-butyl nitrate were compared to those of IPN, *sec*-butyl nitrate, and EGMN [41].

6.2 2-Ethylhexyl Nitrate

2-Ethylhexyl nitrate, also known as EHN, 2-EHN, $CH_3(CH_2)_3CH(C_2H_5)CH_2ONO_2$, nitric acid 2-ethylhexyl ester, CAS RN [27247-96-7], is very useful as a plasticizer for hydroxyl-terminated polybutadiene (HTPB) propellants because it is completely miscible with the R45M prepolymer; not only that, it also solubilizes other plasticizer additives that will improve the mechanical properties of the cured propellant [264]. The solubilities of other plasticizers like GTN, BTTN, TMETN, and TEGDN in R45M are only on the order of one to two parts per hundred.

EHN is now widely used as an ignition enhancer and cetane number improver in diesel fuels. 2-EHN typically is used in a concentration range of 0.05 to 0.40 mass-% and may yield a 3 to 8 cetane number benefit. Other alkyl nitrates, as well as ether nitrates and some nitroso compounds, have also been found to be effective cetane number improvers, but they are not currently used commercially. The use of cetane number improver additives constitutes both a cost-effective and convenient way to accelerate startup, reduce emissions, and improve engine performance. As a result of this application, 2-EHN has become more widely available and can thus be used for rocket propulsion as well as automobile propulsion. The quantity of 2-EHN produced worldwide is now the largest quantity of any alkyl mononitrate currently in use. This explains the large number of recent publications on the thermal stability of EHN, apparently in response to some accidents that happened before mixing the material with diesel fuel.

6.2.1 Preparation of 2-Ethylhexyl Nitrate

Having identified in 1984 a growing demand for a nitrate ester diesel fuel Cetane Improver, the French company SNPE (Société nationale des poudres et explosifs) first began production of 2-EHN at its Sorgues production facility in France. When EURENCO was created in 2004 as an SNPE subsidiary, it was also entrusted with the development of this activity. Close to 30 years after it started, the production of Cetane Improver is a fully integrated and vital part of the Sorgues manufacturing complex. In November 2012, anticipating the growing need for fuel additives offering both technical and economic advantages, EURENCO launched a new subsidiary, VeryOne, to promote its 2-EHN solution, Cetane Improver, and meet the strong market demand worldwide [265].

2-EHN can be produced by nitration of iso-octanol with $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixed acid. Before scaling up the production process, one must better understand the hazards involved with nitration reactions. DSC, ARC, and a reaction calorimeter were used to analyze the thermal stability of 2-EHN and the thermal hazard of iso-octanol nitration [266]. Four samples with different ratios of 2-EHN to mixed acid were tested using DSC. The results indicated that more mixed acid could catalyze the decomposition of 2-EHN. Three samples were tested using ARC, and the results showed that one sample started decomposing at the lowest onset temperature. This showed that there is a high probability of triggering the decomposition of the product 2-EHN from the iso-octanol nitration process. The overall heat generation of these reactions was large, even when keeping the temperature at 318–328 K (45–55 °C). This heat generation makes these semibatch processes difficult to control, especially on a pilot or plant scale. Based on the maximum temperature of the synthesis reaction, the only acceptable semibatch process is the nitration reaction at 283 K (+10 °C).

2-EHN can be made from nitric acid and 2-ethyl hexanol as raw materials and sulfuric acid as catalyst in a microchannel continuous flow reactor [267]. The best synthetic conditions were determined under experiments: 1:2 for the mol ratio of nitric acid and sulfuric acid; 1:1 for the mol ratio of nitric acid and 2-ethyl hexanol; the optimal liquid hourly space velocity obtained was 4000 h^{-1} . In this condition, the yield and purity of 2-EHN were relatively high. Experience gained in the production of 2-EHN can be applied to the production of other alkyl nitrates that are used as rocket propellant ingredients.

6.2.2 Physical Properties of 2-Ethylhexyl Nitrate

Physical properties of 2-EHN are summarized in Table 28.

Table 28: Physical properties of 2-EHN.

	SI units	Other units
Freezing point	228 K	−45 °C
Boiling point	373 K (decomp.)	100 °C (decomposes)
Vapor pressure	27 Pa @ 293 K	0.2 mm Hg @ 20 °C
Vapor pressure	40–53 Pa @ 313 K	0.3–0.4 mm Hg @ 40 °C
Vapor pressure	1.33 kPa @ 355 K	10 mm Hg @ 82 °C
Density	0.96 kg/dm ³ at 293 K	0.96 g/mL @ 20 °C
Kinematic viscosity	0.018 cm ² /s	1.8 cSt @ 20 °C
Solubility in water	12.6 mg/L @ 293 K	12.6 mg/L @ 20 °C
Heat of evaporation	368 kJ/kg	
Coefficient of thermal expansion		1.010 (between 10 and 20 °C at atmospheric pressure)

Data source: Lubrizol® 8090 Data Sheet

6.2.3 Chemical Properties of 2-Ethylhexyl Nitrate

6.2.3.1 Thermal Decomposition of 2-Ethylhexyl Nitrate

2-EHN is thermally unstable. When heated to above 373 K (100 °C), it may undergo a self-accelerating exothermic decomposition.

The thermal decomposition mechanism of 2-EHN, an additive to diesel fuel to improve the cetane number, was investigated in solution and in the gas phase [268]. In *trans*-decalin as a solvent the activation barrier for the thermal decomposition was 163 kJ/mol (39 kcal/mol). The decomposition at temperatures below 373 K (100 °C) was slow. Under high pressure conditions (2.4 kbar), the decomposition rates decreased, in accordance with what would be expected for a radical mechanism. Flash vacuum pyrolysis with subsequent detection of the products via MS or matrix IR spectroscopy identified NO₂, formaldehyde, and several olefins as the major decomposition products.

ARC was used to test the thermal sensitivity of four solid explosives and two liquid energetic materials, including PETN, RDX, HMX, TNT, nitroethane, and EHN [269]. Kinetic and thermodynamic parameters were calculated and analyzed. TMR_{ad} (time to maximum rate under adiabatic condition) was calculated. The thermal sensitivity of four solid energetic materials was decreasing in the order PETN RDX HMX TNT, which was consistent with results obtained using the traditional Wood's alloy bath method. The thermal sensitivity (sensitivity is the opposite of stability) ranking of six energetic materials from high to low was EHN PETN RDX HMX TNT NE.

The thermal decomposition of EHN in air was studied by microcalorimetry [270]. The effect of heating rate on the thermal decomposition of EHN was used to calculate the activation energy of thermal decomposition, TMR_{ad} (time to maximum rate under adiabatic condition) and the self-accelerating decomposition temperature. The results showed that a rise in the heating rate could shift the onset exothermic tem-

perature and peak temperature of EHN, but the reaction mechanisms were the same at all four temperature rise rates. The activation energy of thermal decomposition of EHN ranged from 144 to 214 kJ/mol. The self-accelerating decomposition temperature in typical storage containers was 348–371 K (75–98 °C).

2-EHN when mixed with acids becomes even more unstable. The thermal stability of EHN with concentrated acids under hot process conditions, four samples (pure EHN, concentrated sulfuric acid with EHN, concentrated nitric acid with EHN, and mixed acid with EHN) and three acids (sulfuric acid, nitric acid, and mixed acid) was measured by DSC and ARC [271]. The results indicated that concentrated sulfuric acid, concentrated nitric acid, and mixed acid can all reduce the onset of the exothermic decomposition temperature of EHN, especially concentrated sulfuric acid. DSC results also showed that the heat of EHN decomposition with nitric acid was greater than that of other samples. Based on ARC data, the kinetic parameters and T_{D24} (temperature at which time to maximum rate TMR_{ad} is 24 h) were calculated. The activation energy and T_{D24} of the EHN with acids, especially with concentrated sulfuric acid, were much lower than those of pure EHN. It was concluded that acids could decrease the stability of EHN and may be an important reason for frequent accidents.

2-EHN and nitrocellulose (NC) are commonly used energetic materials that have caused many thermal runaway reactions and explosions worldwide, and their thermal stabilities have always been an important issue. DSC was used to investigate the influence of thermal history during storage on the thermal stabilities of EHN and NC heated at different heating rates [272]. The decomposition kinetics of EHN and NC were determined by the Friedman isoconversional method. The kinetic parameters derived from heat balance were analyzed and used for the simulation of the time to the maximum heat release rate under adiabatic conditions (TMR_{ad}). The results indicated that the thermal history significantly influenced the dynamic DSC curves, decomposition kinetics, and thermal stability of NC, which decomposes autocatalytically, but the influence on EHN was negligible, whose decomposition proceeds according to an n th-order law.

2-EHN is unstable and has caused fire and explosion accidents. The mechanism of EHN thermal decomposition was investigated by DSC under non-isothermal and isothermal conditions, and its thermal decomposition kinetics was calculated [273]. A model for the decomposition reaction was established and verified by an isothermal method. The results indicated that the activation energy for EHN was 154 ± 3 kJ/mol under non-isothermal and 157 ± 7 kJ/mol under isothermal conditions. In addition, there was almost no difference in E_{act} at various extents of the reactant conversion, suggesting that a single-step reaction model is suitable to describe the decomposition reaction. In addition, the temperature of no return and self-accelerating decomposition temperature were calculated under non-isothermal and isothermal conditions. The kinetic parameters under the isothermal conditions were in good agreement with those obtained under the non-isothermal conditions.

6.2.3.2 Analysis of 2-Ethylhexyl Nitrate

Although 2-EHN is not used in liquid rocket propellants, methods for its analysis are listed here because the same methods can be used for the analysis of other alkyl nitrates: [274–276].

6.2.4 Safety Properties of 2-Ethylhexyl Nitrate

2-EHN had a low acute oral toxicity when tested in animals. The median lethal dose (LD50) was 5000 mg/kg (rat), and therefore 2-EHN was not classified as harmful or toxic if swallowed (under OSHA guidelines). The inhalation exposure guideline for 2-EHN is 1 ppm based on an 8-h time weighted average (TWA). In light of the potential temporary effects of overexposure, it was suggested that 1 ppm should also be adopted as reference standard for short-term exposures averaged over 15 min (STEL).

2-EHN is a combustible liquid but is not classified as a flammable liquid. The closed-cup flash point of 2-EHN is above 343 K (70 °C).

2-EHN was found to be biodegradable by microbial communities from refinery wastewater treatment plants but was recalcitrant to those of urban wastewater treatment facilities [277]. Out of 18 hydrocarbon-polluted or non-polluted soil samples, 6 microbial populations were also able to degrade 2-EHN.

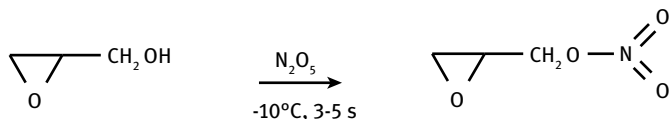
7 Alkyl Nitrates with Ring Structures

7.1 Glycidyl Nitrate

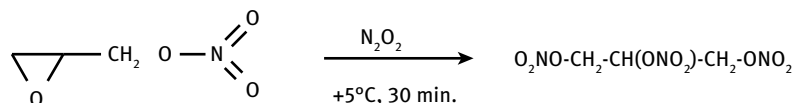
Glycidyl nitrate (GLYN) is a monomer that can be polymerized to a solid energetic binder polyGLYN or can be oligomerized to form lower-molecular-mass oily liquids suitable as energetic plasticizers.

7.1.1 Preparation of Glycidyl Nitrate

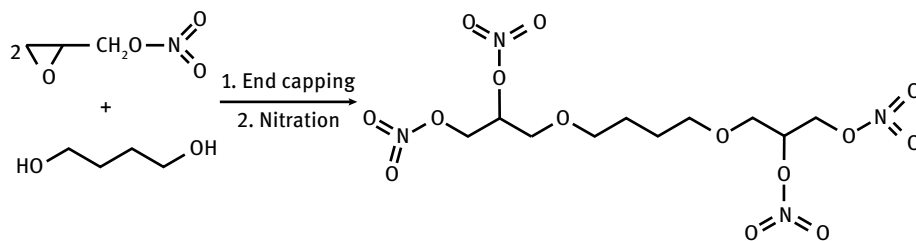
The preparation of GLYN by the nitration of glycidol with dinitrogen pentoxide must be carried out at low temperatures and is usually completed within a few seconds:



Higher temperatures and extended nitration times lead to unwanted ring opening:



GLYN dimer plasticizer can be used for plasticization of polyether binder systems, such as polyGLYN and polyNIMMO [278]. It can be prepared by end-capping a 1,4-butanediol spacer unit with GLYN and then nitrating the terminal hydroxyl groups [279, 280]. Nitration increased both oxygen balance and energy content and prevented unwanted reaction of plasticizer with isocyanate crosslinking agent in polyurethanes. It is normally a mixture of oligomers that has a low T_g and low impact sensitivity compared with nitrate esters such as BTTN and TMETN:



Synthesis of GlyN Dimer

As with the 3-nitratomethyl-3-methyloxetane (NIMMO) oligomer, nitration both increases oxygen balance and energy content and prevents unwanted reaction of the plasticizer with the isocyanate crosslinking agent. GLYN dimer is normally a mixture of oligomers and has a low T_g ($208.2\text{ K} = -64.9^\circ\text{C}$) and impact sensitivity compared with conventional nitrate esters such as BTTN and TMETN.

The traditional method synthesizing GLYN is the partial nitration of glycerol to 1,3-dinitroglycerol, which does not have to be isolated but can be first separated from excess acid, neutralized, and then reacted with sodium hydroxide to achieve the epoxide ring closure [281].

The yield of GLYN from chloro-epoxypropane and diluted nitric acid can be increased in the presence of 5-aminotetrazolium nitrate [282]. The presence of 5-aminotetrazolium nitrate as catalyst and conitrating agent enabled GLYN to be produced smoothly and in excellent yield under mild condition, increasing the yield from 66 to 81%. The product was characterized by FTIR and ^1H NMR spectroscopy.

7.1.2 Physical Properties of Glycidyl Nitrate

The physical properties of GLYN dimer are listed in Table 29.

Table 29: GLYN dimer properties.

	SI units	Other units
Glass transition temperature, T_g	208.2 K	-64.9 °C
Density, dimer	1.38 kg/dm ³	1.38 g/cm ³
Density, monomer	1.332 g/cm ³	
Drop weight sensitivity, 50% H		18.1 cm
Autoignition temperature	440 K	167 °C
Detonation velocity	6900 m/s	
Detonation pressure, P_{C-J}	17.7 GPa	
Enthalpy of formation ΔH_f	-789 kJ/mol	-188.6 kcal/mol

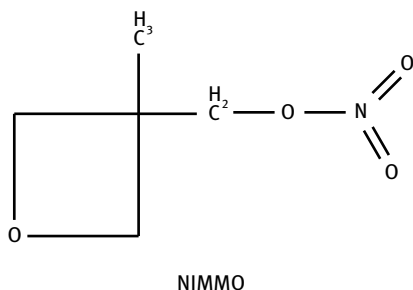
7.1.2.1 Molecular Structure of Glycidyl Nitrate

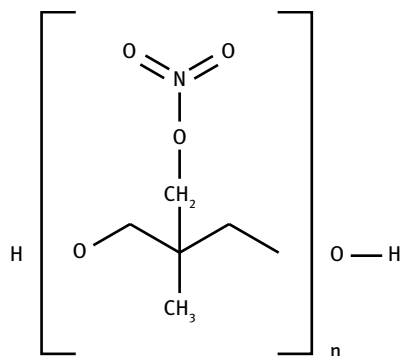
Oligo-GLYN plasticizer offers a number of advantages over traditional nitrate ester plasticizers (TEGDN, TMETN, BTTN) like excellent miscibility with normal-molecular-weight polyGLYN, low volatility, low T_g as compared to normal-molecular-weight polyGLYN, decreased plasticizer mobility, and excellent enthalpies of combustion and explosion characteristics.

The linear GLYN dimer molecule is significantly smaller than polyGLYN and is prepared by end-capping a 1,4-butanediol spacer unit with GLYN and then nitrating the terminal hydroxyl groups [283]. Applications of GLYN polymers as binders in solid propellants will be discussed in future volumes of this series of encyclopedias.

7.2 Oxetane Plasticizers. 3-Nitratomethyl-3-methyloxetane

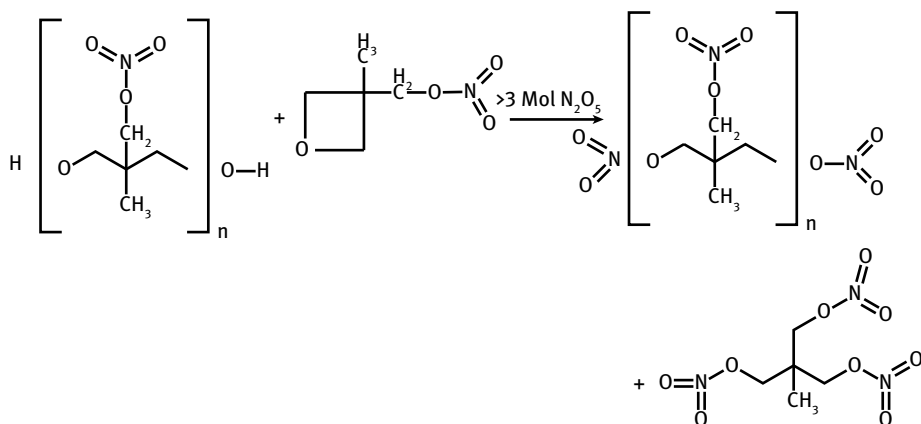
3-Nitratomethyl-3-methyloxetane (NIMMO) is a monomer that can be polymerized to form a high-energy solid propellant binder (polyNIMMO) or oligomerized to form a lower-molecular-mass oily liquid that can be used as a plasticizer.





Linear NIMMO oligomer

Oxetane plasticizers are linear nitratomethyl(methyl)oxetane (NIMMO) oligomers. Linear NIMMO oligomers (consisting of a chain of 1–10 monomers) have lower T_g than the cyclic NIMMO. The most promising energetic plasticizers for use with nitro-substituted polyethers appear to be NIMMO oligomer and GLYN dimer. Linear NIMMO oligomers (1–10 monomer units) are used as plasticizers in polyNIMMO binder systems. To remove the terminal hydroxyl groups and prevent unwanted reaction with the isocyanate crosslinking agent, oligomeric NIMMO has been further nitrated, which also increased the oxygen balance and energy of binder system. This is similar to what had been done with oligomeric GLYN:



7.3 Bridged and Caged Hydrocarbon Nitrates

7.3.1 Cubyl Nitrates

Cubyl nitrates can also be called nitroxycubanes. Similar to nitrocubanes, these are expected to be highly energetic compounds, suitable as explosives and propellants.

The previous chapter on nitro compounds included a section on polynitrocubanes. Along the same track of development, polynitroxycubanes have been studied, although for the time being only by computer. A series of nitroxycubanes, in which the hydrogen atoms on cubane have been progressively substituted for nitrate groups, were studied by computations to predict optimized geometries, vibrational frequencies, enthalpies of formation, and enthalpies of combustion [284]. The results indicated that the enthalpies of formation decreased as the number of nitrate groups increased, which is in direct opposition to what calculations have shown occurs for both the nitroso and the nitrocubane series. Given the difficulty in synthesis of octanitrocubane, octanitroxycubane may still be a more viable candidate for use as a new potential high-energy material once we figure out how to make it.

7.3.2 Adamantyl Nitrates

In parallel with synthesizing nitroadamantane and polynitroadamantanes, efforts have started to prepare adamantyl nitrate and adamantyl polynitrates and evaluate them as energetic materials.

The heats of combustion and enthalpies of evaporation for adamantyl nitrate and adamantandiyil dinitrate were measured by precision calorimetry methods [285]. On the basis of these data, the enthalpies of formation in the standard state and in the gas phase were calculated.

In a similar effort, the heats of formation for 26 adamantyl nitrates were calculated and it was found that the heats of formation of the 26 isomers with the same number of $-\text{ONO}_2$ groups (n) were not correlated well with the corresponding substituted positions [286]. According to the obtained heats of detonation, detonation velocities, and detonation pressures using the Kamlet-Jacobs equations, it was found that when $n = 7\sim 8$, the adamantyl nitrates meet the criterion as high-energy-density compounds. The calculations on BDEs of $\text{N}-\text{O}$ showed that the adamantyl nitrates with geminal ONO_2 groups always had the worst stability among the isomers, and all the adamantyl nitrates with geminal ONO_2 groups had similar stability. Considering the stability requirement, only 1,2,4,6,8,9,10-adamantyl heptanitate was recommended as a feasible high-energy-density compound. *Ab initio* calculations of the electronic structure showed that the $\text{O}-\text{NO}_2$ bond is the trigger bond during thermolysis, which agreed with the result derived from the study of dissociation energies of $\text{N}-\text{O}$ bonds.

8 Higher Alkyl Polynitrates

Alkyl nitrates containing more than one carbon atom and containing more than one nitrate ester group are very energetic compounds and many of these compounds find applications as gun propellants, as rocket propellants, as energetic plasticizers for solid propellants, and eventually also as explosives by themselves. They were also

evaluated as liquid gun propellants. The best known member of this group is glycerol trinitrate (nitroglycerin, NG, GTN). Other examples are nitrocellulose, EGDN, and PETN.

Nitrocellulose can be softened by swelling (gelatinizing) it with GTN, creating extrudable double-base propellants. A large portion of solid propellant literature is dedicated to physical methods of processing (mixing, casting, extruding) that have very little to do with chemistry. Therefore, we are not attempting to include all the details of nitrate ester processing in this book. Also, there are thousands of patents covering these types of double base propellants with and without various performance or processing-improving additives which we chose to ignore.

Energetic plasticizers for double-base propellants, composite-modified double-base propellants, or composite propellants will be discussed in future volumes of this *Encyclopedia of Rocket Propellants*. The following sections are arranged by increasing number of carbon atoms and increasing number of nitrate groups.

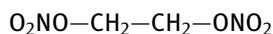
8.1 Higher C_n (n ≥ 2) Alkyl Polynitrates

Alkylene dinitrate compounds were prepared from alkane diols such as 1,6-hexane diol, 1,8-octane diol, 1,10-decane diol, and 2-methyl-2,4-pentane diol using conventional nitration reactions [287]. These dinitrate compounds were tested as cetane improver for diesel fuel. Results showed that the cetane number values had increased about 1 and 3 units for 0.05 and 0.10% by weight of dinitrate compounds, respectively, compared with base diesel fuel. Their efficiency was higher than that of a commercial cetane improver, 2-EHN.

9 C₂ Alkylpolynitrates

9.1 Ethylene Glycol Dinitrate

Ethylene glycol dinitrate, also known as C₂H₄N₂O₆, ethanediol dinitrate, 1,2-ethanediol dinitrate, EGDN, glycol dinitrate, dinitroglycol, nitroglycol, ethyleneglycol dinitrate, ethylene dinitrate, 1,2-dinitratoethane, 1,2-dinitroxyethane, 2,2-oxidiethyl dinitrate, CAS RN [628-96-6], is a viscous, pale yellow to colorless liquid explosive that can be used as a plasticizer for double-base propellants:



It has a perfect oxygen balance of ±0% to oxidize all carbon to carbon dioxide and all hydrogen to water when it burns. It is thermally more stable and less sensitive to

impact than GTN. However, its vapor pressure is higher than that of GTN, and that limits the range of its applications.

It was once used as a freezing point depressant for GTN in low-freezing dynamites and as an energetic plasticizer for double-base propellants. A vast amount of information on EGDN has been collected and published in Fedoroff, *Encyclopedia of Explosives and Related Items*, Vol. 6, p. E259–E279.

Like all alkyl nitrates, EGDN can be prepared by nitration of ethylene glycol with mixed acid or dinitrogen pentoxide. EGDN can be prepared by reaction of ethylene with nitric acid, where a byproduct is 2-nitroethanol nitrate. It can also be prepared by bubbling ethylene gas through the anode space of an electrolyzed calcium nitrate/nitric acid solution.

9.1.1 Physical Properties of Ethylene Glycol Dinitrate

The physical properties of EGDN are summarized in Table 30. Additional physical properties of EGDN are summarized in [288–290].

Table 30: Physical properties of EGDN.

Property	SI units	Other units				References
Molecular mass	152.0630 g/mol	6.5762 mol/kg				[73]
Freezing point	253 K	−20 °C				[74]
	250.8 K	−22.3 °C (supercooling)				[291]
Boiling point	470 K dec.	387 °F dec.				
Density	1.4918 g/cm ³ at 293 K					[10]
Specific gravity ¹⁵ ₁₅	1.4962 g/cm ³					[15]
Viscosity		4.61 cPs at 20 °C				[10]
Refractive index n_D^{20}	1.43235					[10]
Dielectric constant	28.26					[10]
Dipole moment	4.00 D					[10]
Enthalpy of formation	−242.8 kJ/mol	−1596.4 kJ/kg	−58.0 kcal/mol	−381.6 cal/g		[74]
ΔH_{298}^f	−233 kJ/mol	−1532 kJ/kg	−55.7 kcal/mol	−366.2 cal/g		[73]
Enthalpy of evaporation at 343–465 K	55.3 kJ/mol	363.7 kJ/kg	13.2 kcal/mol	86.9 cal/g		[73]

9.1.1.1 Physical-Mechanical Properties of Ethylene Glycol Dinitrate

Twenty determinations of the specific gravity of EGDN at temperatures ranging from 275.7 to 299.8 K (2.6–26.7 °C) were made and, when plotted, indicated a straight-line function from which the following values in Table 31 were read off at regular temperature intervals [291].

Table 31: Density of EGDN.

Temperature		Specific gravity, $x^\circ/15^\circ$, interpolated
K	°C	g/cm ³
273	0	1.5176
278	5	1.5105
283	10	1.5033
288	15	1.4962
293	20	1.4890
298	25	1.4817

Data source: [291]

Table 32 gives the vapor pressure of EGDN in comparison to that of GTN.

Table 32: Vapor pressure of EGDN in comparison to that of GTN.

Temperature, K	288	288	298	298	308	308	318	318	328	328
Temperature, °C	15	15	25	25	35	35	45	45	55	55
Vapor pressure	Pa	mm Hg	Pa	mm Hg	Pa	mm Hg	Pa	mm Hg	Pa	mm Hg
Ethylene glycol dinitrate	3.11	0.0233	9.41	0.0706	29.2	0.2189	59	0.4425	128	0.9619
Glycerol trinitrate	0.17	0.0013	0.24	0.0018	0.61	0.0046	1.72	0.0129	4.80	0.0359

Data source: [15]

The vapor pressure of glycol dinitrate as determined using the air-bubbling method, in which 19 L of air was passed through pure material at a fixed temperature and the loss in weight determined, was found to be 0.93 Pa (0.007 mm Hg) at 273 K (0 °C) and 7.53 Pa (0.0565 mm Hg) at 295 K (22 °C) (Table 33) [291].

EGDN, then, has a vapor pressure approximately 150 times 0.049 Pa (0.00037 mm Hg) at 295 K (22 °C) found for GTN.

Table 33: Vapor pressure of EGDN.

Temperature			Vapor pressure		
K	°C	°F	millibar	Pa	mm Hg
273	0	32	0.006	0.606	0.00456
293	20	68	0.05	5.05	0.038
313	40	104	0.35	35.35	0.266
333	60	140	1.7	171.7	1.292
353	80	176	7.8	787.8	5.928
373	100	212	29	2929	22.04

Data source: [291]

The vapor pressures of EGDN along with those of three solid nitroaromatics were measured by an electron-capture gas-chromatographic method in a temperature range of 240.15 to 298.15 K for EGDN [292]. The temperature dependence of the vapor pressure can be expressed by the equation

$$\log_{10} p = (10.55 \pm 0.08) - (3476 \pm 22)/T$$

where p is the vapor pressure in mm Hg and T is the temperature in kelvin. At one time, EGDN was added to GTN to lower the freezing point and because it was easier to produce from petroleum-derived feedstock (ethylene, ethylene glycol) than glycerol and its trinitrate. However, the increased vapor pressure made dynamite products containing this mixture more difficult to handle [293]. See also [294].

A comparison of vapor pressure data from six papers dealing with vapor pressure measurements of EGDN found that the data from these papers as illustrated in Figure 17 were in very good agreement but that the data from John [294] were not consistent with the rest and had to be excluded from the best fit to Clausius-Clapeyron equations [295]. EGDN melts at 250.8 K (−22.3 °C) and hence the data points at 240 and 243 K (−33 and −30 °C) were excluded. The Clausius-Clapeyron fit of the data for EGDN led to the equation

$$\log P = A - B/T = 10.537 - 3473/T$$

where P is the vapor pressure in mm Hg and T is the temperature in kelvin for the temperature range 251–323 K (−22 to +50 °C). The vapor pressure of EGDN at 298 K was extrapolated to be 7.63×10^{-2} mmHg. The heat of evaporation is 66.5 kJ/mol (15.89 kcal/mol).

EGDN is less viscous than GTN. The viscosity and fluidity of EGDN and GTN were compared on a side-by-side basis at 296 K (23 °C). The fluidity of water was arbitrarily set at 100 (Table 34).

The solubility of EGDN in water is 0.68 g/100 g water at 293 K and 0.92 g/100 g water at 323 K.

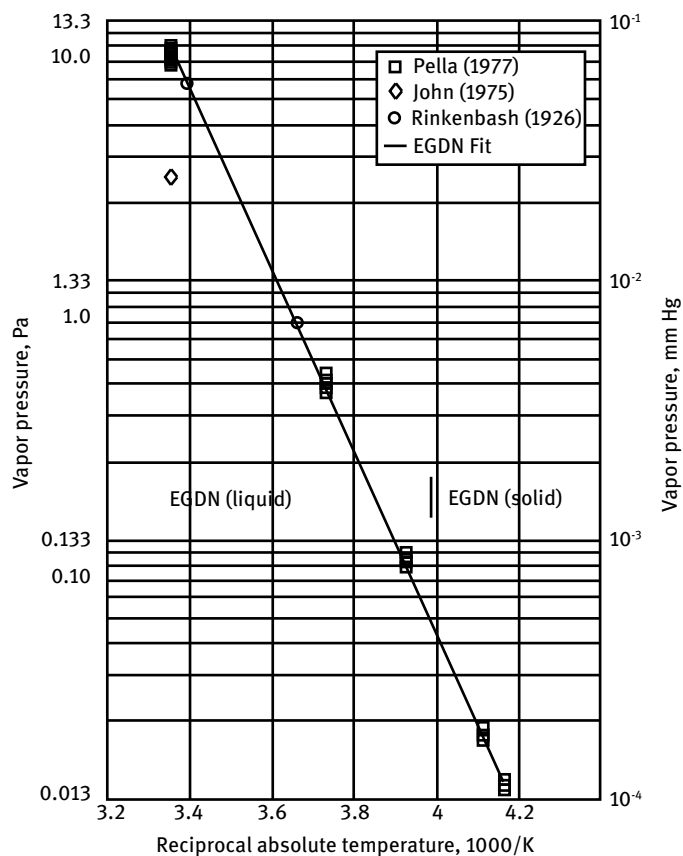


Figure 17: Vapor pressure of EGDN. (Republished and modified from [295], with permission of © 2012 John Wiley Sons – Books; permission conveyed through Copyright Clearance Center Inc.)

Table 34: Viscosity of EGDN and GTN.

Compound	Temperature K	Density g/cm ³	Temperature °C	Viscosity cPs	Fluidity relative to water	References
EGDN	296	1.4833	23	3.63	27.54	[291]
GTN	296	1.587	23	28.8	3.47	[291]
Water	296		23		100	[291]
EGDN	280.2	1.4918	7.1	6.33		[10]
EGDN	293		20	4.23		[10]
EGDN	327.5		54.4	1.98		[10]
GTN	278.2	1.5985	5.1	103.3		[10]
GTN	293		20	35.2		[10]
GTN	328.1		55	8.75		[10]

9.1.1.2 Optical Properties of Ethylene Glycol Dinitrate

The IR spectrum of EGDN is shown in Figure 18.

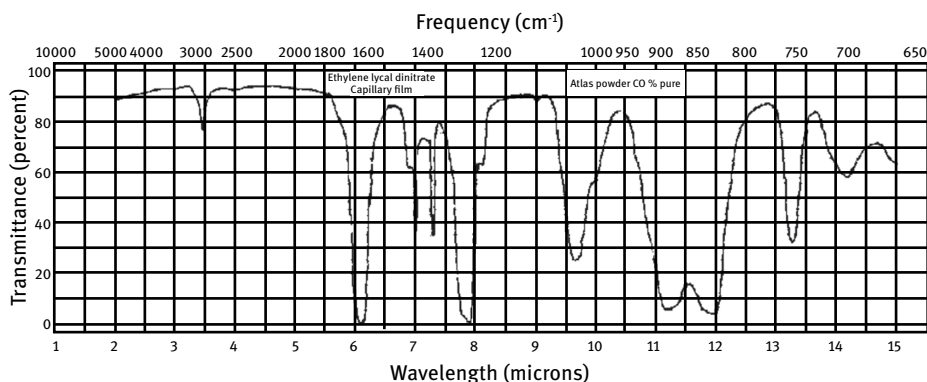


Figure 18: IR spectrum of liquid EGDN. (From [296].)

The MIL SPEC has a similar IR spectrum for EGDN, which contained 0.25% 2-nitrodiphenylamine (2-NDPA) as a stabilizer (Figure 19).

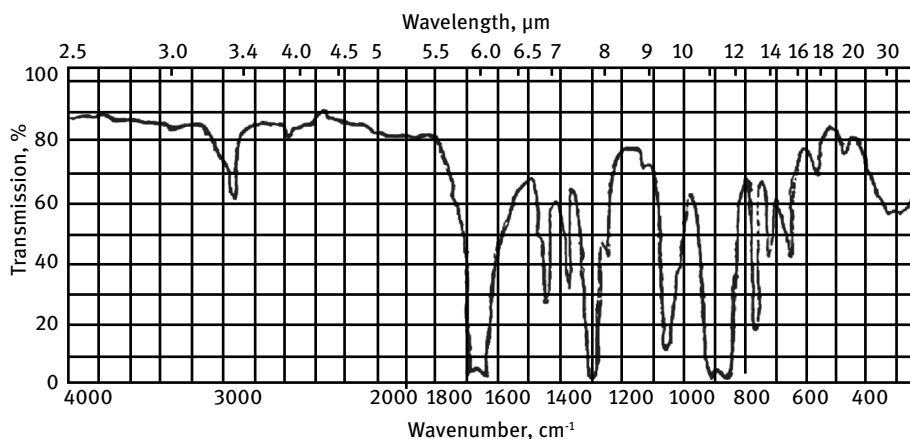


Figure 19: IR spectrum of liquid EGDN. (From MIL-E-48225.)

The IR spectrum of EGDN and six other dinitrate esters were computed by a DFT method. The actual, measured, and predicted, computed IR spectra of EGDN are compared in Figure 20 [297]. Note that the two parts of this figure have different abscissa scale expansions. There are five very strong IR active modes. One is in

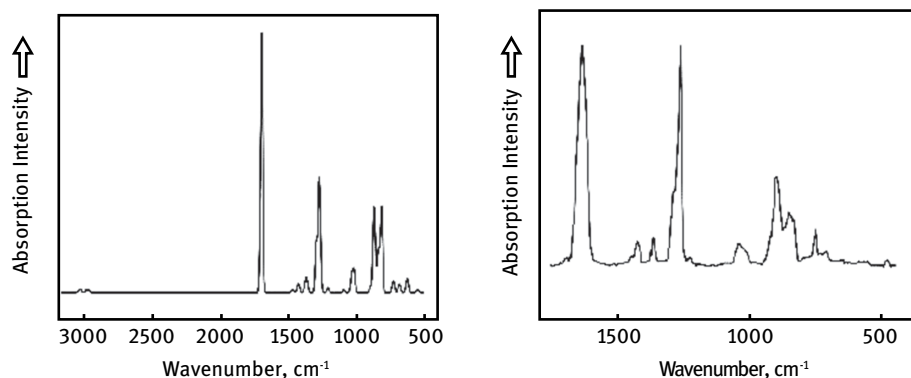


Figure 20: Comparison of calculated (left) and experimental (right) IR spectra of EGDN. (Republished and modified from [37], with permission of © 2009 John Wiley Sons; permission conveyed through RightsLink.)

Note different abscissa scale expansions.

a range of $1682\text{--}1700\text{ cm}^{-1}$, corresponding to --NO_2 asymmetric stretching. Another is in the $1265\text{--}1295\text{ cm}^{-1}$ range, arising from --NO_2 symmetry stretching. The third is located in a range of $1125\text{--}1145\text{ cm}^{-1}$, corresponding to the characteristic peaks of ether groups ($\text{CH}_2\text{CH}_2\text{O}$). The fourth is in a range of $1002\text{--}1034\text{ cm}^{-1}$, corresponding to C—O symmetry stretching. The IR spectra can be used to calculate thermodynamic properties of EGDN vapor. Correlations were established to predict the detonation performance of di-, tri-, tetra-, penta-, and hexa-ethylene glycol dinitrate.

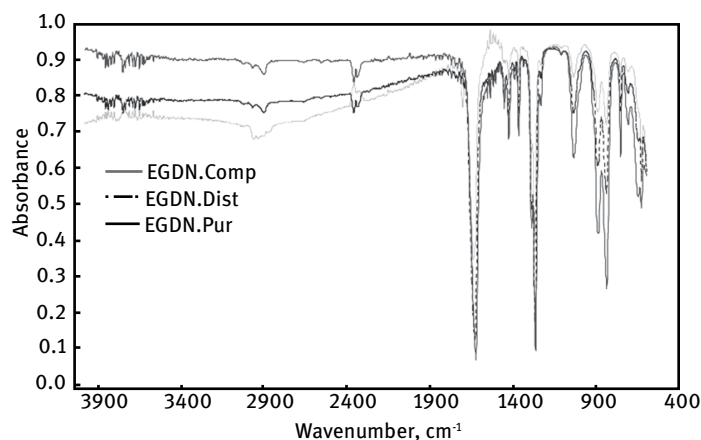


Figure 21: Comparison of IR spectra of three different EGDN samples. (Reproduced and modified from [298]; CEJEM; CC BY-NC-ND 3.0.)

The IR spectra of three different samples of EGDN prepared from ethylene glycol of different origins and different purities are compared in Figure 21 in an effort to support the quality control of this material before it is allowed to be worked into propellants.

For additional discussion of vibrational spectra and conformational composition of EGDN in solid phases, see [299]. EGDN is used as a taggant in some explosives because it is easily detected by its IR spectrum [300].

The refractive index of pure EGDN was measured at 25 points between 276.1 and 310.6 K (3.0 and 37.5 °C) using a water-jacketed refractometer and employing sodium D light. The values were plotted against temperature readings and found to represent a straight-line function. From this straight-line graph the values in Table 35 were interpolated at regular temperature intervals.

Table 35: Refractive index of EGDN with sodium light.

Temperature			Refractive index		
K	°C	n_D	K	°C	n_D
273	0	1.4546	293	20	1.4473
278	5	1.4528	298	25	1.4454
283	10	1.4509	303	30	1.4436
288	15	1.4491	308	35	1.4417

Data source: [291]

The refractive index with white light at 296.3 K (23.2 °C) was 1.4452. Table 36 is a comparison of the refractive indices of three nitrate esters at different temperatures.

Table 36: Refractive indices of nitrate esters.

Temperature, K	Temperature, °C	Glycerol trinitrate	Ethylene glycol dinitrate	Diethylene glycol dinitrate
288	15.0	1.4751	1.4491	1.4536
293	20.0	1.4732	1.4472	1.4517
298	25.0	1.4713	1.4454	1.4498
202	30.0	1.4693	1.4435	1.4479

9.1.1.3 Thermodynamic Properties of Ethylene Glycol Dinitrate

The heat of combustion of EGDN was measured in a calorimeter in comparison to that of GTN (Table 37). NIST recalculated the heat of combustion of EGDN as -1123.3 kJ/mol. The heat of evaporation is 55.3 kJ/mol at 358 K and 68.3 kJ/mol at 255 K.

Table 37: Heat of combustion of EGDN in comparison to that of GTN.

	At constant volume				At constant pressure			
	J/g	cal/g	kJ/mol	kcal/mol	J/g	cal/g	kJ/mol	kcal/mol
EGDN	7380	1763.9	1122	268.22	7332	1752.5	1115	266.48
GTN	6822	1630.4	1549	370.25	6787	1622.1	1541	368.36

Data source: [291]

The enthalpies of formation in Table 38 were obtained from these heats of combustion.

Table 38: Enthalpy of formation of EGDN in comparison to that of GTN.

Compound	Enthalpy of formation			
	J/g	cal/g	kJ/mol	kcal/mol
EGDN liquid	1529	365.5	233	55.580
GTN liquid	1505	359.8	342	81.7

Data source: [291]

The enthalpy of evaporation for EGDN is 66.5 ± 0.38 kJ/mol (15.9 ± 0.09 kcal/mol) as derived from vapor pressure measurements [292]. The heat of evaporation of EGDN reported by an earlier investigator [293] was 68.6 ± 0.5 kJ/mol (16.4 ± 0.13 kcal/mol). The enthalpy of formation of EGDN vapor is -45.3 kcal/mol.

The heat capacity, standard entropy, and standard enthalpy of EGDN vapor derived from IR spectra and statistical thermodynamic/quantum mechanical calculations as a function of temperature can be calculated from [297, 301]:

$$\begin{aligned}
 C_p &= 26.2633 + 0.4616T - 2.2428 \times 10^{-4}T^2 \\
 \Delta S &= 261.8054 + 0.5855T - 1.7774 \times 10^{-4}T^2 \\
 \Delta H &= -5.6124 + 0.0766T + 1.1842 \times 10^{-4}T^2
 \end{aligned}$$

where C_p is the molar heat capacity in $\text{J K}^{-1} \text{mol}^{-1}$, ΔS is the standard molar entropy $\text{J K}^{-1} \text{mol}^{-1}$, ΔH is the standard molar enthalpy in kJ/mol, and T is the temperature in kelvin. The standard molar enthalpy of formation of liquid EGDN is -238.66 kJ/mol. Similar data are available for DEGDN and TEGDN. Other data reported for the heat of combustion of EGDN are 1115 kJ/mol (266.5 kcal/mol) [302].

9.1.1.4 Molecular Structure of Ethylene Glycol Dinitrate

The molecular structure of EGDN is illustrated in Figure 22.

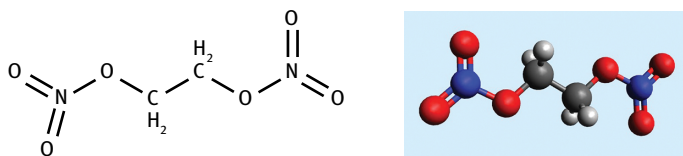


Figure 22: Molecular structure of EGDN.

9.1.2 Chemical Properties of Ethylene Glycol Dinitrate

Although EGDN gelatinizes nitrocellulose faster than GTN, it cannot be used in double-base propellants because its vapor pressure is too high.

9.1.2.1 Thermal Decomposition of Ethylene Glycol Dinitrate

Similar to methyl nitrate and ethyl nitrate being used as model compounds for the decomposition of other, more complex alkyl nitrates, the decomposition of EGDN has also been examined for more academic than practical reasons.

The molecular structure of EGDN and its mono ionic forms were examined by semiempirical and *ab initio*-type quantum chemical computations [303]. The computation revealed that the neutral and anionic forms are exothermic whereas the cation is endothermic. All of the systems were found to be stable, but the calculations indicated that plus and minus charge developments caused drastic geometrical changes in the molecular structures, resulting in bond elongation, possibly bond cleavage in the ester N—O bond.

A DFT method was used to study the geometric and electronic structures, thermodynamic properties, detonation performance, and pyrolysis mechanisms of six dinitrate esters including EGDN [297]. The IR spectra of these compounds were obtained, and the bands were assigned by vibrational analysis. The thermodynamic properties were evaluated based on the principle of statistic thermodynamics. Detonation performances were evaluated by Kamlet-Jacobs equations based on the calculated densities and heats of formation. For the nitrate esters, the O—NO₂ bond is a trigger bond during the thermolysis initiation process.

The activation energy of the thermal decomposition of EGDN in a DSC was 145.06 or 148.04 kJ/mol, depending on which method was used for data reduction [298]. See also [304].

9.1.2.2 Homogeneous Vapor-Phase Decomposition Mechanisms of Ethylene Glycol Dinitrate

Most of the work on ethylene glycol nitrates has been done on the dinitrate. Therefore, it is unusual to find studies on the thermal decomposition of ethylene glycol mononitrate [41].

9.1.2.3 Photolysis of Ethylene Glycol Dinitrate

Most studies on the photolysis of alkyl nitrates were done to investigate their role as a sink of nitrogen in the atmospheric nitrogen cycle and examined the alkyl mononitrates. Surprisingly, the polluted atmosphere may even contain alkylene dinitrates, such as those formed from ethylene or propylene and dinitrogen tetroxide.

9.1.2.4 Military Specifications for Ethylene Glycol Dinitrate

The purity requirements for EGDN for government applications are spelled out in MIL-E-48225 [305], listed in Table 39. That specification also contains recommended methods for analyzing EGDN for assays and contaminants.

Table 39: Specification requirements for EGDN.

Properties	Percent	Method
Nitrogen, minimum	18.06	4.4.1, Method 414.1 of MIL-STD-650
Moisture, maximum	0.25	4.4.2, Method 101.4 of MIL-STD-650
Acidity as nitric acid or alkalinity as sodium carbonate, maximum	0.01	4.4.3, Method 102.3 of MIL-STD-650
Stability, minutes, minimum	8.0	4.4.4

Data source: [305]

9.1.3 Toxicity of Ethylene Glycol Dinitrate

EGDN is a very active poison and has been the cause of numerous poisoning accidents and health complaints following occupational exposure in the workplace. The toxicity of EGDN has been examined very thoroughly, and some observations and recommended workplace controls and cures may apply to other alkyl nitrates or alkylene dinitrates that are used in rocket propellants instead of the manufacture of dynamite. Like the effects of GTN in lowering blood pressure, the body eventually develops a greater tolerance to EGDN with prolonged exposure, but that does not mean that prolonged exposure is safe. An excess mortality from chronic cardio-cerebrovascular diseases among dynamite workers has been reported from the explosives industry. The exposure situation with regard to EGDN and GTN over the course of two decades in one of these factories was correlated to epidemiological statistical evaluation data of medical histories of workers [306]. The mean 8-h TWA concentrations of nitrate esters for

different job types were retroactively calculated from a large number of semiannually measured short-time samples. The concentrations in workroom air were estimated to have been in a range of 0.2–1.1 mg/m³.

EGDN can cause headaches, dizziness, nausea, vomiting, and abdominal pain and may affect the cardiovascular system, causing a decrease in blood pressure, resulting in lightheadedness. High levels can interfere with the blood's ability to carry oxygen (methemoglobinemia). Excessive exposure may result in death. Skin contact can cause a rash or burning feeling on contact. Exposure to small amounts of EGDN and/or NG by skin exposure, inhalation, or swallowing may cause severe throbbing headaches. The effects may be delayed.

EGDN may penetrate through rubber or cotton gloves similar to GTN. It appears that most of the occupational exposure to EGDN has occurred in dynamite production facilities where it was mixed with GTN. Although EGDN and GTN have a similar toxicity, the higher vapor pressure of EGDN caused most complaints to be due to inhalation and skin resorption of EGDN and not to GTN. Headaches have developed in workers exposed to 0.4 to 0.67 mg/m³ for 25 min, and all workers experienced decreases in blood pressure. Both EGDN and NG are vasodilators, and initial exposures result in headache, dizziness, nausea, or decreases in blood pressure. However, workers became tolerant of the vasodilatory activity after 2 to 4 d of exposure.

EGDN can be absorbed through skin contact as well as through inhalation and will cause hypotension, severe headaches, and methemoglobin formation. The rate of resorption through the skin was measured to be 0.4 mg cm⁻² h⁻¹ for humans and 6.5–10 mg cm⁻² h⁻¹ for rats [307]. The rate of resorption of EGDN through the skin was much faster than that of GTN.

9.1.3.1 Maximum Allowable Exposure Levels of Ethylene Glycol Dinitrate

PELs in air: Conversion factor: 1 ppm = 6.22 mg/m³ at 25°C and 1 atm.

The NIOSH REL for EGDN is 0.1 mg/m³ with a skin notation, and the same limit applies as an STEL. The OSHA PEL was 0.2 ppm (1 mg/m³) with a ceiling and a skin notation and was lowered on closer examination in 1989 to 0.1 mg/m³ as a STEL with a skin notation. The 1993-1914 ACGIH TLV was 0.05 ppm (0.31 mg/m³) TWA with a skin notation and was lowered to 0.02 ppm with a skin notation. The original NIOSH (SCP) IDLH was 500 mg/m³, which was lowered on closer examination to 200 mg/m³ and eventually lowered to 75 mg/m³ [308, 309]. The chosen IDLH for EGDN was based on chronic toxicity data concerning the physiological response of animals to EGDN. Rats and guinea pigs survived 6 months of exposure to 500 mg/m³ (80 ppm) EGDN, with the only effect being slight drowsiness and some Heinz body formation. It was stated that EGDN is more toxic for cats and rabbits, and the chosen IDLH is still probably conservative because cats given 2-h daily exposures to 21 ppm (133 mg/m³) EGDN for 1000 d exhibited only marked blood changes. There have been suggestions that these limits should be lowered for worker comfort [310].

The European Maximale Arbeitsplatz-Konzentration (MAK) limit is 0.05 ppm = 0.3 mg/m³. Already concentrations of 0.5 mg/m³ can cause headaches in workers exposed to EGDN vapors.

The intraperitoneal (IP) LD₅₀ in mice was 800 mg/kg and the IP LD₅₀ in rats was 616 mg/kg. The subcutaneous (SC) LD₅₀ in rabbits was 400 mg/kg and the SC LD₅₀ in cats was 100 mg/kg.

There have been extensive surveys of EGDN accumulation in the blood of workers exposed to EGDN vapors in the workplace [311, 312]. Blood samples were taken before, during, and at various intervals after the work shift. Health authorities have specified a maximum allowable EGDN concentration in the blood of workers at the end of the work shift of 0.3 µg EGDN/L blood. This number can be used to establish a biological exposure index (BEI) for monitoring worker health.

9.1.3.2 Toxicokinetics and Metabolism of Ethylene Glycol Dinitrate

EGDN concentrations in the blood and urine of dynamite production workers were measured [313]. Measurement of EGDN concentrations in the blood of 16 workers revealed undetectable levels prior to work in all of them. The amounts of EGDN detected after work were 0–145 ng/mL, high levels being noted in workers who had frequent exposure to skin absorption. Measurement of changes in blood EGDN concentrations and the EGDN excretion in urine in workers during a week revealed no persistent trend in blood EGDN concentrations, but a tendency toward higher EGDN concentration in urine was found in the afternoon. Urine samples are easier to obtain than blood samples and can be correlated to blood levels of EGDN.

Twenty percent of EGDN vapors in inhaled air are absorbed in the lungs, and exhaled air contains little EGDN [314]. At concentrations of 133–428 mg/m³ EDN in air, about 20% of the inhaled EGDN was resorbed in lung tissue with each breath.

The breakdown of EGDN in blood *in vitro* resulted in the liberation of inorganic nitrite and EGMN [315]. The nitrite was oxidized to inorganic nitrate, but the EGMN was more resistant to further degradation. Similar metabolites were produced during the metabolism of EDGN *in vivo*. The nitrate was excreted in the urine and accounted for 60% of the injection. The EGMN released was almost completely metabolized, since only 1.5% of the injection could be detected as EGMN in the urine. Breakdown of EGMN *in vivo* was confirmed when the compound was injected. Less than 0.5% was recovered as EGMN in the urine. Nitrite was released and oxidized to nitrate, which was then excreted in the urine and accounted for 57% of the injection. An injection of EGDN or EGMN caused a fall in blood pressure lasting several hours, EGDN being more effective. Since the fall in blood pressure and the concentrations of EGDN and its metabolites in the blood were determined simultaneously, a correlation between blood pressure and blood concentrations has been attempted. It was suggested that the fall in blood pressure after an injection of EGDN could be the result of the actions of EGDN, EGMN, and nitrite. The initial fall in blood pressure may be due to the intact molecule

of EGDN followed in turn by the effects of nitrite and EGMN released during the breakdown of the EGDN molecule.

During the *in vivo* metabolism of EGDN following repeated administration in the rat, and the *in vitro* metabolism of EGDN and NG following repeated administration in the rat and the dog, no changes were detected in the *in vivo* or *in vitro* metabolism after repeated injection, and the pattern of excretion of EGDN metabolites in the urine did not change [316]. It was suggested that the tolerance that developed to the cardiovascular effects of these compounds might be due to the changing influence of some physiological compensatory mechanisms rather than to any change in the pattern of metabolism.

The SC injection of 65 mg/kg EGDN, once daily, 5 d/week, for 5 weeks in the rat did not lead to any changes in the resting electrocardiogram (ECG), heart rate, or blood pressure once the immediate effects of the presence of unmetabolized EGDN in the blood had passed [317]. Five hours after the last injection of EGDN, the heart of the anesthetized rat was subsensitive to epinephrine-induced arrhythmias, and 24 h after the last injection both the heart and blood pressure were supersensitive to epinephrine. The absence of supersensitivity in the pithed rat indicated that the pressor supersensitivity of the intact, anesthetized rat was not due to the muscle cells of the cardiovascular system *per se* but must have involved the nervous system in some way. It was suggested that there might be some temporary deficiency in the circulatory mechanisms, in the baroreceptors, the higher autonomic centers, or the peripheral ganglia. It was suggested that the pressor supersensitivity might lead to myocardial sensitization in response to the extra-large fluctuation in blood pressure.

The effects of sustained exposure to EGDN at a rate of 50 mg/kg, 10 d on heart rate and mean arterial blood pressure, isolated strips from aorta and vena cava, catecholamine and DOPAC levels in brain, heart, adrenals and plasma, and synaptosomal uptake of noradrenaline have been investigated in rats [318]. Aortic strips showed a lower responsiveness to EGDN than control strips 2, 24, and 96 h after cessation of EGDN. Acute cumulative doses of EGDN induced a decrease in mean arterial blood pressure at all time intervals but 2 h after cessation of chronic EGDN-treatment, while noradrenaline induced a dose-dependent increase in mean arterial blood pressure. Mean arterial blood pressure was lower 2 h after cessation of EGDN than in the control rats, while heart rate was higher. After 24 h, mean arterial blood pressure was slightly higher than in the controls, and the heart rate was still elevated. It was suggested that prolonged exposure to EGDN not only induces tolerance at the cellular level but also interferes with arterial smooth muscle sensitivity to noradrenaline and with resetting of mean arterial blood pressure and heart rate.

The toxic effect of subcutaneously injected EGDN on the heart functions of rabbits was investigated by ECG [319]. The changes in the ECG patterns disappeared at 24 h after injection. The effect of EGDN on the heart tissues or the heart functions still remained days after, while no traces of EGDN were noticed in the blood.

In the EGDN metabolism, EGDN is first converted to EGMN, which converts to ethylene glycol more slowly and remains in the blood longer. There are enzymes that catalyze the hydrolysis of nitrate esters [320, 321].

An excellent summary of the toxicity of EGDN and a thorough compilation of data on which to base the establishment of safe exposure limits in the air of workplaces was published in German and is available for download on the Internet [322].

9.1.4 Handling Safety of Ethylene Glycol Dinitrate

EGDN has a DOT Hazard Classification of 1.1 when desensitized. EGDN must be shipped desensitized with 40% acetone and stabilized with 0.25% 2-NDPA. It can then be shipped under a DOT exemption permit as a Class A, Type 8 High Explosive. Stabilizers can be added on request.

Special gloves that prevent EGDN permeation through gloves must be worn when handling dynamite [323]. Permeation tests were performed on several protective clothing materials with NG- and EGDN-based explosive. Breakthrough times showed that the most resistant material was a nitrile rubber. Washing the gloves between uses was ineffective.

9.1.5 Safety Properties of Ethylene Glycol Dinitrate

The drop weight impact sensitivity of EGDN as measured in the BAM apparatus was 0.2 Nm. In another test with the BAM apparatus, for a steel weight of 1 kg, the tests with pure EGDN were positive for all heights, so sensitive that a “non-standardized” drop weight had to be used [298]. Subsequently, a mass of 0.534 kg, dropped at a height of less than 5 cm, gave six successive negatives. The 50% point with the smaller mass was at 0.133 J.

The friction sensitivity of EGDN as measured in the BAM apparatus was beyond the range of the apparatus, since at the maximum load of 353 N on the pistil no reaction was observed.

Card gap sensitivity tests were done with a 50:50 mix of EGDN:GTN and with Cavea-B in different diameter containers made from different container materials, starting with approximately 1-in. ID × 16-in.-long containers of varying wall thicknesses [324]. For 50–50 NG-EGDN the gap vs. wall thickness relationship for high-velocity detonation (approximately 7500 m/s) was found to have a negative slope in both steel and aluminum containers. This behavior is analogous to results obtained with Cavea-B-110 in steel, aluminum, and copper. For example, with card gaps of approximately 1.5 in. and 0.4 in., high-velocity detonations were observed for NG-EGDN in steel containers whose walls were 0.020 in. and 0.133 in. thick, respectively. Low-velocity reactions (approximately 2000 m/s or less) were obtained with NG-EGDN in 0.020-, 0.035-, and 0.133-in. wall thicknesses at gaps up to and including 12 in. For similar tests, see also [325, 326]. A shock sensitivity scale

for comparing double-base propellant casting solvents was established with the GTN/EGDN/triacetin system [327].

EGDN could be made to explode when tested for impact sensitivity in comparison to GTN and other energetic liquids [263].

In a U-tube adiabatic compression sensitivity test apparatus with variable, preselected push pressure and constant bubble size, the push pressure required to explode EGDN was higher than that of methyl nitrate or GTN, but similar to that of DEGDN [111].

9.1.6 Detonation Properties of Ethylene Glycol Dinitrate

In a lead block test, detonation of EGDN will enlarge the cavity by an impressive $620\text{ cm}^3/10\text{ g}$, one of the highest explosive yields measured by this method. The detonation velocity of EGDN confined in a steel tube is $7300\text{ m/s} = 24000\text{ ft/s}$ at $\rho = 1.48\text{ g/cm}^3$. Detonations in EGDN can propagate by LVD [328].

Theoretical predictions of detonation velocity and detonation pressure of EGDN from the Kamlet-Jacobs equation are 8960 m/s and 35.03 GPa , respectively [297].

9.1.7 Applications of Ethylene Glycol Dinitrate

EGDN was used mostly to lower the freezing point of GTN in the manufacture of dynamite. While initially in the early 1900s only 20% EGDN was in nitrate ester mixtures, the commonly used percentage had increased to 80% EGDN in the 1970s.

It is unfortunate that EGDN is one of the more easily produced liquid explosives for illicit uses. This required a stepped-up effort by the security authorities to detect vapors of EGDN in contraband smuggled by terrorists. The thermal stability and explosive performance of EGDN made in a clandestine laboratory from automobile coolant instead of laboratory-grade ethylene glycol was not much different from the pure substance [298]. The characteristics of the synthetic process (ease, yield), the chemical properties of the synthesized product (purity, spectra), and explosive properties (sensitivities, detonability) of EGDN prepared by various methods were investigated. Comparisons were drawn between clandestine products and the product obtained using pure laboratory ingredients. The explosives were analyzed by GCMS, IR, and DSC. The explosive properties of the pure synthesized products and improvised explosives were tested for their potential use as a priming/booster charge or as a main charge. The anti-corrosion additives in the automotive coolant did not interfere with the synthesis process.

9.2 1,1,2,2-Tetranitrateoethane

Geminal dinitrate esters form during the nitration of the geminal diol hydrated form of aldehydes. They can also be obtained via the addition of N_2O_5 to the double bond of

aldehydes. The other geminal dinitratoalkane is dinitratomethane, a liquid obtained by the nitration of 1,3,5-trioxane in a HNO₃/H₂SO₄ mixture [329].

Tetranitratoethane, tetranitroxyethane, C₂H₂N₄O₁₂, which has an oxygen content of 70.1 mass-% O, was synthesized by nitration of monomeric glyoxal using N₂O₅ and purified by sublimation [330]. Single crystals could be grown from CH₂Cl₂/pentane and were used to determine the structure by XRD. The X-ray structure revealed the material crystallizing in the orthorhombic space group *P*2₁/*c* with a density of 1.991 g/cm³ at 173 K. A DSC test with a heating rate of 5 °C/min indicated the material starting to decompose at 363 K (90 °C). Table 40 gives a comparison of properties of tetranitratoethane and those of other candidate oxidizers.

Table 40: Comparison of tetranitratoethane with other oxidizers.

Compound name	Tetranitratoethane	Ammonium perchlorate	Glycerol trinitrate	Pentaerythritol tetranitrate
Formula	C ₂ H ₂ N ₄ O ₁₂	NH ₄ ClO ₄	C ₃ H ₅ N ₃ O ₉	C ₅ H ₈ N ₄ O ₁₂
FW, g/mol	274.06	117.49	227.09	316.14
Impact sensitivity, ^a J	2	20	0.2	3
Friction sensitivity, ^b N	5	360	360	60
Oxygen balance to CO, %	+52.54	+34.04	+24.66	15.18
Oxygen balance to CO ₂ , %	+40.87	+34.04	+3.5	-10.12
Melting point, °C	62	—	13	141
Melting point, K	395	—	286	414
Decomposition temperature, °C	90	240	185	202
Decomposition temperature, K	363	513	458	475
Density, g/cm ³ , at room temp.	1.954	1.95	1.595	1.75
Heat of formation, kJ/mol	-384.6	-295.8	-311.3	-479.7
<i>I</i> _{sp} ^c , s	272.3	263.8	263.8	256.6

^a BAM drop hammer test apparatus; ^b BAM friction test apparatus; ^c Optimized specific impulse, shifting equilibrium, 15% HTPB

Data source: [330]

Tetranitratoethane has a higher oxygen content than prominent solid oxidizers such as ammonium dinitramide (ADN), KClO₄, NH₄ClO₄, tetranitroacetimidic acid, and even tetranitromethane (TNM). The purified material is stable at room temperature under a dry atmosphere. In air it slowly hydrolyzes, forming nitric acid and glyoxal again. The hydrolysis, however, is slow enough to prevent the material from being hydrolyzed in ice water after quenching the reaction. Summarizing all the physicochemical properties of tetranitratoethane, especially the low thermal stability but also the high sensitivities would probably exclude any practical application of tetranitratoethane. Nevertheless, tetranitratoethane is a solid oxidizer carrying one of the highest oxygen contents ever synthesized.

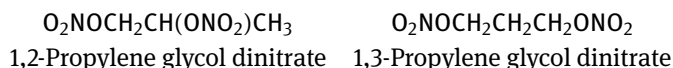
9.3 C₃ Alkylpolynitrates

9.3.1 Propylene Glycol Dinitrates

There are two isomers of propylene glycol, the unsymmetrical 1,2-propylene glycol (the more common one since it is made by hydrolysis of propylene oxide, readily available from propylene) and the symmetrical molecule with the terminal hydroxyl groups in the 1 and 3 positions. Likewise, there are two dinitrate esters. If no other information is given, it is safe to assume that the information contained in publications without more specific nomenclature relates to 1,2-propylene glycol dinitrate (1,2-PGDN).

9.3.1.1 1,2-Propylene Glycol Dinitrate

1,2-Propylene glycol dinitrate, also known as 1,2-dinitratopropane, 1,2-propanediol dinitrate, methylglycol dinitrate, propylene dinitrate, dinitroxypropane, 1,2-PGDN, PGDN, $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2(\text{ONO}_2)$, $\text{C}_3\text{H}_6\text{N}_2\text{O}_6$, molecular mass 166.09 g/mol, CAS RN [6423-43-4], is an important ingredient of a torpedo propellant called Otto Fuel II. Because it would be too sensitive and hot-burning if it was used in the undiluted state, it has been desensitized by addition of a non-energetic fuel with low volatility, di-*n*-butyl sebacate. It has been repeatedly tested as a gas generant for other applications and as a liquid gun propellant. The symmetrical isomer 1,3-PGDN is also called trimethyleneglycol dinitrate (Section 9.3.1.2):



9.3.1.1.1 Preparation of 1,2-Propylene Glycol Dinitrate

1,2-PGDN can be prepared from 1,2-propylene glycol with mixed acid. It can also be prepared by reaction of propylene with dinitrogen pentoxide. This reaction may actually take place uncontrolled to a minute extent in a polluted atmosphere. Products of the gas phase reaction of N_2O_5 with propylene in air were analyzed using a long-path FTIR spectrometer and a GC-EI and CI mass spectrometer [331]. This reaction may occur in the smog of highly polluted air.

To solve the problem of chemical waste during production of 1,2-PGDN with propylene oxide as raw material and a mixture of nitric acid and sulfuric acid as nitrating agent, a new method for preparation of PGDN by nitrating propylene oxide with dinitrogen pentoxide as a clean nitrating agent was developed [332]. This reaction is environmentally more friendly and economical. Effects of the sequence of addition, molar ratio of N_2O_5 to propylene oxide, reaction temperature and solvents on the yield and selectivity of PGDN were studied. The results showed that the optimum reaction conditions are: dropping the propylene oxide into the solution of N_2O_5 in an organic solvent, a molar ratio of N_2O_5 to propylene oxide above 1.1 : 1, the reaction temperature

288 K (15 °C) using dichloromethane as a solvent. Under these optimum conditions the yield of PGDN was about 96%, and the selectivity was nearly 100%.

Hygroscopic but thermally sensitive liquids such as PGDN (1,2-propanediol dinitrate)/DBS (dibutyl sebacate) mixtures can be sprayed at reduced pressure into a stream of dry, warm air to reduce the undesirable water content [333]. The effects of pressure, spraying times, propellant temperature and ventilation condition on spraying method dewatering efficiency were investigated. The results show that the water content in the propellant can be reduced from 0.2428 to 0.0614% under the conditions of 100 g batch size, pressure of 0.08 MPa, propellant temperature of 344 K (71 °C) and ventilation. The recovery was 100% and the treatment did not alter the thermal stability of the propellant.

9.3.1.1.2 Physical Properties of 1,2-Propylene Glycol Dinitrate

The physical properties of 1,2-PGDN are summarized in Table 41. See also [334, 335].

Table 41: Physical properties of 1,2-PGDN.

Property	SI units		Other units		References
Molecular mass	166.0895 g/mol		6.0208 mol/kg		[73]
Freezing point	230.9 K		−42.2 °C	−44 °F	
Boiling point	365 K at 1.33 kPa		92.2 °C at 10 mm Hg	198 °F at 0.19 psia	
Density			1.368 g/cm ³		[74]
Density	1.3774 g/cm ³ at 293 K				[10]
Specific gravity 15/15 °C			1.3939 g/cm ³		[15]
Vapor pressure at 298 K	11.6 Pa		0.087 mm Hg		[336]
Vapor pressure at 298 K	13.1 Pa		0.0984 mm Hg		[15]
Refractive index n_D^{20}	1.42720				[10]
Viscosity			4.65 cPs		[10]
Enthalpy of formation ΔH^f , solid	−296.9 ± 9.3 kJ/mol	−1788 ± 56 kJ/kg	−70.96 ± 2.22 kcal/mol	−427.3 ± 13.3 cal/g	[10, 337]
Heat of evaporation at 288–328 K	63.8 kJ/mol	384.1 kJ/kg	15.2 kcal/mol	91.8 cal/g	[338]
Dielectric constant at 293 K (20 °C)	26.80				
Dipole moment	4.24 D				[10]

Vapor pressure data for PGDN in comparison to the vapor pressures of other glycol polynitrates were already shown in Table 6 above and Table 58 below.

The solubility of PGDN in water is 1.3 g/L. An IR spectrum of PGDN is shown in Figure 23.

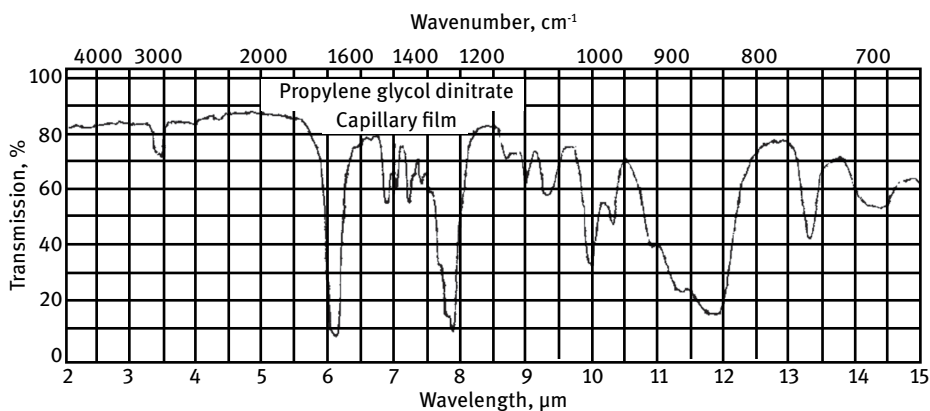


Figure 23: Infrared spectrum of 1,2-PGDN. (Reproduced and modified from [296].)

The IR spectrum of PGDN in the gas phase differs appreciably from that of the neat liquid [331]. Comparison of the spectra indicated that three prominent peaks at about 1672, 1280, and 838 cm^{-1} in the PGDN spectrum can be assigned to the anti-symmetric NO_2 stretch, symmetric NO_2 stretch, and N—O stretch of PGDN (Figure 24).

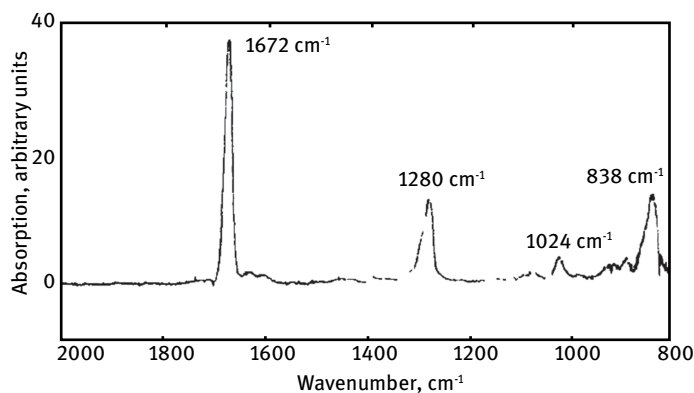


Figure 24: IR spectrum of PGDN vapor. (Reproduced and modified from [331], with permission of Chemical Society of Japan.)

The IR spectrum of PGDN and six other dinitrate esters were computed by a DFT method [297].

A Raman spectrum of PGDN was shown in Figure 2 above in comparison to the Raman spectrum of GTN [25, 26].

9.3.1.1.3 Physical Properties of 1,2-Propylene Glycol Dinitrate Mixtures

The most prominent mixture of 1,2-PGDN is Otto Fuel II, a torpedo propellant used mostly in the US Navy's MK-46 and MK-48 torpedoes, but also in torpedoes of other navies worldwide. Otto Fuel II consists nominally of 76% 1,2-PGDN as the energy source, 22.5% dibutyl sebacate as a desensitizer, and 1.5% 2-NDPA as a stabilizer.

Because so many publications deal with the chemistry of Otto Fuel II, it has even been assigned its own Chemical Abstracts System Registry Number, CAS RN [106602-80-60]. The properties of Otto Fuel II are summarized subsequently in Section 9.3.1.1. 1,2-PGDN forms an azeotrope with water, which enhances its volatility.

9.3.1.1.4 Chemical Properties of 1,2-Propylene Glycol Dinitrate

The oxygen balance of 1,2-PGDN is -28.9%, and the nitrogen content is 16.87 mass-% N.

Analysis of 1,2-Propylene Glycol Dinitrate

The purity requirements for PGDN that is to be used for torpedo propellants such as Otto Fuel II are spelled out in [339]. Analytical methods per DOD-P-82671 used to verify the purity of PGDN include the following methods: total nitrogen content per MIL-STD 286B, Method 209 (16.82–16.92 mass-%N), free acidity (or alkalinity) (0.001 mass-% max.), moisture content by Karl Fischer reagent (0.5 mass-% H₂O max.), and thermal storage stability as indicated by a potassium iodide-starch paper test strip suspended in the gas space above the sample heated to 355.3 K (82.2°C) (no reaction within 10 min).

1,2-PGDN, the main ingredient in Otto Fuel II, can be detected and quantified in aqueous solution down to the ppm level by HPLC separation and UV detection [340]. The method developed was applied to evaluate the efficiency of organic solvent extractions of PGDN from wastewater solutions generated at CFAD Bedford during maintenance of the MK37 and MK44 torpedoes. The results indicated that less than 1 ppm PGDN remained in solution following extraction.

A rapid and specific polarographic method for analyzing PGDN in wastewater uses a portable and inexpensive digital polarograph and monitoring system for the field analysis of PGDN in effluent water from a Navy carbon column cleanup process to remove the PGDN from Otto Fuel wastewater [341–343]. Data obtained by this method of analysis and field equipment compared favorably with data obtained by a more time-consuming vapor-phase GC method on the same samples of effluent water.

PGDN in the air of workplaces can be detected by a sensitive piezoelectric quartz crystal microbalance with a coating that has high affinity toward PGDN [344]. The in-

strument is sensitive to below 0.05 ppm and selective for PGDN and suffers no interference from humidity.

Mono- and dinitrated propylene glycols can be separated and detected using either a gas chromatographer equipped with a nitro-specific thermal energy analyzer (GC/TEA) or a HPLC equipped with an electrochemical detector in reductive mode (LC/EC) [345]. The GC/TEA exhibited a linear range of response of three orders of magnitude and provided detection limits in the $\mu\text{g/mL}$ range for these three compounds. The LC/EC had a linear response over two orders of magnitude and was best suited for the determination of PGDN.

1,2-Propanediol dinitrate poisoning in blood at concentrations ranging from 10 ng/mL up to 25000 ng/mL can be analyzed by GC with electron-capture detection using double ether extraction with manual shaking in order to complete sample preparation within 5 min [346].

Photolysis of 1,2-Propylene Glycol Dinitrate

Surprisingly, mono- and difunctional alkyl nitrates are common products of atmospheric reactions of NO_3 radicals with unsaturated hydrocarbons. The UV absorption spectra of several organic dinitrates and keto nitrates have been measured in the gas phase at 298 K and atmospheric pressure: 1,2-propanediol dinitrate, $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2(\text{ONO}_2)$; 1,2-butanediol dinitrate, $\text{CH}_3\text{CH}_2\text{CH}(\text{ONO}_2)\text{CH}_2(\text{ONO}_2)$; 2,3-butanediol dinitrate, $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}(\text{ONO}_2)\text{CH}_3$; and five others [347]. Although the UV spectra of the nitrates were all very similar in shape, the cross sections of the dinitrates were a factor of 2 higher than those reported in the literature for the corresponding alkyl mononitrates. The UV absorption cross sections of the difunctional nitrates were used in combination with solar actinic flux data to estimate photolysis frequencies and, consequently, atmospheric lifetimes for these compounds. The results indicated that for the saturated difunctional nitrates, photolysis will generally be somewhat more important than reaction with $\cdot\text{OH}$ radicals as an atmospheric removal process.

9.3.1.1.5 Safety Properties of 1,2-Propylene Glycol Dinitrate

Although PGDN is used mostly for underwater propulsion and not above ground or even in space, the safety properties of PGDN are summarized here in detail because they may relate to the safety properties of other nitrate esters that are actively being used as rocket propellant ingredients. Methods of analysis and safety evaluation for all these alkyl nitrates would be very similar.

Most safety tests for 1,2-PGDN were done in connection with its use in Otto Fuel II. The current section and a similar section specifically for Otto Fuel II further down overlap to some extent.

Toxicity of 1,2-Propylene Glycol Dinitrate

Most toxicity tests for 1,2-PGDN have been done in connection with its use in Otto Fuel II. As a matter of fact, in a few instances Otto Fuel II was used as a source of PGDN vapor because the other ingredients have only negligible vapor pressure. The current section and a similar one specifically for Otto Fuel II overlap to some extent. 1,2-PGDN is a systemic toxicant with effects on the cardiovascular and central nervous systems. Its vasodilatory action results in headaches during human exposure. Dizziness, loss of balance, nasal congestion, eye irritation, palpitations, and chest pains have been reported. The air-odor threshold in healthy human subjects is 0.2 ppm, but warning properties are poor inasmuch as olfactory fatigue sets in after as little as 5 min [348]. PGDN is rapidly and completely metabolized *in vivo* and eliminated primarily in the urine as inorganic nitrate within 24 h of exposure. Inhalation or resorption of PGDN through the skin causes headaches and cumulative disruption of the visual evoked response, marked impairment of balance and coordination, and eye irritation at exposure levels of 0.2 ppm or greater. The *per os* (PO) LD₅₀ in rats is 250 mg/kg.

An excellent review of toxicity evaluation of PGDN and Otto Fuel II is given in [349].

The ACGIH recommended TLV/TWA was 0.02 ppm = 0.2 mg/m³ in air but the more recent NIOSH REL TWA is 0.05 ppm (0.3 mg/m³) with a **skin** notation.

Two excellent summaries on the toxicity of PGDN were prepared by the National Research Council US Subcommittee and used as the basis to establish tolerable level of exposure of humans to PGDN in the workplace. One was used to establish Acute Exposure Guideline Levels (AEGs) for PGDN [350]. The two books were posted on a web site of the National Center for Biotechnology Information and provided as e-books as PDFs for download by the general public. Those publications, just one of the five or six chapters in each book, are the best summaries on the toxicity of any rocket propellant or energetic material referenced in our book. The style of the publication is accurate, comprehensive, and (as of 2002 and 2009) up to date. Several sections of those studies would fit right in here without any modification. Several sentences have been selected for inclusion in this book. A few years after the first book, an updated summary of toxicity of PGDN as it may affect submarine atmospheres was published by the National Research Council [351]. That book's Chap. 6 summarized epidemiologic and toxicological studies of PGDN. It presented selected chemical and physical properties, toxicokinetic and mechanistic data, and recommended inhalation-exposure threshold levels from the National Research Council and other agencies. The committee considered all that information in its evaluation of the US Navy's 1-h, 24-h, and 90-d exposure guidance levels for PGDN and issued recommendations for PGDN EEGL and CEGl exposure levels shown in Table 42.

Because PGDN is the primary and most toxic component of Otto Fuel II and because only PGDN is relatively volatile compared to the other components, AEGs have been derived in terms of PGDN with the notation that the values are appropriate for Otto Fuel II as well (Table 43). Additional information is in the meeting minutes of

Table 42: Emergency and continuous exposure guidance levels for PGDN.

Exposure level	US Navy Values ppm	Committee recommended values ppm
EEGL 1-h	0.15	0.2
EEGL 24-h	0.02	0.02
CEGL 90-day	0.01	0.004

CEGL = Continuous Exposure Guidance Level; EEGL = Emergency Exposure Guidance Level

Data source: [351]

Table 43: Summary of AEGL values for PGDN (Otto Fuel II).

Classification	Units	10 min	30 min	1 h	4 h	8 h	End point	References
AEGL-1 ^a , Non-disabling	ppm	0.33	0.33	0.17	0.05	0.03	Mild headaches in humans	[348]
	mg/m ³	2.3	2.3	1.1	0.34	0.17		
AEGL-2, Disabling	ppm	2.0	2.0	1.0	0.25	0.13	Severe headaches and slight unbalance in humans	[348]
	mg/m ³	14	14	6.8	1.7	0.8		
AEGL-3, Lethal	ppm	16	16	13	8.0	5.3	Convulsions in monkeys	[353]
	mg/m ³	114	114	93	57	38		

^a The distinctive odor of PGDN will be noticeable to most individuals at the 0.33- and 0.17-ppm concentrations.

Data source: [350]

the National Advisory Committee for Acute Exposure Guideline Levels for Hazardous Substances [352].

Experimental Animal Exposure Tests

In a study of the acute toxicological parameters of PGDN, EGDN, and GTN both *in vivo* and *in vitro*, the LD50 was determined in a strain of albino female mice by IP injection of a 2% solution of each compound in a 10% soy oil emulsion [354]. Twenty mice were dosed in each group. Five dose levels were set at logarithmic increments. LD50 determinations revealed PGDN at 930 mg/kg (800–1075, 95% confidence interval), EGDN at 800 mg/kg (661–964), and GTN at 194 mg/kg (164–228). GTN was about four times as toxic to mice as the other two nitrated esters. Mice exposed to GTN expired within 1 h of injection and suffered convulsions. Expiring animals in the groups exposed to PGDN and EGDN did not exhibit premorbid convulsions and most exceeded 1 h to demise. For a study of the blood elimination in 2.5-kg rabbits, each compound was injected

as a single dose of 1 mg/kg body weight in one femoral vein, while serial arterial and venous samples were taken on the contralateral side. Samples were assayed for each compound by GC. At 1 min, 15% of injected PGDN was found in arterial blood and 3 to 5% in venous samples. By 2 min, the rates of elimination for PGDN, EGDN, and GTN were the same. This indicated an extremely rapid breakdown, exhibiting first-order kinetics with only slight differences among PGDN, EGDN, and GTN.

The LD₅₀ values of PGDN were determined in the rat, mouse, and cat [355]. Injection of LD₅₀ in rat caused almost complete conversion of the hemoglobin to methemoglobin, indicating that methemoglobinemia was the principal cause of death following PGDN administration. The metabolism of PGDN *in vitro* and *in vivo* gave rise to inorganic nitrite and inorganic nitrate, and the 1- and 2-isomers of propylene glycol mononitrate. The 2-isomer predominated, and it was suggested that there was a reaction favoring its formation. *In vivo* the mononitrates were themselves metabolized with the result that only small amounts are excreted. The major urinary metabolite was inorganic nitrate, accounting for 56% of the original injection of PGDN. PGDN is a potent vasodilator in animals, inducing a maximal fall in blood pressure usually 30 min after injection. An injection in the rat gave rise to a fall in blood pressure lasting several hours that might have been due to the combined influence of the intact molecule of PGDN and its metabolites. It was concluded that there was little to distinguish the metabolism and pharmacology of PGDN from those of EGDN. Rats treated with lethal oral or subcutaneous doses of PGDN were prostrate, anoxic, and cold and had signs of methemoglobinemia and respiratory depression. At high oral or parenteral doses, deaths from anoxia due to almost complete conversion of hemoglobin to methemoglobin have been observed. Death consistent with anoxia occurred up to 48 h after PGDN administration. Oral doses of PGDN that were lethal to half the animals ranged from 250 to 1190 mg/kg in rats.

Comparing the toxicity of TEGDN and PGDN it was observed that in most species the LD₅₀ of TEGDN was two to five times as high as that of PGDN [356]. Both compounds produced methemoglobinemia and hypotension in rats. PGDN-poisoned rats were lethargic and did not convulse. Chronic daily dermal applications to rabbits of 21 mmol/kg of either dinitrate caused death in 2 to 3 weeks. PGDN-treated rabbits gained weight normally, while those treated with TEGDN lost 20 to 30% of their body weight. The toxic responses of these two dinitrates were sufficiently different to preclude simple comparisons in hazard evaluations.

Bolus injections of PGDN were made intravenously to dogs at four (4, 10, 40, and 100 mg/kg) dose levels [357]. Dynamic effects were dose related and both physiological and biochemical in nature. The physiological changes were maximized during the fast distribution phase of PGDN in the central compartment. These included the vasodilation effects of decreased systolic, diastolic, and pulse blood pressures. A reflex increase in heart rate ensued, which was significantly dose related with a maximum attainable increase of 129.5 beats/min. One biochemical manifestation of PGDN intoxication was an increase in methemoglobin. Urine production, presumably changed

due to blood pressure, decreased inversely with PGDN dose. An unexpected occurrence associated with this decrease was the appearance of whole blood cells in the urine.

Inhalation Toxicity and Behavioral Changes

Inhalation exposure of eight male Sprague-Dawley-derived rats to PGDN at about 10 ppm 7 h/d, 5 d/week for a total of 30 exposures did not result in death or adverse clinical signs [353]. Weight gain, hematologic values, and histopathologic examinations of heart, lungs, liver, spleen, and kidneys did not reveal adverse effects immediately after exposure (four rats) or 2 weeks later (four additional rats). In the exposed 4 species of animals used for inhalation tests, 9 male squirrel monkeys, 2 male beagles, 15 male and 15 female Sprague-Dawley-derived rats, and 15 male and 15 female Hartley-derived guinea pigs per exposure concentration to PGDN at 10, 16, or 35 ppm continuously (24 h/d) for 90 d, physiological and biochemical changes noted were anemia, pigment deposition in various organs, fatty changes in the liver, methemoglobin formation, and greatly increased serum and urinary inorganic nitrates. Three trained male squirrel monkeys were exposed to PGDN continuously for 90 d at 39 ppm. The animals were removed from the exposure chambers for a 2-h period once a week and tested. There were no changes in avoidance behavior in the monkeys.

Free operant avoidance behavior and visual evoked responses of rhesus monkeys exposed to 2–33 ppm PGDN vapors on either an acute or chronic schedule were monitored for several weeks [358]. Free operant avoidance was not affected at any dose level.

Rats were evaluated as a model animal to measure PGDN-induced motor performance decrement and to determine whether direct application of PGDN to neural tissue would be a useful alternative to other routes of exposure [359]. PGDN was injected onto the cisterna magna of adult rats trained on the accelerod, a test of motor performance. Three groups of 13 or 14 male rats each received a single dose of either 5 or 10 μ L PGDN or 25 μ L sterile saline (control) while anesthetized with halothane. Accelerod performance was measured 12 min after IC injection, then hourly for 6 h and at 24 h. A significant decrease in performance occurred during the first 2 h following injection of 10 μ L PGDN compared to the control and the 5- μ L groups. No significant differences were seen between the 5- μ L and control groups. The data indicated that IC injection may be an effective alternative to other routes of dosing exposure.

Nitrate ester explosives block monoamine oxidase (MAO) MAO metabolism and nerve conduction. The effect of the organic nitrate explosives GTN, PGDN, EGDN, and their metabolites on mitochondrial MAO activity of rabbit liver was studied *in vitro* with a method using tryptamine labeled with radioactive carbon as a substrate. The MAO activity was inhibited by the three explosives, while their metabolites had no such effect [360, 361]. See also [362, 363].

Blood Toxicity

Methemoglobinemia has been observed at the highest concentrations used in exposure studies with animals. Interspecies variability of PGDN-induced methemoglobin formation was studied *in vitro* employing erythrocytes from four separate species [364]. In a series of *in vitro* assays using blood, hemolysates, and partially purified hemoglobin solutions, the formation of methemoglobin was greatest in the dog and less in the guinea pig, followed by the rat; the human was either the least sensitive or as sensitive as the rat. The net rate of methemoglobin formation was significantly different among species with dog guinea pig rat human.

Oral Toxicity

The PO toxicity of PGDN in rats and the ocular and dermal irritation effects of PGDN on rabbits were determined in carefully conducted animal exposure tests [353]. Rats, guinea pigs, rabbits, squirrel monkeys, and dogs were exposed to the vapors of PGDN in acute, repeated, and continuous inhalation exposures.

Rats treated with lethal oral doses of PGDN were prostrate, anoxic, and cold and had signs of methemoglobinemia and respiratory depression. At high oral doses, deaths from anoxia due to almost complete conversion of hemoglobin to methemoglobin have been observed. Oral doses of PGDN that were lethal to half the animals ranged from 250 to 1190 mg/kg in rats.

Mutagenicity of Otto Fuel II

Otto Fuel II was examined for mutagenic activity in a series of *in vitro* microbial assays employing *Salmonella* and *Saccharomyces* indicator organisms [365]. The low dose in all cases was below a concentration that demonstrated any toxic effect. The dose range employed for the evaluation of this compound was from 0.005 to 10 μ L per plate. The compound was toxic to all the strains except TA-1538 and D4 at 5 and 10 μ L per plate. Toxicity was also observed with the strain TA-1535 at 1 μ L per plate. The results of the tests conducted on the compound in the absence of a metabolic system were all negative. The results of the tests conducted on the compound in the presence of the rat liver activation system were all negative. The test was repeated with TA-100 at the three lowest doses and intermediate doses of 0.05 and 0.5 μ L per plate, and the repeat tests were also negative.

Carcinogenicity of Otto Fuel II

In a 1-year industrial type (6h/d, 5d/week) of test animal inhalation exposure to evaluate the oncogenic potential of Otto Fuel II, the exposure levels were 1.4 and 240 mg/m³ [336]. Dogs (male and female beagle), rats (male and female Fischer 344), and mice (male and female C57BL/6) were exposed to the lower concentration, while only rats and mice were exposed to the higher concentration. Dogs appeared to be the most sensitive species tested with measurable reductions in RBC, hematocrit, and hemoglobin levels. Mildly increased methemoglobin was also observed in dogs

exposed to 1.4 mg/m^3 and rats exposed to 240 mg/m^3 . No other significant effects were noted in rats exposed at either concentration. Microscopic examination of tissues collected from dogs, rats, and mice exposed to Otto Fuel II vapors failed to suggest any significant exposure-related non-neoplastic changes. Similarly, exposure to Otto Fuel II also failed to increase the incidence of neoplastic changes.

Teratogenicity of Otto Fuel II

Four groups of time-mated rats were treated dermally at rates of 0, 400, 2000, and $4000 \text{ mg kg}^{-1} \text{ d}^{-1}$ with Otto Fuel II to study developmental toxicity in the fetuses [366]. A significant reduction in maternal body weight was seen at necropsy in dams receiving 2000 and $4000 \text{ mg kg}^{-1} \text{ d}^{-1}$ of Otto Fuel II. Fetuses from these dams also weighed significantly less than control fetuses. Phase II of the investigation involved dosing of artificially inseminated rabbits with Otto Fuel II. The fuel was administered to the skin of the animals' back at the rate of 0, 100, 316, and $1000 \text{ mg kg}^{-1} \text{ d}^{-1}$. Maternal toxicity was evidenced by a significant reduction in the body weight of the dams in the $1000 \text{ mg kg}^{-1} \text{ d}^{-1}$ dose group on days 20 and 25 of gestation. There were no significant differences observed in maternal weight or fetal weight at necropsy. Morphological examination of both rat and rabbit fetuses failed to reveal significant evidence of fetal malformations.

Human Volunteer Exposure Tests

At low concentrations, PGDN has been reported to cause cardiovascular, irritant, and central nervous system effects including headaches, nasal congestion, eye irritation, and dizziness in humans.

Primarily young male volunteers were exposed to PGDN vapors under carefully controlled conditions at various concentrations (0.03, 0.1, 0.2, 0.35, 0.5, and 1.5 ppm) for 1 h or longer [348, 367]. Three of six volunteers or research staff members who were exposed to PGDN at 0.5 ppm for 1–1.25 h developed mild headache but had no other adverse effects. At 1.5 ppm, eight subjects reported mild eye irritation within 40 min of exposure, which resolved on cessation of exposure. Marked impairment in balance became noticeable after exposure to 0.5 ppm for 6.5 h, while 40 min of exposure to 1.5 ppm added eye irritation to the list of symptoms. All the volunteers developed severe frontal headaches after only 30–90 min of exposure, so all exposures were terminated after 3 h, at which time the headaches were described as nearly incapacitating. The headaches persisted for 1–7.5 h in the absence of continued exposure. Coordination tests were abnormal while the subjects were experiencing severe headaches. The visual evoked response in all volunteers showed a dramatic increase (of 10–70%) in amplitude in the peak-to-peak voltage of the 3-4-5 complex after 45–90 min of exposure. The amplitude shifted toward normal after cessation of exposure but was still altered 48 h after exposure. Those data indicated a threshold after a 1-h exposure to PGDN at 0.5–1.5 ppm for the induction of severe headaches that can be incapacitating and impair function.

The air-odor threshold in healthy subjects was 0.2ppm, but warning properties were poor inasmuch as olfactory fatigue was reported to set in after as little as 5 min [348].

Occupational Exposure Monitoring

The neurophysiologic effects of acute and chronic exposure to PGDN of 87 workers employed in US Navy torpedo facilities were evaluated by interviews and review of medical records [368]. Prior to the evaluation, the subjects reported subjective symptoms of frequent or occasional headaches (65% of respondents), nasal congestion (31%), eye irritation (26%), and dizziness (13%). Palpitations, dyspnea, chest pain, and loss of balance were reported by small percentages of workers. For chronic exposure, evaluation of the workers included both quantitative oculomotor functions (eye tracking movements) and ataxia tests. Comparisons were made with a control group consisting of 21 non-exposed personnel from the same facilities. Results of the tests indicated no evidence of chronic neurotoxicity in either the study population or a subgroup of 28 workers with the longest exposure to PGDN. Acute effects were evaluated in a subgroup of 29 workers by comparing test values before and after a torpedo maintenance procedure. The maintenance procedures lasted 30–60 min. During this time, PGDN concentrations, as indicated by approximately 400 grab samples taken in the work area, ranged from 0.00 to 0.22 ppm (average value of 0.06 ppm; 88% were ≤ 0.1 ppm, 50% were ≤ 0.05 ppm, and only one sample was above the ACGIH TLV-Ceiling value of 0.2 ppm, which was in effect at that time).

Unintentional Human Exposure Epidemiological Studies

Epidemiological studies evaluated cardiac morbidity among the US Navy's torpedoman's mates, a group of servicemen potentially exposed to PGDN while engaged in torpedo maintenance work [369–371]. Cardiovascular events in this group were compared with both a non-exposed group of torpedomen and a non-exposed group in the job category of fire control technician. The torpedoman's mate group consisted of 1352 men, with an average yearly population of 822; hospitalization records were available for 10 years. The non-exposed-torpedomen control group consisted of 14336 individuals over the 10-year period with a yearly average of 4906. The fire control technician control group consisted of 29129 individuals with a yearly average of 11198. Measured concentrations of PGDN included those of the Horvath et al. [368] study and more recent surveys in which 8-h TWA were below 0.05 ppm. Cardiac incidents considered were myocardial infarction, angina pectoris, and cardiac arrhythmia. There were higher incidences of hospitalizations for myocardial infarctions and angina pectoris but not cardiac arrhythmias in the torpedoman's mates group than in either control group. Relative risk and stress in working with explosive devices were significant for myocardial infarction and angina pectoris when compared with the torpedoman's control group (2.6 and 3.8, respectively; $p < 0.05$) but not when compared with the fire control technicians. When incidences

of myocardial infarction and angina pectoris were combined, relative risk was significant when compared with both the unexposed torpedoman's and fire control technician control groups (2.6 and 2.9, respectively; p 0.05).

Environmental Effects of 1,2-Propylene Glycol Dinitrate

Soil Degradation of 1,2-Propylene Glycol Dinitrate

Previously, bacterial cultures were isolated that had the ability to degrade the nitrate ester GTN. An attempt was made to induce *Bacillus* sp. ATCC 51912 to degrade the more recalcitrant nitrate ester PGDN [372]. It was observed that the PGDN-denitrating activity was expressed during growth, even when sensitized cells were cultured in the absence of nitrate esters. Using cell-free extracts, PGDN was observed to be sequentially denitrated to propylene glycol mononitrate and propylene glycol with the second denitration step proceeding more slowly than the first.

Investigation of the biodegradability of PGDN, the major component of Otto Fuel II, has shown that this compound was resistant to biodegradation by microorganisms found in sewage sludge, a pure culture of *Pseudomonas aeruginosa* (previously shown to capable of biodegrading nitroaromatic explosives), and a commercially available inoculum, used for the degradation of nitrogen-containing organic wastes [373]. However, PGDN is photolabile in ultraviolet, decomposing to pyruvic and lactic acids. In biodegradation experiments, PGDN rapidly evaporated from aqueous solutions. This unexpected volatility of PGDN, which poses a potential health hazard, was attributed to the formation of a PGDN-water azeotrope, whose presence was demonstrated by partition experiments.

Explosive Sensitivity of 1,2-Propylene Glycol Dinitrate

PGDN will detonate if initiated with a No. 8 blasting cap. The impact sensitivity was 57.5 cm using a 5-kg mass. In the Allegheny Ballistics Laboratory (ABL) sliding friction test apparatus (metal to metal), the material did not ignite at the maximum setting of the apparatus 4.36 kN (980 lb_f). In the electrostatic sensitivity tester, all tests were negative at 8.75 J.

9.3.1.1.6 Explosive Performance of 1,2-Propylene Glycol Dinitrate

1,2-PGDN is shock sensitive and is a liquid explosive. In the lead block test, the enlargement of the cavity was 540 cm³/10 g, which was 92% of that of NG or 157% of that of TNT. The detonation velocity of confined PGDN was 6885 m/s at 1.38 g/cm³.

9.3.1.1.7 Propellant Mixtures with 1,2-Propylene Glycol Dinitrate

The main application of 1,2-PGDN is as a monopropellant in Otto Fuel II, a torpedo propellant. Although 1,2-PGDN by itself would be a powerful monopropellant, it is too sensitive to be used in the undiluted state. The diluent (solvent, desensitizer) used to desensitize PGDN is di-*n*-butyl sebacate. Although we would rather go up than go

down, the properties of Otto Fuel II are listed here because there may be other applications for it.

Composition of Otto Fuel II

The nominal composition of Otto Fuel II as specified by MIL-O-82672A [374] is listed in Table 44, along with a list of military specifications that cover the procurement of the ingredients to be mixed in making Otto Fuel II.

Table 44: Nominal composition of Otto Fuel II.

Ingredient	Requirement		as per MIL SPEC
	Minimum, mass-%	Maximum, mass-%	
1,2-PGDN	75.8	76.2	DOD-P-82671
2-Nitrodiphenylamine	1.4	1.6	MIL-N-3399B
Di- <i>n</i> -butyl sebacate	22.2	22.8	DOD-B-82669
Sodium		0.8 ppm	—
Moisture		0.1	—

Production of Otto Fuel II

The US Naval Surface Warfare Center's Indian Head Division (NSWC IHD) closed out a chapter in its long history with a commemorative ceremony that marked the final operation for a five-decade old nitration facility in 2011. Constructed in 1954, the Bi-azzi Nitration Facility allowed Indian Head to make NG in a continuous as opposed to batch process. In the early 1960s, the Bi-azzi plant was modified to produce Otto Fuel II for torpedoes and has been the sole producer of that fuel since 1971. Otto Fuel II is (was) used in many of the US Navy's torpedoes and was also used by 26 US allies. For several years, NSWC IHD ramped up production of Otto Fuel II to cover any potential shortfall while a new state-of-the art nitration facility was being built. The new facility, which will be remotely operated, modernized nitration procedures, is safer to operate and significantly reduced the facility's environmental footprint. As of 2011, NSWC IHD produced Otto Fuel II for all domestic and foreign allies' torpedoes [375].

Physical Properties of Otto Fuel II

A useful summary of physical properties of Otto Fuel II over a wide range of temperatures and pressures was given in [376]. Several of the graphs in this section of our book were copied from that source.

Dry Otto Fuel II freezes at 241 K (−32°C). The melting point depends on water impurity levels and may range from 241 to 237 K (−32 to −36°C).

Physical properties of Otto Fuel II are summarized in Table 45.

Table 45: Physical properties of Otto Fuel II.

Property	SI units	Other units
Freezing point	241 K	−32 °C
Density at 298 K	1.2314 g/cm ³	
Isothermal compressibility at 101 kPa	5.324 × 10 ^{−7} kPa ^{−1}	
Viscosity at 273 K	0.011 Ns/m ²	11.0 cPs
Viscosity at 293 K	0.005 Ns/m ²	5.0 cPs
Viscosity at 298 K	0.004 Ns/m ²	4.04 cPs
Surface tension	34.45 × 10 ^{−5} N/cm at 298 K	34.45 dyn/cm at 25 °C
Thermal conductivity at 278 K	1490 W m ^{−1} K ^{−1}	
Thermal conductivity at 333 K	1400 W m ^{−1} K ^{−1}	
Specific heat at 303 K	1.88 J g ^{−1} K ^{−1}	0.45 cal g ^{−1} °C ^{−1}
Dielectric constant at 296 K	18.8	
Electrical conductivity at 296 K	14.2 μ MHO/m	

Data source: [376, 336]

The density as a function of temperature in the range 258 to 338 K (−15 to +65 °C) can be calculated from the equation

$$\rho = 1.2595 - 0.001155t$$

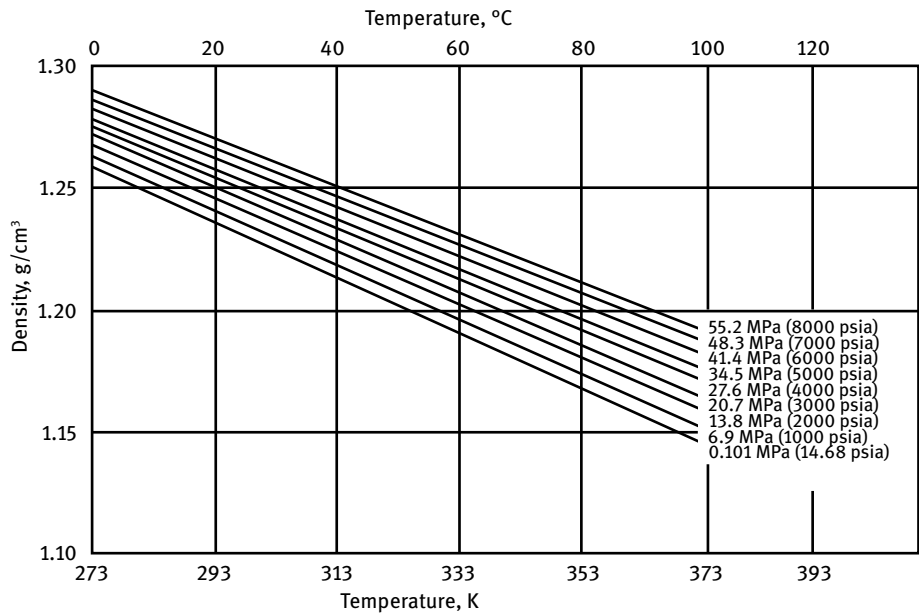


Figure 25: Density of Otto Fuel II as a function of temperature with pressure as auxiliary parameter. (Reproduced and modified from [376].)

where ρ is the density in g/cm³ and t is the temperature in °C. The density of Otto Fuel II as a function of temperature with the pressure as auxiliary parameter is shown in Figure 25.

The thermal coefficient of expansion of Otto Fuel II is illustrated in Figure 26.

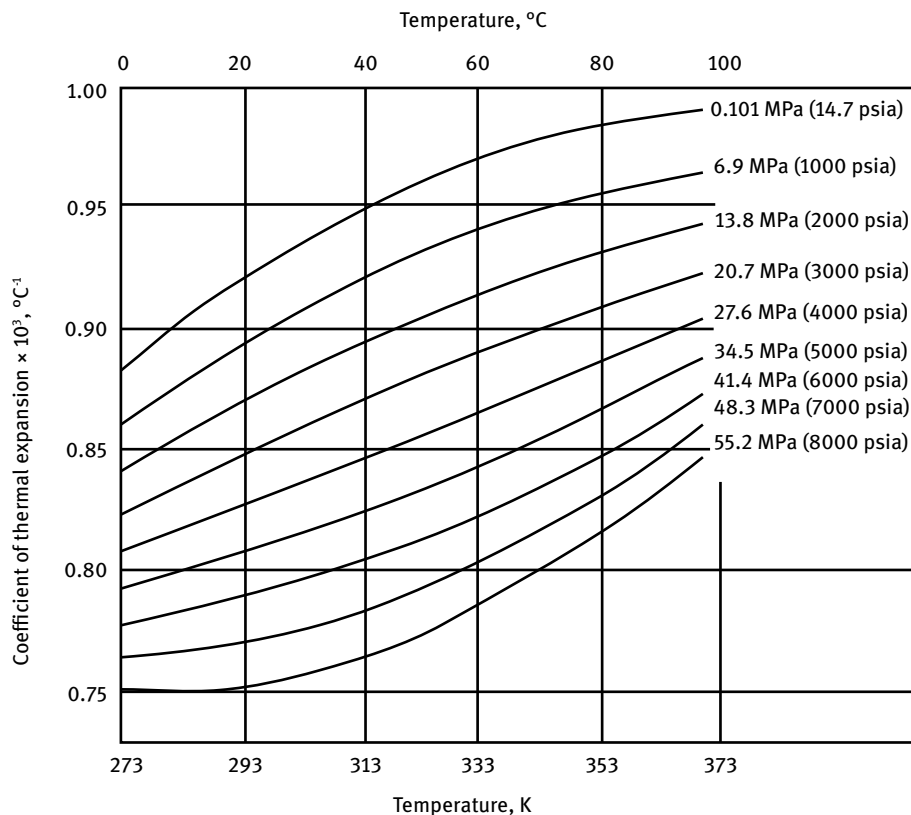


Figure 26: Thermal coefficient of expansion of Otto Fuel II. (Reproduced and modified from [376].)

The compressibility of Otto Fuel II is shown in Figure 27.

The vapor pressure of Otto Fuel II that is not perfectly dry is caused mostly by the low water content. The vapor pressure of freshly dried Otto Fuel II is very low, 9.7 Pa (0.0728 mm Hg) at 298 K (25 °C) and 456 Pa (3.424 mm Hg) at 348 K (75 °C). The vapor pressure of its most hazardous ingredient, pure PGDN, in the absence of the desensitizer at 298 K (25 °C) would be 13 Pa (0.09844 mm Hg). The dynamic viscosity of Otto Fuel II is illustrated in Figure 28.

The maximum dissolved water content in Otto Fuel II before phase separation occurs is 0.31 mass-% H₂O at 298 K.

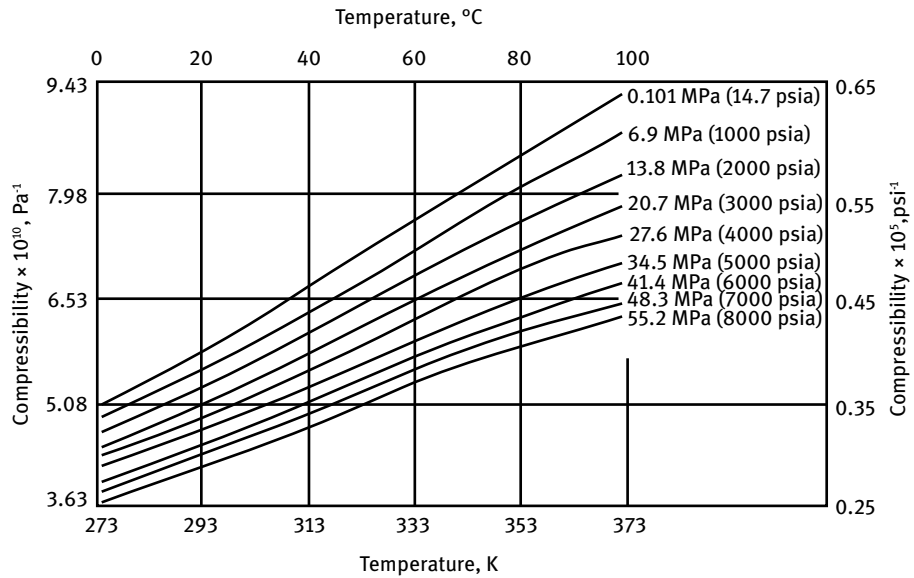


Figure 27: Compressibility of Otto Fuel II. (Reproduced and modified from [376].)

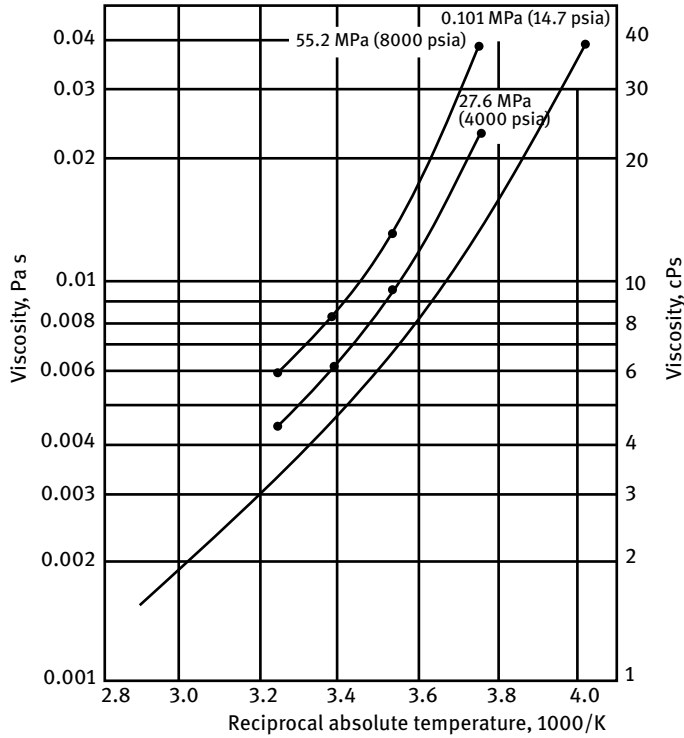


Figure 28: Dynamic viscosity of Otto Fuel II. (Reproduced and modified from [376].)

Thermodynamic Properties of Otto Fuel II

Table 46: Heat of formation of Otto Fuel II assuming additive behavior.

Ingredient	Composition	Molecular mass g/mol	Enthalpy of formation		
	Mass-%		kJ/mol	J/g	J/%g
1,2-PGDN	76	166.09	-296.9 ± 9.3	-1788 ± 56	
2-Nitrodiphenylamine	1.5	214.22	+121.0	+565	+8.472
Di- <i>n</i> -butyl sebacate	22.5	314.47	-1156.7	—	—
Total	100				

The US Navy PEP computer program ingredient list PEPCODED.DAF lists three different sets of data for Otto Fuel II, but we don't know which one is the more accurate one [377]:

Name	Formula		cal/g	lb/cu. in.
726 OTTO II	471C 876H 5520 155N	00	-696	.0452
727 OTTO II	274C 526H 3060 ~94N	00	-696	.0452
728 OTTO II GARY	295C 565H 3280 100N	00	-526	.0448

It is not known which of the three sets is the most accurate to be used for performance calculations.

Chemical Properties of Otto Fuel II

The chemical properties of Otto Fuel II are determined mostly by its main ingredient, 1,2-PGDN. As such, it will react with bases and strong acids.

Decomposition Reactions of Otto Fuel II

In this section we only cover the slow decomposition of Otto Fuel II during storage and thermal stability tests. The strand burning of 1,2-PGDN and its mixtures such as Otto Fuel II will be discussed in *Encyclopedia of Monopropellants*.

Thermal Stability of Otto Fuel II

Otto Fuel II is thermally stable at temperatures up to 339 K (150 °F) for several years, up to 355 K (180 °F) for a few months and up to 394 K (250 °F) for perhaps 30 min. Above 394 K (250 °F) there is a danger of instant exothermic decomposition in a runaway reaction. The AIT of Otto Fuel II is 394 K (121 °C).

Storage Stability of Otto Fuel II

A sample of Otto Fuel II has been held at a temperature of 323 K (122 °F) for over 7 years with no sign of deleterious effects. In another test, Otto Fuel II in a Mark 46 Mod 1 torpedo tank was stored at 336 K (145 °F) for 6 months with only minor changes [378].

The long-term storage properties of Otto Fuel II were investigated by elevated-temperature aging tests, natural environment storage tests and hydrothermal environment metal compatibility (causticity) tests [379]. Results showed that its safe storage life estimated at 303 K (30 °C) is not less than 11 years and its ingredients unchanged after stored for 2.4 years under ambient environment conditions. The water content in Otto Fuel II was nearing saturation after stored at 333 K (60 °C), 85% relative humidity for 30 d, but the content of the stabilizer and nitric acid ester was constant.

Analysis of Otto Fuel II

The nominal composition of Otto Fuel II as specified by MIL-O-82672A [374] is listed in Table 47.

Table 47: Specification requirements for Otto Fuel II.

Requirement	Minimum, mass-%	Maximum, mass-%
PGDN	75.8	76.2
2-Nitrodiphenylamine	1.4	1.6
Di- <i>n</i> -butyl sebacate	22.2	22.8
Sodium		0.8 ppm
Moisture		0.1

The methods for the chemical analysis of Otto Fuel II for quality control are described in Military Specification MIL-O-82672A. The PGDN content in Otto Fuel II can be determined by one of two methods, either the nitrometer method or an HPLC method. The 2-NDPA content in Otto Fuel II can be determined by one of three methods, a spectrophotometric method (only for freshly manufactured propellant), a volumetric bromination method, or an HPLC method. Moisture content is determined by the Karl Fischer titration method. There is no specific method for di-*n*-butyl sebacate analysis, which is assumed to make the difference up to 100% after the other two ingredients and moisture have been quantified.

2-NDPA is made from *o*-chloronitrobenzene (OCNB) and aniline, but some of the raw material is carried over into the product and eventually ends up in Otto Fuel II, where 2-NDPA is used as a stabilizer. OCNB has been reported to cause tumors in male and female rats. A sample of Otto Fuel II was found to contain 0.00165% OCNB by HPLC analysis [380].

Safety Properties of Otto Fuel II

The desensitizer used in Otto Fuel II was intentionally insoluble in water. There was concern that if Otto Fuel II was spilled on a ship and the spill was washed away with sea water, the residue left behind after leaching out of a water-soluble desensitizer would be sensitive to detonation.

Although it has been proven that Otto Fuel can be made to detonate, the conditions and stimulus energy required are so extreme that it is considered a non-explosive, relatively low fire hazard for shipping and storage purposes. Otto Fuel II is routinely shipped by commercial carriers as a non-regulated item, Not Otherwise Indexed By Name (NOIBN).

Drop Weight Impact Sensitivity of Otto Fuel II

Drop weight impact sensitivity data reported for Otto Fuel II in the literature vary widely:

- 8.5 to 34.2 kg-cm (50% point) with a 2-kg mass in JANNAF (ASTM D-2540-70) Drop Weight Test
- 21 kg-cm (50% point) with a 2-kg mass in JANNAF (ASTM D-2540-70) Drop Weight Test
- 98 kg-cm (50% point) with a 2-kg mass in JANNAF (ASTM D-2540-70) Drop Weight Test

Adiabatic Compression Sensitivity of Otto Fuel II

Some of the early work by Princeton Combustion Research Laboratory (PCRL) on adiabatic compression sensitivity of liquid gun propellants included Otto Fuel II and NOS365 for comparison. In all these propellants, adiabatic compression sensitivity is dependent on the amount of pressurant gas saturation. In a liquid that is saturated with gas, the easy release of bubbles aids the propagation of low velocity detonations.

PCRL studied compression-ignition sensitivity of NOS365 and Otto Fuel II at pressure levels and pressure rise rates comparable to those of liquid propellant gun systems, particularly during the start-up phase of the ballistic cycle [381].

Most of the Navy-sponsored work on compression ignition sensitivity of liquid gun propellants conducted until 1986 used Otto Fuel II or NOS365 instead of XM46 or LP1845. See also [382].

Cap Sensitivity of Otto Fuel II

Otto Fuel II would not detonate when it was attempted to initiate it with a No. 8 blasting cap.

Shock Sensitivity with Unattenuated Booster Charges

Otto Fuel II can be detonated when a sufficiently strong booster charge is employed. The size of craters formed when detonating large boosters adjacent to 5-gal cans of Otto Fuel II were compared to the crater formed when the 5-gal pail was filled with water [383]:

- 75 lb Composition C-4 stacked on top of a 5-gal can of Otto Fuel II created a 6-ft diameter × 3-ft depth crater

- Five 5-gal cans, each containing 75lb C-4, surrounding a 5-gal can of Otto Fuel II created a 5-ft diameter × 3-ft depth crater
- 75lb C-4 stacked on top of a 5-gal. can of water created a 2-ft diameter × 1-ft depth crater.

A comparison of the crater sizes clearly indicated that the exploding Otto Fuel II made a substantial contribution to crater formation.

When Otto Fuel was formulated in the 1960s, it would sustain detonation in a schedule 40 pipe with an ID of 34.9 mm. More recently, shock loading experiments with 95.2 and 50.8 mm diameter, pressed (1.56 g/cm^3) pentolite donors were conducted on Otto Fuel II while heavily confined by thick-wall steel tubes with an ID of 50.6 mm [384]. When the donor shock was attenuated to the detonation pressure of Otto Fuel II, the larger donor produced a high-velocity detonation. The smaller donor produced a low-velocity detonation, indicating that recently produced Otto Fuel II was less detonable than it was in the 1960s. Other shock loading experiments using the smaller pentolite donor were conducted with less confinement from a thick-wall Lexan tube surrounding an aluminum tube with an ID of 25.4 mm. Reaction had failed within 100 mm for a shock loading near the detonation pressure of Otto Fuel II. When the aluminum tube was lined with bubble pack, which introduced an average but non-uniform porosity of 25%, violent reactions were attained for shock inputs ranging from 112 to 22 kbar.

Card Gap Sensitivity of Otto Fuel II

For tests in a slightly modified Naval Ordnance Laboratory (NOL) card gap test, since the critical diameter of Otto Fuel II is near 1.5 in., the usual card board containers of 1.44-in. diameter had to be replaced by a 2-in.-diameter × 1/4-in. wall thickness × 12-in. length pipe [383]. Table 48 shows the card gap data obtained at three temperatures for bubble-free Otto Fuel II and one value when carbon dioxide was bubbled through the liquid.

Table 48: Card gap sensitivity test data for Otto Fuel II.

Material	Temperature		
	−45 °F 230 K	80 °F 300 K	78 °C 351 K
Otto Fuel II	26.3 (0)	13.3 (0)	38.7 (0 to 13)
Otto Fuel II and CO ₂ bubbles		46.3 (26)	

2-in. diameter × 0.25-in. wall thickness × 12-in. length steel tube.

Numbers in parentheses are the number of cards at 1.44 in. in diameter (standard NOL test).

Data source: [383].

Accident History of Otto Fuel II

An accidental explosion involving a torpedo test vehicle occurred at a test facility in February 1995 [385]. The test vehicle was operating inside of a pressure vessel with 3-in.-thick walls when the incident occurred. The pressure vessel failed catastrophically, with the resulting high-speed fragments causing extensive damage to the reinforced concrete test cell. The 18-in.-thick cell walls and roof were completely perforated by the fragments. An investigation was performed to document the damage and assist the US Navy in determining the cause of the accident. This investigation included reconstruction of the pressure vessel and major portions of the test vehicle. Calculations were performed to estimate the source energy necessary to produce the observed amount of damage.

A summary paper [386] listed three Otto Fuel II explosions, including the description of one of the incidents:

Otto Fuel II fuel tank explosion during static testing; explosion in transfer pipeline in fire; explosion of propellant tank in fire finite propagation of low velocity detonation with heavy confinement or ullage (blast and fragment hazards similar to Class 1.1); minor explosion with lower confinement (near field fragment hazards)

but details on the other two incidents could not be obtained.

Handling of Otto Fuel II

The official document for the safe handling of Otto Fuel II on shore and shipboard is the *Technical Manual for Otto Fuel II – Safety, Storage, and Handling Instructions* [387]. This supersedes an older version [388].

Materials Compatibility with Otto Fuel II

Chapter 7 of Volume 3 of the CPIA Publ. 394, Hazards of Chemical Rockets and Propellants, Liquid propellants manual contains a detailed summary of handling instructions and compatible and incompatible materials of construction for Otto Fuel II [389].

Disposal of Otto Fuel II

During maintenance of torpedoes, large quantities of contaminated rinse water are created that need to be disposed of in a safe manner. Activated carbon has been found to be effective in removing Otto Fuel from water [390]. Preliminary pilot runs using Filtrasorb 400 show a low carbon cost per unit of wastewater treated as compared to the high cost of disposal by incineration. A carbon adsorption stage was planned to be used in the design of an Otto Fuel wastewater treatment plant several decades ago.

Toxicity of Otto Fuel II

The acute, short-term inhalation toxicity of Otto Fuel II is determined by its most volatile ingredient, 1,2-PGDN. The toxicity of PGDN by itself was discussed earlier in Section 9.3.1.1.5. The additional concern about the long-term toxicity of Otto Fuel

II stems from the carcinogenic properties of 2-NDPA and contaminants carried over from its manufacture. This is the reason why a significant effort was launched to find a non-carcinogenic replacement for 2-NDPA in Otto Fuel II and other solid propellant applications.

When Otto Fuel II was first introduced into the US arsenal, the sailors were warned that Otto Fuel II was toxic, and extrapolating from animal tests to humans was difficult. The problem was handled thus (quote [391]): "It has been estimated that ingestion of 2 ounces of Otto Fuel II would kill a man-sized rabbit." The tests resulted in a series of guidelines and recommendations for handling the material that were incorporated in the Safety and Handling Procedures OP 3368.

The toxicity of Otto Fuel II is described in S 6340-AA-MMA-0101 (as quoted in MIL-O-82672A). The LD50 (oral) is 332 mg/kg.

The CPIA/M4 Unit 35 manual stated "Carcinogenicity: none of the components of Otto Fuel are suspected carcinogens," but it must be pointed out that not the original component, but the **nitrosamine** that forms during storage, aging, and gradual stabilizer degradation of 2-NDPA is indeed a carcinogen.

Additional information on the toxicity of Otto Fuel II and its components is available from several US government reports [392]. The toxicological profile of Otto Fuel II and its components published by the Agency for Toxic Substances and Disease Registry (ATSDR) in 1995 is a very thorough compilation of toxicity data and recommended safe handling practices for Otto Fuel II [393].

Environmental Effects of Otto Fuel II

Environmental Fate. Otto Fuel is a chemically stable liquid that is insoluble in water. Its transport in the environment in water would be expected to be very limited, due to this hydrophobicity. In a land spill, Otto Fuel would probably absorb into clays and biological particles rather than leach downstream. In a surface water spill, Otto Fuel would be adsorbed into bottom sediments. In small concentrations, Otto Fuel should be biodegradable both in surface water and in soil. In the environment, a simple nitrate ester would be biodegradable. However, the other constituents of Otto Fuel may cause it to be somewhat more persistent.

The factor that controls the rate of buildup of Otto Fuel vapor in the atmosphere of any environment in which Otto Fuel II is spilled is the rate of evaporation of material from the spill. To obtain more information on the quantitative aspects of the problem, the evaporation rate of Otto Fuel II at 298–300 K (25–27 °C) was determined by weight loss measurements in a nitrogen atmosphere [394]. After an initial period of 3–4 h, the evaporation rate was found to be $0.18 \text{ g h}^{-1} \text{ ft}^{-2}$ of the spill. An initially higher weight loss was attributed in part to water that was dissolved in Otto Fuel II and in part to the presence of a volatile impurity that could not be removed by drying the liquid with calcium sulfate. The observed evaporation rate was in good agreement with the rate of $0.52 \text{ g h}^{-1} \text{ ft}^{-2}$ reported for PGDN at 308 K (35 °C) and with the rate of $0.135 \text{ g h}^{-1} \text{ ft}^{-2}$ calculated for PGDN at 298 K (25 °C) using Langmuir's method of calcu-

lating the evaporation rate of liquids into a stagnant atmosphere. A new technique, based on differential pulse polarography, was developed for the quantitation of the rate of PGDN diffusion in sea water. This technique was used to follow the diffusion of Otto Fuel II through a stagnant layer of sea water. Under favorable circumstances (i.e., complete coverage, no agitation), the covering of an Otto Fuel II spill with sea water reduced the evaporation rate by a factor of 1/10000.

PGDN spilled on the ground and soaking into soil will eventually disappear by biodegradation [395, 396].

9.3.1.1.8 Other Propellant Mixtures with 1,2-Propylene Glycol Dinitrate

Torpedo fuels similar to Otto Fuel II have been used by other navies [397].

9.3.1.2 1,3-Propylene Glycol Dinitrate

1,3-Propylene glycol dinitrate, 1,3-propanediol dinitrate, 1,3-dinitroxypropane, trimethylene glycol dinitrate, $\text{O}_2\text{NO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{ONO}_2$, $\text{C}_3\text{H}_6\text{N}_2\text{O}_6$, PGDN, CAS RN 3457-90-7, is a colorless oil. Like GTN, it can be used as a gel-forming (gelatinizing) solvent for nitrocellulose. The physical properties of 1,3-PGDN are summarized in Table 49.

1,3-PGDN is less volatile than EGDN but more volatile than GTN. It is less impact-sensitive than GTN and more stable during storage at high environmental temperatures. In the BAM impact sensitivity test apparatus, no reaction could be observed at energies up to 20 N m.

In the lead block test, detonation of 1,3-PGDN caused an enlargement of the cavity by $540 \text{ cm}^3/10 \text{ g}$, which is a very high number.

Table 49: Physical properties of 1,3-PGDN.

	SI units	Other units	References
Molecular mass	166.0895		
Freezing point	243.61 K	-29.49 °C	
Density	1.393 g/cm ³		
Density	1.3952 at 293 K		[10]
Specific gravity 15/15 °C	1.4708 g/cm ³		
Vapor pressure at 298 K	5.3 Pa	0.03980 mm Hg	
Viscosity		9.4 cPs at 6.3 °C	[10]
Viscosity		5.8 cPs at 20 °C	[10]
Viscosity		2.75 cPs at 54.4 °C	[10]
Refractive index n_D^{20}	1.43476		[10]
Dielectric constant	18.97		[10]
Dipole moment	3.50		[10]
Enthalpy of formation at 298 K	-1743 kJ/mol		
Heat of evaporation at 293–313 K	74.3 ± 4.6 kJ/mol		
Heat of evaporation at 293–313 K	75 ± 5 kJ/mol	17.9 ± 1.1 kcal/mol	
Deflagration point	498 K	225 °C	

9.4 Glycerol Trinitrate (Nitroglycerin)

Glycerol trinitrate, also known as $\text{C}_3\text{H}_5(\text{ONO}_2)_3$, $\text{C}_3\text{H}_5\text{N}_3\text{O}_9$, nitroglycerin, nitroglycerine, NG, glycerin trinitrate, GTN, 1,2,3-propanetriol trinitrate; trinitrate, propane-1,2,3-triyl; 1,2,3-glyceryl trinitrate, CAS RN [55-63-0], is a pale yellow liquid explosive with a legendarily high sensitivity to impact and other stimuli. The common name is *nitroglycerin* (abbreviated as NG), but that is a misnomer and chemically incorrect since this is not a *nitro* compound. We are slowly shifting to the correct name *glycerol trinitrate* and hope that readers will go along on this new trend. Glycerin trinitrate is also sometimes used as the name for this compound.

Alfred Nobel's invention that GTN can be desensitized by absorbing it on kieselguhr or porous pumice led to the widespread use of dynamite and enriched Nobel's wealth and worldwide fame. GTN can be gelled with various additives (including nitrocellulose) to form blasting gelatin and propellants like cordite and ballistite, precursors for modern double-base propellants.

GTN is one of the few organic compounds with a positive oxygen balance. The oxygen balance for combustion to CO_2 is +3.5%. It contains more oxygen than is needed to burn all carbon to carbon dioxide and all hydrogen to water.

9.4.1 Production of Glycerol Trinitrate

GTN is produced in large quantities industrially by the nitration of glycerol with nitrating acid, a mixture of concentrated nitric acid and sulfuric acid. Once produced, it is usually consumed as a captive product by secondary processes on site and is not shipped as such (except in thriller movies). The literature on the safe production of GTN is voluminous and cannot be included in detail in this book. References to a few typical publications may suffice [398].

The use of dinitrogen pentoxide instead of mixed acid as the nitrating agent avoids the problem of having to dispose of spent acid [399].

Sometimes glycerol is not nitrated all the way to GTN, but it may be desirable to stop the nitration at the dinitrate level to make glycerol dinitrate (GDN), an intermediate for the synthesis of GLYN that is used to make an energetic binder. To optimize the yield of dinitrate and prevent the last step from leading to trinitrate, it is necessary to better understand the kinetics of the nitration process. Therefore, the equilibrium constants of seven sequential-parallel reactions of conversion of glycerol into GTN in HNO_3 were measured [400]. The effect of the acidity of the medium on the equilibrium nitration constants was correlated with processes of protonation of glycerol and its nitrates. The equilibrium nitration constants were higher for primary hydroxides than for secondary hydroxides, and they decreased in both series in going from glycerol to its dinitrates.

Glycerol can be treated to make 1,3-GDN as an intermediate product to produce polyGLYN. Nitration of glycerol to 1,3-dinitroglycerin was studied in the temperature

range 283–303 K (10–30 °C), a molar ratio of nitric acid to glycerol 1/1 to 7/1, and nitric acid concentration of 69% [401]. Seven reaction kinetic rate terms represented the reactions that occurred in the nitration of glycerol. The position of the hydroxyl group in the glycerol molecule caused different reaction rates. The primary hydroxyl group was more reactive than the secondary hydroxyl group.

The nitration of glycerol was modeled by fitting the kinetic model with six parameters, the rate constant at an average temperature and the activation energy [402]. The reaction rate was assumed to be governed by three reactions: the formation of **(1)** GMN, **(2)** GDN, and **(3)** GTN.

9.4.2 Physical Properties of Glycerol Trinitrate

The physical properties of GTN at a fixed temperature (usually 298 K) are summarized in Table 50. More detailed data, in particular the variation of key physical properties over a wider range of temperatures, are discussed in individual sections below. Additional properties of GTN are discussed in [403–405].

Table 50: Physical properties of GTN.

Property	SI units	Other units			References
Molecular mass	227.0865	4.4036 mol/kg			[73]
Freezing point	286 K	+13 °C			
Freezing point (stable modification)	286.3 K	+13.2 °C	55.8 °F		[74]
Freezing point (unstable modification)	275.3 K	+2.2 °C	35.6 °F		[74]
Boiling point	398 K		257 °F		
Density	1.5931 g/cm ³ at 293 K				[10]
Density	1.591 g/cm ³				[74]
Specific gravity 15/15 °C	1.599 g/cm ³				[15]
Viscosity		37.8 cPs at 20 °C			[10]
Refractive index n_D^{20}	1.45731				[10]
Dielectric constant	19.25				[10]
Dipole moment	3.82				[10]
Enthalpy of formation ΔH_{298}^f	–370.7 kJ/mol	–1632.4 kJ/kg	–88.6 kcal/mol	–390.2 cal/g	[74]
Heat of evaporation	92.0 ± 2.1 kJ/mol	405 J/g	22 kcal/mol	96.8 cal/g	
Heat of fusion	21.85 kJ/mol	96 J/g	5.22 kcal/mol	23 cal/g	[406]

9.4.2.1 Freezing Point and Melting Point of Glycerol Trinitrate

The freezing point of GTN in its stable modification is 286 K (+13 °C). Early in the history of NG, it was discovered that liquid NG could be “desensitized” by cooling it to about 278 to 283 K (5 to 10 °C = 40 to 50 °F). At this temperature NG freezes, contracting upon solidification. However, thawing it out can be extremely tricky, especially if impurities are present or if the rate of warming is too rapid. One of the methods to avoid freezing is to add freezing-point-depressing additives that are compatible with GTN. These additives are usually nitrate esters of similar aliphatic polyols.

It is difficult to explain why there are two different versions of GTN that differ in stability and freezing points. GTN may crystallize in two allotropic modifications, a metastable, labile form and a stable form, of which only the first can be converted into the other. This conversion occurs readily, so that there is a monotropic allotropy. Chemically pure GTN is more difficult to crystallize, but it always crystallizes in the labile form. Less pure NG, on the other hand, freezes more readily but mostly in the stable form. On contact with a crystal of the stable form, the labile-form liquid converts to the stable form immediately, or, without such contact, after a certain time at an optimum temperature for the conversion to take place. Thus, any nitrate-ester-plasticized propellant that has been embrittling for some time will contain the stable, higher freezing and melting crystal form because of this spontaneous conversion.

Most published data on alkyl nitrate freezing points were done by cooling the sample, but most alkyl nitrates tend to supercool and the freezing points vary considerably. Also, some alkyl nitrates freeze to a metastable form that is not identical with the stable form formed during long-term storage. It would be more accurate to measure the melting points of frozen alkyl nitrates. The melting points of five different frozen nitrate ester samples were determined by visual observation and in a low-temperature DSC [407]. All samples were preconditioned to 230 K (−43 °C) and stored at that temperature. Table 51 is a summary of melting points (both visually observed and DSC measurement) of GTN in comparison to four other nitrate esters that are also commonly used as plasticizers in double-base propellants.

Many alkyl nitrates and polynitrates have a tendency to supercool and do not crystallize voluntarily. Therefore, it is difficult to determine a freezing point by cooling a liquid sample. A systematic study was conducted of four nitrate esters, GTN, BTTN, TMETN, and TEGDN, which are used to better control the crystallization phenomena of plasticizers in propellants [406]. The tests were done to determine the melting characteristics of these four frozen compounds and to compare new measurements to the old data in the literature, which were sometimes incomplete or unreliable. The influence of temperature on the rate of crystal growth was studied for four nitric esters by photographic observation, while nucleation was specifically considered for GTN and TMETN, two nitrate esters that exist in allotropic modifications and may form two crystallographic different varieties, depending on the mode of nitration and the tem-

Table 51: Melting points of alkyl nitrate esters.

Compound	Visual observations				DSC major endotherm onset	
	Start K	Start °C	End K	End °C	K	°C
GTN	282.7	9.6	286.3	13.2	284	10.9
DEGDN	274.3	1.2	276.6	3.5	276.4	3.3
					262.6 ^a	−10.5 ^a
BTTN	265.5	−7.6	270.3	−2.8	267.2	−5.9
TMETN	286	12.9	289.2	16.1	286.1	13
					276.9 ^a	3.8 ^a
TEGDN	258.7	−14.4	263.7	−9.4	261.5	−11.6
	250.2	−22.9	253.6	−19.5	—	—

^a Labile crystals formed during immediate rescan of melted and quickly frozen original samples

Data source: [407]

perature/time history. The melting point of frozen unstable GTN was 276 K (+3 °C), the melting point of the stable form was 288 K (15 °C), and the heat of fusion was 21.85 kJ/mol = 96 J/g = 5.22 kcal/mol = 23 cal/g. The heat of fusion of GTN was the highest among the four alkyl nitrates tested. If GTN is supercooled and seed crystals are inserted into the liquid to induce solidification, different forms of GTN are obtained depending on the type of seed crystal inserted. Seed crystals of potassium nitrate gave only the metastable form, but seed crystals of sodium salicylate gave a mixture of both allotropes with more of the stable form. If a sample of supercooled GTN is conditioned at 233 K (−40 °C) for 3 h to 8 weeks, and samples are taken and seeded to induce crystallization, initially the solidification exotherm occurs only at 277–278 K (4–5 °C), but with increasing age of the sample the exotherm at 277–278 K disappears and is replaced by one at 288 K (15 °C). The rate of crystallization of supercooled GTN was measured as a function of the preconditioning temperature between 233 and 283 K. Liquid GTN samples that have been aged at different temperatures for 2 h and then induced to crystallize will crystallize the fastest if aged at 268 K (−5 °C).

9.4.2.2 Vapor Pressure of Glycerol Trinitrate

The vapor pressure of GTN between 400 and 524 K can be calculated from the Antoine equation

$$\log_{10}(P) = 4.07588 - (2508.448 / (T - 39.235))$$

where P is the vapor pressure in bar and T is the temperature in kelvin. Other vapor pressure data for GTN are in Table 52, 53, and 54. See also [294, 408].

Table 52: Vapor pressure of GTN.

Temperature			Vapor pressure		
K	°C	°F	Pa	millibar	mm Hg
293	20	68	0.033	0.00033	0.00025
323	50	122	0.97	0.0097	0.007
353	80	176	13	0.13	0.097
363	90	194	31	0.31	0.23

Data source: [74]

Table 53: Vapor pressure and heat of evaporation of GTN.

Compound	Vapor pressure, Pa			Vapor pressure, μ m Hg			Heat of evaporation	
	Temperature, K			Temperature, °C			kJ/mol	kcal/mol
	293	303	313	20	30	40		
Glycerol trinitrate I	0.03	0.11	0.4	0.21	0.82	3.2	105 $\pm$ 6	25.1 $\pm$ 1.4
Glycerol trinitrate II	0.03	0.15	0.5	0.2	1.1	3.5	109 $\pm$ 11	26 $\pm$ 2.7

Data source: [12]

Table 54: Vapor pressure of GTN in comparison to EGDN.

Temperature, K	288	288	298	298	308	308	318	318	328	328
Temperature, °C	15	15	25	25	35	35	45	45	55	55
Vapor pressure	Pa	mm Hg	Pa	mm Hg	Pa	mm Hg	Pa	mm Hg	Pa	mm Hg
Glycerol trinitrate	0.17	0.0013	0.24	0.0018	0.61	0.0046	1.72	0.0129	4.80	0.0359
Ethylene glycol dinitrate	3.11	0.0233	9.41	0.0706	29.2	0.2189	59	0.4425	128	0.9619

Data source: [15]

A comparison of several papers reporting the vapor pressure of NG illustrated in Figure 29 showed general satisfactory agreement among data from different authors, except that the Clausius-Clapeyron fit of the data by John [294] and Crater [15] had to be excluded because they were outliers [295]. The Clausius-Clapeyron fit of the data led to the equation

$$\log P = A - B/T = 11.88 - 4529/T$$

where P is the vapor pressure in mmHg and T is the temperature in kelvin for the temperature range 286–356 K (13–93 °C). The vapor pressure at 298 K was extrapolated to 4.81×10^{-4} mmHg. The heat of evaporation is 86.7 kJ/mol. In light of its importance in the explosive industry and known health effects, surprisingly no recent papers have

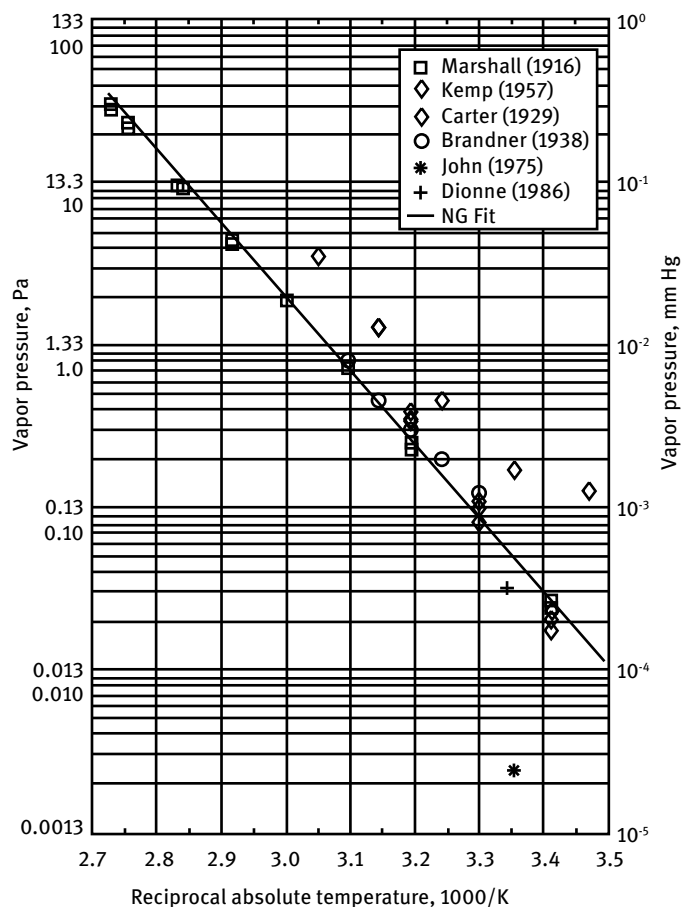


Figure 29: Vapor pressure of GTN. (Republished and modified from [295], with permission of © 2012 John Wiley Sons – Books; permission conveyed through Copyright Clearance Center Inc.)

dealt with the room temperature vapor pressure of NG. NG freezes at 285.9 K (12.8 °C), but no data on the vapor pressure of solid NG could be found.

9.4.2.3 Optical Properties of Glycerol Trinitrate

An IR spectrum of GTN is shown in Figure 30. The self-association of GTN in the liquid state and in tetrachloroethane solution (at various dilutions) was studied by IR spectra, especially focusing on the vibrations of the $-\text{NO}_2$, $-\text{ONO}_2$, and C–H bonds [409]. The formation of dimers and higher aggregates changes with dilution. As in the crystal state, associations appear to take place within the NO_2 groups by interaction between an O atom of one of the ester groups and the N atom of a second ester group. Hydrogen-bonded associations appeared only in concentrated and bulk solutions and

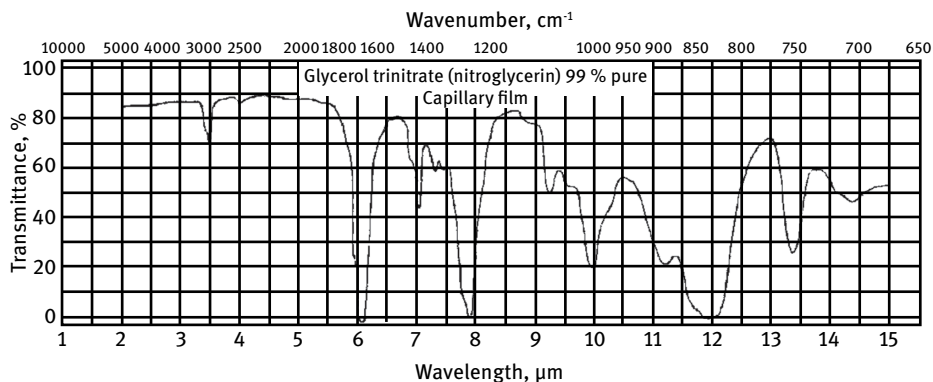


Figure 30: IR spectrum of GTN. (From [296].)

were less stable. In liquid GTN at room temperature, the concentrations of monomer and dimer are small, with tetramer and trimer dominating.

In the near-IR spectra from 1000 to 2500 nm of GTN and other explosives, particularly intense and complex were the bands corresponding to the first combination region (2500–1900 nm) and first overtone stretching mode of C–H and N–H bonds (1750–1450 nm) [410].

The Raman spectra of GTN and glycerol mononitrate (GMN) were described in [25] and [26].

9.4.2.4 Thermodynamic Properties of Glycerol Trinitrate

The thermodynamic properties of GTN are summarized in Table 55.

The heat evolved during the production of GTN by the nitration of glycerol must be carefully managed to prevent runaway reactions in the nitration vessel. The real

Table 55: Thermodynamic properties of GTN.

Quantity	Value	Units	References
Heat capacity, liquid	1.318	J g ⁻¹ K ⁻¹	[10]
ΔH_f° liquid	-370 ± 2	kJ/mol	[411]
ΔH_f° liquid	-371.1 ± 1.7	kJ/mol	[412]
ΔH_f° liquid	-375	kJ/mol	[302]
ΔH_f° liquid	-372 ± 4	kJ/mol	[413]
ΔH_f° liquid	-400	cal/g	[377]
ΔH_f° vapor	-279.1 ± 2.7	kJ/mol	[412]
ΔH_f° vapor	-66.7	kcal/mol	[37]
Heat of combustion	6784.4	J/g	[412]
Heat of combustion	1525.9 ± 0.8	kJ/mol	[412]
Heat of evaporation at 298 K	92.0 ± 2.1	kJ/mol	[412]
Heat of evaporation at NBP	44.1	kJ/mol	[412]

enthalpies of seven sequential-parallel reactions of glycerol nitration into glycerol mono-, di-, and trinitrate were found by the combination of the heats of the reactions obtained by the thermochemical method and with the equation for the isobar of the chemical reaction, and the standard enthalpies of formation of glycerol nitrates were calculated with them [411, 414, 415]. The difference in the enthalpies of nitration with respect to different positions in glycerol and its nitrates basically determines the difference in the corresponding equilibrium constants of the nitration reactions.

9.4.2.5 Molecular Structure of Glycerol Trinitrate

Proton magnetic resonance (PMR, ¹H NMR) spectra at a frequency of 294 MHz for glycerol and its mono-, di-, and trinitrates have been measured in nitric and sulfuric acids and in deuteroacetonitrile [416]. The conformational composition weakly depends on the medium, temperature, and number of nitrate groups in the molecule. Conformers with CH₂ and OH (or ONO₂) located in a *trans* position have a certain preference.

9.4.3 Chemical Properties of Glycerol Trinitrate

9.4.3.1 Thermal Decomposition of Glycerol Trinitrate

9.4.3.1.1 Experimental Studies of Thermal Decomposition of Glycerol Trinitrate

GTN decomposes in the vapor phase at 403–423 K (130–150 °C) at a rate proportional to its vapor pressure, and the rate decreases with time according to first-order reaction kinetics [417]. In the presence of liquid-phase GTN, the rate of gas formation in the same interval of temperature is smaller; it gradually increases with time and depends on the pressure of the decomposition products whether or not they are vented. When the decomposition reaches a certain critical pressure of the trapped decomposition products, the rate of gas formation increases proportionally to the square of the pressure. The critical pressure is ~27 kPa at 373 K (~200 mm Hg at 100 °C). The sharp increase in the rate is due to the effect of the pressure on the accumulation of gaseous decomposition products (H₂O and HNO₃) in the liquid phase. The presence of these products accelerates hydrolytic and chemical reactions, whose rates are much faster than the rate of initial thermal decomposition of pure GTN. If all the decomposition products remain trapped in the liquid phase, the accelerated runaway reaction rate of the decomposition of GTN begins at 373 K (100 °C) after ~9 h. Accelerated gas formation is associated mainly with the accumulation of HNO₃. Neutralization of the acid with Na₂CO₃ eliminated the acceleration. The time for the onset of acceleration was considerably shortened in the presence of HNO₃ and H₂O.

The thermal decomposition of NG was investigated in the vapor and liquid states over a temperature range of 388–433 K (115–160 °C) [418]. Above 413 K (140 °C) the decomposition in the vapor phase was first order, but in the liquid phase the order was only approximately first order. At all temperatures the rates were found to vary markedly with the ratio of the mass of NG to the volume of the reactor, indicating wall effects and free radical chain termination. Below 413 K (140 °C) the decomposition

was autocatalytic with free HNO_3 catalyzing the reaction. A mechanism was proposed for the vapor-phase reaction that was in agreement with the experimental data.

The slow thermal decomposition of GTN at 383 K (110 °C) was examined by GC analysis of gas evolution and showed mostly CO_2 but no free NO_2 [419]. NO was seen only during the first hour of the test. Time-resolved IR spectrophotometry for 72 h at 383 K showed that the O— NO_2 band had diminished, but the C=O bands had increased due to evolution of ketones and aldehydes. GC/MS identified N_2 , CO_2 , HCHO, HCOCOH , HCOOH , HOCH_2COOH , and HOCCOOH as decomposition products.

GTN samples were mixed with different organic and inorganic compounds that it might encounter as contaminants or propellant ingredients and investigated by heat flow calorimetry [420]. The timing and severeness of the autocatalytic reaction were very dependent on the nature and amount of the added contact material. NMR analyses of GTN and its decomposition products proved that the main reaction can be characterized by a homolytic split of the nitrate ester bond, preferably in the center position. The distribution of reaction products (1,3-dinitroglycerin and 1,2-dinitroglycerin) and the further decomposition products (dinitroglycerol carboxylic acid, mononitroglycerol carboxylic acids) was dependent on neither the structure nor the amount of contact material, nor was it a function of the reaction time. But the severeness of the decomposition reaction was dependent on the type of additive. Some contact materials changed the mechanism of the decomposition reaction. The addition of basic substances led to an increase of ester bond hydrolysis. The addition of radical scavengers (4-methoxyphenol) effectively prevented the formation of nitroglycerol carboxylic acids. As mentioned in other publications, an increase of diphenylamine (DPA) to over 1% did not result in a stabilizing effect. Other stabilizers (2-NDPA, N-NO-DPA) showed a much better stabilizing effect in binary mixtures. Also, non-reactive bases like carbonates stabilized GTN very well. Compared with GTN, other nitrate esters (ethyl nitrate, BBTN) were much more stable.

A dual-shutter ion mobility spectrometer operating at atmospheric pressure and interfaced to a gas chromatograph for sample introduction has been used to study the reaction of Cl^- with nitrate esters in explosive vapor-detecting mass spectrometers [421]. Of particular interest was an investigation of the formation of NO_3^- from the reaction of the Cl^- with GTN. The adduct $\text{GTN}\cdot\text{Cl}^-$ together with NO_3^- and $\text{GTN}\cdot\text{NO}_3^-$ compose the mobility mass spectrum. Over the temperature range 374–395 K (111–122 °C), $\text{GTN}\cdot\text{NO}_3^-$ was stable, but $\text{GTN}\cdot\text{Cl}^-$ decomposed to NO_3^- and 1,2-dinitro-3-chloropropane. The activation energy and preexponential factor for this first-order decomposition was $80 \pm 3 \text{ kJ/mol}$ and $1.3 \times 10^{12} \text{ s}^{-1}$, respectively.

9.4.3.1.2 Computations Relating to Thermal Decomposition of Glycerol Trinitrate

DFT calculations were performed to determine various decomposition channels for GTN [422]. For the unimolecular decomposition mechanism of GTN, two main mechanisms were found: **(1)** homolytic cleavage of O— NO_2 to form $\cdot\text{NO}_2$ and $\text{CH}_2\text{ONO}_2\text{CHONO}_2\text{CH}_2\text{O}\cdot$, which subsequently decomposes to form $\cdot\text{CHO}$, $\cdot\text{NO}_2$, and $2\text{CH}_2\text{O}$; and **(2)** successive HONO eliminations to form HONO and CHO—CO—CHO ,

which subsequently decomposes to form $\text{CH}_2\text{O} + 2\text{CO}_2$ and $\cdot\text{CHO} + \text{CO}$. The former channel has slightly lower activation energy than the latter one. The calculated rate constants of the initial process of the two decomposition channels showed that the $\text{O}-\text{NO}_2$ cleavage pathway occurred more easily than the HONO elimination pathway.

9.4.3.2 Reactions of Glycerol Trinitrate with Inorganic Reactants

The hydrolysis of GTN may be an undesirable reaction during storage of GTN-containing propellants in moist areas, or it may be used with advantage in the decontamination of GTN-containing wastewaters from the production or demilitarization of GTN and GTN-containing propellants. The hydrolysis is aided by alkaline conditions.

The reaction between GTN and NaOH in aqueous solution at various mol ratios was followed UV spectrophotometrically and the loss of GTN determined polarographically after several hours of reaction time [423]. The initial reaction of GTN occurred by an α -hydrogen elimination with the formation of a carbonyl and nitrite ion NO_2^- . A slow reaction with the formation of NO_2^- occurred concurrently with α -H elimination.

9.4.3.3 Analysis of Glycerol Trinitrate

9.4.3.3.1 Assay and Purity Control of Glycerol Trinitrate

The analytical methods for determination of assay and contaminants in GTN are described as part of Military Specification MIL-N-246B.

GDN contamination in GTN can be separated by thin-layer chromatography and identified by IR [424]. The main impurity was glycerol 1,3-dinitrate, CAS RN [623-87-0], with only traces of glycerol 1,2-dinitrate, CAS RN [621-65-8].

9.4.3.3.2 Trace Detection of Glycerol Trinitrate in Workroom Air

As it turns out, workplace exposure to GTN either by inhalation or skin resorption occurs not only in the explosives and propellant industry, but also in pharmaceutical companies where GTN is formulated into tablets and skin patches as a medicine for lowering acutely high blood pressure in human patients. Beyond that, detection of GTN and other explosive nitrate esters in improvised explosive devices suspected to be used by terrorists is an important task to assure security of the general public, in particular for the safety of air travel. The industry has developed very sensitive instruments to detect traces of explosive vapors. Instruments that were initially developed for security forces can now be used beneficially to monitor workroom air in a controlled environment. Similar methods can now be used to monitor workroom air in propellant factories and munitions storage magazines.

Liquid chromatography-mass spectrometry (LC-MS) with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) in negative-ion mode were investigated for the analyses of three widely used nitrate ester explosives, PETN, GTN, and EGDN, as well as six additional nitrate esters [425]. In ESI, ammonium nitrate and ammonium chloride promote the formation of characteristic adduct ions of the

respective nitrate esters. In APCI, chlorinated agents, dichloromethane, chloroform, carbon tetrachloride, and ammonium chloride, are used, forming more easily ionizable chloride attachment adduct ions. For comparison, three authentic forensic samples, Booster DYN0, Semtex, and Smokeless Powder, were analyzed to demonstrate the validity of the developed LC-MS methods.

The two closely related ion spectrometric methods used in explosive detection and analysis include MS and ion mobility spectrometry [426]. The four fundamental requirements: speed, selectivity, sensitivity, and ease of sampling can be fulfilled with each of these methods.

The recommended analysis methods for analysis of GTN (and EGDN) in workroom air are NIOSH 2507 [427, 428] and OSHA43 [429]. In these methods, which are suitable for a concentration range 0.6 to 3.2 mg/m³ in a 15-L air sample, the analyte is first adsorbed from the air on a solid sorbent Tenax-filled tube and then extracted with ethanol and analyzed by GC.

9.4.3.3.3 Trace Detection of Glycerol Trinitrate in Body Fluids

The desirable ability to monitor GTN exposure of workers in the workplace by taking blood or urine samples at the end of the work shift and the establishment of a BEI with a maximum allowed GTN concentration depends on the availability of sensitive analytical methods. The occupational health aspects of BEI will be discussed subsequently in Section 9.4.4. The current section deals only with analytical instrumentation. In addition to monitoring GTN in blood or urine of propellant factory workers and military personnel, the same methods will also help physicians to select a safe dosage of GTN pills or dermal patches for patients with high blood pressure. Patients may metabolize GTN at different rates, so the maintenance dosage must be adjusted individually.

A sensitive method for the quantitative determination of GTN in human plasma was developed in which GTN and an internal standard (BTTN) were first extracted from plasma with *n*-pentane [430]. The extracts were analyzed by GC-MS using fused silica capillary columns and electron capture negative ion chemical ionization. The quantitation limit of the method was about 50 pg/mL. Linear calibration curves were obtained in a range of 50–1600 pg/mL. Precision at the level of 100 pg/mL was 4%. A similar method used *n*-hexane instead of pentane for extraction, with identical results [431].

A method for the quantitative determination of GTN in human plasma by GC-MS was developed that added (¹⁵N)GTN as internal standard, extracted with a mixture of pentane and methyl acetate, purified by partition between, first, the extraction solvent and a mixture of acetonitrile and water (60:40) and, secondly, the resultant aqueous phase and benzene [432]. The solvent was evaporated to a small volume before injection. The fragment ions at *m/z* 46 and 47 were monitored for the measurement of the [NO₂]⁺ and [¹⁵NO₂]⁺ ions using electron impact ionization. The mean recovery in blind plasma samples spiked with amounts in the concentration range 0.35–3.52 nmol/L was 97.4% (*n* = 58). Concentrations in plasma could be estimated down to

about 0.2 nmol/L (50 pg/mL). Recovery of doped samples in duplicate determinations in the range 0.5–1.96 nmol/L was 99.4% ($\pm 6.0\%$ relative) ($n = 80$).

GTN is metabolized in the body to glycerol 1-nitrate and glycerol 2-nitrate, which can be determined by a GC method that is suitable for a variety of biological samples and can detect nitrates down to the low nanogram range [433]. An extract of the sample to be analyzed was treated with phenylboronic acid. The GMNs rapidly formed cyclic boronate derivatives, with five- and six-membered rings, respectively, which could then be separated by GC and detected by an electron-capture detector.

A sensitive GC/electron-capture detection method for the simultaneous determination of GTN and its dinitrate metabolites (1,2-GDN and 1,3-GDN) was developed in which human plasma samples (1 mL) spiked with 2,6-dinitrotoluene as an internal standard were extracted with 10 mL of a methylene chloride/pentane mixture (3:7 v/v) [434]. The limits of detection by this method for GTN, 1,2-GDN, and 1,3-GDN in plasma were 0.025, 0.1, and 0.1 ng/mL, respectively. A similar method that also separated the three compounds can be found in [435].

A sensitive, specific capillary GC-electron-capture detection method for the simultaneous determination of GTN, 1,2-GDN, and 1,3-GDN and 1- and 2-glyceryl mononitrate (1-GMN and 2-GMN, respectively) with a minimum quantifiable concentration for GTN, GDNs, and GMNs of 0.4 ng/mL in plasma, with extraction recoveries for GMNs 76% and for GTN and the GDNs 95% was developed to be used in pharmacokinetic studies [436]. Following controlled addition of GTN to human blood, the ratio of 1,2-GDN to 1,3-GDN maximum concentrations was ca. 7:1, reflecting preferential denitration of the GTN molecule at the primary positions, while the ratio of 2-GMN to 1-GMN in this system was ca. 6:1, representing a highly selective if not specific primary denitration of the 1,2-GDN molecule. Following the intravenous administration of 1,2-GDN to five healthy male volunteers, 2-GMN/1-GMN ratios averaged 8.8:1, representing a highly selective but not specific formation of 2-GMN from the 1,2-GDN molecule. The assay will find utility in *in vitro* studies attempting to address the molecular pharmacology of GTN and its metabolites and in *in vivo* clinical pharmacology studies attempting to address the relationship between pharmacokinetics of GTN and its metabolites.

A method for the quantitative analysis of NG and its dinitrate metabolites (1,2- and 1,3-GDN) in urine would first extract the analytes by liquid-liquid extraction and then analyze them by GC-MS with negative ion chemical ionization [437]. The method was able to detect 0.3 nmol/L for all analytes and was linear over the range of at least 0–44 nmol/L. The method was then used to determine metabolite levels in a subject using NG therapeutically for the treatment of angina. Metabolites were stable in urine for at least 6 d at room temperature.

An HPLC-MS method for the simultaneous determination of GTN and its active metabolites 1,2-GDN and 1,3-GDN for a range of GTN and GDN concentrations of 0.5–15 ng/mL also used BTTN as an internal standard [438]. The lower limit of quantification was about 0.01 ng on column. An application of this method was illustrated during *in vitro* studies of GTN metabolism in cultured media and human vascular smooth

muscle cells at 310 K (37 °C). With this method, the degradation half-life of GTN in rat plasma at 310 K (37 °C) was 26.8 ± 1.8 min, consistent with previous values obtained using GC instead of HPLC.

GTN, and its two main metabolites, 1,2-GDN, CAS RN [621-65-8], and 1,3-GDN, CAS RN [623-87-0], in human plasma can be analyzed using a capillary GC method with an electron-capture detector [439]. Linear calibrations were obtained for 1,3-GDN from 0.14 to 3 ng/mL, for 1,2-GDN from 0.06 to 6 ng/mL, and for GTN from 0.01 to 0.3 ng/mL in plasma samples. The calculated limits of quantification values for GTN, 1,2-GDN, and 1,3-GDN were 0.03, 0.2, and 0.15 ng/mL, respectively.

Besides 1,2-GDN, 1,3-GDN, and GMN, the nitration product 3-nitrotyrosine has been observed in human plasma or urine as a result of GTN exposure and can be used as a marker in a BEI for GTN exposure.

9.4.3.3.4 Analysis of Glycerol Trinitrate Mixtures

In many applications GTN is not used in the pure state but is desensitized by the addition of desensitizers and is stabilized by the addition of stabilizers. The contents of diluents and stabilizers must be carefully controlled by chemical analysis to maintain safe conditions. The composition of GTN/BTTN mixtures can be determined by HPLC [440].

9.4.3.4 Specifications for Glycerol Trinitrate

The purity requirements for GTN are specified in MIL-N-246B, which also contains the analytical methods recommended for the quality control of GTN [441]. This specification covers two types of NG for use in propellants: Type I uses Grade B glycerol, and Type II uses partially polymerized glycerol (diglycerin). For Type I, the nitrogen content must be 18.4% minimum. For Type II, the nitrogen content must be 17.8–17.9%. When subjected to a 355.3 K (82.2 °C) heat test, the GTN will not change the color of the standard potassium iodide starch paper in less than 10 min.

9.4.4 Toxicity of Glycerol Trinitrate

At room temperature, GTN is an oily, colorless to pale yellow liquid with a sweet, burning taste. GTN has very toxic effects following inhalation, skin contact, or ingestion [442]. It is a most useful drug to treat angina pectoris, congestive heart failure (particularly acute myocardial infarction), and hypertension. In industrial situations, inhalation of vapor by airways and skin contact are potential exposure routes. Data concerning GTN concentrations in workplace air date from the second half of the 20th century. Concentrations measured at that time in workplaces were 0.1–4.0 mg/m³. Data on human exposure indicated that blood vessel dilation is a critical effect of GTN exposure and is its major effect when used as medication. Headache, blood pressure decrease, and nausea are GTN exposure symptoms that result from blood vessel dilation. In occupational settings, these symptoms were observed in workers exposed to 0.3–4.0 mg/m³ GTN. Similar symptoms were noted in persons following dermal exposure

(patches releasing 5 mg GTN). The absorbed dose corresponds to a GTN air concentration of 0.5 mg/m^3 , assuming lung ventilation is 10 m^3 in an 8-h shift. Higher concentrations could induce depression, methemoglobinemia, and cyanosis. After decreasing workplace air GTN concentrations to 0.1 mg/m^3 (0.01 ppm), no adverse effects were observed in workers. There were no reliable data on increased human risks of coronary and cerebrovascular diseases induced by GTN. Study results were conflicting. Some cohort studies suggested the incidence of these diseases is generated by EGDN, often used together with GTN. There was also a lack of data on repeated inhalation exposure of experimental animals. In animals, methemoglobinemia and toxic liver and testes effects were observed following intragastric GTN administration in high doses. Rat and dog studies helped determine the value of no observed adverse effect level for GTN in the dose range of $25\text{--}40 \text{ mg kg}^{-1} \text{ d}^{-1}$ for systemic effects, including reproductive toxicity, which corresponded to much higher GTN concentrations in air than concentrations inducing toxic effects in humans. *In vitro* study results of its mutagenic effect have not shown strong or even slight mutagenic effects; all *in vitro* studies of mutagenic effect produced negative results. The International Agency for Research on Cancer has not classified the carcinogenicity of GTN to humans. In Germany, GTN has been categorized into Group 3B for carcinogenicity. The Scientific Committee on Occupational Exposure Limits classified GTN as a carcinogenic compound (Group C), a genotoxic carcinogen for which it is possible to set an admissible practical value based on existing data. There are no data concerning the GTN effect on the human reproductive system. In a three-generation reproductive toxicity study in rats, the F0 generation showed no effect of GTN on reproduction. Major reproduction disorders were observed in the F1 group administered the highest GTN dose, which was associated with inhibition of spermatogenesis and significant decrease in testes mass. Other studies revealed no effect of GTN on reproduction. In Germany GTN was categorized in Group C, a substance not expected to damage embryos and fetuses if the Maximum Allowable Concentration (MAC) value is strictly observed. GTN enters the body through airways and skin; its through-skin absorption capacity in humans is 68–76%. There are no data concerning airway GTN absorption. Results of occupational studies showing no adverse effects of GTN exposure at concentrations 0.095 mg/m^3 (0.01 ppm) have been suggested as the basis for setting GTN MAC values. It has been suggested to adopt a 0.095 mg/m^3 (0.01 ppm) GTN concentration as MAC value. It has been suggested that a 0.19 mg/m^3 (0.02 ppm) concentration be adopted as STEL, since irritation effects were observed in workers exposed to $\sim 0.3 \text{ mg/m}^3$ GTN.

9.4.4.1 Animal Exposure Tests with Glycerol Trinitrate

In experimental animal exposure tests, the LD₅₀ was $1888 \pm 76 \text{ mg/kg}$ (mice, male, intragastric), LD₅₀: $1055 \pm 63 \text{ mg/kg}$ (mice, female, intragastric), LD₅₀: $822 \pm 54 \text{ mg/kg}$ (rats, male, intragastric) and LD₅₀: $844 \pm 61 \text{ mg/kg}$ (rats, female, intragastric). GTN is an experimental teratogen.

The rate of resorption of GTN through the skin was measured in rats [443]. From a gelled explosive that contained 93% GTN and 7% NC, the GTN was resorbed at a rate

of $0.85 \text{ mg cm}^{-2} \text{ h}^{-1}$, which was much slower than the rate of resorption of EGDN that had been tested in earlier experiments.

9.4.4.2 Mutagenicity of Glycerol Trinitrate

GTN is mutagenic in the Ames test with *S. typhimurium* strain TA1535. GTN increased the number of His⁺ revertants to a maximum of four times over background at a GTN dose of $5 \mu\text{mol/plate}$ [444]. Hamster liver S9 enzyme depressed the toxicity of high GTN doses but increased the maximum number of revertants to five times over background at $10 \mu\text{mol/plate}$. GTN did not cause significant reversion in any of the six other *S. typhimurium* strains tested, although signs of toxicity were observed. Therefore, the mutagenicity of GTN was manifest only in the repair-deficient strain, which is responsive to single base changes. A similar mutational spectrum was seen previously with nitric oxide (NO)-releasing chemicals. This suggested that NO, which can be derived from GTN via metabolic reduction, may be responsible for GTN's mutagenic action.

9.4.4.3 Carcinogenicity of Glycerol Trinitrate

GTN was reported to induce hepatocellular carcinoma (HCC) in rats after prolonged feeding. Additional experiments were undertaken to evaluate the histogenesis and molecular biology of these tumors and the possible role of nitric oxide (NO), a GTN metabolite, in their development [445]. Male F344 rats received a single intragastric (IG) intubation of GTN (1.2 g/kg) at 6 weeks of age and/or a diet containing 1% GTN from 8 weeks of age until necropsy, i.e., for up to 78 weeks. Some animals were subjected to 2/3 partial hepatectomy at 9 weeks of age. Five sequential sacrifices (14, 32, 52, 78, and 84 weeks of age) were performed. No liver tumors developed in control rats or in rats that received GTN only by a single IG intubation. Preneoplastic foci, mainly of clear cell and mixed cell type (identified as positive for glutathione S-transferase placental form), were found from 14 weeks of age in rats receiving GTN in the diet. HCCs were seen beginning at 78 weeks of age, but only in rats receiving dietary GTN. Incidence of HCC in the latter animals was 50–75%. Most HCCs were well differentiated. The fact that tumors arose only on prolonged feeding of this potentially bioactive agent at massive doses seems consistent with a more complex mechanism involving multiple (i.e. genetic and/or epigenetic) factors in carcinogenesis by GTN.

9.4.4.4 Human Exposure Incidents and Epidemiological Studies

In a workplace environment, GTN is toxic by inhalation and absorption through skin. Several occupational exposure studies showed that skin resorption is a more likely pathway for intoxication than inhalation. It is very important to use proper gloves and replace them frequently. GTN causes severe headaches in exposed workers and a lowering of blood pressure.

Plasma GTN concentrations were studied in 12 volunteers in a gunpowder factory [446]. Serial blood samples were obtained from the cubital vein before and during work at two sites of production. High concentrations of GTN were detected in most plasma. Control specimens from a femoral vein contained much less GTN, indicat-

ing that blood in the cubital vein was enriched by dermally absorbed GTN. In the roll mill area concentrations of GTN in the cubital vein were higher than in the press area, but individual factors were also important since some workers consistently had higher concentration of GTN than others. Differences in absorption were more important than differences in the metabolism of GTN since only a small variation in disappearance rate was found after a controlled sublingual test dose of GTN given in a location away from the workplace. The major discomfort experienced was a headache that increased during working hours, but this was not significantly related to GTN concentrations in the air or in the blood from the cubital vein. The observations implied that major efforts should be made to reduce dermal contact with GTN during propellant production work.

Like the effects of EGDN in lowering the blood pressure, the body eventually develops a greater tolerance to GTN with prolonged exposure, but that does not mean that prolonged exposure is safe. An excess mortality from chronic cardio-cerebrovascular diseases among dynamite workers has been reported from the explosives industry [306]. The exposure situation with regard to EGDN and GTN during two decades in one of these factories has been correlated to epidemiological statistical evaluation data of worker medical histories. The mean 8-h TWA concentrations of nitrate esters for different job types were retroactively calculated from a large number of semiannually measured short-time samples. See also [447, 448].

9.4.4.5 Government Regulations for Maximum Allowable Glycerol Trinitrate Vapor Concentrations

The following vapor exposure limits for GTN were established by various agencies:

- ACGIH: 0.05 ppm (skin) (1994)
- NIOSH: STEL 0.1 mg/m³ (skin)
- NIOSH REL: ST 0.1 mg/m³ (skin)
- OSHA: Ceiling 0.2 ppm (skin)
- OSHA PEL: Ceiling 0.2 ppm (2 mg/m³) (skin)
- OSHA PEL-CL: 0.02 ppm (skin), TLV TWA: 0.05 ppm or 0.5 mg/m³ (skin)
- OSHA TLV-STEL: 0.1 ppm or 1.0 mg/m³ (skin).

For conversions from one unit to another, it is helpful to have the conversion factor 1 ppm = 9.29 mg/m³ @ NTP.

Based on the carcinogenicity of GTN observed in animal tests with rats, German health authorities in 2005 categorized GTN as a Category 3B carcinogen and suspended the TLV TWA of 0.005 mL/m³ that had been in effect since 1995 [449, 450]. The BEI values of 0.5 µg/L 1,2-GDN and 1,3-GDN in blood plasma were also repealed.

A very thorough summary of observed health problems in workers in dynamite and gunpowder factories is contained in the criteria document that NIOSH used to arrive at a recommended maximum allowable concentration of GTN (and EGDN) in workroom air [451].

The original NIOSH IDLH of 500 ppm was lowered by almost one order of magnitude to 75 ppm after a review of the literature and after additional data became available [452, 453]. Where data for GTN were lacking, quite often a comparison with EGDN was made to arrive at presumably safe levels of emergency exposure.

9.4.4.6 Biological Exposure Indices for Glycerol Trinitrate

Traditional practices with respect to the use of protective gloves at US Army ammunition plants that manufacture and incorporate GTN were critically reviewed, and the availability of alternate and presumably superior types of gloves was examined [454]. A literature review with respect to exposure indices suggested that it may be possible to monitor GTN exposure with GTN and/or its metabolites in plasma and urine, but that further research would be necessary before any of these control options could be routinely used. Urinary NG metabolites represented the best prospect for BEI monitoring since urine is easier to collect than plasma and is not complicated by factors such as the site of collection, which must be considered for blood. Before urine could be used for routine BEI monitoring, additional human studies of the characteristics of metabolites and the time course of their appearance/disappearance in urine during dermal exposure under controlled conditions would be necessary.

BEI monitoring to assess worker exposure workers to GTN has been difficult due to the short half-life of NG and its metabolites. A method to assess NG and its metabolites (GDNs) in urine would make biological monitoring more feasible. Samples taken from three sites using GTN, two munitions manufacturing sites and a pharmaceutical manufacturing site, were analyzed, and the samples taken at the two munitions sites contained 0.9–18 and 0–4.7 $\mu\text{mol/mol}$ creatinine, respectively, and the one at the pharmaceutical site contained 0–0.9 $\mu\text{mol/mol}$ creatinine [455]. The presence of glycerol di- and mononitrates in the urine of workers despite the use of personal protective equipment and local exhaust ventilation showed the usefulness of biological monitoring to assess the efficacy of any controls already in place and the continued potential of dermal absorption of NG.

The effects of inhaled or percutaneously administered NG on coronary flow in the coronary artery, left ventricular pressure, and ECG in dogs was measured by Doppler flow probes and implantable pressure transducers [456, 457]. It was shown that dogs exposed to NG by inhalation suffered pressure drop symptoms slightly, but that dogs treated percutaneously with 1.0 g NG daily did not show symptoms. The percutaneous treatment produced marginal changes in pressure and flow, slowing of the heart rate, and a progressive deterioration of the ECG patterns. Studies on uptake of tritiated NG confirmed that NG was absorbed through the skin, but later it could not be detected in the blood.

9.4.5 Safety and Hazard Properties of Glycerol Trinitrate

There have been numerous explosion accidents in the manufacture, transportation, and usage of GTN [458]. The strand burning of liquid GTN will be discussed in *Encyclopedia of Monopropellants*.

9.4.5.1 Drop Weight Impact Sensitivity of Glycerol Trinitrate

The drop weight impact sensitivity of GTN in the BAM tester is $0.02 \text{ kg m} = 0.2 \text{ N m}$ [74].

The impact sensitivity of liquid NG (50% point) was observed to be near 1.8 kg-cm or $3.3 \times 10^3 \text{ J/m}^2$ [459]. The impact sensitivity of solid NG (50% initiation level) was observed by extrapolation to be near 200 kg-cm or $4.4 \times 10^5 \text{ J/m}^2$. The impact sensitivity of a mixture of solid and liquid GTN was comparable to solid GTN at the two stimulus levels tested. Thus, the presence of solid GTN reduces the impact sensitivity of liquid GTN. See also [263, 460].

9.4.5.2 Shock Sensitivity of Glycerol Trinitrate Mixtures

The shock sensitivity of GTN and other liquid explosives depends on the shock pressure and the sonic velocity of the medium [461]. It may also depend on the amount of gas saturation and bubbles release of the liquid.

9.4.5.3 Card Gap Sensitivity of Glycerol Trinitrate Mixtures

Low-velocity reactions can often be observed in containers of high sound velocity such as glass, iron, and aluminum ($5000\text{--}6000 \text{ m/s}$) but not in containers of low sound velocity, like lead and Lucite (1200 and 2500 m/s , respectively). Copper was observed to be intermediate in sound velocity (3500 m/s). The container material affects the results of detonability testing.

While both GTN and EGDN by themselves are used as plasticizing agents for double-base propellants, it was hoped that mixtures of the two nitrates would be less sensitive and less prone to accidental explosions during processing of double-base propellants. Studies were conducted at 298 K (25°C) with a 50–50 mixture of GTN and EGDN (GTN-EGDN) in approximately 1-in.-ID $\times$ 16-in. L steel or aluminum containers of varying wall thicknesses [462]. The card gap was plotted as a function of wall thickness of the containment vessel. For 50-50 GTN-EGDN the gap versus wall thickness relationship for high-velocity detonation (approximately 7500 m/s) was found to have a negative slope in both steel and aluminum containers, as with other liquid explosives. Low-velocity reactions (approximately 2000 m/s or less) were obtained with NG-EGDN in 0.51-, 0.89-, and 3.4-mm (0.020-, 0.035-, and 0.133-in.) wall thicknesses at gaps up to and including 30.5 cm (12 in.), and data points were scattered all over the graph. The detonation velocity with zero gap was 7550 m/s .

9.4.5.4 Friction Sensitivity of Glycerol Trinitrate

Testing the friction sensitivity of GTN in the BAM friction sensitivity test apparatus was somewhat surprising in that no reaction was observed at the maximum load of the machine with a pistil load of 353 N [74].

9.4.6 Disposal of Glycerol Trinitrate

The epoxides glycidol and GLYN are formed during chemical desensitization of GTN-containing waste streams with calcium hydroxide [463]. The epoxide rings of both

compounds are unstable to heat in aqueous solutions and the rings open up to form glycerol 1-mononitrate and some glycerol. These transformations are accelerated by microbiological activity. Glycerol 1-mononitrate is slowly denitrated to form glycerol. Glycidol and GLYN caused base pair substitutions in the Ames test for mutagenicity while glycerol 1-mononitrate tested negative.

The safe disposal of spent acid from the manufacture of GTN is a major environmental challenge. It is not sufficient to simply dilute and neutralize the spent acid before releasing it to surface water since it contains some GTN that was dragged over from the separator.

9.4.7 Biodegradation of Glycerol Trinitrate

GTN spilled on the ground or leached from abandoned propellants and soaking into the soil will deteriorate naturally by bacterial action. GTN is biotransformed through a series of successive denitration steps, including GDN and GMN isomers, with each successive step slower than the previous step [395, 396, 464]. Glycerol is mineralized by biological systems. Glycidol and glycidol nitrate, formed by the chemical desensitization of GTN, are also mineralized. The biotransformation pathway of these compounds proceeds from GLYN to 1-mononitrate to glycerol, with slower rates at each succeeding step.

One method to reduce environmental pollution from GTN in wastewater from explosives and propellant factories would be to treat the water in holding ponds with active bacteria cultures capable of reducing GTN and hydrolysis products.

Bacteria capable of metabolizing GTN were isolated under aerobic and nitrogen-limiting conditions from soil, river water, and activated municipal sewage sludge [465]. One of these strains, from sewage sludge, chosen for further study was identified as *Agrobacterium radiobacter* subgroup B. A combination of HPLC and NMR analyses of the culture medium during the growth of *A. radiobacter* on basal salts-glycerol-GTN medium showed the sequential conversion of GTN to GDNs and GMNs. Isomeric glycerol 1,2-dinitrate and glycerol 1,3-dinitrate were produced simultaneously and concomitantly with the disappearance of GTN, with significant regioselectivity for the production of the 1,3-dinitrate. Dinitrates were further degraded to glycerol 1- and 2-mononitrates, but mononitrates were not biodegraded. Extracts of broth-grown cells contained an enzyme which in the presence of added NADH converted GTN stoichiometrically to nitrite and a mixture of GDNs. The specific activity of this enzyme was increased 160-fold by growth on GTN as the sole source of nitrogen.

Four axenic bacterial species capable of biodegrading GTN were isolated from soil samples taken from a wash water soakaway at a disused GTN manufacturing plant [466]. The isolates were identified by 16S rRNA gene sequence homology as *Pseudomonas putida*, an *Arthrobacter* species, a *Klebsiella* species, and a *Rhodococcus* species. Each of the isolates utilized GTN as its sole nitrogen source and removed

nitro groups sequentially from GTN to produce GDNs and mononitrates (GMN), with the exception of the *Arthrobacter* strain, which achieved removal of only the first nitro group within the time course of the experiment. The *Klebsiella* strain exhibited a distinct preference for the removal of the central nitro group from GTN, while the other five strains exhibited no such regioselectivity. All strains that removed a second nitro group from glycerol 1,2-dinitrate showed regiospecific removal of the end nitro group, thereby producing glycerol 2-mononitrate. Most significant was the finding that the *Rhodococcus* species was capable of removing the final nitro group from GMN and thus achieved complete biodegradation of GTN. Such complete denitration of GTN was previously shown only in mixed bacterial populations and in cultures of *Penicillium corylophilum* supplemented with an additional carbon and nitrogen source. This was the first report of a microorganism that can achieve complete denitration of GTN.

During a study of the reactions of the old yellow enzyme and reduced flavins with organic nitrate esters, it was found that reduced flavins reacted readily with GTN and PGDN, with rate constants at pH 7.0, 298 K = 25 °C of 145 and 5.8 mol⁻¹ s⁻¹, respectively [467]. With GTN, the secondary nitrate was removed reductively six times faster than the primary nitrate, with liberation of nitrite. With PGDN, on the other hand, the primary nitrate residue was three times more reactive than the secondary residue. In the old yellow enzyme-catalyzed NADPH-dependent reduction of GTN and PGDN, rapid-reaction studies of mixing reduced enzyme with the nitrate esters showed that a reduced enzyme-substrate complex is formed before oxidation of the reduced flavin. The rate constants for these reactions and the apparent K_d values of the enzyme-substrate complexes revealed that the rate-limiting step in catalysis is a reduction of the enzyme by NADPH. Reduction of the primary nitrate in both GTN and PGDN was favored by comparison with the free-flavin reactions. See also [468, 469].

9.4.8 Transportation of Glycerol Trinitrate

In pure form, GTN is too sensitive and unstable for indefinite storage or transport and must be quickly used as soon as it is received or produced. GTN is not usually transported but used immediately at the location of its production. Transportation of GTN makes for a good plot element in thrillers such as *The Wages of Fear* (*Le Salaire de la peur*, 1953 [470]), one of the author's favorite movies. The consequences of explosion of a truckload of GTN destined for snuffing out a burning oil well were graphically illustrated.

For shipment, GTN must be desensitized with not less than 40% of a non-volatile, water-insoluble phlegmatizer per UN 0143.

9.4.9 Explosive Performance of Glycerol Trinitrate

The detonation velocity of GTN at a density of 1.59 g/cm³ is 7750 m/s. Detonations in GTN can propagate by LVD [328].

9.5 Glycerol Dinitrate

The two glycerol dinitrates, also known as GDN, dinitroglycerin, glycerol dinitrate, $C_3H_6N_2O_7$, isomers may be found as contaminants in GTN due to incomplete nitration or premature hydrolysis or partial biodegradation and digestion. GDN is also made deliberately as a less-sensitive additive to propellant formulations. It is the raw product from which GLYN can be made by dehydration, which is then used to make polyGLYN, an energetic binder. 1,2-GDN is prepared by the nitration of glycerol with nitric acid, but such nitrations mostly yield mixtures of di- and trinitroglycerin. 1,2-GDN is a product of GTN metabolism where GTN was used as a medication to lower blood pressure. The metabolic products are 1,2-GDN, CAS RN [621-65-8], 1,3-GDN, CAS RN [623-87-0], and 1-GMN, CAS RN [624-43-1].

9.5.1 Physical Properties of Glycerol Dinitrate

The molecular mass of GDN is 182.1 g/mol. GDN is a viscous liquid that freezes at 243 K ($-30^\circ\text{C} = -22^\circ\text{F}$). The density of the liquid at room temperature is 1.51 g/cm^3 .

9.5.2 Chemical Properties of Glycerol Dinitrate

GDN is a viscous liquid but is more volatile and more soluble in water than GTN. It is hygroscopic and may be used as a gelatinizer of certain types of nitrocellulose in the preparation of double-base propellants. It is thermally more stable than GTN. Its vapors are just as toxic as GTN's and cause headaches.

While GTN is oxygen rich, its less nitrated precursor GDN is underoxidized and the oxygen balance is -17.58% for combustion to CO_2 .

9.5.2.1 Analysis of Glycerol Dinitrate

The historically used methods for the determination of GTN in cordite are not specific for that particular ester of nitric acid; the reagents will act in the same way on every organic nitrate, including the dinitrate of diethylene glycol. The isolation of the free polyvalent alcohol by reductive hydrolysis with alkali sulfite and their identification through crystalline derivatives are tedious and would lead to complications when mixtures of two nitrates are present. A comparison of IR spectra of NG and DEGDN showed that while either will exhibit the same absorption bands characteristic of the C—O—NO_2 group, only in the latter is the ether group C—O—C present. The ether group has a specific absorption at about 1130 cm^{-1} . Analysis of the spectra showed that both substances have a common IR absorption band between 1270 and 1280 cm^{-1} [NG 1273 cm^{-1} ($7.68\mu\text{m}$), DEGDN 1278 cm^{-1} ($7.3\mu\text{m}$)], and that only DEGDN shows an additional peak at 1140 cm^{-1} ($8.77\mu\text{m}$). This absorption band can, therefore, serve to indicate the presence of DEGDN in propellant mixtures that contain both NG and DEGDN [471].

9.5.3 Explosive Properties of Glycerol Dinitrate

The drop weight impact sensitivity in the BAM machine is 1.5 Nm, less sensitive than GTN, which has a 50% chance of ignition at a stimulus of only 0.2 Nm. If initiated to explosion in the lead block test, the resulting cavity volume is 450 cm³/10 g. Other sources give the lead block indentation as 500 cm³, which is 82% of that of GTN.

10 C₄ Alkyl Polynitrates

10.1 1,3-Butanediol Dinitrate

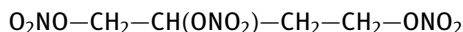
1,3-Butanediol dinitrate, also known as 1,3-butylene glycol dinitrate, C₄H₈N₂O₆, BDN, BDDN, CAS RN [6423-44-5], is a colorless oily liquid, with a density of 1.32 g/cm³, insoluble in water, but soluble in most solvents that are also used for GTN. It is more volatile than GTN. Nitrocellulose is readily gelatinized. The nitrate is very easily destroyed by oxidation, and sometimes the reaction mixture during its attempted synthesis decomposed generating heat and nitrous gases. The product cannot be obtained under industrial conditions and for this reason has not found any practical applications.

1,3-Butanediol dinitrate is a powerful explosive with a lead block cavity enlargement of 370 cm³/10 g. The flame reactions of the two isomeric dinitrates of butanediol have been investigated [472].

The structural isomer 1,4-butanediol dinitrate, CAS RN [3457-91-8], could not be made to explode when tested for impact sensitivity in comparison to GTN and other energetic liquids [263].

10.2 1,2,4-Butanetriol Trinitrate

The most common C₄ energetic plasticizer is 1,2,4-butanetriol trinitrate (BTTN), butane-1,2,4-triyl trinitrate, C₄H₇N₃O₉, BTTN, CAS RN [6659-60-5], *M* = 241.1131. BTTN is essentially a GTN with an extra methylene group inserted between two of the carbons that bear nitroxy groups:



The additional methyl group makes the molecule less reactive than GTN. BTTN is a pale yellow oily liquid with a density of 1.52 g/cm³ and a solidification point of 246 K = -27 °C = -17 °F. It has a lower vapor pressure than GTN and was sometimes used in double-base propellants intended for operation in tropical climates where NG might have bled (=exuded) out of the propellant grains during storage.

Less frequently used isomers of 1,2,4-butanetriol trinitrate are 1,2,3-butanetriol 1,2,3-trinitrate, α-methylglycerol trinitrate, O₂NOCH₂CH(ONO₂)CH(ONO₂)CH₃, CAS RN [84002-64-2], with a density of 1.489 g/cm³ at 293 K (20 °C) and 1,3-propanediol,

2-[(nitrooxy)methyl] dinitrate = trimethylolmethane trinitrate $\text{O}_2\text{NOCH}_2\text{CH}(\text{CH}_2\text{ONO}_2)=\text{CH}_2\text{ONO}_2 = \text{CH}(\text{CH}_2\text{ONO}_2)_3$, CAS RN [82975-75-5].

10.2.1 Physical Properties of 1,2,4-Butanetriol Trinitrate

The physical properties of BTTN are summarized in Table 56. See also [473, 474].

Table 56: Physical properties of 1,2,4-butanetriol trinitrate.

Property	SI units	Other units	References
Molecular mass	241.1131	241.1131	[73]
Freezing point	246 K	$-27^\circ\text{C} = -17^\circ\text{F}$	Manufacturer's data sheet
Melting point	267.2 K	-5.9°C	[407]
Boiling point	503 K	446 °F	Manufacturer's data sheet
Density at 293 K	1.52 g/cm ³		Manufacturer's data sheet
Vapor pressure	0.147 Pa @ 293 K	0.0011 mm Hg at 20 °C	Manufacturer's data sheet
Viscosity at 293 K	0.059 N s m ⁻²	59 cPs	Manufacturer's data sheet
Refractive index n_D^{25}	1.4738		Manufacturer's data sheet
Heat of formation		-386 cal/g	[377]
Heat of formation	-374.5 kJ/mol	$-371.2 \text{ kcal/kg} =$ -89.5 kcal/mol	[74]
Heat of formation	-414 kJ/mol	-98.9 kcal/mol	[302]
Heat of combustion, solid	2176 kJ/mol	520.2 kcal/mol	[302]
Heat of combustion, liquid	2311 kJ/mol	552.3 kcal/mol	[302]

Most previously published data on freezing points of nitrate esters were obtained by freezing point measurements instead of melting point measurements. These data tend to be low because of the strong tendency for nitrate esters to supercool and also because of low-melting-point, metastable, allotropic crystal formation by the pure materials. The melting points of stable-form, nitrate ester crystals were measured by DSC and confirmed by visual observations [407]. These data were already shown in Table 51 in the GTN section of this book. Similar data were obtained on GTN/BTTN and TMETN/BTTN mixtures.

Many alkyl nitrates and polynitrates have a tendency to supercool and don't crystallize voluntarily. Therefore, it is difficult to determine a freezing point by cooling a liquid sample. A systematic study was conducted of four nitrate esters, GTN, BTTN, TMETN, and TEGDN, which are used to better control the crystallization phenomena of plasticizers in propellants [406]. The tests were conducted to determine the melting characteristics of these four frozen compounds and to compare new measurements to the old data in the literature, which were sometimes incomplete or unreliable. The influence of temperature on the rate of crystal growth was studied for four nitric esters by visual observation, and nucleation was specifically considered for GTN and

TMETN, the two nitrate esters that exist in allotropic modifications and may form two crystallographic different varieties, depending on the mode of nitration and the temperature/time history. The melting point of frozen BTTN was 263 K (−10 °C), and the heat of fusion was 15.1 kJ/mol = 63 J/g = 3.62 kcal/mol = 15 cal/g.

10.2.2 Chemical Properties of 1,2,4-Butanetriol Trinitrate

10.2.2.1 Thermal Stability of 1,2,4-Butanetriol Trinitrate

The steady-state combustion of BTTN has been modeled using a one-dimensional model and detailed kinetics [475, 476]. A global decomposition reaction for the condensed phase has been postulated based on experimental data and the evaporation of BTTN was included in the model. A detailed gas-phase kinetic mechanism consisting of 534 reactions and 83 species has been used. The combustion has been modeled over a pressure range of 5–100 atm and initial temperatures of 298 ± 50 K. The calculated combustion characteristics included the burning rate, pressure exponent, temperature sensitivity, surface and flame temperatures, temperature and species profiles, and condensed- and gas-phase heat release. The calculated values were compared to the available experimental data on BTTN and other similar nitrate esters. The strand burning rates of BTTN and BTTN mixtures will be discussed in *Encyclopedia of Monopropellants*.

There are three different locations of the —ONO₂ groups in the molecular structure of BTTN: α-O—NO₂, β-O—NO₂, and δ-O—NO₂. The cleavage of each of the three O—NO₂ bonds must be considered when building a model of the decomposition of BTTN. In addition to the dissociation of the O—NO₂ bond, there will be a competitive HONO elimination one NO₂ group from BTTN. Therefore, six possible competitive initial decomposition pathways of BTTN must be considered. Homolysis of one of the O—NO₂ bonds occurs to form •NO₂ and CH₂ONO₂CHONO₂CH₂CH₂O•, which subsequently decomposes to form CH₃CHO + •CHO + 3NO₂ + HCHO. In the second, successive HONO elimination reactions yield three HONO and OHCCH₂CHONO₂CH₂ONO₂ fragments, which subsequently decompose to form CH₃CHO + 2CO + 3HONO. The first pathway has a slightly lower activation energy than the second. The results showed that the pathway involving O—NO₂ cleavage is slightly more energetically favorable than that involving HONO elimination. Computations gave the BDEs required for the departures of α-NO₂, β-NO₂, and δ-NO₂ as 139.81, 140.46, and 132.15 J/mol, respectively [477]. Thus, it became apparent that the homolytic cleavage of δ-O—NO₂ would be preferred in the decomposition of BTTN. For HNO elimination, the activation energies of the three possible elimination pathways were 156.65, 153.77, and 149.37 J/mol, respectively. Again, this showed that the cleavage of δ-O—NO₂ is preferred in the decomposition of BTTN.

10.2.2.2 Reactions of 1,2,4-Butanetriol Trinitrate

The supermolecular systems of BTTN with polyethylene glycol (PEG), HTPB, glycidyl azide polymer (GAP), poly(3-azidomethyl)-3-methyl-oxetane (AMMO), and poly(3,3-bis(azidomethyl)-oxetane) (BAMO) were calculated by semiempirical molecular orbital theory methods [478]. The binding energies of the optimized geometrical structures were obtained with dispersion energies being corrected. The binding energies (absolute values) of BTTN with HTPB and AMMO increased as the molecular chain of polymers increased. However, there was a deviation from the preceding rule on the binding energies of BTTN with BAMO, GAP, and PEG with increases in the molecular chain. The binding energies of BTTN with GAP, AMMO, and BAMO were slightly larger than those of BTTN with the other two polymer binders (PEG and HTPB).

10.2.2.3 Analysis of 1,2,4-Butanetriol Trinitrate

Impurities in the raw material 1,2,4-butanetriol and in the finished product 1,2,4-BTTN can be analyzed by ion chromatography (IC), HPLC, NMR, capillary GC, and GC/MS [479].

A GC method for the separation and quantitative determination of glycerol and 1,2,4-butanetriol conitration products by a method using external standard calibration achieved a relative standard deviation of less than 1% [480, 481].

10.2.3 Handling of 1,2,4-Butanetriol Trinitrate

BTTN must be diluted to a maximum of 80% BTTN with methylene chloride for shipment. It can be shipped under a limited-time exemption permit as a Class A, Type 8 high explosive liquid (Federal Register 59, #249:67395, Dec. 29, 1994). A stabilizer is not required, but 2-NDPA or ethyl centralite can be added prior to shipment on special request.

10.2.4 Toxicity of 1,2,4-Butanetriol Trinitrate

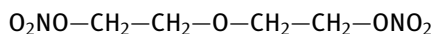
In parallel tests with 1,2,4-butanetriol 1,2,4-trinitrate by oral gavage to rats, the LD50 was 1587 mg/kg in one test and 1027 mg/kg in another test.

10.2.5 Explosive Properties of 1,2,4-Butanetriol Trinitrate

The drop weight impact sensitivity of BTTN as determined in the Bureau of Mines apparatus with a 2-kg mass was 58 cm. In the Picatinny Arsenal apparatus, the sensitivity was 25 mm (1 in.) with a 2-kg mass. In a ballistic mortar, the performance of BTTN was 137% of that of TNT.

10.3 Diethylene Glycol Dinitrate

Diethylene glycol dinitrate, also known as DEGDN, C₄H₈N₂O₇; ethanol, 2,2'-oxybis-, dinitrate; diglycol dinitrate, CAS RN [693-21-0], is a highly energetic material that can be used either as an explosive by itself or, most often, as an energetic plasticizer in double-base solid propellants. It is slightly underoxidized with an oxygen balance of -40.8%:



DEGDN was used extensively in WWII by the German side as one of the main components of double-base propellants [482]. Fedoroff, *Encyclopedia of Explosives and Related Items*, Vol. 5, contains only relatively little information on DEGDN on pages D1232-D1233.

One book on liquid explosives contains illustrations of equipment used for production of DEGDN [39].

10.3.1 Physical Properties of Diethylene Glycol Dinitrate

The physical properties of DEGDN are summarized in Table 57. See also [483, 484].

Table 57: Physical properties of DEGDN.

Property	SI units	Other units	References
Molecular mass	196.1155 g/mol	5.099 mol/kg	[73]
Freezing point, stable modification	275 K	2 °C	35.6 °F
Freezing point, unstable modification	262.2 K	-10.9 °C	+12.4 °F
Melting point, stable modification	276.4 K	3.3 °C	[407]
Density at 293 K	1.38 g/cm ³		[74]
Density at 289 K	1.3890 g/cm ³		[10]
Specific gravity 15/15 °C	1.3908 g/cm ³		[15]
Vapor pressure at 20 °C (68 °F)	480 Pa	0.0048 mbar	[74]
Vapor pressure at 60 °C (140 °F)	17 kPa	0.17 mbar	[74]
Viscosity		8.1 cPs at 20 °C	Manufacturer's Datasheet
		13.3 cPs at 6 °C	[10]
		7.27 at 20.4 °C	[10]
		3.37 at 54.4 °C	[10]
Refractive index n_D^{25}	1.4498		[74]
Refractive index n_D^{21}	1.4505		[10]

The vapor pressure of DEGDN is shown in Table 58 in comparison to that of PGDN and trimethylene glycol dinitrate.

Table 58: Vapor pressure of DEGDN and other glycol polynitrates.

Temperature, K	288	288	298	298	308	308	318	318	328	328
Temperature, °C	15	15	25	25	35	35	45	45	55	55
Vapor pressure	Pa	mm Hg	Pa	mm Hg	Pa	mm Hg	Pa	mm Hg	Pa	mm Hg
Diethylene glycol dinitrate	0.29	0.0022	0.79	0.0059	1.97	0.0148	3.8	0.0284	12	0.0867
1,2-Propylene glycol dinitrate	5.15	0.0386	13.1	0.0984	33.8	0.2532	66.1	0.4955	133	0.9951
Trimethylene glycol dinitrate	1.55	0.0116	5.31	0.0398	8.28	0.0621	19.5	0.1466	43	0.3222

Data source: [15]

The solubility of DEGDN in water is 0.40 g/100 g water at 298 K. The IR spectrum of DEGDN is shown in Figure 31.

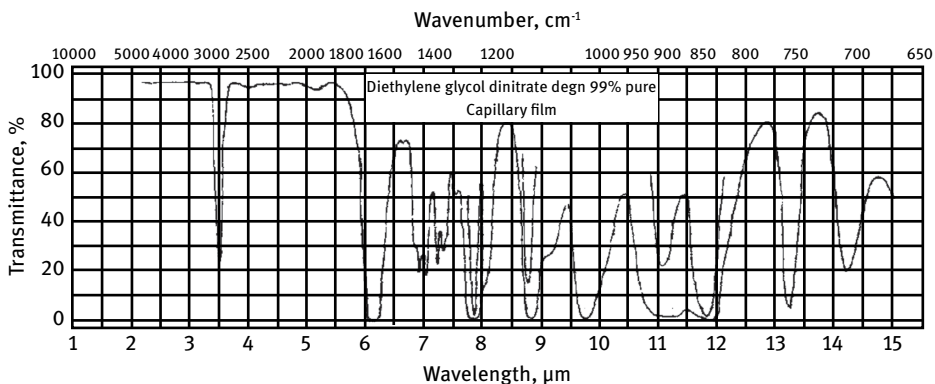


Figure 31: IR spectrum of DEGDN. (From [296].)

The IR spectra of DEGDN and six other dinitrate esters were computed by a DFT method [297].

A Raman spectrum of DEGDN in comparison to the spectra of TMETN and PGDN was shown in [26].

10.3.1.1 Thermodynamic Properties of Diethylene Glycol Dinitrate

The thermodynamic properties of DEGDN are summarized in Table 59.

Table 59: Thermodynamic properties of DEGDN.

Property	SI units		Other units		References
Enthalpy of formation at 298 K, liquid	-433 kJ/mol	-2208 kJ/kg	-103.5 kcal/mol	-528 kcal/kg	[74]
Enthalpy of formation at 298 K, liquid	-451.0 kJ/mol	-2300 kJ/kg	-107.8 kcal/mol	-550 cal/g	[73]
Enthalpy of formation at 298 K, liquid	-426.7 kJ/mol	-2176 kJ/kg	-102.0 kcal/mol	-520 cal/g	[377]
Enthalpy of formation at 273 K, solid	-476.1 kJ/mol	-2428 kJ/kg	-113.8 kcal/mol	-580 cal/g	[377]
Enthalpy of formation at 298 K, liquid	-436.7 kJ/mol	-2227.3 kJ/kg	-104.4 kcal/mol	-532.3 cal/g	
Enthalpy of formation at 273 K, solid	-476.1 kJ/mol	-2428 kJ/kg	-113.8 kcal/mol	-580 cal/g	[337]
Heat of combustion, liquid	2291 kJ/mol	11682 kJ/kg	547.6 kcal/mol		[302]
	2261 kJ/mol	11529 kJ/kg	540.4 kcal/mol		[302]
	2291 kJ/mol	11682 kJ/kg	547.6 kcal/mol		[291]
Heat of evaporation, 293–333 K	94.3 kJ/mol		22.5 kcal/mol	115 kcal/kg	[338]
Heat of fusion at 276.5 K	25.4 kJ/mol		6.07 kcal/mol	30.9 kcal/kg	[73]

The heat capacities of liquid, glassy, and crystalline DEGDN were measured in a vacuum adiabatic calorimeter in the range 80–320 K [485]. Two crystal modifications were identified, and their melting points and enthalpies were determined. The $H_0(T) - H_0(0)$, $S_0(T)$, and $G_0(T) - H_0(0)$ thermodynamic functions of crystalline and liquid DEGDN were calculated in the range 0–320 K.

10.3.1.2 Magnetic Properties of Diethylene Glycol Dinitrate

A complete analysis of the ¹H NMR spectra of 21 nitrate esters including DEGDN and GTN was not possible [27]. A small number, like the corresponding fluorides, gave deceptively simple spectra. In others the resolution was not sufficient to allow all the NMR parameters to be evaluated. It would be difficult to use NMR in the analysis of nitrate ester mixtures.

10.3.1.3 Molecular Structure of Diethylene Glycol Dinitrate

A DFT method was used to study the geometric and electronic structures and pyrolysis mechanisms of six dinitrate esters including DEGDN (DEGDN), TEGDN, Tetra-EGDN, pentaethylene glycol dinitrate (Penta-EGDN), and hexaethylene glycol dinitrate (Hexa-EGDN) [297]. The IR spectra of these compounds were obtained and the bands were assigned by vibrational analysis. Based on the principle of statistic thermodynamics, the thermodynamic properties were evaluated, which were linearly related to the number of repetitive $\text{CH}_2\text{CH}_2\text{O}$ groups as well as the temperature, showing good group additivity. The thermal stability and the pyrolysis mechanism of the dinitrate esters were investigated by calculating the BDEs. For the nitrate esters, the $\text{O}-\text{NO}_2$ bond is a trigger bond during a thermolysis initiation process. In the series $\text{O}_2\text{NO}-[\text{CH}_2\text{CH}_2\text{O}]_n\text{CH}_2\text{CH}_2\text{ONO}_2$, the enthalpy of formation ΔH_m increases on an average by 10.45 kJ/mol for each $\text{CH}_2\text{CH}_2\text{O}$ group that is added, which showed good group additivity of thermodynamic functions.

The interactions between nitrate plasticizer ingredients GTN, DEGDN, and TEGDN were investigated theoretically and experimentally [486]. DFT and second-order perturbation theory (MP2) calculations showed that intermolecular $\text{N}-\text{O}$ electrostatic interactions and hydrogen bonding between alkyl hydrogens and oxygen atoms govern the dimer structures, which predicted binding energies ranging from 20.6 to 39.3 kJ/mol. Vibrational frequencies observed in the nitrate band fingerprint region of the IR spectra were in good agreement with the DFT scaled harmonic frequencies. The relative volatility observed in thermogravimetric analysis (TGA) measurements of the pure ingredients, and their 1:1 mixtures showed reasonable correlation with the DFT dimer binding energies. The similarity in the dimer binding energies of all three plasticizers suggested that their mixtures should be uniformly miscible.

10.3.2 Chemical Properties of Diethylene Glycol Dinitrate

DEGDN is miscible at ordinary temperatures with GTN, EGDN, ether, acetone, methanol, chloroform, and benzene. It is not miscible with ethanol and is sparingly soluble in carbon tetrachloride. It has a low hygroscopicity and is sparingly soluble in water but more soluble in water than GTN. Its vapors produce headaches, though not as strong as those produced by EGDN vapors.

10.3.2.1 Decomposition of Diethylene Glycol Dinitrate

The thermal stability and thermal decomposition properties of four alkyl nitrates, including DEGDN and TEGDN, was examined by ARC under adiabatic conditions [185]. The onset temperature, the initial temperature rise rate and the maximum temperature rise rate were recorded. The apparent activation energy and preexponential factors of the thermal decomposition were calculated. The self-accelerating decomposition temperatures (SADT) of four nitrates in three different containers (4.5-L iron drum, 25-L iron drum, and 210-L fiber drum) were calculated. It was concluded that the on-

set temperatures of TEGDN and DEGDN were 423.7 and 423.7 K (both 150.6 °C), respectively, while the maximum temperature rise rates of TEGDN and DEGDN were 59.7 and 209.8 °C/min, with the apparent activation energy of TEGDN and DEGDN being 226.4 and 214.5 kJ/mol. The thermal stability of the four nitrates was ranked (from worst to best): DEGDN TEGDN NPN IPN.

10.3.3 Safety Properties of Diethylene Glycol Dinitrate

10.3.3.1 Toxicity of Diethylene Glycol Dinitrate

As of 1983, the completeness of health and toxicity information on three widely used energetic plasticizers (DEGDN, TEGDN, and TMETN) left some to be desired, and the need for additional research was outlined [487].

10.3.3.1.1 Oral Toxicity of Diethylene Glycol Dinitrate

The acute oral toxicity of DEGDN was determined in rats by the oral gavage single-dose method [488]. The LD₅₀ was 990.4 ± 30.0 mg/kg for male rats and 753.1 ± 35.9 mg/kg for female rats. Similar tests in mice indicated an LD₅₀ of 1395 ± 59 mg/kg for male mice and 1321 ± 74 mg/kg for female mice [489]. Clinical signs produced by DEGDN intoxication included twitching, tremors, hypertonia, squinting, lacrimation, depression of grasping and righting reflexes, jumping, increased startle reflex, ataxia, cyanosis, and prostration. The extent of the neurotoxic component of these clinical signs suggested that DEGDN possesses additional pharmacological properties in addition to those routinely associated with other nitrate esters. Most animals were exhibiting signs within 2 h after dosing and had either perished or cleared by 72 h after dosing.

10.3.3.1.2 Dermal Toxicity of Diethylene Glycol Dinitrate

The acute dermal toxicity of DEGDN was evaluated in rabbits by applying DEGDN topically to the clipped dorsal skin surface under a semioclusive wrap for 24 h [490]. A limit dose of 2 g/kg did not produce deaths or clinical (systemic or dermal) signs during the 2-week observation period that could be attributed to administration of DEGDN.

In a similar test, the primary dermal irritation potential of DEGDN was determined in rabbits using a modified Draize procedure with a 4-h application period [491] or in guinea pigs [492]. Neither edema nor erythema, or any other recognizable skin reaction, was detected at any time during the 72-h observation period. Similar tests were conducted for triethylene glycol dinitrate (Section 12.1.4.1).

The DEGDN eye irritation potential was evaluated in rabbits using a modified Draize method [493]. DEGDN produced no irritation upon direct contact with the eye. Slight iridial vasodilation and slight conjunctival vasodilation and swelling, indicative of mild inflammation, were the most serious responses observed. DEGDN was classified as a non-irritant under conditions of this study.

10.3.3.1.3 Mutagenicity of Diethylene Glycol Dinitrate

DEGDN was not mutagenic under conditions of the Ames *Salmonella*/mammalian microsome mutagenicity testis test with doses ranging from 5 to 0.0016 $\mu\text{L}/\text{plate}$ [494].

10.3.4 Explosive Properties of Diethylene Glycol Dinitrate

10.3.4.1 Impact Sensitivity of Diethylene Glycol Dinitrate

The drop weight impact sensitivity of DEGDN is 0.1 Nm, which is on the same order of magnitude as that of GTN. In the Picatinny apparatus with a 2-kg mass the impact sensitivity was 100 cm. DEGDN could be made to explode when tested for impact sensitivity in comparison to GTN and other energetic liquids [263].

10.3.4.2 Adiabatic Compression Sensitivity of Diethylene Glycol Dinitrate

In a U-tube adiabatic compression sensitivity test apparatus with variable, preselected push pressure, and constant bubble size, the push pressure required to explode DEGDN was higher than that of methyl nitrate or GTN, but similar to that of EGDN [111].

10.3.5 Explosive Performance of Diethylene Glycol Dinitrate

In the lead block test, explosion of 10 g DEGDN will widen the cavity to hold 410 cm^3 of water. The detonation velocity of unconfined DEGDN is 6600 m/s at a density of 1.38 g/cm^3 .

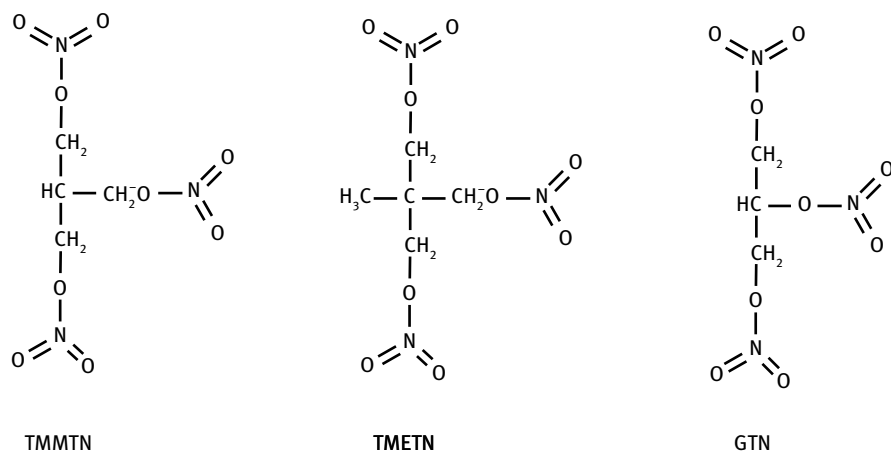
Mixtures of DEGDN with nitric acid exist during the nitration of diethylene glycol and may be more detonable than the product itself. The detonation of mixtures of concentrated (94–100%) nitric acid with DEGDN was studied, and the detonation failure diameter was measured in glass tubes [495]. The critical diameter of a stoichiometric mixture of nitric acid with DEGDN was 1 mm.

A DFT method was used to predict the explosive performance of six dinitrate esters including DEGDN, TEGDN, Tetra-EGDN, Penta-EGDN, and Hexa-EGDN [297]. Detonation performances were evaluated by the Kamlet-Jacobs equations based on the calculated densities and heats of formation. It was found that density, detonation velocity, and detonation pressure decreased with the increase in the number of $\text{CH}_2\text{CH}_2\text{O}$ groups. The predicted detonation velocity of DEGDN at a density of 1.59 g/cm^3 was 7.78 km/s, and the detonation pressure was 24.89 GPa, compared to 8.96 km/s and 35.03 GPa for EGDN.

10.4 Trimethylolmethane Trinitrate

Trimethylolmethane trinitrate, also known as 1,3-propanediol, 2-[(nitrooxy)methyl] dinitrate, 2-[(nitrooxy)methyl]propane-1,3-diyl dinitrate, $\text{C}_4\text{H}_7\text{N}_3\text{O}_9$, TMMTN, $\text{O}_2\text{NO}-\text{CH}_2\text{CH}(\text{CH}_2\text{ONO}_2)\text{CH}_2\text{ONO}_2 = \text{CH}(\text{CH}_2\text{ONO}_2)_3$, CAS RN [82975-75-5], has been syn-

thesized as an experimental chemical, but due to the limited availability of the parent polyol, TMMTN has not yet found widespread application as an energetic plasticizer. It is not to be confused with methyltrimethylolmethane trinitrate, which will be described subsequently in Section 11.1. TMMTN is an isomer of BTTN. Since a non-energy-contributing methyl group has been removed, the oxygen balance and energy content of TMMTN is improved over that of the homolog TMETN. All nitrate groups in TMMTN are connected to a primary carbon atom. The weak link in GTN is the nitrate group on the central, secondary carbon atom. TMMTN does not have such a nitrate group and thus should be thermally more stable than GTN:

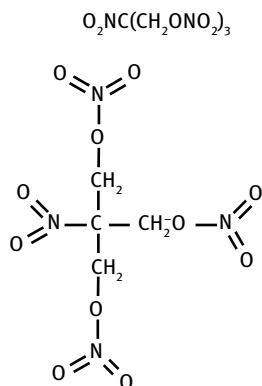


The enthalpy of formation of TMMTN has not been determined experimentally, but because it is a structural isomer of 1,2,4-BTTN, it was assumed that the enthalpy of formation of TMMTN was identical to that of BTTN, which is $-397 \text{ kJ/mol} = -95 \text{ kcal/mol}$.

TMMTN is a clear liquid at room temperature with a density of 1.53 g/cm^3 . Only very pure samples can be induced to crystallize when the sample is cooled to $285\text{--}286 \text{ K}$ ($+12\text{--}13^\circ\text{C}$). It is insoluble in water but soluble in most organic solvents except tetrachloromethane. It is less volatile than TMETN, which in turn is less volatile than GTN. This is an advantage for its intended use as an energetic plasticizer in double-base propellants, where the migration of GTN has been a long-standing problem.

10.5 Nitroisobutylglycerol Trinitrate

Nitroisobutylglycerol trinitrate, also known as nitroisobutylglyceryl trinitrate, NIBGT, C₄H₆N₄O₁₁, nib-glycerin trinitrate, 2-nitro-2-nitroxymethyl-propane-1,3-diol dinitrate, nitroisobutanetrinitrate, NIBTN, CAS RN [20820-44-4], is a yellow viscous oil:



2-nitro-2-nitroxymethyl-propane-1,3-diol dinitrate

We were looking for the best place in this book to reference alkyl nitrates that also carry a nitro group in the alkyl group. Should they be listed under alkyl nitro compounds, or should they be listed under alkyl nitrates? Since the reactivity of these compounds is more determined by the more labile nitroxy group, we have listed them under alkyl nitrates. A few of these compounds were also discussed in the sections on aliphatic nitro compounds.

NIBGT can be prepared by the condensation of formaldehyde with NM, followed by nitration of the nitroisobutylglycerol product under the same conditions as GTN. If during the condensation with formaldehyde only one instead of two methoxy groups are attached, the product is 2-nitro-2-methyl-1,3-propanediol, which upon nitration gives 2-nitro-2-methyl-1,3-propanediol dinitrate. This is likely to accompany NIBGT as a contaminant. The nitration and stabilization procedures are very difficult because of incipient decomposition reactions and the difficulty of separating the aqueous and non-aqueous phases after washing with sodium carbonate or sodium sulfite to remove excess acid [496].

The physical properties of NIBGT are summarized in Table 60. See also [497].

NIBGT is less volatile than GTN, which is an advantage, but it is thermally less stable than GTN, which is a disadvantage. It is practically insoluble in water and petroleum ether, but soluble in alcohol, acetone, diethyl ether, benzene, or chloroform. It is a good gelatinizer of nitrocellulose for the preparation of double-base propellants. Its explosive strength is close to that of GTN.

NIBGT is one of the few energetic plasticizers that are stoichiometrically balanced with an oxygen balance of $\pm 0\%$. Adding NIBGT to a double-base propellant formulation will therefore not cause the overall oxygen balance to drop as it would when conventional plasticizers were in use.

The thermal stability of NIBGT was evaluated and compared to that of other nitrate esters [498]. The thermal stability of NIBGT was compared to that of other nitrate

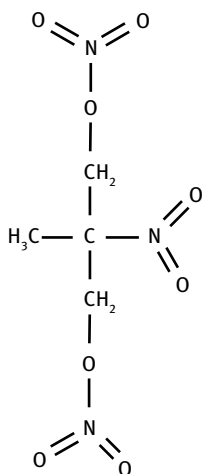
Table 60: Physical properties of nitroisobutylglycerol trinitrate.

Property	SI units		Other units		Refer- ences
Molecular mass	286.1				
Freezing point	238 K		−35 °C	−31 °F	[74]
Density			1.68 g/cm ³		
Refractive index n_D^{20}					
Enthalpy of formation ΔH_{298}^f	−228 kJ/mol	−797.5 kJ/kg	−54.6 kcal/mol	−190.8 cal/g	[74]
Enthalpy of formation ΔH_{298}^f	−226 kJ/mol	−790 kJ/kg	−54.02 kcal/mol	−188.8 cal/g	[73]
Heat of combustion	2205.2 kJ/mol	7707 kJ/kg	527 kcal/mol	1842 cal/g	[73]
Heat of evaporation	72.9 kJ/mol at 313–353 K	255 kJ/kg	17.4 kcal/mol	61 cal/g	[338]

esters in an effort to explain the relationship between molecular structure and thermal stability [56].

10.6 Nitromethylpropanediol Dinitrate

2-Nitro-2-methylpropane-1,3-diol dinitrate, also known as methylnitropropanediol dinitrate, C₄H₇N₃O₈, CAS RN [4055-94-1], can be prepared by the condensation of nitroethane with formaldehyde and subsequent nitration of nitromethylpropanediol:



2-Nitro-2-methylpropane-1,3-diol dinitrate

Nitromethylpropanediol dinitrate has an oxygen balance of -24.9% and a nitrogen content of 18.67 mass-% N. The physical properties of 2-nitro-2-methylpropane-1,3-diol dinitrate are summarized in Table 61.

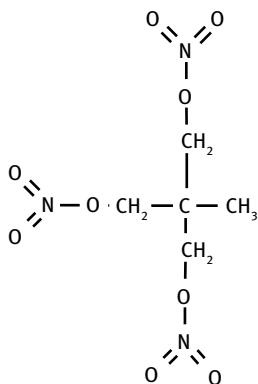
Table 61: Physical properties of 2-nitro-2-methylpropane-1,3-diol dinitrate.

Property	SI units	Other units	References
Molecular mass	225.1137 g/mol	4.4422 mol/kg	
Enthalpy of formation ΔH_f^{298}	-374 ± 2.2 kJ/mol	-89.39 ± 0.53 kcal/mol	[499]
Heat of combustion	2200 ± 2.2 kJ/mol	525.8 ± 0.53 kcal/mol	[499]

11 C₅ Alkylpolynitrates

11.1 Trimethylolethane Trinitrate

Trimethylolethane trinitrate, also known as C₅H₉N₃O₉, CH₃—C(CH₂—O—NO₂)₃, 2-methyl-3-nitrooxy-2-(nitrooxymethyl)propyl nitrate, methyltrimethylolmethane trinitrate, 2-methyl-2-[(nitroxy)methyl]1,3-propanediol dinitrate; 1,3-propanediol, 2-methyl-2-[(nitrooxy)methyl]-, dinitrate; nitropentaglycerin, 2-methyl-2-nitroxy-methyl-1,3-dinitroxyropane, METN, TMETN, metriol trinitrate, metriole trinitrate, 1,1,1-trimethylolethane trinitrate; 1,3-propanediol, 2-(hydroxymethyl)-2-methyl-, trinitrate; 1,3-propanediol, 2-methyl-2-[(nitrooxy)methyl]-1,3-dinitrate; 1,3-propanediol, 2-methyl-2-[(nitrooxy)methyl]-, dinitrate (ester); CAS RN [3032-55-1], is a nitrate ester that can be used as a substitute gelatinizer for GTN. TMETN is a structural isomer of 1,2,5-pentanetriol trinitrate (C₅H₉N₃O₉). TMETN can be made by nitration of the alkanetriol trimethylolethane [500]:



TMETN is a high explosive similar to GTN but more stable to heat. It is a clear oily liquid, colorless to light brown. TMETN is a solid at subzero temperature and is often used in combination with BTTN or DEGDN/TEGDN. It has the advantage of being relatively insensitive to impact and friction. TMETN has been synthesized by nitrating 1,1,1-trimethylolethane (metriol) at 263 K (10 °C) with mixed acid (45% HNO₃ and 55% H₂SO₄) in 93% yield. Metriol in turn is prepared by the condensation of propanal with formaldehyde in a manner similar to that employed in the synthesis of pentaerythritol. Because of its low vapor pressure, TMETN does not induce headaches as badly as other nitrate esters do. It can be used in some solid propellants and smokeless powders as a plasticizer and gelatinizer together with, or as an alternative to, TEGDN.

TMETN was first prepared and patented in Italy under the name *Metriolo*. Germany began producing it even before WWII after TMETN (in combination with TEGDN) showed its usefulness as an erosion and flash-reducing agent in smokeless tube weapon propellants, in particular in those intended for use in hot climates. TMETN is insoluble in water, but readily soluble in acetone or NM.

TMETN can be initiated by friction, impact, and electrostatic discharge. It can be used as a high-viscosity plasticizer-binder together with nitrocellulose, but its poor colloiding properties may require adding an inert plasticizer and an auxiliary, but unfortunately more volatile, solvent/colloiding agent.

11.1.1 Physical Properties of Trimethylolethane Trinitrate

The physical properties of TMETN are summarized in Table 62. See also [69, 278, 501].

Similarly to GTN, TMETN crystallizes in a stable and a metastable form, one melts at 273.6 K (+0.5 °C) and the other at 288 K (+15 °C) [406]. The heat of fusion of TMETN is 15.1 kJ/mol = 63 J/g = 3.62 kcal/mol = 15 cal/g, similar to that of BTTN. Freezing points listed in the literature are probably the result of substantial supercooling before the sample solidified.

The vapor pressure of TMETN as a function of temperature can be expressed by the following equation [503]:

$$\log p = A - B/T$$

in which p is the pressure in μmHg , T is the absolute temperature in kelvin, and A and B are constants: $A = 14.6237$ and $B = 4603.4$. Table 63 has the raw data of the measured vapor pressure of TMETN in comparison to data interpolated with the foregoing equation.

Table 62: Physical properties of TMETN.

Property	SI units		Other units		References
Molecular mass	255.1397 g/mol		3.919 mol/kg		[73]
Freezing point	258 K		−15 °C	+5 °F	[74]
	255.7 K		−17.5 °C		[502]
Melting point, stable allotrope modification	286.1 K		13 °C		[407]
Boiling point	443–446 K		170–175 °C		
	455 (decomp.)		182 °C (dec.)		
Density	1.46 g/cm ³	at 298 K			[74]
	1.543 g/cm ³ at 298 K		1.543 g/cm ³ at 25 °C		[502]
Density at 25 °C/4 °C	1.4607 g/cm ³				[503]
Vapor pressure	0.016 Pa	at 288 K	0.00012 mm Hg	at 15 °C	[502]
	0.024 Pa	at 299 K	0.183 μm Hg	at 26 °C	[503]
Index of refraction n_D^{25}	1.4748	at 298 K			[503]
Enthalpy of formation	−425 kJ/mol	−1666 kJ/kg	−101.6 kcal/mol	−398.2 cal/g	[74]
	−443.7 kJ/mol	−1739 kJ/kg	−106.0 kcal/mol	−415.5 cal/g	[74]
	−443 kJ/mol	−1736 kJ/kg	−105.9 kcal/mol	−415 cal/g	[377]
	−450.2 kJ/mol	−1764 kJ/kg	−107.6 kcal/mol	−421.7 cal/g	[504]
Heat of combustion	2811 kJ/mol		671.8 kcal/mol		[302]
Heat of evaporation	88.2 ±		21.07 ±		[503]
	0.1 kJ/mol		0.03 kcal/mol		
Heat of evaporation 299–345 K	88.1 kJ/mol		21.06 kcal/mol		[338]

The solubility of TMETN in water at 298 K is 0.01 g TMETN/100 g H₂O. TMETN is miscible with diethyl ether or acetone. It is completely miscible with acetone, diethyl ether, methanol, toluene, or xylene. The IR spectrum of TMETN is shown in Figure 32.

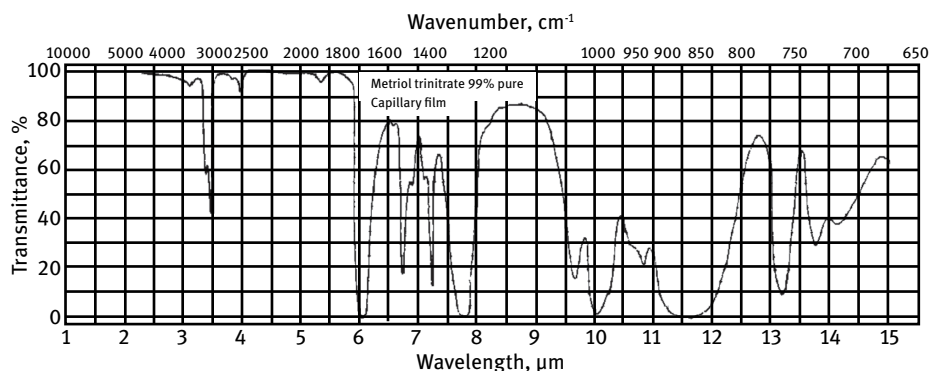
A Raman spectrum of TMETN was already shown earlier in Figure 2 in comparison to the spectra of EGDN and PGDN [26].

The physical properties of TMETN and its higher homolog, TMPTN, are compared in Table 64 (repeating some of the data already shown in an earlier table).

Table 63: Vapor pressure of TMETN.

Temperature		Measured	Interpolated	Deviation
K	°C	μm Hg	μm Hg	%
299.66	26.51	0.183	0.183	0
302.93	29.78	0.268	0.268	0
304.06	30.91	0.305	0.305	0
308.61	35.46	0.503	0.51	-1.4
313.4	40.25	0.863	0.862	0.1
319.31	46.16	1.623	1.612	0.7
323.93	50.78	2.616	2.588	1.1
329.4	56.25	4.494	4.457	0.8
337.19	64.04	9.37	9.373	0
340.23	67.08	12.35	12.41	-0.5
343.41	70.26	16.59	16.56	0.2
345.3	72.15	19.46	19.61	-0.8

Data source: [503]

**Figure 32:** IR spectrum of TMETN. (From [296].)**Table 64:** Physical properties of TMETN and trimethylolpropane trinitrate.

Compound name	Trimethylolethane trinitrate TMETN	Trimethylolpropane trinitrate TMPTN
Gross formula	C ₅ H ₉ N ₃ O ₉	C ₆ H ₁₁ N ₃ O ₉
Molar mass	255.1397 g/mol 3.919 mol/kg	269.4 g/mol 3.712 mol/kg
Oxygen balance	-34.5%	-50.5%
Density at 293 K	1.47 g/cm ³	1.5 g/cm ³
Melting point	270 K = -3 °C	324 K = 51 °C
Enthalpy of formation	-1739 kJ/kg = -443.7 kJ/mol	-1783 kJ/kg = -480.3 kJ/mol

11.1.2 Chemical Properties of Trimethylolethane Trinitrate

With an oxygen balance of -34.5% , TMETN detracts some of the available oxygen in double-base propellants, but due to its positive enthalpy of formation it improves the performance of the propellant.

11.1.2.1 Reactions of Trimethylolethane Trinitrate

11.1.2.1.1 Hydrolysis of Trimethylolethane Trinitrate

Hydrolysis with alkaline ethanol solutions is a safe method for the disposal of TMETN [505]. Instead of the expected triol, a cyclic 3-methyl-oxetane methanol was formed as the hydrolysis product.

11.1.2.2 Thermal Stability of Trimethylolethane Trinitrate

The thermal decomposition of TMETN was investigated by pressure DSC [506]. The results showed that, even though TMETN has a structure similar to that of GTN, TMETN has totally different thermal decomposition characteristics. At normal pressure, TMETN has an exothermic decomposition peak, while NG has an endothermic peak. Under pressure, TMETN has two exothermic peaks. The shape, temperature, and quantity of heat of the two peaks change with the increase of pressure. The kinetic parameters of TMETN were obtained, and TMETN's decomposition mechanism has also been analyzed.

The thermal stability of TMETN was compared to that of other nitrate esters in an effort to explain the relationship between molecular structure and thermal stability [56].

11.1.2.3 Analysis of Trimethylolethane Trinitrate

The purity of TMETN for propellant applications is controlled by MIL SPEC WS 12798, Weapon Specification WS 12798 Metriol Trinitrate.

11.1.3 Safety Properties of Trimethylolethane Trinitrate

11.1.3.1 Toxicity of Trimethylolethane Trinitrate

As of 1983, the completeness of health and toxicity information on three widely used energetic plasticizers (DEGDN, TEGDN, and TMETN) left something to be desired, and the need for additional research has been outlined [507].

11.1.3.1.1 Oral Toxicity of Trimethylolethane Trinitrate

The acute oral toxicity of TMETN suspended in corn oil was determined in male and female ICR mice using the oral gavage single-dose method with doses ranging from 562 to 1590 mg/kg [508]. The calculated median lethal dose LD₅₀ for male mice was 829.0 ± 42.5 mg/kg and for female mice it was 658.4 ± 32.7 mg/kg. The LD₁₀ in male mice was 643.3 ± 54.8 mg/kg. TMETN had a strong effect on the nervous system, as indicated by the incidence of convulsions, tremors, twitching, writhing, jumping, and catalepsy.

These signs were observed within 2 h of dosing and the majority had resolved within 72 h of dosing. Deaths were observed acutely, with 86% occurring within 4 h of dosing; no deaths were observed after 24 h. Similar tests in rats gave an LD₅₀ of 1587 ± 191 mg/kg for male rats and 1027 ± 64 mg/kg for female rats [509, 510]. Again, clinical signs observed following TMETN administration were inactivity, tremors, irritability, clonic convulsions, depression of grasping and righting reflexes, changes in the startle reflex, disorientation, and hunched posture. Most animals exhibited signs within 2 h of dosing and had either died or returned to normal by 72 h after dosing.

Other sources give the toxicity of TMETN as LD₅₀ (mice): 562 mg/kg, 655–828 mg/kg; LD₅₀ (rats): 1030–1519 mg/kg, 2390–3100 mg/kg (oral).

11.1.3.1.2 Dermal Toxicity of Trimethylolethane Trinitrate

While other nitrate esters can be resorbed through the skin by handling plasticized propellants without glove protection, TMETN had only a very slight potential of permeation when tested for 24-h applications in rabbits at a topical dose of up to 2 g/kg [511]. There was no evidence of percutaneous absorption of quantities sufficient to produce systematic toxicity or death. In topical application tests, there was no recognizable skin reaction (visible irritation) at any time during the 14-day observation period in exposed rabbits [512, 513]. Slight primary eye irritation is caused by TMETN in rabbits [514].

TMETN was evaluated for its potential to produce dermal sensitization in male guinea pigs or guinea pigs [515]. The Buehler test, which utilizes repeated closed patch inductions with the test compound, was used for this evaluation. No evidence of TMETN-induced sensitization was observed.

11.1.3.1.3 Mutagenicity of Trimethylolethane Trinitrate

TMETN showed no mutagenic activity in the Ames *Salmonella*/mammalian microsome mutagenicity test [516].

11.1.3.2 Explosive Sensitivity of Trimethylolethane Trinitrate

The explosion of TMETN can be initiated by friction, impact, or electrostatic discharge. Autodecomposition of TMETN begins at the deflagration point of 455 K = 182 °C = 360 °F. The open-cup flash point of TMETN is 299.8 K = 26.7 °C.

The impact sensitivity of TMETN when impacted in the Olin Technoproducts tester with a 2-kg mass is 47 cm. In the Bureau of Mines impact tester with a 2-kg mass it is 40 cm. In the BAM tester the drop weight sensitivity is 0.2 Nm. It can be detonated with a No. 6 blasting cap.

In the electrostatic discharge sensitivity test, TMETN was negative at 12.42 J [502].

11.1.4 Explosive Performance of Trimethylolethane Trinitrate

When detonated in a lead block test, the resulting cavity enlargement is $400 \text{ cm}^3/10 \text{ g}$. The fully developed detonation velocity is 7050 m/s . In the lead block test, the indentation with TMETN was $400 \text{ cm}^3/10 \text{ g}$, which is 139% of that of picric acid or 140% of that of TNT.

The shock initiation of TMETN was tested in comparison to GTN and ethyl nitrate [158]. The donor charges were 3.5-cm-diameter Composition B pellets, 10 to 12.5 cm in length; the interruptors were 6.5×8.0 -cm square glass plates of varying thicknesses S_1 (3.2–9.3 mm) and the receptor explosive was contained in 4- to 7.5-cm-diameter glass cylinders. The initial wave velocity and delay to detonation were measured with a streak camera and were 4470 – $4970 \text{ mm}/\mu\text{s}$; the delays were 0.6 – $0.7 \mu\text{s}$.

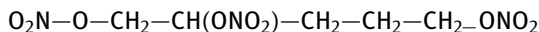
11.1.5 Applications of Trimethylolethane Trinitrate

TMETN can be used as an energetic plasticizer in insensitive solid propellants [517].

TMETN (MTN) is used as a plasticizer in PBXN-103 per MIL-E-82756(OS). The nominal MTN content is 23%.

11.2 1,2,5-Pentanetriol Trinitrate

1,2,5-Pentanetriol trinitrate, $\text{C}_5\text{H}_9\text{N}_3\text{O}_9$, CAS RN [98071-55-7], is an energetic plasticizer, but, owing to the nitroxy group on a secondary carbon atom, its thermal stability is inferior to some of the other alkyl polynitrates in this category:



The physical properties of 1,2,5-pentanetriol trinitrate are summarized in Table 65.

Table 65: Physical properties of 1,2,5-pentanetriol trinitrate.

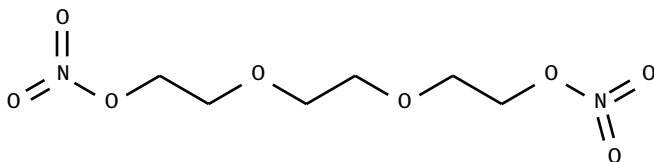
Property	SI units		Other units	References
Molecular mass	255.1397 g/mol	3.919 mol/kg		[73]
Vapor pressure at 293 K	0.02 Pa		0.16 $\mu\text{m Hg}$	[12]
Heat of combustion	2814 kJ/mol		672.6 kcal/mol	[302]
Heat of evaporation 293–313 K	$41.7 \pm 2.1 \text{ kJ/mol}$		$9.97 \pm 0.50 \text{ kcal/mol}$	[338]
Heat of evaporation	$42 \pm 2 \text{ kJ/mol}$		$10 \pm 0.5 \text{ kcal/mol}$	[12]

12 C₆ Alkylpolynitrates

12.1 Triethylene Glycol Dinitrate

Triethyleneglycol dinitrate, also known as TEGDN, Tri-EGDN, O₂NO—CH₂—CH₂—O—CH₂—CH₂—O—CH₂—CH₂—ONO₂, C₆H₁₂N₂O₈, triglycol dinitrate, triethyleneglycol dinitrate, nitrotriglycol, 2,2-bis(ethylenedioxy)diethyl nitrate; ethanol, 2,2'-[(1,2-ethanediyl)bis(oxy)]bis-1,1'-dinitrate; CAS RN [111-22-8], is used as a plasticizer for double-base propellants as a replacement for GTN. One of the many advantages of TEGDN is its insensitivity to detonation. TEGDN is also superior to NG with respect to withstanding cold temperatures under arctic conditions. The oxygen balance is -66.6% for combustion to CO₂ and -27% for combustion to CO.

TEGDN was the main ingredient in an experimental liquid monopropellant NOSET-A:



12.1.1 Production of Triethylene Glycol Dinitrate

TEGDN was first prepared in 1863 by Leurenco. Already during WWII it was used by Germans and Italians as a plasticizer in double-base propellants [518]. TEGDN is manufactured by nitrating triethylene glycol (TEG) under controlled conditions with mixed acid. The difficult point in the production process is treating the spent acid. TEGDN is highly soluble in spent acid (~9%), more so than any of the other commonly made alkyl nitrates, and the mixture is relatively unstable. Safe spent acid treatment is important to ensure safe conditions for TEGDN manufacture. EURENCO Vihtavuori in Finland is using a continuous Biazzi process with a production capacity of 500 kg/h [519].

A modification of common preparation methods allowed for continuous nitration [520]. This procedure recommended the use of sufficient CHFCl₂ to maintain the temperature below 316 K (43 °C = 110 °F) and ensure a safe degree of dilution of the product. The reaction temperature is limited by the boiling point of the refluxing solvent. The triethylene glycol and the mixed acid nitrating agent were separately dispersed in CHFCl₂ prior to mixing. The 74% yield was recovered after evaporation of the CHFCl₂. See also [521].

12.1.2 Physical Properties of Triethylene Glycol Dinitrate

Table 66 shows a comparison of the properties of TEGDN and GTN. Additional physical properties of TEGDN are listed in Table 6, 51, and 67. See also [522, 523].

Table 66: Comparison of physical properties of TEGDN and GTN.

Physical property	TEGDN	Glycerol trinitrate
Molecular mass	240.1	
Solidification point	257.1 or 250.1 K (−19 or −23 °C)	286.3 K (+13.2 °C) stable modification 275.3 K (+2.2 °C) unstable modification
Boiling point	600 K (327 °C) (760 mmHg), calculated, dec.	418 K (145 °C)
Density	1.335 g/cm ³	1.591 g/cm ³
Vapor pressure at 293 K = 20 °C	0.001 mmHg	0.00025 mmHg
Viscosity at 293 K = 20 °C	13.2 cPs	37.8 cPs
Decomposition temperature	501 K (228 °C) (760 mmHg)	323–333 K (50–60 °C) unstable modification 453–473 K (180–200 °C) stable modification
Flash Point	420 K (146.9 °C)	285 K (12 °C)

Data source: [519]

Table 67: Physical properties of TEGDN.

Property	SI units	Other units	References
Molecular mass	240.1681 g/mol	4.1637 mol/kg	[73]
Freezing (glass) point	250 K	−23 °C	Manufacturer's data sheet
Melting point	261.5 K	−11.6 °C	[407]
Density at 298 K/273 K (25 °C/4 °C)	1.3194 g/cm ³		[503]
Density at 293 K (20 °C)	1.335 g/cm ³		Manufacturer's data sheet
Density at 289 K (16 °C)	1.3291 g/cm ³		[10]
Vapor pressure at 303.4 K (30.3 °C)	0.025 Pa	0.188 μm Hg	[503]
Viscosity	0.0132 N·s/m ² at 293 K	13.20 cPs at 20 °C	Manufacturer's data sheet
Viscosity at 279 K (6 °C)		25.7 cPs	[10]
Viscosity at 293.4 K (20.3 °C)		11.9 cPs	[10]
Viscosity at 327.3 K (54.2 °C)		1.5 cPs	[10]
Refractive index n_D^{24}	1.4527		[503]
Refractive index n_D^{20}	1.4540		Manufacturer's data sheet

Vapor pressure data for TEGDN in comparison to the vapor pressures of other glycol polynitrates were already shown earlier in Table 6 and 51.

Like most other nitrate esters, TEGDN tends to supercool on cooling before it crystallizes. It is more accurate to determine a melting point of frozen TEGDN than rely on the freezing point data in the literature. Freezing points listed in the literature are probably the result of substantial supercooling before the sample solidified. The melting point of frozen TEGDN is 248 K (–25 °C) [406]. The heat of fusion of TEGDN is 18 kJ/mol = 75 J/g = 4.3 kcal/mol = 18 cal/g, between that of GTN and BTTN. The visual start- and end-of-melt temperatures for 2-week-old as-received TEGDN crystals were 250.2 and 253.6 K (–22.9 and –19.5 °C), respectively, but 8 months later they had increased to 258.7 and 263.7 K (–14.4 and –9.4 °C), respectively (Table 51 in GTN preceding section).

The vapor pressure of TMETN as a function of temperature can be expressed by the following equation [503]:

$$\log p = A - B/T$$

in which p is the pressure in $\mu\text{m Hg}$, T is the absolute temperature in kelvin, and A and B are constants: $A = 14.4792$ and $B = 4614.7$.

Figure 33 shows an IR spectrum of TEGDN.

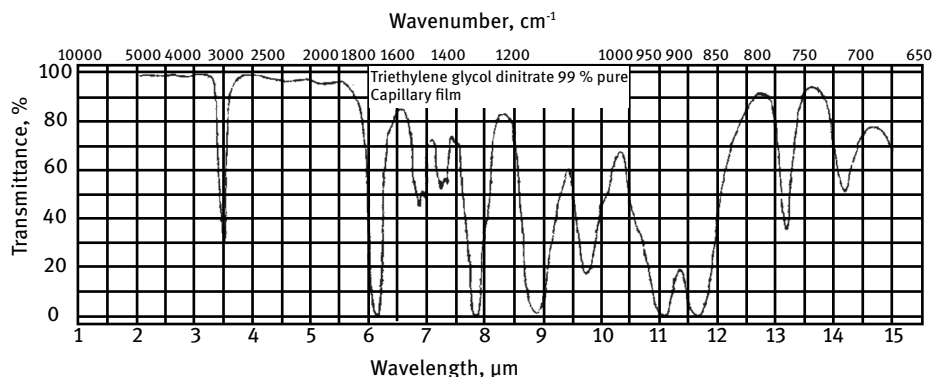


Figure 33: IR spectrum of TEGDN. (Reproduced from [296].)

The IR spectra of TEGDN and six other dinitrate esters were computed by a DFT method [297].

A Raman spectrum of TEGDN was compared to Raman spectra of 7 other alkyl nitrates and 24 other explosives as described in [26].

12.1.2.1 Molecular Structure of Triethylene Glycol Dinitrate

A DFT method was used to study the geometric and electronic structures and pyrolysis mechanisms of six dinitrate esters, including TEGDN [297]. The IR spectra of these compounds were obtained and the bands were assigned by vibrational analysis. Based on the principle of statistic thermodynamics, the thermodynamic properties were evaluated, which were linearly related to the number of repetitive $\text{CH}_2\text{CH}_2\text{O}$ groups as well as the temperature, showing good group additivity. Thermal stability and the pyrolysis mechanism of the dinitrate esters were investigated by calculating the BDEs. For the nitrate esters, the $\text{O}-\text{NO}_2$ bond is a trigger bond during a thermolysis initiation process.

12.1.2.2 Thermodynamic Properties of Triethylene Glycol Dinitrate

The thermodynamic properties of TEGDN are summarized in Table 68.

Table 68: Thermodynamic properties of TEGDN.

Property	SI units		Other units		References
Molecular mass	240.1681 g/mol		4.1637 mol/kg		[73]
Enthalpy of formation	-606.3 kJ/mol	-2526 kJ/kg	-144.9 kcal/mol	-603.7 cal/g	[74]
	-628.9 kJ/mol	-2619.2 kJ/kg	-150.3 kcal/mol	-626.0 cal/g	[74]
ΔH_{298}^f	-580.86 kJ/mol		-138.83 kcal/mol		[524]
Heat of combustion	3495 kJ/mol		835.4 kcal/mol		[302]
	3410 kJ/mol	14.57 kJ/g	815 kcal/mol	3483 cal/g	
Heat of evaporation	88.37 kJ/mol	367.9 kJ/kg	21.12 ±	87.94 cal/g	[503]
			0.03 kcal/mol		
Heat of fusion	18 kJ/mol	75 J/g	4.3 kcal/mol	18 cal/g	[406]

12.1.3 Chemical Properties of Triethylene Glycol Dinitrate

The oxygen balance of TEGDN is -66.7%, and the nitrogen content is 11.67 mass-% N.

12.1.3.1 Thermal Stability of Triethylene Glycol Dinitrate

An examination of the thermal decomposition of TEGDN by pressurized DSC showed that at atmospheric pressure, TEGDN had an exothermic decomposition process with a peak temperature of ~489 K (~216 °C) [525]. When the pressure was increased to 2 MPa, the peak shape became very sharp, the peak temperature increased by about 5 °C and shifted from low temperature to high temperature, and the output of the exotherm was over two times that of a peak at atmospheric pressure. If the pressure was increased further, the peak shape, temperature, and exothermic output changed very little.

The thermal behavior and kinetic parameters of the decomposition reaction of TEGDN in a temperature-programmed mode at different pressures (0.1, 2, 4, and 6 MPa) were investigated by DSC and TG-DTG [526]. The results showed that the thermal decomposition of TEGDN was affected by a change in pressure. The kinetic model function, the apparent activation energy E_a , and preexponential factor A of this reaction were $2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$, 106.54 kJ/mol and $10^{9.17} \text{ s}^{-1}$ at 0.1 MPa, and 120.82 kJ/mol and $10^{10.56} \text{ s}^{-1}$ at 2 MPa, respectively. The critical temperature of thermal explosion of TEGDN obtained by the onset temperature and the peak temperature (when the heating rate tends to zero) are 464 and 483 K (191 and 210 °C) at 0.1 MPa and 480.7 and 494.7 K (207.6 and 221.6 °C) at 2 MPa, respectively. On a hot plate with rapid heating, the deflagration point is at 468 K (195 °C = 383 °F).

Quantum chemical computational methods were employed to investigate the equilibrium geometry, frontier orbital energy, and energy gap, as well as the BDEs, of TEGDN and Tetra-EGDN [527]. The thermal stability of two nitrates and the corresponding radicals were analyzed. The calculated O—NO₂ BDEs of TEGDN and Tetra-EGDN were close to the real values. That the experimental thermolysis of two nitrates is only a unimolecular homolytical dissociation of the O—NO₂ bonds is corroborated by the finding that the present results of BDEs were well coincident with the experimental results of activation energies from literature.

12.1.4 Safety Properties of Triethylene Glycol Dinitrate

In the card gap test, confined in a Schedule 40 steel pipe 24.4 mm in diameter and 15 cm long, TEGDN went high order with a velocity detonation of 6400 m/s at zero cards but failed to propagate after only a few inches as soon as a gap of 3.3 mm cards was between the donor and the acceptor charge [528].

When examining the detonation threshold properties of liquid monopropellant NOSET-A, a mixture of TEGDN/dibutyl sebacate/ethyl centralite (96/3/1%) in small-scale detonation and wedge tests, it was concluded that the detonation velocity of the propellant was strongly affected by the sample temperature [529]. For example, when heavily confined at 289 K (60 °F), NOSET-A exhibited a detonation velocity of 5950 m/s; however, no detonation occurred under the same confinement at 271.5 K (29 °F). The detonation pressure of NOSET-A at 285.9 K (55 °F) was 170 kbar, and wedge tests indicated a detonation threshold at 110–130 kbar for transmitted shock pressure.

In the ESD test apparatus, TEGDN was negative at 12.42 nJ. For the adiabatic compression sensitivity of NOSET-A, see [530]. The results were already shown earlier in the IPN section.

12.1.4.1 Toxicity of Triethylene Glycol Dinitrate

TEGDN is as toxic as other nitrate esters like GTN and DEGDN. The toxicological properties of aliphatic nitrates are similar, differing only in intensity, onset, and duration of effect. As of 1983, the completeness of health and toxicity information on three

widely used energetic plasticizers (DEGDN, TEGDN, and TMETN) left something to be desired, and the need for additional research was outlined [531]. Table 69 lists a comparison of toxicity values of TEGDN and GTN.

Table 69: Toxicity of TEGDN and GTN.

Toxicity	TEGDN	References	Glycerol trinitrate
LD50, intraperitoneal, mouse	945 mg/kg	[356]	104 mg/kg
LD50, oral, mouse	1866 mg/kg		115 mg/kg
LD, skin, rabbit	2000 mg/kg		280 mg/kg
LD50, intraperitoneal, rabbit	796 mg/kg	[356]	189 mg/kg
LD50, oral, rat	1000 mg/kg	[356]	105 mg/kg
LD50, subcutaneous, rat	2520 mg/kg	[356]	94 mg/kg

Secondary data source: [519]

Comparing the toxicity of TEGDN and PGDN, it was observed that in most species the LD50 of TEGDN was two to five times as high as that of PGDN [532]. Both compounds produced methemoglobinemia and hypotension in rats. However, TEGDN-poisoned rats trembled violently and expired, apparently in respiratory arrest, after acute convulsive episodes. PDGN-poisoned rats were lethargic and did not convulse. Chronic daily dermal applications to rabbits of 21 mmol/kg of both dinitrates caused death in 2 to 3 weeks. PGDN-treated rabbits gained weight normally, while those treated with TEGDN lost 20 to 30% of their body weight. Guinea pigs receiving as little as 100 mg/kg of TEGDN IP daily had decreased food intake and retarded weight gain. The toxic responses of these two dinitrates are therefore sufficiently different to preclude simple comparisons in hazard evaluations.

12.1.4.1.1 Oral Toxicity of Triethylene Glycol Dinitrate

TEGDN is very toxic. It acts as a violent poison when ingested by rats or as a peripheral nerve block when selectively applied [533]. Dermal application of 21 mmol/kg of body weight in rabbits caused death in 2 to 3 weeks. In a later study, the 24-h IP LD50 in rats was found to be 995 on average, range 932–1063 mg/kg of body weight.

The acute oral median lethal dose (MLD) of TEGDN as measured by an oral gavage single-dose method was 1330 ± 42 mg/kg for male rats and 1116 ± 40 mg/kg for female rats [534] and 2036.5 ± 101.1 mg/kg for male mice and 1866.3 ± 86.2 mg/kg for female mice [535]. Clinical signs included hunched posture, inactivity, tremors, twitching, and hypotonia. Most animals exhibited signs within 2 h after dosing and either they had perished or the signs had cleared by 72 h after dosing.

12.1.4.1.2 Inhalation Toxicity of Triethylene Glycol Dinitrate

A male rhesus monkey was exposed to NOSET-A (which is mostly TEGDN) aerosol for 4 h at a concentration of 2.4 ppm [536]. Visual evoked response and Sidman avoidance task data were collected after 2 h and again after 4 h of exposure. The visual evoked response was not affected, but a significant increase in response rate on the Sidman avoidance task occurred. These data indicated that inhalation of NOSET-A has neurobehavioral effects of potentially serious consequences. NOSET-A was intended as a torpedo propellant.

12.1.4.1.3 Dermal Toxicity of Triethylene Glycol Dinitrate

The acute dermal toxicity of TEGDN was evaluated in rabbits by applying 2 mL TEGDN/kg topically to the clipped dorsal skin surface under a semioclusive wrap for 24 h [537] or by using a modified Draize method [538]. Very slight erythema was observed in eight of eight rabbits and very slight edema in five rabbits 0.5–1 h after dosing. Percutaneous absorption was insufficient to produce any systemic toxicity or death. Several of the rabbits exhibited very slight to slight erythema 0.5 h after wrap removal, and all but one had cleared by 72 h. No other recognizable skin reaction was detected at any time during the 14-d observation period. TEGDN was a mild irritant under conditions of this study. TEGDN has the potential to produce slight dermal irritation, as well as in the eyes [539], but there is no allergic sensitization to repeated skin exposures after the first insult has cleared [540]. Similar tests were conducted with DEGDN.

12.1.4.1.4 Mutagenicity of Triethylene Glycol Dinitrate

The mutagenic potential of TEGDN was assessed using the Ames *Salmonella*/mammalian microsome mutagenicity test [541]. Tester strains TA98, TA100, TA1535, TA1537, and TM538 were exposed to doses ranging from 5 μ L/plate to 0.0016 μ L/plate, in both the presence and absence of metabolic enzyme activation. The test compound was not mutagenic under conditions of this test.

12.1.5 Explosive Properties of Triethylene Glycol Dinitrate

The explosive properties of TEGDN are summarized in Table 70. A thermal stability test at 373 K = 100 °C indicated that TEGDN was considerably less sensitive to temperature than GTN. TEGDN was unaffected in the Bureau of Mines pendulum friction test with a metal or fiber shoe. Impact resistance was much better than for NG. The Bureau of Mines impact test indicated a drop weight sensitivity of over 100 cm. In the BAM impact test machine, beginning reaction was observed at 12.7 N m.

Table 70: Explosive properties of TEGDN compared to GTN.

Explosive property	TEGDN	Glycerol trinitrate
Explosion temperature (5 s)	225 °C	222 °C
Detonation gas volume	1202 L/kg	782 L/kg
Detonation velocity	2000 m/s	7600 m/s
Heat of explosion	725 kcal/kg	1616 kcal/kg
Impact SENSITIVITY (2 kg)	100 cm+ (US Bur. Mines) 43 cm+ (Picatinny Arsenal) 65 cm+ (BAM, Germany)	15 cm
Lead block test	320 cm ³ /10 g	520 cm ³ /10 g
Vacuum stability 100 °C	45 mL in 40 h	least stable of all standard military explosives
Vacuum stability 120 °C	0.8–0.99 mL in 8 h	
Heat test, 100 °C first 48 h	1.8%	3.6%
Heat test, 100 °C second 48 h	1.6%	3.5%
Friction pendulum test, steel shoe	Unaffected	No reaction up to 353 N
Friction pendulum test, fiber shoe	Unaffected	—
Critical diameter (steel sleeve test)	26.7 mm	24 mm
Card Gap test	0.48 cm (0.19 in)	2.31 cm (0.91 in)

Data source: [519]

12.1.5.1 Detonation Properties of Triethylene Glycol Dinitrate

In the lead block test, the explosion of TEGDN caused an increase in the cavity volume by 320 cm³/10 g. TEGDN is relatively insensitive to detonation. In some tests, TEGDN failed to detonate with a No. 8 blasting cap. No detonation occurred in samples placed in light steel tubing with a diameter of 3.175 cm at a density of 1.33 g/cm³. When heavily confined, the detonation velocity was less than 2000 m/s.

In the NOL card gap test, TEGDN was tested in comparison to RDX, C-4, and an NC/TEGDN/AP/Al solid propellant [542]. With heavy confinement (steel pipe), the critical diameter was 26 D_c 35 mm (1.05 D_c 1.38 in.) and the NOL card gap sensitivity 50% point was at 57 cards.

A DFT method was used to predict the explosive performance of six dinitrate esters, including TEGDN [297]. Detonation performances were evaluated by the Kamlet-Jacobs equations based on the calculated densities and heats of formation. It was found that density, detonation velocity, and detonation pressure decreased with increases in the number of CH₂CH₂O groups. The predicted detonation velocity of TEGDN at a density of 1.55 g/cm³ was 7.25 km/s, and the detonation pressure was 21.23 GPa, compared to 8.96 km/s and 35.03 GPa for EGDN.

12.1.6 Propellant Mixtures with Triethylene Glycol Dinitrate

TEGDN is widely used as a plasticizer for double-base propellants and Composite Modified Double Base (CMDB) propellants.

NOSET-A consisted of 96% TEGDN, 3% di-*n*-butyl sebacate as desensitizer, and 1% ethyl centralite as stabilizer. The vapor pressure of NOSET-A at 298 K was 0.33 Pa (0.0025 mm Hg). The nominal density of NOSET-A at 298 K was 1.31 g/cm³.

12.2 Trimethylolpropane Trinitrate

1,1,1-Trimethylolpropane trinitrate, also known as 2-ethyl-2-(hydroxymethyl)-1,3-propanediol trinitrate, C₆H₁₁N₃O₉, H₃CCH₂C(CH₂ONO₂)₃, TMPTN, CAS RN [2921-92-8P], can be prepared by the nitration of 1,1,1-trimethylolpropane with nitric acid [543]. Using 98% nitric acid as the nitrating reagent, with a molar ratio of trimethylolpropane to nitric acid of 10:1, a reaction time of 2h, and a reaction temperature of 0–20 °C, the yield of TMPTN reached as high as 99.7%. The product was characterized by IR, NMR, and elemental analysis.

12.2.1 Physical Properties of Trimethylolpropane Trinitrate

The physical properties of TMPTN and its lower homolog, TMETN, are compared in Table 71.

Table 71: Physical properties of TMETN and TMPTN.

Compound name	Trimethylolethane trinitrate TMETN	Trimethylolpropane trinitrate TMPTN
Gross formula	C ₅ H ₉ N ₃ O ₉	C ₆ H ₁₁ N ₃ O ₉
Molar mass	255.1397 g/mol 3.919 mol/kg	269.4 g/mol 3.712 mol/kg
Oxygen balance	–34.5%	–50.5%
Density at 293 K	1.47 g/cm ³	1.5 g/cm ³
Melting point	270 K = –3 °C	324 K = 51 °C
Enthalpy of formation	–1739 kJ/kg = –443.7 kJ/mol	–1783 kJ/kg = –480.3 kJ/mol

The heat of combustion at a constant volume of 1,1,1-tris(hydroxymethyl)propane trinitrate is 3469 kJ/mol = 829.2 kcal/mol, and that of its parent triol, 1,1,1-tris(hydroxymethyl)propane, is 3613 kJ/mol = 863.5 kcal/mol [544].

12.2.2 Thermal Stability of Trimethylolpropane Trinitrate

The thermal decomposition of TMPTN was investigated by high pressure DSC [545, 546]. It was shown that even though the structure of TMPTN is similar to that of NG and TMETN, the thermal decomposition characteristics of TMPTN are different from those of NG and TMETN. TMPTN began to decompose at 409.9 K (136.8 °C). At normal

pressure, the DSC curve of TMPTN had two peaks: one was a melting endothermic peak ($481\text{ K} = 208^\circ\text{C}$ at $10^\circ\text{C}/\text{min}$) and the other was an exothermic decomposition peak, while NG had only an endothermic peak and TMETN had an exothermic decomposition peak, without a melting endothermic peak. At high pressure, TMPTN had two similar peaks, but the melting endothermic peak was not evident compared to that at normal pressure. The shape, temperature, and quantity of heat of decomposition peak greatly changed with different pressures. The peaks were broad at 101 kPa but became sharp at 7 MPa. The activation energy of TMPTN decomposition at 101 kPa was 181.1 kJ/mol .

12.3 Other Polynitrate Esters

Theoretically cellulose polynitrate, nitrocellulose would belong in this chapter, but the properties of nitrocellulose will be postponed to future volumes of the *Encyclopedia of Rocket Propellants* in conjunction with double-base propellants and the ingredients for making double-base propellants. Similarly, dextrin nitrate and polydextrin nitrate will be treated in future volumes.

PETN is primarily used as an explosive and not as a propellant. For this reason it was not included in this book. Its properties have frequently been cited in comparison to other propellant ingredients, but it is not covered in its own section in this book. The same applies to several other primary explosives.

The nitration of tris(hydroxymethyl)aminomethane (Tris) gives a group of energetic nitrates [547]. The new nitrates were fully characterized by NMR, IR, MS, DSC, and elemental analysis. The structure of each compound was confirmed by single-crystal XRD. The energies of formation were calculated with the Gaussian program package, and the detonation parameters were predicted using EXPLO5 computer code. Because of the positive oxygen balance of these compounds, their performance data as oxidizers were compared to the common oxidizer ammonium perchlorate.

12.3.1 Nitroalkyl Nitrate Esters

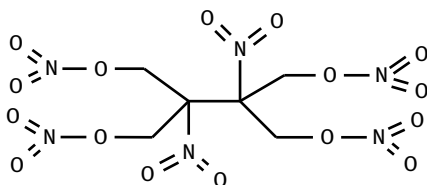
2,2-Dinitro-1,3-bis(nitroxy)propane, also known as $\text{O}_2\text{NOCH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{ONO}_2$, $\text{C}_3\text{H}_4\text{N}_4\text{O}_{10}$, dinitropropyldinitrate, DNPN (not to be confused with NPN for *n*-propyl nitrate), is a candidate energetic plasticizer because of its high oxygen balance (+12.5%) and low T_g ($191.5\text{ K} = -81.5^\circ\text{C}$, midpoint) [548]:



However, the thermal stability of DNPN has been insufficient and the search for a suitable stabilizer for DNPN is ongoing.

A castable polynitrate ester, tentatively identified as 2-nitratomethyl-2-nitro-3-nitratomethyl-3-nitro-butane(1,4)diol dinitrate, was prepared in a three-stage

synthesis [549]. Compared to PETN, it had a relatively low melting point, which makes it suitable as a castable explosive. It had a density of 1.917 g/cm³ and a melting point of 358–359 K (85–86 °C). The heat of formation was measured to be –371 kJ/mol by combustion bomb calorimetry. The predicted detonation velocity was 9.1 km/s (similar to HMX), and the predicted detonation pressure was 40 GPa:



2-nitratomethyl-2-nitro-3-nitratomethyl-3-nitro-butane(1,4)diol dinitrate

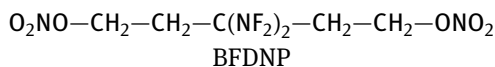
The heat of combustion at constant volume of 2-ethyl-2-nitro-1,3-propanediol dinitrate, $\text{O}_2\text{NOCH}_2\text{C}(\text{NO}_2)(\text{C}_2\text{H}_5)\text{CH}_2\text{ONO}_2$, is 2902 kJ/mol = 693.5 kcal/mol, while that of its parent diol, 2-ethyl-2-nitro-1,3-propanediol is 2944 kJ/mol = 703.7 kcal/mol [544].

12.3.2 Fluoroalkyl Nitrate Esters

The oxygen balance of energetic plasticizers can be improved by replacing some of the hydrogen in the alkyl groups with fluorine or azido groups. Fluoroalkyl nitrate derivatives have higher densities, better thermal stability, and lower shock sensitivity than the all-hydrogen analogs. Thermally stable energetic plasticizers have been synthesized that contain terminal fluoroalkyl groups. Alkyl nitrate esters with terminal trifluoromethyl groups have good thermal stability and good energy content. These compounds are of interest as replacements for dinitrato propane in Otto Fuel II or as plasticizers in double-base propellants or PBX explosives.

12.3.3 Difluoroaminoalkyl Nitrate Esters

Energetic plasticizers containing 3,3-bis(difluoroamino)-1,5-(dinitrato)pentane (BFDNP) have a T_g of around 186 K (–87 °C) and an onset of exothermic decomposition at 459 K (186 °C) and can be used as improved plasticizers with excellent performance potential [550].



12.3.4 Azidoalkyl Nitrate Esters

The oxygen balance of energetic plasticizers can be improved by replacing some of the hydrogen in the alkyl groups with azido groups. Azidoalkyl nitrate derivatives have higher densities and more energy than the all-hydrogen analogs. Thermally stable en-

ergetic plasticizers have been synthesized that contain terminal azido groups in addition to nitrate ester groups.

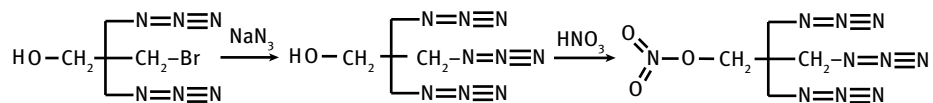
These compounds could just as well be treated in the chapter on organic azide compounds (*Encyclopedia of Liquid Fuels*, "Azido Compounds"), but the primary location is here under alkyl nitrates. Both the nitroxyl group and the azido group are very active. Usually we file these multi-substituent compounds under the group that is more reactive. In this case, the two groups seem to be equally reactive (and will cause premature decomposition of many energetic materials).

12.3.4.1 Pentaerythritol Diazido Dinitrate

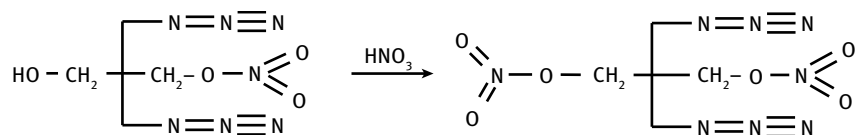
PETN is a well-characterized energetic material. In the search for liquid energetic materials with lower melting points than PETN, a group of azidoalkyl nitrates was investigated. Most emphasis was placed on characterizing pentaerythritol diazido dinitrate as an energetic plasticizer [551, 552].

Pentaerythritol diazido dinitrate, $\text{O}_2\text{NO}-\text{CH}_2-\text{C}(\text{CH}_2\text{N}_3)_2-\text{CH}_2-\text{ONO}_2$, $\text{C}_5\text{H}_8\text{N}_8\text{O}_4$, 1,3-dinitroso-2,2-diazidomethyl-propane, is a colorless oil. It has an oxygen balance of -46.35% and a nitrogen content of 40.57%.

Diazido derivatives of pentaerythritol can be prepared by reacting 3,3-bis(azidomethyl) oxetane with inorganic acids such as hydrobromic or nitric acid [553]. The resulting diazido monobromide can be reacted with sodium azide to produce pentaerythritol triazide, which can be subsequently nitrated to pentaerythritol triazido mononitrate. The pentaerythritol diazido mononitrate produced by the reaction of nitric acid with the aforementioned oxetane can be further nitrated with nitric acid to produce pentaerythritol diazido dinitrate, a thoroughly investigated energetic compound. These diazido and triazido derivatives of pentaerythritol can be utilized as energetic azido plasticizers *per se* or can serve as intermediates for the production of such plasticizers. Pentaerythritol triazido mononitrate is an intermediate product, but it can also be used by itself as is. The pentaerythritol diazido mononitrate produced by the reaction of nitric acid with the aforementioned oxetane can be further nitrated with nitric acid to produce pentaerythritol diazido dinitrate. Pentaerythritol diazido monobromide can be reacted with sodium azide to produce pentaerythritol triazide, and the latter can be subsequently nitrated with nitric acid to produce pentaerythritol triazido mononitrate, as noted below:



Pentaerythritol diazido mononitrate can be further nitrated with nitric acid to produce the desired pentaerythritol diazido dinitrate as shown here:



Pentaerythritol diazido dinitrate is a low-melting-point substance, depending on the purity, with a density of 1.507 g/cm^3 and a refractive index of $n_D^{22.5}$ of 1.5161. Later reports using a different method of synthesis obtained a purer product that melted at 312.7 K (39.6°C) [554]. The heat of combustion is 14259 J/g , and the enthalpy of formation is $+825.42\text{ kJ/mol}$.

A different technique of preparing pentaerythritol diazido dinitrate (PDADN) proceeded via bromidation reaction of pentaerythritol as the starting material, azidation of 2,2-bromomethyl-1,3-propanediol, and nitration of 2,2-azido-1,3-propanediol [555]. The structure of PDADN was characterized by IR, ^1H NMR, and elemental analysis.

The thermal decomposition of PDADN was examined using TGA, DSC, pressure DSC, and rapid scanning FTIR spectroscopy [556]. The results showed that **(1)** the extrapolated onset temperatures, peak temperatures, and enthalpy of decomposition increased with a change in pressure from 0.1 to 2 MPa. Over the range of pressures from 2.0 to 6 MPa, the thermal behavior of PDADN did not seem to be very affected by the pressure; **(2)** the apparent activation energy and the preexponential constant of thermal decomposition of PDADN at a pressure of 0.1 MPa were 134.9 kJ/mol and $10^{12.7}\text{ s}^{-1}$, respectively; and **(3)** the pressure affected the magnitude of the apparent activation energy.

The structure of PDADN was studied by FTIR, MS, and NMR [557]. The molecular geometries and electronic structures of the four conformations of PDADN were fully optimized using a semiempirical AM1-MO method [558]. Among the four conformations, the structure with one $-\text{ONO}_2$ group at *trans* conformation and another $-\text{ONO}_2$ and two $-\text{N}_3$ groups at *cis* conformations was the most stable. When all four groups, two $-\text{ONO}_2$ and two $-\text{N}_3$, were at *trans* conformations, the nuclei repulsion energy was lower, and the dipole moment was smaller than those in other conformations.

The molecular geometries, electronic structures, and IR spectra at the four conformations of pentaerythritol diazido dinitrate were calculated using a DFT B3LYP method [559]. Among the four conformations, the one whose structure consisted of one $-\text{NO}_2$ group at the *cis* position and the other $-\text{NO}_2$ group and two $-\text{N}_3$ groups at the *trans* position was the most stable. The calculated IR absorption band frequencies of $-\text{NO}_2$ groups and $-\text{N}_3$ groups in the IR spectra were in agreement with the corresponding experimental data.

The thermal decomposition of PDADN was investigated by DSC-TGA-FTIR [560]. The time-resolved TGA-IR curves of the change of the IR characteristics and relative absorption intensity of decomposition gas products as a function of temperature yielded the kinetic parameters and mechanism functions of PDADN decomposition.

The mechanism of PDADN thermal decomposition was analyzed based on the *isokinetic point* of the formation rate among all the decomposition gas products.

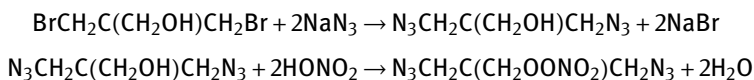
Five structurally similar $-\text{ONO}_2$ and $-\text{N}_3$ derivatives of pentaerythritol, including tetraazido pentaerythritol (TAPE), pentaerythritol triazido nitrate (PTAN), PDADN, pentaerythritol azido trinitrate (PATN), and PETN were studied by a molecular orbital computational method [561]. The molecular geometric configurations were optimized, and vibration analyses were conducted, and the densities, heats of formation, thermodynamic functions, detonation performances, and specific impulses were calculated. The BDE of the possible trigger bond and the activation energy of the hydrogen transfer reaction were computed. The results showed that in comparison with PTAN, PDADN, PATN, and PETN, TAPE has the highest heat of formation among the five derivatives and a specific impulse level approaching that of PETN. The detonation performance and stability of PATN were close to those of PETN and better than that of other derivatives, including PDADN. The pyrolysis of TAPE is most likely initiated from the transfer of H to $-\text{N}_3$, which leads to the elimination of N_2 , and has an E_a of 130.57 kJ/mol. The pyrolysis of other derivatives containing $-\text{ONO}_2$ groups most likely starts from the rupture of the $\text{O}-\text{NO}_2$ bond with a BDE of 130.91–137.45 kJ/mol. These energy values satisfy the common stability requirements for these energetic compounds.

12.3.4.2 1,3-Diazido-2-nitroxypropane

1,3-Diazido-2-nitroxypropane, also known as 1,3-diazidopropan(2)ol nitrate, 1,3-diazido-2-nitryloxypropane, DANG, $\text{N}_3\text{CH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{N}_3$, $\text{C}_3\text{H}_5\text{N}_7\text{O}_3$, is an energetic plasticizer that has not yet found any application. It has an oxygen balance of -47.04% and a nitrogen content of 52.34% . Its freezing point is below 258 K (-15°C), and its density is 1.0059 g/cm^3 at 293 K. The onset of thermal decomposition exotherm is at 461 K (188°C) [562]. 1,3-diazido-2-nitroxypropane can be prepared with 1,3-dichloro-2-propanol as starting material via azidation and nitration with 1,3-diazido-2-propanol as an intermediate [563, 564].

12.3.4.3 1,3-Diazido-2,2-dinitroxypropane

1,3-Diazido-2,2-dinitroxypropane, also known as neopentyl glycol diazido dinitrate, $\text{N}_3\text{CH}_2\text{C}(\text{CH}_2\text{OONO}_2)\text{CH}_2\text{N}_3$, was synthesized by a one-pot process, which consisted of two steps, i.e., nucleophilic substitution of 1,3-dibromo-2,2-dihydroxymethylpropane with sodium azide and nitration of the substituted intermediate (1,3-diazido-2,2-dihydroxymethylpropane) with nitric acid, but carried out in one pot without separating the intermediate [565]:



The factors affecting the yield and purity of neopentyl glycol diazo dinitrate, such as the ratio of 1,3-dibromo-2,2-dihydroxymethylpropane/sodium azide/nitric acid, nitration temperature, and time, were optimized. The optimized process conditions were as follows: 1,3-dibromo-2,2-dihydroxymethylpropane/sodium azide/nitric acid (molar ratio) = 1.0/2.1/8.0, $T = 268\text{--}292\text{ K}$ ($15\text{--}19\text{ }^{\circ}\text{C}$), and $t = 18\text{ min}$. The yield and purity of the resulting neopentyl glycol diazo dinitrate could be up to 84 and 98%, respectively, and the structure was identified with IR, NMR, and elemental analysis.

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Nitrate Oxidizers

1 Introduction – Solid Nitrate Oxidizers

Like any oxidizer for rocket propellants, oxidizers for solid propellants need to have a high percentage of excess oxygen. However, while in the case of liquid oxidizers the lack of excess oxygen can be adjusted by changing the oxidizer-to-fuel liquid propellant flow rates, that choice is not available for solid propellants. This is because the binder that holds the oxidizer granules together is generally an organic fuel type that can hold only a limited amount of solids before its mechanical properties deteriorate and it cracks under the load of acceleration during transportation and launch. One of the key parameters characterizing a solid propellant is the *percent solids loading*. For optimum performance, there has to be at least sufficient oxidizer to achieve complete combustion of the binder to CO, water, and nitrogen. High-density oxidizers allow more binder to be used, resulting in better mechanical properties.

The oxidizers for solid propellants are mostly the perchlorates and nitrates of ammonium compounds. Alkali metal perchlorates [1] and nitrates may be used for pyrotechnic igniter charges, but they are rarely used in modern rocket propellants because the high molecular mass and the particulate nature of the alkali metal oxides in the exhaust lowers the specific impulse. Solid propellants for model rockets and toy rockets may still use potassium nitrate in formulations similar to the old “black powder” that has been used for almost 1000 years. In the past 20 years, two new oxidizing anions have been added to the inventory: dinitramide (dinitramidate) and nitroformate. They can be combined with ammonium, hydroxylammonium, hydrazinium, or heterocyclic cations to form solid salts. These new oxidizers were not included in older books on rocket propellants, and the current book at hand provides the first comprehensive summary on the properties of these new oxidizers.

Discussions about the production of various solid-propellant oxidizers are contained in the following sections on individual oxidizers, usually as one of the very first subsections of each section. While most other industrial applications of these chemicals are not affected by the particle (crystal) size and shape, these properties do affect the processability and burning rates of solid propellants and need to be carefully controlled. If a solid-propellant oxidizer in the as-supplied state does not have the desired particle size or shape, it will have to be recrystallized or ground (pulverized) to the required size. A very useful chapter on the crystallization of chemicals with special reference to solid-propellant oxidizers is contained in [2]. It includes nicely illustrated information on the best crystallization methods for ammonium nitrate (AN), ammonium dinitramide (ADN), hydrazinium nitroformate (HNF), 3-nitro-1,2,4-triazole-5-one (NTO), hexanitrohexaazaisowurtzitane (CL-20), and many other energetic materials. For

instance, the crystal shape of various energetic materials can be changed in the desirable direction by changing the solvent and the cooling rate. Ultrasound might be used during crystallization to induce nucleation at lower supersaturation levels. Quite often the optimum solids loading of solid propellants can be achieved only with bimodal or even multi-modal particle size distribution of the oxidizer.

During the past two decades, development in the field of solid-propellant oxidizers was driven not only by the need for higher specific impulse but also by the desire to reduce air pollution from toxic rocket-propellant exhaust such as HCl and AlOCl . Chlorine-free, environmentally-friendly oxidizers have received a lot of attention but are still several steps away from practical application.

1.1 Comparison of Solid-Propellant Oxidizers

The properties of solid-propellant oxidizers are summarized in Table 1. The most important evaluation criterion for any oxidizer, solid or liquid, is the percentage of oxygen available for the combustion of a fuel the oxidizer is paired with in a rocket-propellant formulation. One can express the percentage of available oxygen as weight (mass) percent, as oxygen balance, or as the oxygen deficiency number, which in the case of oxidizers actually is an oxygen excess number, so it carries a positive instead of a negative sign. If the oxidizer contains a halogen in addition to oxygen, the halogen also has oxidizing potential and can be added to the oxygen balance (a formality), but one will need to explain how the oxygen balance was calculated (with or without inclusion of the halogen).

Table 1 contains a column for available oxygen, expressed in mass-%. In most cases this number is smaller than the total oxygen content because some of the oxygen may be consumed by the cation if it contains metals or hydrogen. In the case of alkali metal perchlorates, it is safe to assume that the halogen will bond with the alkali metal to form an alkali metal halide; thus, all oxygen should be available. In the case of perchlorates of nitrogen-hydrogen cations such as ammonium and hydrazinium, extra credit should be given in the available oxygen column for the chlorine, which can bind some of the hydrogen. This is indicated by the designation (+ Cl).

Table 1: Useful oxygen content and physical properties of solid oxidizers.

Compound name	Formula	Molec- ular mass, g/mol	Total oxygen content, mass-% O	Available oxygen, mass-% O	Melting point		Density, g/cm ³ , at °C	Enthalpy of formation	
					K	°C		kJ/mol	kcal/mol
Lithium nitrate	LiNO ₃	68.94	69.62	58.02	525	252	2.38 (25°)	-482.4	-115.3
Lithium perchlorate	LiClO ₄	106.39	60.15	52.64 (+ Cl)	512	239	2.429	-380.3 ± 1.2	-90.89 ± 0.29
Sodium nitrate	NaNO ₃	84.99	56.47	47.06	585	312	2.257	-424.7	-101.5
Sodium perchlorate monohydrate	NaClO ₄ •H ₂ O	140.45	56.96	39.87 (+ Cl)	403 (decomp.) (decomp.)	130	2.02	-382.7 ± 0.9	NaClO ₄ anhydrous: -91.48 ± 0.22 -117.7
Potassium nitrate	KNO ₃	101.10	47.47	39.56	607	334	2.109 (16.0°)	-492.5	
Potassium perchlorate	KClO ₄	138.55	46.19	40.42 (+ Cl)	883	610	2.52	-433.5	-103.6
Ammonium nitrate	NH ₄ NO ₃	80.04	59.97	19.99	442.7	169.6	1.725 (25°)	-367.9	-87.93
Ammonium dinitramide	NH ₄ N(NO ₂) ₂	124.06	51.58	25.8	365.6	92.44	1.824	-365.6	-87.38
Ammonium perchlorate	NH ₄ ClO ₄	117.49	54.47	27.24 (+ Cl)	Decomp.	Decomp.	1.95	-135.0	-32.26
Hydroxylammonium nitrate	NH ₃ OHNO ₃	96.04	66.63	33.31	315.4	42.2	1.92	-295.9	-70.74 ± 0.32
Hydroxylammonium perchlorate	NH ₃ OHClO ₄	133.49	59.93	23.97 (+ Cl)	354	81	~2	-399	-95.3
Hydrazinium(1+) nitrate	α-N ₂ H ₅ NO ₃	95.06	50.49	8.42	343.8	70.7	1.685	-278.2	-66.5
Hydrazinium(1+) perchlorate	N ₂ H ₅ ClO ₄	132.51	48.30	30.19 (+ Cl)	410	137	1.939	-246.2 ± 0.96	-58.86 ± 0.23
Hydrazinium(2+) diperchlorate	N ₂ H ₆ (ClO ₄) ₂	232.96	54.94	34.34 (+ Cl)	463	190	2.21	-177.8	-42.5
Hydrazinium(1+) nitroformate	N ₂ H ₅ C(NO ₂) ₃	183.08	52.43	13.11	403.9	130.8	1.869	-293.3 ± 4.1	-70.1 ± 1.0
Nitrosyl perchlorate	NOClO ₄	129.46	61.8	61.8 (+ Cl)	Decomp.	Decomp.	2.169	-72.8	-17.39
Nitronium perchlorate	NO ₂ ClO ₄	145.45	66.0	66.0 (+ Cl)	398 (decomp.) (decomp.)	125	2.25	-154	-36.8
								+37.2 ± 1.0	+8.88 ± 0.25

2 Ammonium Nitrate

There is increasing interest in the development of ecologically-friendly solid-propellant systems that can replace the existing ones in applications, particularly when the rockets have to be fired in close proximity of military personnel and smokeless HCl-free burning is desired. Avoiding HCl in the exhaust will lead to cleaner burning propellants with no contrail and low signature, thus not revealing the launch site to the enemy. Therefore, ammonium nitrate (AN) is receiving renewed attention as a possible substitute for ammonium perchlorate (AP) oxidizer in view of the hazardous nature of other candidates such as nitramines and the non-availability of substances such as ammonium dinitramide in requisite quantities and at affordable prices. With an oxygen balance of +19.99%, AN is a moderately good oxidizer for solid rocket propellants, and it is not at the top of the list when it comes to evaluating solid oxidizers based on their useful oxygen content alone.

Although ammonium and hydrazinium nitrates and perchlorates can burn by themselves if the decomposition is accelerated by burning rate additives, using AN by itself does not offer any advantages over formulations that contain organic binders. The strand-burning decomposition of pure hydrazinium salts can spontaneously transition into a detonation. In addition to the complications caused by polymorphism and phase changes, AN is very hygroscopic, and if stored in bulk, it has a tendency to cake. For the various applications of AN, what the industry wants is a free-flowing granular material. For this reason, AN intended to be used as a fertilizer is often prilled in spherical form (melt spraying) and coated with anti-caking agents. Anti-caking agents often used include clay, zeolites, diatomaceous earth, and aluminosilicates. Anti-caking agents may interfere with the intended applications of AN in rocket propellants, gas generants, or explosives.

Because AN is an important propellant and explosive ingredient and industrial bulk commodity, several conferences and literature summaries have been devoted exclusively to this chemical [3–5].

2.1 Natural Occurrence of Ammonium Nitrate

Ammonium nitrate occurs naturally as an intermediate product during the bacterial oxidation of ammonia. The nitrification by nitrifying bacteria that occurs in the soil where aqueous or gaseous ammonia has been applied as fertilizer in the field is undesirable because nitrate is leached by rain or irrigation water and carried away faster than ammonia, which remains adsorbed to clay in the soil until it is taken up by the roots of the plants. Ammonium nitrate can form naturally in sewage and other nitrogen-rich environments. Aerosols of AN and ammonium sulfate form in polluted air and play a significant role in atmospheric smog chemistry. Much of the natural nitrogen fixation in the form of NO_x is the result of atmospheric lightning electrical

discharges. The formation of AN in a model nitrogen atmosphere containing oxides of nitrogen, ammonia, water vapor, and oxygen present in parts-per-million (ppm) quantities has been investigated [6]. The measured amounts of nitrate produced were compared with those predicted by use of a kinetic model for the reacting system. For any temperature, there was an initial pressure of ammonia below which AN was not found. At higher pressures of nitrogen dioxide, equilibrium was quickly attained, but at low pressures, nitrate was not always formed in the time of contact of reactants. Water vapor enhanced the rate of formation of nitrate.

2.2 Production of Ammonium Nitrate

Ammonium nitrate, NH_4NO_3 , AN, CAS RN [6484-52-2], is a bulk industrial production chemical [7]. It is produced industrially in large quantities by neutralization of aqua ammonia or anhydrous ammonia gas with diluted or concentrated nitric acid. This neutralization reaction is violent and very exothermic and has led to accidental explosions [8]. Of course, the combination of anhydrous ammonia and white fuming nitric acid could be used as a bipropellant rocket combination. For making solid AN, after the solution is formed, typically at about 83% concentration, the excess water is evaporated to an AN content of 95 to 99.9% concentration (AN melt), depending on purity grade and intended application. The AN melt can then be made into “prills” or small beads in a spray tower or into granules by spraying and tumbling in a rotating drum. The prills or granules may be further dried and are cooled and then coated to prevent caking and moisture absorption. These prills or granules are the typical AN products in commerce.

Of all AN produced from nitric acid, the majority (86%) is used in the nitrogen-based fertilizer industry, either as a direct fertilizer or in the production of fertilizer blends with ammonium sulfate or urea ammonium nitrate. In looking at the usage statistics, after the demand of the fertilizer industry is accounted for, the balance of the AN derived from nitric acid is used mainly for manufacturing explosives and blasting agents (“ANFO”; ammonium nitrate–fuel oil mixture). Relatively little AN is used in rocket propellants or gas generants.

2.2.1 Crystallization of Ammonium Nitrate

Crystallization of AN can occur either from saturated solutions or from the melt. For propellant applications, it is very important to obtain water-free AN in the desired particle size and phase. Quite often, phase-stabilizing additives are co-crystallized with the AN. Therefore, the crystal growth habits of AN by itself and AN with additives have been investigated. The growth rate of NH_4NO_3 phase III crystals from saturated solutions was measured and interpreted using two models: The first was a standard crystal growth model based on a spiral growth mechanism, and the second was based on

the new concept of kinetical roughening [9]. As the crystal surface becomes rough, a critical supersaturation point can be determined, and from this step a value for the free energy can be derived. Another model for the morphology of phase III AN crystals was based on the concepts of periodic bond chain, F face, and a connected net of ions [10].

Much of the phase behavior of AN is influenced by how it is crystallized the first time. Changes in the crystal structure of freshly crystallized AN take place for several hours after the material has first solidified. By examining freshly crystallized AN using scanning electron microscopy (SEM), it was observed that aging for >1 h led to the growth of secondary grains along the boundaries of primary grains (140–200 μm) [11]. After 6 h of aging, no more grain growth along grain boundaries could be observed. Instead, distinct clusters with morphologies similar to the secondary grains were formed. The secondary growth occurs to relieve strain at the grain boundaries and to minimize interfacial tension between the grains.

The AN crystal shape depends on the conditions of cooling and supercooling and the presence of seed crystals or nuclei. It was possible to crystallize phase I and phase II AN as dendrites from a melt containing 0–4.5 and 4.5–12 mass-% water, respectively [12]. *In situ* microscopic measurements showed that the characteristic ratio S/ρ (where S is the side branch spacing near the tip and ρ is the dendrite tip radius) for dendrites varies between 2.3 and 5.1 for both AN(I) and AN(II). This agreed reasonably well with a theoretically derived value of 2.8 reported in the literature. The water concentration had a strong influence on the crystal shape as expressed by the relation between the side-branch spacing near the tip, S , and the tip growth rate, v , of the dendrites. These observations matched, at least qualitatively, the theoretically predicted relationship between S and v . Ammonium nitrate phase II crystals growing from an AN solution containing 5.7 mass-% water develop as dendrites in the ab -plane and in the c -direction and are referred to as ab - and c -dendrites, respectively. Experimental data have suggested that the growth form of the ab -dendrites growing in pure aqueous solutions results from the instability of the growth directions along the a - and b -axes and can be altered by the presence of additives [13, 14]. If the growth rate of c -dendrites is sufficiently retarded by additives, the ab -dendrite tips are stable, do not split, and grow along the a - and b -axes. If side branches growing in the c -direction are less retarded, the ab -dendrites show tip splitting, finally resulting in growth directions deviating from $\langle 100 \rangle$ and being approximately $\langle 410 \rangle$. The tip growth rates as well as the side branch spacings depend on the amount of undercooling.

Ammonium nitrate nanoparticles can be made by employing a surfactant templating method [15]. For example, about 10 g bulk AN is dissolved in 10 mL deionized water. About 2 mL PEG-400 is added to this solution, and the solution is thoroughly mixed. This solution is kept in an oven at 333 K (60 °C) for several hours to slowly evaporate the water. The resultant material is then stirred vigorously while adding 2-propanol from a burette at a rate of 1 mL/min, which forms a white precipitate that

is then washed with excess 2-propanol several times to remove almost all of the PEG-400. The precipitate is then dried completely at 333 K (60 °C) to obtain a dry powder. Ammonium nitrate is highly hygroscopic, so these nanoparticles tend to recrystallize to form bulk crystals. Therefore, it is best to keep AN nanoparticles in a vial sealed under vacuum to prevent moisture absorption.

2.2.2 Prilling of Ammonium Nitrate

AN is often converted to the desired particle shape by spraying and atomizing molten AN (with or without the addition of phase-stabilizing additives) into a tall tower, where the falling droplets assume a spherical shape before they solidify and are carried away by a cooling gas stream. The operating temperature during this prilling process must be carefully controlled to ensure that all AN is molten yet not overheated to the point of incipient decomposition. Prilling produces a range of particle sizes from 20 to 400 μm . The prilled and coated near-spherical particles have the advantage that they are free flowing, which makes it easier to transfer fertilizer grade AN from storage silos to hopper cars and fertilizer spreaders. Supercooling of droplets in the prilling tower must be avoided. Therefore, nucleating (seed) agents are added to avoid supercooling of the melt and to initiate crystallization. Aluminum silicate and silica have been tested as nucleating agents. In addition, 1% fumed silica or tricalcium phosphate can be applied as an anti-caking agent. All of these must be expected as contaminants if industrial-grade AN is to be used for propellants.

Freshly prepared prills flow freely; however, the phase IV $\leftrightarrow$ phase III phase change during storage and transport causes the prills to fracture and fragment. The benefit of coatings (e.g., anti-caking or hydrophobic coating) of the prills is forfeited once they fracture and uncoated surface is exposed. If only 10% of the spherules fracture, the benefit of coatings is lost, and the bulk material is likely to set up into a monolithic mass. If the prills run through several phase-transition cycles, they convert to powder, which is more likely to form a monolithic cake that is hard to remove and disperse. The addition of phase stabilizers to AN is therefore of importance not only for AN as a rocket propellant and gas generant but also for most other applications of AN.

A different process used for both AN and ADN is the prilling by spraying droplets of molten salts into a stirred pool of an inert, cool liquid in which the droplets can assume a spherical shape before they solidify. This process can be applied to a wide range of energetic materials as well as AN and ADN [16, 17].

For optimum packing in a solid propellant grain, it is best to use spherical oxidizer particles. Besides the spraying of molten AN into a prilling tower, spheres can be shaped by melting AN in a two-phase system. In this case, the molten AN is dispersed in a continuous, inert phase that is not miscible with AN. The surface tension and interfacial tension cause the molten droplets to assume a spherical shape. The solidification of the molten droplets to spherical prills takes place during the cooling

to a temperature below the melting point of AN. By proper choice of suitable oil-bath fluids and spray nozzles and by optimizing the process parameters, spherical AN particles with mean particle sizes from 10 to 800 μm can be manufactured reproducibly, similar to a process used for ADN [18–22]. The inert fluid prilling process consists of two stages: In the first stage, molten AN is dispersed in a continuous phase in which AN is insoluble. The droplet size produced can be controlled by varying the force of agitation. The influence of the different process parameters, such as dispersion rate, dispersion power, emulsification time, influence of emulsifying agents, and the rheological behavior of the continuous phase were studied to optimize the process. In the second stage of the process, crystallization of the emulsified AN droplets to spherical, solid particles is obtained by quickly lowering the temperature of the system. This process also gives spherical AN particles with mean sizes of 10–800 μm . Fumed silicon dioxide can be used as a protective colloid to promote emulsification.

Instead of producing prilled stabilized AN in a batch process, it is possible to conduct this as a continuous process with adequate process controls for a reproducible product [23, 24]. Similar continuous processes have been developed for the prilling of ADN.

Prilled and stabilized AN is of interest as a propellant ingredient for gas generants in airbag inflators [25]. However, failure to prevent intrusion of moisture into the gas generators or insufficient desiccant in the cartridge allowed phase changes to take place and caused numerous fatalities in airbag inflator explosions.

2.2.3 Coating of Ammonium Nitrate

Ammonium nitrate is often coated to reduce its hygroscopicity, to prevent it from caking, and to achieve a better bond with the solid-propellant binder.

A systematic study has been made of the interaction mechanisms of amine type surfactants and AN by using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) [26]. The results indicated that octadecylamine adsorbs on the surface of powdered AN in the form of octadecylammonium nitrate. Bromo-hexadecyltrimethylamine also adsorbs on AN through rather strong chemical affinity action, providing a good anti-caking effect of amine-type surfactants on powdered AN.

Octadecylamine at a concentration of 2×10^{-4} mol/L in xylene was selected as a monolayer-forming material to coat AN crystals [27, 28]. After a self-assembling monolayer was formed through hydrogen bonding, Coulomb forces, and polarization at the interface of xylene and AN, a monolayer of octadecylamine is assumed to have self-assembled itself on the surface of AN crystals. The rate of moisture absorption of AN after surface modification was only 58% of that of untreated AN.

Ammonium nitrate was coated with a wetting agent Si-K and polymer material Polymer B [29]. Surfaces of the coated AN particles were characterized by SEM and XPS. The hygroscopicity and caking tendency of the coated AN were measured, and

the experimental results showed that the hygroscopicity and caking tendency of AN particles could be effectively reduced through this type of coating.

A liquid-phase separation technique was used to coat AN with polyvinyl butyral (PVB) [30]. A study of the properties of coated AN showed that the water absorptivity and caking tendency were greatly reduced. The differential scanning calorimetry (DSC) peak of the crystal phase transition of II $\rightarrow$ III shifted to higher temperature and even disappeared.

A polymer and a wetting agent were used to coat phase-stabilized AN (PSAN) by means of a spraying and drying technique in order to lower the moisture absorption of AN [31]. The characterization of the modified PSAN was performed by measuring the hygroscopicity, contact angle, and mass fraction of the coating layer and by using XPS and SEM. The results showed that the composite modification of both the polymer and the wetting agent can effectively reduce the moisture absorption of PSAN by up to 46%. This indicated that spraying and drying technology is better than liquid-phase separation coating techniques.

The crystal properties of AN modified by treatment with surfactants were analyzed by SEM, DSC, and XRD, and their specific surface area, hygroscopicity, caking, and explosion properties were examined [32]. The results showed that, compared to conventional AN, the modified AN crystals have different shapes and larger specific surface areas. They contain a larger number of gas pockets, but they are also less hygroscopic and have less tendency to cake, which are desirable properties for all explosive applications.

AN particles were coated with polyvinyl acetate and ethyl cellulose in order to improve wetting between AN particles and the binder [33]. This was done to prepare AN-based propellants with higher solids loading by the use of coated AN.

To decrease the surface polarity and hygroscopicity of AN, a surfactant, a wetting agent, and a polymer were used to coat AN particles [34]. A spraying–drying technique was used to coat the fluidized granules. The surface polarity, surface structure, and hygroscopic water absorption rate of the coated AN particles were studied by surface energy measurement, SEM, and controlled moisture storage experiments. It was shown that the coated AN particles possessed low surface polarity and low rates of hygroscopic water absorption.

Gravimetric analyses of AN coated with eight different waterproofing materials in comparison to uncoated AN were conducted at different relative humidity and exposure durations [35]. The results indicated that mineral jelly is a promising waterproofing material for AN among the materials tested, which included calcium stearate, dioctyl phthalate, kaoline, diethyl phthalate, dinitrotoluene, shellac varnish, and beeswax. Coated AN was characterized using differential thermal analysis (DTA) and XRD.

Ammonium nitrate has been modified by evaporative recrystallization from a solution containing hexadecyl trimethyl ammonium bromide and sodium dodecyl sulfate surfactants [36]. The physical property of the modified compound was

investigated by SEM, DSC, specific surface area, and particle size measurements. The results showed that compared with common AN, the modified AN had an irregular crystal shape, greater specific surface area, better particle size distribution, lower heat of crystal pattern transition, and higher phase-change transition temperature. This indicated that the modified AN had a mesoporous structure with good self-sensitizable, anti-hygroscopic, and anti-caking performance as an oxidizer in industrial ANFO explosive.

Ammonium nitrate was coated by precipitation polymerization of styrene in chloroform solution [37], and the effects of the polymerization process conditions on the hygroscopicity of the coated AN were investigated. The results showed that the hygroscopicity of the coated AN decreased at first and then increased with an increase of the styrene concentration and polymerization temperature. The minimum hygroscopicity was attained with a styrene concentration of 4% and a polymerization temperature of 333 K (60 °C). The hygroscopicity rate of water absorption was reduced by 88.8% in comparison with uncoated AN. The hygroscopicity of the coated AN was also affected by the particle size of the uncoated AN. Within the scope of the experiments, the hygroscopicity of the coated AN was lower the smaller the particle size.

In order to strengthen the bond strength between PSAN and a binder, a silane bonding agent that can form hydrogen bonds with PSAN was selected to coat the PSAN particles [38]. Modified PSAN was characterized by SEM and XPS. It was shown that the surface morphology of coated PSAN changed greatly, and the coating caused the contact angles of nitroglycerine (NG) and diethylene glycol dinitrate (DEGDN) on the surface of modified PSAN to be reduced by about 56 and 63%, respectively. At the same time, the rate of moisture absorption of modified PSAN was reduced by about 15%. Processing the modified PSAN into PSAN/3,3-bis (azidomethyl)oxetane-tetrahydrofuran copolymer (BAMO-THF) propellants, the test results showed that tensile strength of the propellants was improved by about 65%, and the amount of dewetting was reduced by about 20%.

A supercritical fluid solvent/anti-solvent process was used to coat AN with nitrocellulose, using acetone as co-solvent and supercritical CO₂ as anti-solvent [39]. The effect of temperature, pressure, and speed of precipitation on the quality of the coating was investigated using SEM and moisture absorption measurements. The results showed that the temperature in the process is a key factor affecting the coating quality. The optimum conditions of the process were temperature, 304 K (31 °C); pressure, 10 MPa; and CO₂ release rate, 10–15 kg/h. The mass fraction of nitrocellulose in the finished product was about 1%. Such coatings reduced the hygroscopicity of AN remarkably. The hygroscopicity, fluidity, and dispersibility properties of coated AN were greatly improved.

To improve the mechanical properties of propellants containing PSAN, ethylenediamine (EDA) was reacted with the surface of PSAN particles to prepare reactively-coated PSAN [40]. The extent of the chemical reaction between EDA and AN was confirmed by Fourier-transform infrared spectroscopy (FTIR), and the coating effect was

characterized by hygroscopicity and contact angle measurements. The results showed that the surface polarity of coated PSAN particles decreased and that the hygroscopicity was much less than that of untreated PSAN. When coated PSAN was used for making PSAN/BAMO-THF propellants, the best improvements of the mechanical properties of the propellants were with PSAN coated with 0.2 mass-% EDA. The maximum stress increased by about 46%, and the elongation increased by about 83%. Similar coatings were achieved using diethylamine and triethylamine [41].

For improving the hygroscopicity and surface polarity of PSAN, EDA, diethylamine, and triethylamine were selected to react with the surface of PSAN particles to prepare reactively-coated PSAN. The coating effects were characterized by measuring the rate of moisture absorption, contact angles, and propellant tensile strength. It was shown that the hygroscopicity and surface polarity of PSAN reactively coated by diethylamine gave the best results compared with the others. The rate of moisture absorption in 8 h declined by 60.5 and 63.6% in the atmospheres of 75.3 and 92.5% relative humidity, respectively. The polar component of surface free energy declined by about 87%, and the non-polar component increased by about 145%. Using reactively-coated PSAN powders in PSAN/BAMO-THF propellants, it was found that the propellants using the PSAN coated by EDA had the best mechanical properties, and the maximum stress (σ_m) could be obtained at 0.2% coating mass of EDA. The chemical reactions between amines and AN were confirmed by surface FTIR

AN can be coated by dispersing AN particles in a non-polar solvent (petroleum ether or cyclohexane) at a mass ratio of 1:(2–20) at 293–333 K (20–60 °C); dissolving a coating agent in a polar solvent (ethyl acetate, acetone, methanol, ethanol, or tetrahydrofuran) at a mass ratio of 1:(100–5000); dripping the coating-agent solution into the AN solution at a coating agent/AN weight ratio of (0.0001–0.1):1; stirring; allowing reaction for several hours; and then removing the solvent and vacuum drying at 333 K (60 °C) to obtain coated AN [42]. The coating agent can be an organic primary amine, secondary amine, or tertiary amine, such as ethylenediamine, diethylene triamine, triethylene tetramine, triethylamine, diethylamine, hexamethylenediamine, or octadecylamine. The coating method is also suitable for coating ammonium perchlorate or ammonium dinitramide particles. The coated AN has reduced moisture absorption and lowered surface polarity, resulting in improved mechanical properties of propellants produced with it.

The fluidized bed technology allows the production of composite particles consisting of layers of different energetic materials. Spherical AN particles could be coated with ultraviolet (UV)-curing polymers (urethane oligomer [meth]acrylate monomer blend), which lead to mechanically stable core-shell structures [43]. The mean particle-crushing strength could be increased from 21.9 to 31.9 N/mm² by adding only 3% of the coating material. Figure 1 shows uncoated and coated AN particles at three different magnifications.

Polyvinyl acetate (PVAC), sliced paraffin (wax), and polyethylene glycol (PEG) were evaluated as coating materials using the liquid coating technology [44]. The

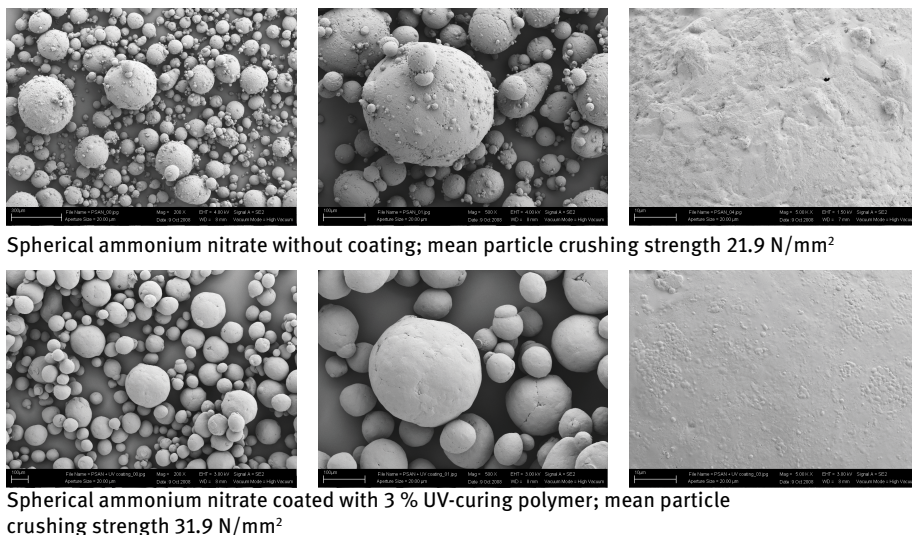


Figure 1: Coated and uncoated spherical ammonium nitrate. (Reproduced from [43] with permission from Fraunhofer Institute of Chemical Technology.)

coated samples were characterized by SEM and DSC. The experimental results showed that the modification effects of PVAC and wax were good, but PEG did not coat very well. The appearance of modified AN presented spherical particles, but free-flowing properties were better. The moisture absorption rate decreased by 30.6 and 23.3% respectively, after 24 h at ambient temperature (303 K [30 °C]) and in a relative humidity of 75%.

The surface of AN was modified by heating, melting, and applying modified paraffin as coating material [45]. The structure and surface properties of coated AN were characterized by infrared (IR), SEM, contact angle, and hygroscopicity measurements. Results showed that the gap of AN coated with modified paraffin was significantly reduced. When the mass fraction of modified paraffin was 0.5%, the film covered most of the surface. When the mass fraction of modified paraffin was 2.5%, the film was uniform and perfect, the water-wetting surface tension decreased from 9.04×10^{-2} to 1.883×10^{-2} N/m, and the amount of moisture absorption after 24 h decreased by 88%. However, what the researchers did not test was the detonability, since the composition of the paraffin-coated AN would now be similar to that of ANFO.

A phase-separation physical coating method was used for coating AN particles with polystyrene [46]. The effects of the volume ratio of toluene and *n*-hexane, the mass ratio of polystyrene and AN, the ratio of AN and mixed solvent, and the precipitating-agent addition rate on the coating of AN particles were optimized. The results showed that the optimum process conditions of polystyrene-coated AN were a 1 : 3 volume ratio of toluene and *n*-hexane, a 3.5 mL/g ratio of mixed solvent and AN, room

temperature, and 6 s/drop for the addition rate of the precipitating agent. When the 60-mesh AN was coated with polystyrene and the mass ratio of polystyrene and ammonium nitrate was 1.54%, the reduction in the moisture absorption rate was 75%.

A phase-separation method for the physical and chemical coating of AN with shellac used *n*-butyl alcohol as the solvent and *n*-hexane as the precipitant [47]. The coating was characterized by measuring the moisture-absorption rate of coated AN. The results showed that the preferred process conditions for making shellac-coated AN were a 1:3 volume ratio of *n*-butyl alcohol to *n*-hexane, 5.0 mL/g for the mass ratio of mixed solvent and AN, and 6 s/drop for the precipitation agent addition rate. The absorbed shellac amount was inversely proportional to the particle size. The moisture absorption was reduced by 55% for shellac-coated ammonium nitrate under the preferred coating conditions.

An excellent review of the available information on various coating methods for the surface modification of AN for reducing its hygroscopicity summarizes the recent advances and issues involved in AN surface modification by physical, chemical, and encapsulation coating methods [48]. Coating materials, process conditions, and the hygroscopicity test conditions are extensively discussed along with summaries of the advantages and disadvantages of each coating method. The findings indicated that the investigation and development of anti-hygroscopicity coatings of AN may require further research in order to further reduce the hygroscopicity. In physical coating methods, the hydrophilic tails of the surfactant materials attach to the polar surface of AN particles and make a hydrophobic uniform membrane on the surface. The success of this process mainly depends on the solubility of the surfactant and the insolubility of AN, as well as on the suspension of particles in aqueous solution.

2.2.3.1 Anti-Caking Agents for Ammonium Nitrate

Historically, attempts to reduce the caking tendency of AN have depended on the following:

1. keeping the AN dry, either by preparing it almost completely free from moisture and protecting the granules with a coating of organic waterproofing agent by adding a desiccating agent, e.g., anhydrous copper sulfate, or
2. adding a coating of a finely powdered, insoluble material of good covering power to the salt in order to separate the crystals from one another or to absorb the liquid phase present in the moist salt, or
3. preparing the granules so they are as uniform in size as possible so that crystallization on standing, due to the increased solubility of finely divided particles as compared with coarse granules, is avoided, or
4. preparing the granules as uniform spherical particles so that the number and area of contacts between granules are minimized; any saturated solution inclusions may be distributed over the large surface areas of the particles and held by surface tension forces in the interstices, or

5. adding crystal habit modifying dyes, which when dissolved in the saturated saline solutions in small concentration (about 0.10%) can bring about very marked changes on the habit of crystallization of these salts [49, 50]. Ammonium nitrate IV, the modification of the salt stable between 305.4 and 255 K (32.3 and -18°C), normally crystallizes as rhombic bipyramids elongated on (001) faces, with the facial development being almost entirely along (110) faces. Dyes capable of modifying the crystal habit of AN, e.g., acid magenta (sodium or ammonium salts of di-sulfonic and tri-sulfonic acids of pararosaniline) eliminated the elongation on (001), and in place of the normal facial development, a platy habit on (010) with a dendritic growth mechanism was produced, but the crystal habit of AN phase III stable above 305 K (32°C) was not greatly affected by acid magenta.

The most widely used anti-caking agent for AN is clay or kaolin [51] in different forms, mostly mineral grade from the nearest clay pit, and is often poorly defined. Diatomaceous earth has been tested as an anti-caking coating. Any of these may be acceptable for fertilizer-grade AN, but they have caused rejections for AN that was to be used in propellants or blasting agents.

Claims that anti-caking agents will not only prevent caking but at the same time also prevent phase transitions have been made, but XRD will usually prove otherwise. Anti-caking agents with this property include fumed silica with a large surface area $250\text{--}350\text{ m}^2/\text{g}$ and a pore size of $100\text{--}250\text{ \AA}$ that also absorbs some of the moisture [52].

Surfactants such as quaternary salts of alkylsulfonic acids have been added to change the crystal habits of AN and prevent caking. Stearyl amine is an anti-caking agent for AN and can be coated on the prills or crystals [53]. The combination of stearyl amine with some fine powders and coating agents can effectively prevent the caking of AN.

Prilled fertilizer-grade AN is often coated with limestone or dolomite powder as an anti-caking agent. The coating affects the thermal decomposition of coated prills [54]. Chemical interactions occur during thermal decomposition of AN prills coated with limestone or dolomite powder.

Quite often, additives that will prevent or shift the $\text{IV} \leftrightarrow \text{III}$ phase change will also prevent caking. One of these additives is zinc oxide or the zinc tetrammino nitrate formed therefrom in the molten AN.

2.2.3.2 Porous Ammonium Nitrate

For certain applications, mostly explosives and blasting agents, it is desirable to use AN that has a controlled porosity. In the case of ANFO, this would allow the fuel oil to be absorbed into the granules, and it would be held by capillary forces instead of seeping out and segregating in a tall column of explosive in a borehole.

However, porous AN (even before the fuel oil is added) may have a higher cap sensitivity than nonporous, granular AN. It was even proposed to increase the porosity of AN to a point that it would become “self-sensitized,” i.e., cap sensitive without a fuel and without a booster (Section 2.8.3). Porous AN is not typically used in rocket propellants, although it may help to obtain higher burning rates but at the expense of increased sensitivity and reduced propellant density.

Porous AN is also sometimes called “expanded AN” or “foamed AN.” Expanded AN in fine crystalline form having a specific surface area greater than $500\text{ cm}^2/\text{g}$ can be prepared by vacuum flash evaporation or crystallization from an aqueous solution in the presence of a surfactant such as laurylamine acetate [55–57].

In addition to purity and crystal structure of the material, physical properties of porous AN must be characterized by measuring the void volume, average pore size, pore size distribution, active surface area, and crush strength [58].

The wettability and porosity of AN prills is one of the primary factors determining the physical stability and detonation behavior of ANFO and how AN bonds to its binder in solid propellants. The wettabilities of various types of AN prills were compared using capillary penetration measurements [59]. Additional SEM imagery and thermogravimetric analysis (TGA) tests were performed to explain the observed differences in wettability. The wettability of AN was found to be affected by several factors, including surface tension, viscosity, density, and purity of the liquid used, as well as by surface composition, porosity, bulk density, particle size, moisture content, and thermal history of the AN samples.

In order to study the self-sensitizing structural characteristics of AN used for industrial blasting agents, the pore-structure characteristics (such as porosity, pore diameter, specific surface area, and pore distribution) and particle shape of three types of AN prills were investigated using the mercury penetration method and SEM [60]. Results showed that there are numerous pores, and the pore quantity whose size is within the effective hot-spots range is much higher in expanded AN samples, where its self-sensitizing characteristic due to adiabatic compression of pores (low-velocity detonation) is obvious. In another expanded AN sample, there were also many pores, but the pore size was much smaller and the pore size distribution was narrow. A third expanded AN sample was similar to common commercial AN, i.e., the porosity and surface area were much lower, and the pore fraction within the effective hot-spots range was less.

2.3 Physical Properties of Ammonium Nitrate

The physical properties of AN have been thoroughly investigated, in particular physical properties relating to the phase changes that AN undergoes with changes in temperature. Ammonium nitrate is hygroscopic, so it is important to measure properties

on absolutely dry samples of the material and to work in a dry box or even under dry nitrogen. Properties of AN are summarized in [61–63].

The molecular mass of AN is 80.043 g/mol (IUPAC 1962 atomic mass $^{12}\text{C} = 12.000$), which corresponds to 12.493 mol/kg.

2.3.1 Melting Point and Phase Changes of Ammonium Nitrate

2.3.1.1 Melting Point of Pure Ammonium Nitrate

Literature sources give the melting point of AN as 442.75 K (169.6 °C or 337.3 °F) Once it melts, AN begins to decompose under formation of nitrous oxide (Section 2.4.6.1).

2.3.1.2 Polymorphism and Solid State Phase Changes of Pure Ammonium Nitrate

Although the fact that AN shows polymorphism and undergoes multiple phase changes has been known for a very long time [64], the study of its phase changes and how to modify or avoid them continues to this date. Hundreds of publications on this subject can be found in the literature, and it is not our intent to collect them all for this book. Uncontrolled phase changes adversely affect our ability to use AN as a rocket propellant, so we must understand it before we select it as a propellant ingredient. Ammonium nitrate exists in five different phases, and each has a different crystal structure and density. The phases are often described by lowercase Greek letters or Roman numerals, but the sequence of numbering of the two numbering systems runs in opposite directions, shown here along with the phase transition temperature:

	–18 °C		+32.1 °C		84.2 °C		125.2 °C		169.9 °C	
Tetragonal	↔	Orthorhombic	↔	Orthorhombic	↔	Tetragonal	↔	Cubic	↔	Liquid
α		β		γ		δ		ϵ		
V		IV		III		II		I		

The temperatures at which the phase transformations take place depend somewhat on the method used to measure them. Thus, dilatometric methods, XRD, and DTA may report slightly different transition temperatures. Although there are two tetragonal and two orthorhombic structures, the crystal lattice parameters are still different. Phase changes of AN are one of the reasons that AN has not been used more widely in rocket propellants and gas generants. Swelling and shrinking as a consequence of repeated phase changes cause debonding of oxidizer particles from the binder or delaminating of a solid propellant grain from the casing, resulting in uncontrollable burning behavior that often leads to explosions. Additional information on density changes of AN as the result of phase changes is summarized in Section 2.3.11.1. A significant amount of effort has been devoted to finding phase stabilizers for AN that will prevent phase changes or at least shift the temperature at which they occur (Section 2.4.1). The crystal structures of the various phases of AN and its solid solution phases with poten-

tial stabilizers are discussed in Section 2.3.11.6. Methods used for the study of phase changes are summarized in Section 2.3.11.3.

The phase changes in high-purity AN were studied by a DTA apparatus designed for constant heating and cooling rates and continuous repeated cycling for ~3-g samples [65]. Based on an analysis of DTA and XRD data, a very consistent phase-change behavior was observed. Phase IV $\rightarrow$ III transformation on heating in the range of 316–324 K (43–51 °C) and phase II $\rightarrow$ IV transformation on cooling in the range of 322–326 K (49–53 °C) were demonstrated repeatedly. The III $\rightarrow$ II transition at about 359 K (86 °C) was seen even with repeated temperature cycling. This repeatable behavior was not consistently seen by other investigators using different techniques, and it is believed that it was due to the high-purity material and constant heating and cooling rates used in this particular study.

Pure AN has five different solid phases and undergoes four different solid–solid phase transitions before melting. An excellent summary of the phase transitions of AN and potassium nitrate (KN) was published by the National Bureau of Standards (now the National Institute of Standards and Technology) [66]. In that book, the chapter on AN in pages 24–30 contains a detailed description of AN phase changes, supported by 77 mostly historical literature references. Another good summary was published by Chien [67, 68] as part of a study of the AN/KN binary system (Section 2.3.11.6).

Differential scanning calorimetry was used alone and in conjunction with Raman spectrophotometry for simultaneous calorimetric and spectral measurements to study the solid state phase transitions of ammonium nitrate between 223 and 373 K (–50 and 100 °C) [69]. On heating, two transition paths were observed between 233 and 273 K (–40 and 0 °C): one showing two separate peaks on DSC and the other showing only a single peak. The latter path became dominant when samples were thermally cycled. There was little hysteresis when going through several cycles. The double transition was followed by transition IV $\rightarrow$ II at 324 K (51 °C) and the single transition by transitions IV $\rightarrow$ III $\rightarrow$ II at higher temperatures at about 323 and 360 K (50 and 87 °C). Raman spectra showed that there were two phases present between the two DSC peaks at low temperature. The first endotherm peak was attributed to a transition from the phase designated as V to phase IV, and the second peak to a transition from V to IV. The single peak below 273 K (0 °C) was due to the transition V $\rightarrow$ IV. In continuation of this work, it was noted that the solid state phase transition path of AN is influenced by the crystallization history [70]. Slow crystallization from water gave ideal crystals, which behaved differently from crystals prepared by rapid crystallization from the melt.

The effect (if any) of crystallization methods on the IV $\leftrightarrow$ III transition of AN has not been unanimously accepted in the crystallographic community. To clarify this problem, AN was crystallized in three different ways, recrystallization, evaporative crystallization, and melt crystallization, and was characterized by DTA, XRD, and SEM [71]. When the samples were crystallized from saturated aqueous solution, ideal crystals were formed, which behaved differently from the crystals formed by the other methods. The DTA examination of the crystals showed that the crystals have differ-

ent phase-transition behavior. The moisture uptake of the samples was influenced by the mode of crystallization. The samples were further analyzed by XRD and SEM. The results showed that parameters such as thermal history, number of previous transformations, and moisture content have a very negligible influence on the IV $\leftrightarrow$ III transition of AN compared to the method of crystallization.

In a comparison of DSC results with an identical sample of AN performed in four different laboratories, the agreement between phase transition temperatures and enthalpies of transition for four phase transitions was remarkably close [72]. See also [73–77].

Pressure Dependence of Solid State Phase Changes of Pure Ammonium Nitrate

Phase diagrams between 273 and 473 K at pressures between 0.98 bar (1 kg/cm^2) and 11.77 kbar (12000 kg/cm^2) showed a previously unknown modification of AN [78, 79]. Some second-order phase transitions do not occur under conditions of hydrostatic compression but can take place when a shear stress is applied in addition to isostatic pressure. A diamond anvil cell used without a gasket around the sample is an excellent device for studying shear stress-induced transitions. Under hydrostatic conditions, AN does not undergo a phase transition at pressures up to 5.0 GPa. However, under shear stress conditions, a shear-induced transition was observed at 2.94 GPa [80]. Under shear stress, AN showed an upward break in the shear stress vs. pressure curve at 29.4 kbar, indicating a shear-induced transition. This transition was also observed at 3.0 GPa using IR spectroscopy of a thick film under non-hydrostatic conditions in a non-gasketed diamond-anvil cell [81]. Failure to observe this shear-induced transition in very thin films of sample is probably due to the very small amount of sample in the film actually experiencing pressures above 30 kbar.

A new modification VI was detected during a study of the phase transformations of AN by DTA at high pressures at 0–35 kbar and 223–623 K [82]. The univariant lines of the I $\rightarrow$ VI, IV $\rightarrow$ VI and I $\rightarrow$ IV transitions were found to intersect at a triple point near 19.5 kbar and 529 K.

The temperature range of stability of three modifications used for a pressure-effect study was V = α ($T < 255 \text{ K}$), IV = β (255–305.1 K), and III = γ (305.1–357.2 K). The average value for the increase in the volume expansion for the IV $\rightarrow$ III transition at atmospheric pressure was found to be 6.5%. In studying the effect of pressure on the polymorphic transformations of AN between stable modifications and the compressibility of different modifications of AN under isothermal conditions, it was found that the temperature for the start of the IV $\rightarrow$ III transition was shifted from 305 K at 101 kPa to 316 K at a pressure of 392.24 bar = 400 kg/cm^2 [83]. It was also found at pressures between 100 and 6000 kg/cm^2 that modification IV, which is stable between 255.1 and 305.2 K (–18 and 32.1 °C), does not show relaxation under pressure because of a very small change in molar volume. The modification III, which is stable from 305.2 to 357.3 K (32.1 to 84.2 °C), possesses the largest molar volume of all known crystal modifications of this salt and easily transforms to modification IV at 323 K [84].

The solid-state transition mechanisms of ammonium nitrate IV, III, and II were studied by measuring samples simultaneously using Raman spectrometry and DSC [85]. The spectral data of the transitions were collected simultaneously with the calorimetric data in the temperature-scanning mode of the calorimeter and then isothermally between transitions. The phase transition from phase IV to phase III occurred through an intermediate phase II*, whose lifetime was 7 min maximum when the onset temperature of the reaction was close to the phase-transition IV → II onset temperature. It was concluded that there is always an intermediate phase II* between IV and III. Simultaneous Raman measurements were shown to be an effective tool for interpreting complex DSC curves.

Bulk sound speed measurements, isothermal volume compression/XRD experiments, and shock loading experiments (maximum pressure ~20 GPa) were performed for high initial density ($\geq 94\%$ theoretical density) AN and AP [86]. The experimental data, and the full-density Hugoniot calculated from that data, suggested the presence of low-pressure shock-induced phase transitions in both AN and AP. The AN phase change occurs at a shock pressure of less than 3.5 GPa, but the associated volume change is relatively large, indicating the presence of a previously unidentified high-pressure, high-density phase.

Besides the known six phases at atmospheric pressure, there are five phases at high pressures. Phase VI occurs at temperatures above 442 K and pressures greater than 0.9 GPa. Phase VIII, which is stable between 0.45 and 2.7 GPa, transforms into phase IX above 2.7 GPa and room temperature. However, the crystallographic information of phases VI, VIII, and IX is unclear. A shock-induced phase change at 3.5 GPa has been observed, but the structure is uncertain. A metastable isostructural transition (IV–IV') at about 20 GPa under non-hydrostatic compression was suggested, but there is no phase transition until 35 GPa under hydrostatic compression.

The influence of pressure on phase transitions, melting, and thermal decomposition characteristics of pure AN was measured using a pressure-differential scanning calorimeter under ambient conditions and up to a maximum inert pressure of 68.03 atm [87]. The temperatures of the three phase transitions occurring above room temperature were distinctly shifted with increasing pressure, went through a maximum around 40 atm, and then dropped again (Table 2).

The shape of the DSC thermogram curves of AN changed with increasing pressure (Figure 2a–d). The most pronounced change at the highest pressure tested is the appearance of a sharp exothermic decomposition peak at 586 K (313 °C) at 68 atm (Figure 2d). Note that the four thermograms have different ordinate scale expansions.

Using a combination of XRD and neutron diffraction techniques augmented by vibrational spectroscopy, structural information of fully deuterated d-AN was obtained at pressures up to ~8 GPa [88, 89]. High-pressure measurements have been conducted on ammonium nitrate up to 7.85 GPa, showing no phase transitions. An equation of state has been determined over this pressure range. Under hydrostatic conditions, AN remained in the ambient phase IV at pressures up to 7.0 GPa. Significant changes in the

Table 2: Effect of pressure on phase transition, melting, and decomposition temperature of AN.

Sample no.	Pressure atm	DSC peak temperature (°C) for				
		Phase transition			Melting	Decomposition
		IV → III	III → II	II → I		
1.	1	43.47	92.08	130.70	168.89	292.54
2.	13.61	42.05	93.50	129.37	170.19	311.40
3.	20.41	39.14	93.21	129.09	170.48	320.13
4.	27.21	46.73	94.51	130.65	172.50	312.33
5.	40.82	50.01	92.39	133.26	175.75	310.66
6.	54.42	51.17	90.16	134.56	175.33	311.15
7.	68.03	45.44	90.86	131.16	157.54	313.55

Data source: [87]

extent of hydrogen bonding between the ammonium and nitrate ions were observed over this pressure range. In a sequence of powder patterns obtained for fully deuterated AN with increasing pressure up to 7.85 GPa, all of the patterns could be indexed to the orthorhombic unit cell (space group *Pmmn*) of phase IV. Full-profile Rietveld refinements of the neutron powder diffraction patterns enabled refinement of the crystal structures. Over this relatively limited pressure range, there were no changes in the primary bond lengths for the ND_4^+ and NO_3^- ions. Instead, the effect of pressure was to modify the hydrogen bonding interactions. The O1...D2 contact distance is reduced from 2.256(25) Å at ambient pressure to 1.888(9) Å at 7.03 GPa. This contact has a significant component along the *b*-axis and so explains why this axis is the most compressible over this pressure range.

Ammonium nitrate phase changes have been studied under both hydrostatic and non-hydrostatic conditions using diamond anvil cells combined with micro-Raman spectroscopy and synchrotron XRD [90]. The refined-powder X-ray data indicated that under hydrostatic conditions, AN-IV (orthorhombic, *Pmmn*) is stable to above 40 GPa. The structures of phase IV and IV' were similar, with a subtle difference in the hydrogen-bonding network; that is, a noticeably shorter N1...O1 distance was seen in phase IV'. On the basis of this comparison, it was postulated that a chemical reaction or phase transition may occur in AN under dynamic pressure conditions at 22 GPa.

The pressure–temperature (P-T) phase diagram of AN has been determined using synchrotron XRD and Raman spectroscopy measurements [91]. Phase boundaries were established by characterizing phase transitions to the high-temperature polymorphs during multiple P-T measurements using both XRD and Raman spectroscopy measurements. At room temperature, the ambient pressure orthorhombic (*Pmmn*) AN-IV phase was stable up to 45 GPa, and no phase transitions were observed. AN-IV phase was also observed to be stable in a large P-T phase space. The phase boundaries were steep, with a small phase stability regime for high-temperature phases. A pressure–volume–temperature (P-V-T) equation of state was obtained by simulta-

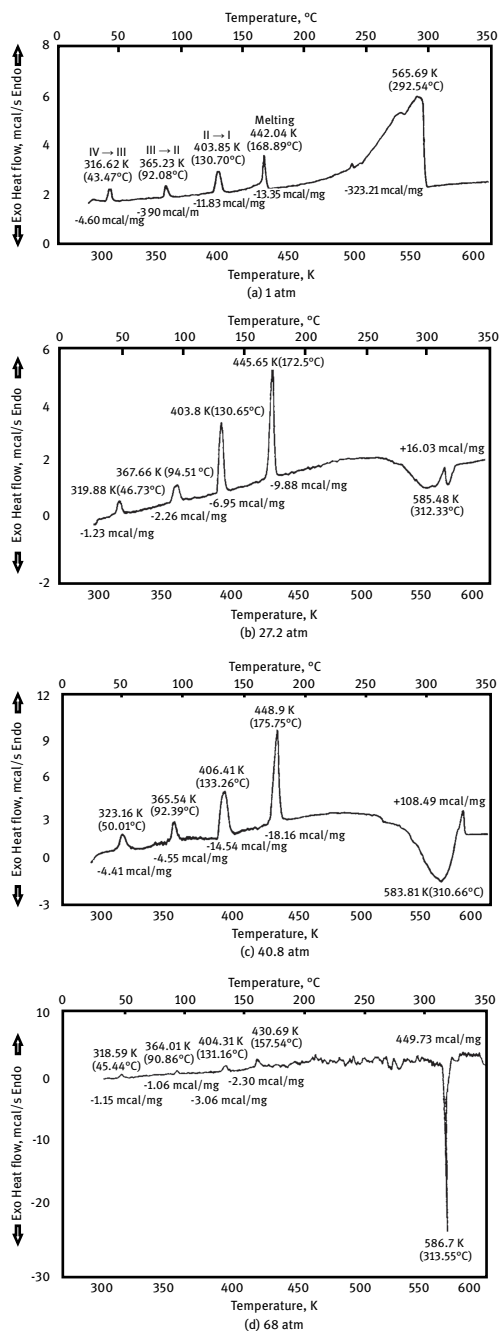


Figure 2: DSC thermograms of AN at increasing pressure. (a) 1 atm, (b) 27.2 atm, (c) 40.8 atm, (d) 68 atm (Reproduced and modified from [87] with permission from © Indian Chemical Society 2003; Permission granted 14-Apr-2021.)

neously fitting the P-V isotherms at 298, 325, 446, and 467 K; thermal expansion data at 1 bar; and volumes from P-T ramping experiments. Anomalous thermal expansion behavior of AN was observed at high pressure with a modest negative thermal expansion in the 3–11 GPa range for temperatures up to 467 K, probably due to vibrational anharmonicity.

An investigation of the phase stability of AN at high pressures and temperatures, using diamond anvil cells and micro-Raman spectroscopy, confirmed the existence of a phase IV-to-IV' transition above 17 GPa and provided new constraints for the melting and phase diagram of AN up to 40 GPa and 673 K (400 °C) [92, 93]. Pure AN decomposed at the onset of melting of phase I, whereas phase IV' showed an unusual turnover of the decomposition temperature well below the melting. There were strong chemical effects on the phase transitions and chemical decomposition of AN.

Effect of Moisture and Humidity on Solid State Phase Changes of Pure Ammonium Nitrate

Phase changes in AN are greatly accelerated by the presence of traces of moisture. For all practical applications, it is virtually impossible to eliminate moisture during propellant processing, transportation, and storage. AN is very hygroscopic, and other than applying vapor barrier coatings, there are few things one can do to AN to make it less hygroscopic [94].

Perfectly dry phase IV AN stabilized with 9% KN was heated from room temperature to 333 K for 300 h, with samples withdrawn periodically and analyzed by XRD. The perfectly dry samples did not show any phase changes, but a sample that was allowed to absorb 0.1% moisture at 298 K underwent phase change under the same conditions [95].

Other sources [96] have reported that the IV → III transformation is very slow in perfectly dry samples, requiring months at 306 K (33 °C) and 0.5 h at 313 K (40 °C). However, opinions differ on the critical moisture content that accelerates or retards the transition. Others state that in a perfectly dry sample transitioned at 328 K (55 °C) (mainly IV + III) but with more than about 0.1% moisture present, a constant transition temperature of 308 K (35 °C) was observed. The III → II transition is not affected by the presence of water [97].

The IV → III phase transition takes place in saturated-solution aqueous slurries of AN crystals [98]. There have been many previous studies of the IV → III phase transition, and water is known to play a mechanistic role. The effect of other solvents and additives on the transition kinetics of single crystals was examined, and these data were combined with structural information to examine the overall mechanism of the transition [99]. The data were consistent with a theory about solvent mediation in which the interface between phases is a microscopic layer of AN solution.

AN aerosols may form in highly polluted atmospheres. Solid AN exists in five stable polymorphic forms (designated as phases I, II, III, IV, and V) below its melting point at around 443 K (170 °C). Phase IV is stable in a temperature range of 256 to ~305 K

(-17 to ~32°C). The IV ↔ III phase transition of NH_4NO_3 and the effects of relative humidity on the transition path and the transition temperatures were examined using *in situ* microscopic FTIR spectroscopy [100]. Two kinds of NH_4NO_3 samples – powder produced from grinding of commercially produced chemicals and single particles obtained by efflorescence of droplets on polytetrafluoroethylene filters – were studied. The powder samples exhibited the IV ↔ III phase transition, and the transition temperature depended on the relative humidity, whereas the single-particle samples exhibited only the IV ↔ II transition at about 325 K (52°C) (forward) and 321 K (48°C) (reverse), bypassing phase III, with transition temperatures independent of the relative humidity. However, grinding of the particles produced through efflorescence resulted in the IV ↔ III transitions becoming visible. Differences in crystal structure and moisture content may explain the distinct phase-transition behaviors of the two types of samples. These results suggest that solid and pure NH_4NO_3 aerosol particles are stable in phase IV under ambient conditions.

Effect of Grain Size on Solid State Phase Changes of Pure Ammonium Nitrate

The reproducibility of the DTA curves of AN as a function of its grain size and the surrounding atmosphere during the measurements was studied, and the temperatures and the areas of the peaks assigned to the modification transitions IV → III (peak 1), III → II (peak 2) and II → I (peak 3) were evaluated [101]. It was found that for some unground samples, the area of peak 2 decreased markedly. In an atmosphere of moist air, the temperature of peak 1 was lowered. The temperatures of lumpy and loose samples did not differ appreciably.

2.3.1.3 Melting Point of Binary Ammonium Nitrate Systems

Many different methods can be used to construct phase diagrams of binary systems. For example, the T-X phase diagram is based on the van't Hoff equation, and the H-X phase diagram is based on the mixture law. The construction of an H-X phase diagram is quicker and simpler than that of a T-X phase diagram. However, an H-X phase diagram cannot be used to determine the composition of a mixture or its melting temperature. A T-X phase diagram describes the relationship between the composition and the melting temperature.

Melting Point of Ammonium Nitrate/Water System

The eutectic point in the AN/water system is at 58 mass-% (23.7 mol-%) AN, with a melting point of 256 K (-17°C). These data are very similar to those for ADN.

Melting Points of Binary Ammonium Nitrate Systems with Other Nitrates

Numerous alkali metal nitrates and other metal nitrates have been studied as additives to AN in order to shift or totally avoid some of the troublesome phase changes that make it difficult to use AN as a rocket propellant or gas generant in airbag inflators (Section 2.11). Nitrates evaluated include potassium nitrate and magnesium nitrate.

Potassium nitrate would be acceptable as a stabilizer because it is an oxidizer in its own right and would not detract too much from the value of AN as an oxidizer in rocket propellants or gas generants. Magnesium nitrate is not preferred because it is very hygroscopic.

The phase diagram of the system $\text{NH}_4\text{NO}_3/\text{KNO}_3$ is extremely complex and has been measured repeatedly, not always with identical results. The following pages provide a comparison of AN/KN phase diagrams from different sources. These diagrams do not all use the same nomenclature for the various phases. Some of the diagrams extend over the entire range of AN/KN compositions, whereas others examine only the AN-rich side of the system. This is why so many different diagrams are shown in the following pages and why they are so difficult to compare. One of the earliest phase diagrams of this system is shown in Figure 3; [102].

The transition curve $\text{II}'\text{A} \rightarrow \text{IVA}$ in the system $(\text{NH}_4)_x\text{K}_{1-x}\text{NO}_3$ was measured in the range $1 > x > 0.75$ [103]. The suffix A or K is used to differentiate phases, which otherwise have the same denomination by their crystallographic properties (e.g., II_A = tetrago-

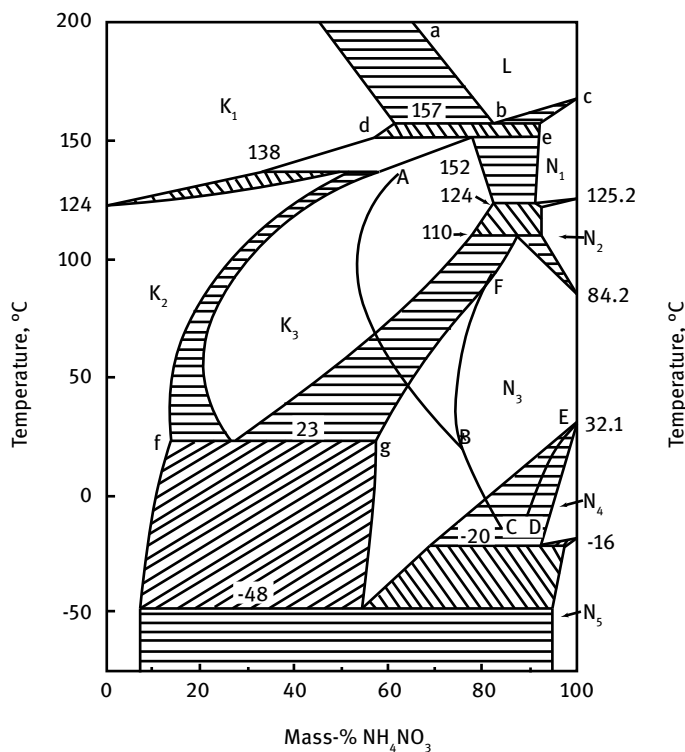


Figure 3: Phase diagram of the system $\text{NH}_4\text{NO}_3/\text{KNO}_3$. (Republished and modified from [102], with permission from © 1932 John Wiley & Sons; permission conveyed through RightsLink.)

nal and II_K = rhombic). A single phase II' of AN-rich mixed crystals was observed in the completely miscible range from $x = 1$ to 0.918 (where x is the molar fraction of AN). From $x = 0.913$ to 0.750, two phases occurred simultaneously: II'_A as an ammonium-rich phase and II_K as an undercooled potassium-rich phase. The stable phase at room temperature III_A formed readily on cooling. The complete miscibility range of phase III_A extended over the entire range mentioned above. It is assumed that homogenization of the formerly phase-separated crystals takes place by ion diffusion in the solid state. In the Figure 4 phase diagram, the striated areas represent the occurrence of each phase in the metastable phase diagram. The names of the phases are given next to the three legend boxes at the top, showing the different fill patterns.

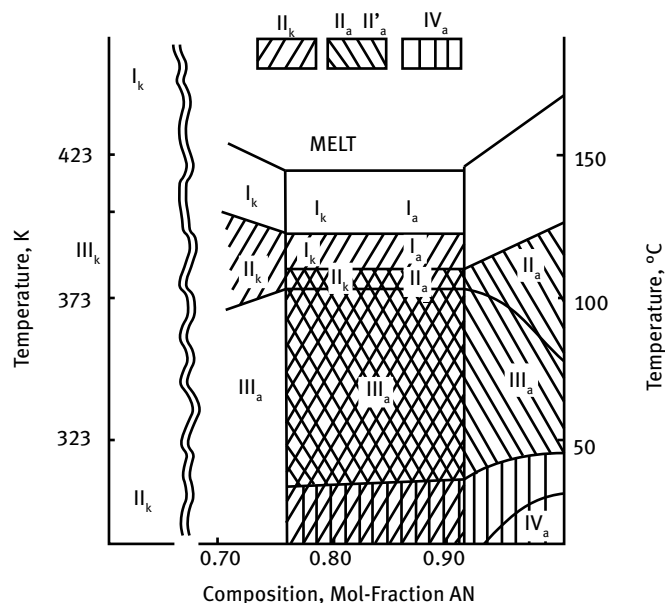


Figure 4: Phase diagram of the AN-rich side of the system $(\text{NH}_4)_x\text{K}_{1-x}\text{NO}_3$. (Reproduced and modified from [103], with permission from Schweizerische Geologische Gesellschaft 17-Jul-2021.)

The melting point vs. composition curve (Figure 2 in Leone [103], but not shown here) has an inflection and slope change at $x = 0.918$, dividing the graph into two zones: the zone of complete miscibility for phase II'_A up to $X = 1$ and the zone of partial miscibility, where II'_A coexists with II_K . In the range $0.75 < x < 0.918$, two types of crystals of modification III_A , having different compositions, will form. Phase changes are accompanied by considerable change in the refractive index and birefringence.

The AN/KN phase diagram in Figure 5 was constructed from visual observations with a hot-stage microscope [104]. Only a portion of the binary-phase diagram for the system AN/KN with up to 30 mass-% potassium nitrate has been determined from

218 to 458 K (−55 to +185 °C). The AN/KN mixtures were prepared by dissolving KN in molten AN and quick-freezing the clear melt by pouring it onto a Teflon sheet. The KN concentration was limited to 30 mass-% KN because the temperature required to dissolve KN, which increases rapidly at this concentration, has reached the point at which significant AN decomposition begins to take place.

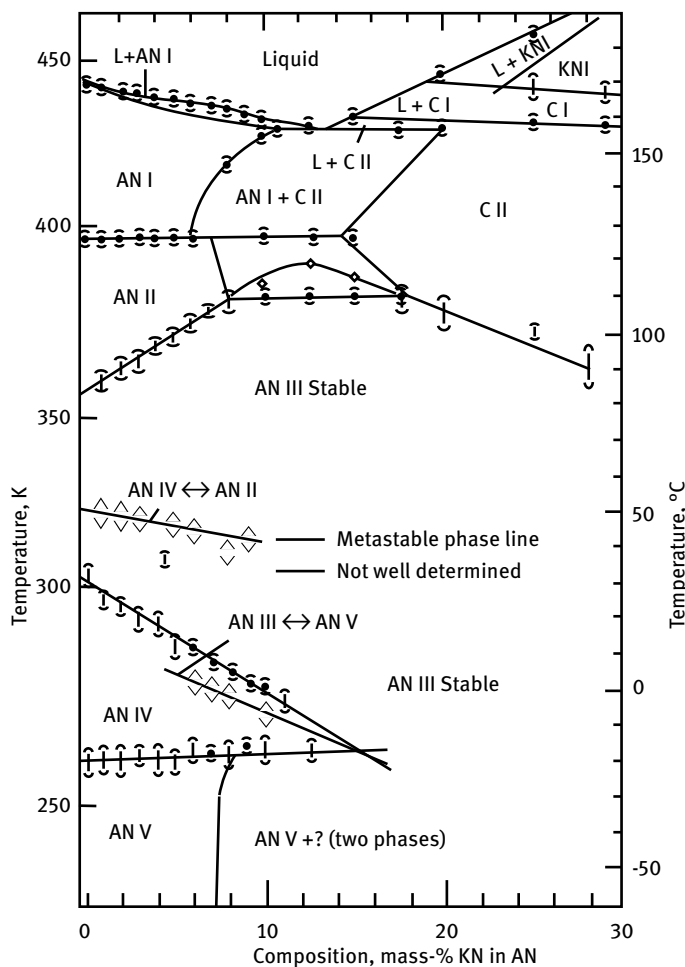


Figure 5: Phase diagram of the AN/KN binary system. (Republished and modified from [104], with permission of © 1981 Wiley VCH; permission conveyed through Copyright Clearance Center, Inc.)

The lengths of the vertical data-point bars in Figure 5 represent the temperature difference between an observation in which the lower-temperature phase was clearly stable and an observation in which the higher-temperature phase was clearly stable.

Single-ended data-point bars indicate that the transformation was observed in only one direction. Phase boundaries between stable phases are indicated by solid lines when their positions are known and by dotted lines when their positions could be inferred only by extrapolation. Dashed lines indicate boundaries between metastable phases.

A very detailed AN/KN phase diagram over the entire range of compositions was obtained by using DSC and *in situ* high-temperature XRD [67, 68] (Figure 6). That paper also contains a thorough list of references from the literature. The enthalpies of phase transformations were measured along with the phase transformation onset and peak temperatures. The phase diagram that is the result of both DSC and XRD measurements showed that there are seven invariant equilibria: one eutectic at 16 mass-% KN and 429 K; two eutectoids, at 39 mass-% KN and 373 K and at 88 mass-% KN and 393 K; three peritectoids at 14 mass-% KN and 390 K, at 55 mass-% KN and 380 K, and at 8 mass mass-% KN and 400 K; and one congruent transition at 72 mass-% KN and 415 K.

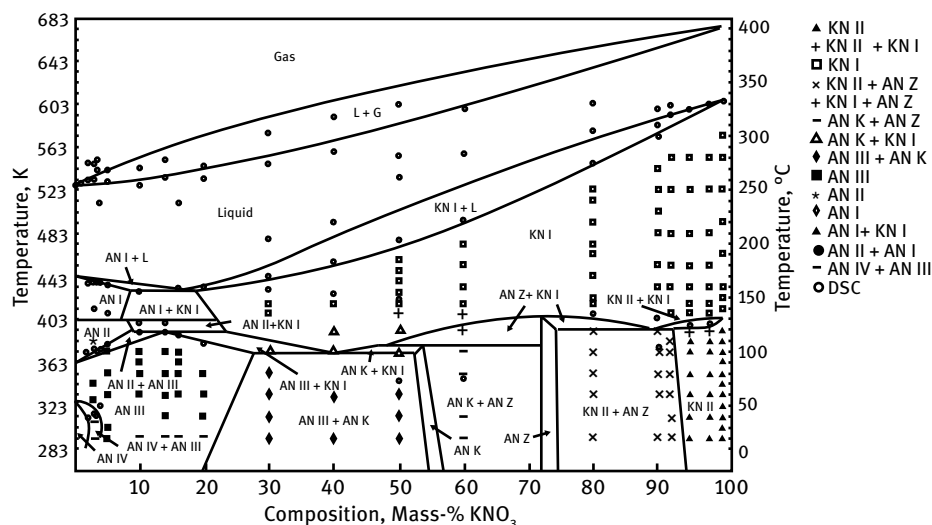


Figure 6: Phase diagram of the AN/KN system. (Republished and modified from [68], with permission of © 2005 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

Earlier publications [104] reported an AN/KN phase diagram for the AN-rich end up to 30 mass-% KN. Comparison of the AN/KN phase diagram of Cady 1981 with Chien's data shows reasonable agreement in the 0–30 mass-% KN region. The phase diagram in Figure 6 supersedes older data and is quite different from AN/KN phase diagrams reported in the older literature. These older data from [105], obtained by differential thermal analysis curves, and from [106], obtained by XRD, are in poor agreement with Chien's results. See also [107] and [108]. The phase III region of AN/KN is stable be-

tween 5 and 20 mass-% KN up to ~ 373 K, which is an important finding for the intended use of phase-stabilized AN in gas generants for airbag gas generators and other applications.

See also [109–114]. Other authors have investigated the potassium-rich end of the system, but that is of less interest as a rocket propellant. A detailed summary of properties of AN/KN binary systems, as well as information on their use in fertilizer mixtures and a summary of phase diagrams published by various earlier investigators, is provided in [63].

Melting Points of Binary Ammonium Nitrate Systems with Other Non-Nitrate Salts

AN is a versatile oxidizer, and it is being tested in mixtures with many other energetic materials, preferably with materials with which it will form solid solutions and eutectic mixtures with which it will not segregate into separate phases on cooling.

AN forms a eutectic with the ethylenediammonium salt of 5-nitrotetrazole that is of interest as a melt-castable explosive [115, 116]. This eutectic mixture, which contains 87.8 mol-% of ammonium nitrate, is close to the CO_2 -balanced composition of 90 mol-% and has a relatively low melting point of 383.65 K (110.5 C), making it readily castable.

A cylindrical oxidizer grain made from a eutectic AN/AP mixture was used in an inverse hybrid rocket engine [117]. The eutectic mixture did not exhibit explosive behavior during melting or casting.

Ammonium nitrate is a cheap oxidizer. Its performance can be improved by adding perchlorates. Solid propellants containing both AN (or PSAN) and AP are called dual-oxidizer composite propellants. The AN and AP can be mixed in as individual powders, or the two salts can be co-crystallized from water and then ground to the desired particle size. AN and AP can be co-crystallized by freeze-drying [118]. AN adheres to the less-soluble AP particles during the drying process to form combined AP/AN particles. The AN content of the combined AP/AN samples dominates particle properties, including shape, hygroscopicity, thermal decomposition behavior, and ignition sensitivity.

Several propellants were formulated with the co-crystallized oxidizer and compared to conventional AP-based propellants [119]. The DTA thermogram of the co-crystallized oxidizer shows peaks that differ from those of its pure constituents:

- peak at 371 K (98 °C): beginning of the phase transition III $\rightarrow$ II of AN
- peak at 400 K (127 °C): beginning of AN phase transition II $\rightarrow$ I
- peak at 408 K (135 °C): fusion of the eutectic mixture AN/AP
- peak at 418 K (145 °C): fusion of AN
- peak at 454 K (181 °C): beginning of the first stage of exothermic decomposition
- peak at 468 K (195 °C): beginning of full exothermic decomposition

No peak was observed at 305 K (32 °C), and that is an important observation!

The phase diagrams of AN/AP and AN/sodium perchlorate were examined [120]. The melting point in the AN/AP system does not drop significantly until the AN concentration reaches 80% AN. Then the melting point drops sharply toward a eutectic containing 90% AN and melting at 419 K (146 °C). Volume 1, *Encyclopedia of Oxidizers*, chapter “Perchlorate Oxidizers” contains a melting-point diagram of the AN/AP binary system. AN/AP or AN/ NaClO_4 mixtures can be used as oxidizers for solid propellants with reduced HCl output. The system $\text{NH}_4\text{NO}_3/\text{NaClO}_4$ has a eutectic point at 10% NaClO_4 , melting at 402 K (129 °C) (Figure 7).

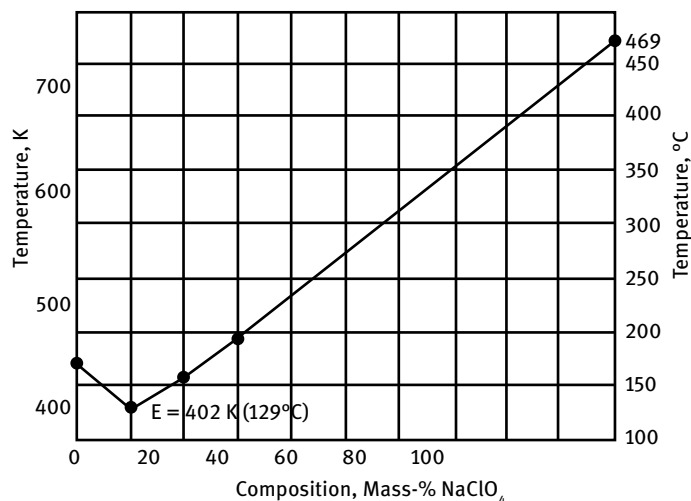


Figure 7: Phase diagram of the ammonium nitrate/sodium perchlorate system. (Reproduced and modified from [120].)

A phase diagram of the AN/ammonium dinitramide binary system is shown in Volume 1, *Encyclopedia of Oxidizers*, chapter “Dinitramide Oxidizers.”

2.3.1.4 Melting Point of Ternary Ammonium Nitrate Systems

Ternary systems containing AN and water and a third ingredient could be ternary mixtures containing two oxidizers and a solvent or systems containing one oxidizer, a fuel, and a solvent. The third ingredient could have a salting-out effect (as in the case of adding ethanol or methanol) or a salting-in effect (only a few additives improve the solubility of AN).

A previously undescribed modification of AN/ KN solid solution crystals was discovered when analyzing supernatant liquids and solid precipitates in two-phase AN/ $\text{KN}/\text{H}_2\text{O}$ solutions for different AN:KN ratios and at different saturation temperatures [102]. The mixed crystals have the same crystal form as that of KN when it is subjected to high pressures >115 atm.

Ternary ammonium nitrate systems have been developed both as solid and liquid oxidizers. Solid oxidizers contain two additional components as phase stabilizers or to improve other properties. Liquid oxidizers contain a solvent and one additional dissolved oxidizer to achieve low freezing points and high densities.

A continuation-in-part of an earlier patent application by Wagaman issued as U.S. patent 6299711 [121] describes AN/hydrazinium nitrate (HN)/H₂O solutions as oxidizers. It is similar to work by Mueller and Wagaman [122], except it does not use hydroxylammonium nitrate (HAN) but also includes methylhydrazinium nitrate as a potential constituent. OXSOL-3 is a mixture containing AN, HN, and water. Figure 8 is a freezing-point diagram of the AN/HN/H₂O system.

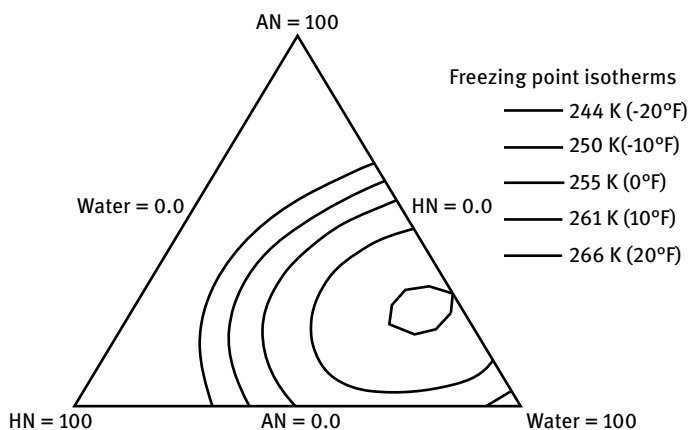


Figure 8: Freezing-point diagram of ternary AN/HN/H₂O oxidizer solutions. (Reproduced and modified from [121].)

Three different OXSOL-3 compositions were listed as examples in performance calculations (Table 3).

Table 3: Composition of OXSOL oxidizer solutions.

Composition, mass-%			Freezing point		Density
AN	HN	H ₂ O	°C	K	g/cm ³
25.0	55.0	20.0	17	290.1	1.422
41.2	43.1	32.7	19	292.1	1.441
46.4	32.7	20.8	18	291.1	1.398

Data source: [121]

These may have favorable densities, storage stabilities, and oxygen contents, but the freezing points are much higher than those of comparable ternary blends containing HAN instead of AN. Instead of dissolving AN in water, a more powerful oxidizer called PERSOL-1 can be obtained by dissolving AN in hydrogen peroxide/water mixtures [123, 124]. The freezing-point diagram of the ternary system AN/H₂O₂/H₂O is shown in Figure 9.

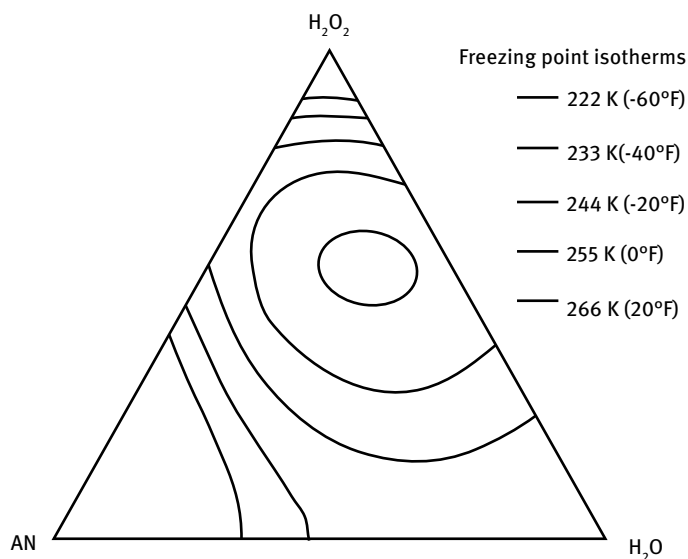


Figure 9: Freezing-point diagram of ternary AN/H₂O₂/H₂O oxidizer solutions. (Reproduced and modified from [124].)

One preferred composition of PERSOL-1 contains 55.6% AN, 22.2% H₂O₂, and 22.2% H₂O. This blend freezes at 276 K (+3 °C) and has a density of 1.361 g/cm³. It can serve as an oxidizer for bipropellants or hybrids. Monopropellants can be formulated by emulsifying it with hydrocarbons or by dissolving amine nitrate salts such as alkylammonium nitrate or alkanolammonium nitrates having one, two, or three carbon atoms. Adducts of AN with H₂O₂ are referred to as *peroxides* or persalts. The AN:H₂O₂ = 1:1 adduct is a solid at room temperature. Such adducts may be used as oxidizers in propellants, explosives, and pyrotechnics [125]. The ignition delays of solutions of AN or ADN in high-test peroxide with an ionic liquid fuel, 1-allyl-3-methylimidazolium dicyanamide, have been measured [126].

While it may have been the objective of some of the previous inventions to develop oxidizers that are less corrosive and less toxic than nitric acid, this does not apply to the following ternary AN solutions called ANNA (for ammonium nitrate nitric acid)

[127]. Unfortunately, the patent does not give the complete freezing-point diagram for the ternary system AN/NA/H₂O as it does for the other nitrate solutions patented by the same inventor, but it does give the density data in tabular form. ANNA-30-40 and ANNA-28-52 have favorable performance and handling properties. The solutions are stable up to about 413 K (140 °C). ANNA oxidizers were proposed as oxidizers with kerosene and water injection steam generators for powering catapults on aircraft carriers.

Ternary mixtures containing AN, water, and methanol have been considered as monopropellants (*Encyclopedia of Monopropellants*).

The phase diagram for a ternary system consisting of AN with 15 mass-% potassium nitrate (AK15)/ethylenediamine dinitrate (EDDN)/nitroguanidine (NQ) has been determined from room temperature to the melting point [128]. The ternary eutectic temperature, measured for a mixture containing 67.24 mol-% AN, 25.30 mol-% EDDN, and 7.46 mol-% NQ was found to be 372 K (98.9 °C). The binary phase diagrams for the systems AK15/EDDN, AK15/NQ, and EDDN/NQ were also determined.

Low-melting ternary blends of AN with other energetic materials are of interest as melt-castable explosives, replacing trinitrotoluene (TNT). A ternary blend containing 26.33 mass-% ethylenediammonium salt of 5-nitrotetrazole, 47.54 mass-% AN, and 26.13 mass-% EDDN has a melting point of 362.6 K (89.5 °C) [115]. The phase diagram was determined for a ternary system consisting of diethylenetriamine trinitrate (DETN)/EDDN/AN with 15 mass-% potassium nitrate (AK15). The eutectic mixture containing 40 mass-% AK15, 35 mass-% DETN, and 25 mass-% EDDN was subjected to small-scale sensitivity and performance tests [129].

Ternary systems containing AN, potassium nitrate, and sodium nitrate show similar shifts or disappearance of phase transitions [130]. A very good summary of binary and ternary molten salt systems including AN and other nitrates is given in [131].

2.3.2 Density of Ammonium Nitrate

The density of solid AN at 298 K is 1.725 g/cm³. This is the density of the IV phase, which is stable at room temperature. Ammonium nitrate exists in five different phases, and each has a different density. The specific volumes (the reciprocal densities) of the different phases of AN are illustrated in Figure 10, and calculated data are summarized in Table 4. Phase changes of AN are one of the several reasons why AN has so far not been used more widely in rocket propellants and gas generants. Swelling and shrinking as the consequence of repeated phase changes result in debonding of oxidizer particles from the binder or debonding of a solid propellant grain from the casing, resulting in uncontrollable burning behavior that often leads to explosions. A significant amount of effort has been devoted to finding phase stabilizers for AN (Section 2.4.1). Dilatometric analyses are performed to demonstrate the effectiveness of phase stabilizers and to measure the coefficients of thermal expansion between phase changes.

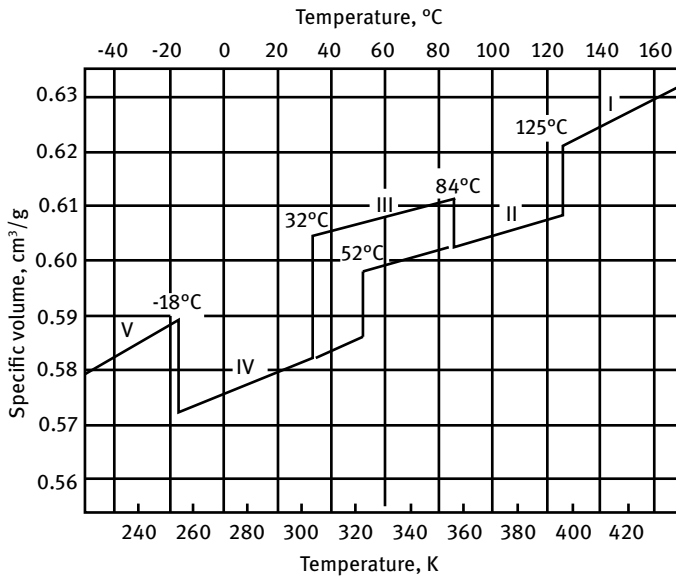


Figure 10: Specific volume of ammonium nitrate and phase changes

Table 4: Computed specific volumes of AN phases at different temperatures

Phase	Volume of unit cell $\times 10^{-23}$	Specific volume	Temperature	
	cm ³	cm ³ /g	°C	K
IV	15.4394	0.5792	22	295
III	32.3108	0.6080	45	315
II	16.1347	0.6070	82	355
I	8.3224	0.6262	150	423

Data source: [87]

It is clearly seen that the IV $\rightarrow$ III and II $\rightarrow$ I phase transitions result in an increase in volume, whereas the III $\rightarrow$ II transition causes only a negligible decrease. The energy release (absorption) associated with the various phase changes was also measured.

2.3.2.1 Coefficient of Thermal Expansion of Crystalline Ammonium Nitrate

The thermal expansion of AN crystals is anisotropic and depends on which phase the crystal is currently in. For instance, crystals of phase IV on heating show a slightly shrinking parameter a length and a strongly expanding parameter b length. Such behavior is difficult to explain.

2.3.2.2 Density of Binary Ammonium Nitrate Solutions

Density of Aqueous Ammonium Nitrate Solutions

If the density of AN solutions is plotted against the mass fraction of AN, the curve is slightly concave. Figure 11 shows the density of aqueous AN solutions at 323 K in comparison to densities of two other oxidizers at 298 K. The AN data were obtained at higher than room temperature because AN is less soluble in water than the other two oxidizers.

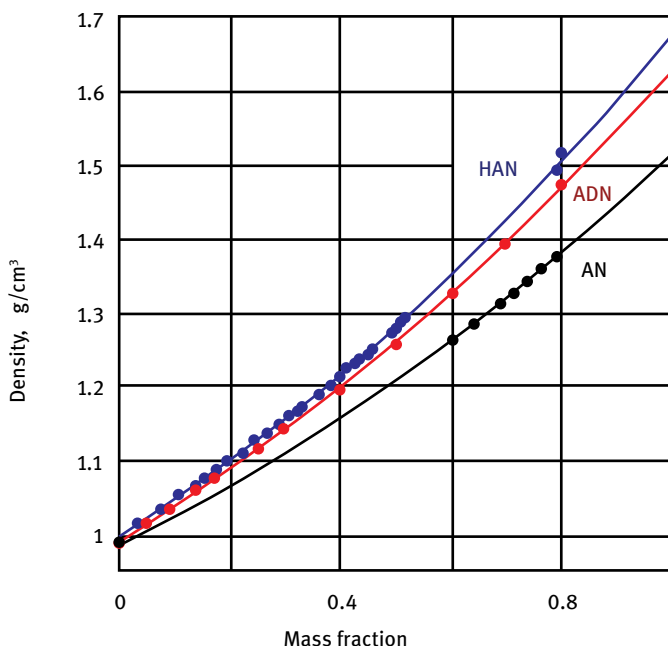


Figure 11: Density of AN solutions in comparison to other oxidizers. (Reproduced and modified from [132] with permission from Dr. Charles Kappenstein.)

The molar volumes of AN and other oxidizers were measured so that the theoretical density of oxidizer/fuel/water mixtures in monopropellants could be calculated assuming additive behavior of the molar volumes in mixtures. As a start, the reciprocal density (i.e., the specific volume) was plotted vs. the mol fraction of oxidizer, as shown in Figure 12.

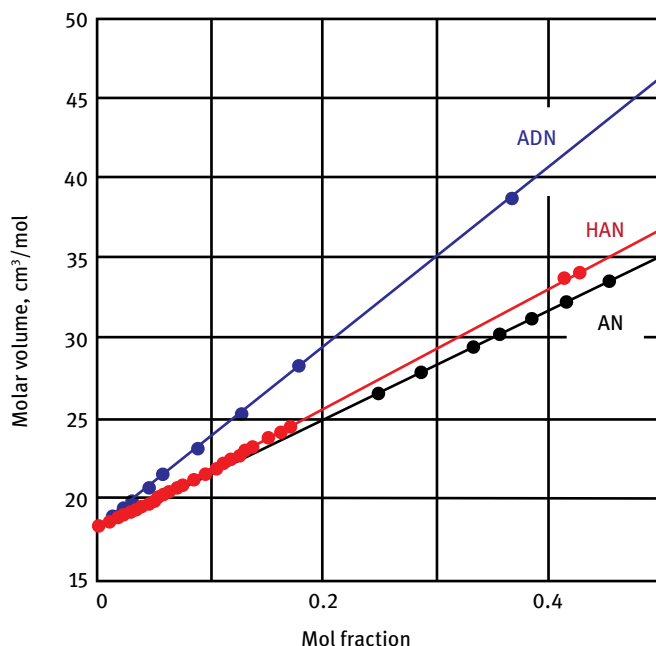


Figure 12: Molar volume of AN solutions vs. mol fraction of AN in comparison to other oxidizers. (Reproduced and modified from [132] with permission from Dr. Charles Kappenstein.)

The curves in Figure 12 are straight lines such that their shape can be expressed by a simple linear function:

$$Vm = Vm_{\text{H}_2\text{O}} \times X_{\text{H}_2\text{O}} + Vm_{\text{AN}} \times X_{\text{AN}}$$

$$Vm = Vm_{\text{H}_2\text{O}} + (Vm_{\text{AN}} - Vm_{\text{H}_2\text{O}}) \times X_{\text{AN}}$$

The molar volumes of the salts were derived from the intercept of the lines. The results are summarized in Table 5.

Table 5: Extrapolated molar volume and density of pure ionic liquid oxidizers.

Compound name	Formula	Molar volume, mL/mol	Density of pure ionic liquid (no solvent), g/cm ³
Ammonium nitrate	NH ₄ NO ₃	52.00(15) ^a	1.539(5) ^a
Ammonium dinitramide	NH ₄ N(NO ₂) ₂	74.06(13)	1.675(3)
Hydroxylammonium nitrate	NH ₃ OH NO ₃	55.45(19)	1.732(6)

^aNumbers in parentheses designate the standard deviation of the last digits.

Data source: [132]

The densities of the AN-water system for water ratios R varying between 1.2 and 3.0 mol H₂O per mol of AN were measured [133]. At a given R , density ρ is a linear function of temperature, and the coefficients A and B are listed in Table 6:

$$\rho = A - B(T - 300)$$

Table 6: Empirical parameters of the least-squares-fit equations for the densities of the NH₄NO₃–H₂O system.

Mols of water R	Temperature range, K	A	$10^3 \times B$
1.2	320–345	1.39268	0.68742
1.4	315–345	1.37450	0.69481
1.6	300–345	1.35608	0.70401
2.0	300–345	1.32788	0.67619
2.5	295–345	1.30150	0.67313
1.8	300–345	1.34033	0.65436
3.0	295–345	1.27736	0.66006

Data source: [133]

The variation of ρ with R can be expressed by a polynomial equation of the type

$$\rho = a + bR + cR^2$$

where a , b , and c are empirical constants listed in Table 7. The molar volume of the AN-water system exhibited ideal behavior.

Table 7: Empirical parameters of the density–concentration equations for the AN-water system.

Temperature, K	a	$b \times 10$	$c \times 10$
323.2	1.48414	0.61416	–4.77017
328.2	1.48706	0.38516	–4.57249
333.2	1.45736	1.20525	–5.20867
338.2	1.52627	–1.04973	–5.46928
343.2	1.50200	–0.40526	–3.95904

Data source: [133]

The apparent molar volume of a solution is the sum of the partial molar volumes of the solute and of the solvent (water). A good correlation can be obtained by plotting the partial molar volumes against a concentration parameter χ

$$\chi = \frac{\sqrt{X}}{1 + \sqrt{X}}$$

where X is the mol fraction AN (Figure 13). This correlation was used at Olin Chemicals for calculating not only the densities of AN, HAN, and triethanolammonium nitrate solutions but also the densities of XM46 formulations with excess nitric acid [134]. The intercept at infinite dilution at 298 K (25 °C) is at 48.285 cm³/mol. See also [135].

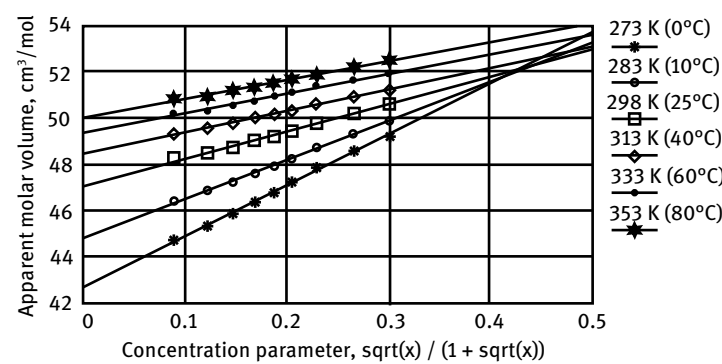


Figure 13: Partial molar volumes of AN as a function of concentration parameter χ and temperature. (Reproduced and modified from [134], based on CRC Handbook p. D247 data.)

Density of AN Solutions in Ammonia

The densities of saturated solutions of AN in liquid ammonia are summarized in Table 8, based on two data sets from two different sources. The measurements were made

Table 8: Densities of saturated solutions of ammonium nitrate in liquid ammonia.

Temperature		Concentration	Density	Temperature		Concentration	Density
K	°C	Mass-% AN	g/cm ³	K	°C	Mass-% AN	g/cm ³
273.1	0	54.33	1.2640	293	20	66.1	1.3115
283.1	10	58.85	1.2909	313	40	73.3	1.3415
288.1	15	62.51	1.3003	333	60	80.2	1.3519
293.1	20	65.63	1.3103	353	80	85.9	1.3940
298.1	25	68.29	1.3200	373	100	91.0	1.4145
303.1	30	70.74	1.3303	393	120	94.7	1.426
305.1	32	71.72	1.3345	413	140	97.4	1.432
305.4	32.3	71.87	1.3351	433	160	99.4	1.436
307.1	34	72.35	1.3380	443	170	100	1.437
309.1	36	73.05	1.3411				
311.1	38	73.85	1.3438				
313.1	40	74.79	1.3464				

Data source: [136]

in closed bombs to prevent loss of ammonia at the higher temperatures. The vapor pressures of these solutions above room temperature are substantially above atmospheric pressure.

2.3.2.3 Density of Ternary Ammonium Nitrate Solutions

The density of the ternary AN/HN/H₂O system is shown in Figure 14. The temperature at which these density data were taken was not stated, but it is assumed that the densities are of the liquids at their freezing points.

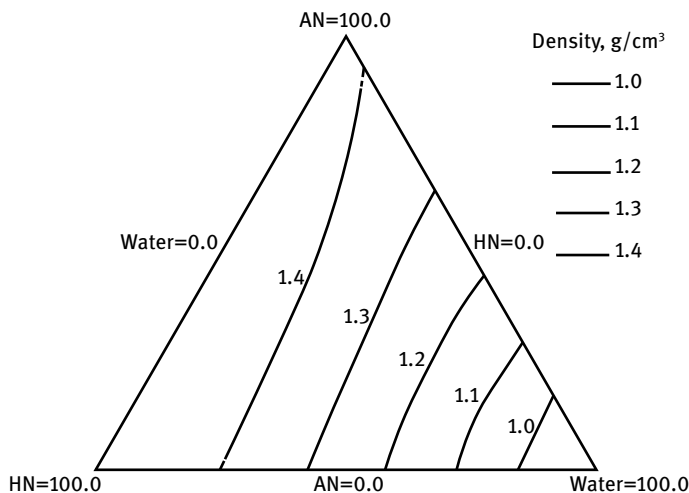


Figure 14: Density of ternary AN/HN/H₂O oxidizer solutions. (Reproduced and modified from [121].)

The density of the ternary AN/nitric acid (HNO₃)/H₂O system can be calculated from the equation

$$\rho = 1.355 \text{ AN} + 1.722 \text{ HNO}_3 + 0.976 \text{ H}_2\text{O} + 0.188 \text{ AN HNO}_3 + 0.211 \text{ AN H}_2\text{O} - 0.173 \text{ HNO}_3 \text{ H}_2\text{O}$$

where ρ is the density in g/cm³, and AN, HNO₃, and H₂O are the mass fractions in the solution. The density ternary diagram is shown in Figure 15.

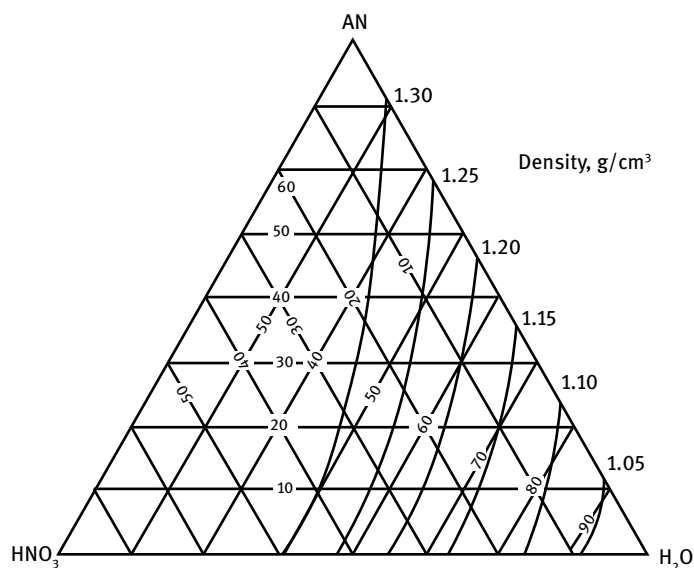


Figure 15: Density of ternary AN/HNO₃/H₂O oxidizer solutions. (Based on data from [127])

2.3.3 Compressibility and Equation of State of Solid Ammonium Nitrate

The equation-of-state properties and initiation behavior of neat AN were measured in a series of gas gun–driven plate-impact experiments on pressed neat ammonium nitrate at a density of 1.72 g/cm³ [137]. No evidence of initiation was observed under shock loadings up to 22 GPa. High-pressure XRD in diamond anvil cells provided some insight into the high-pressure phase behavior over a pressure range up to 25 GPa, as well as a static isotherm at ambient temperature. From the isotherm and thermodynamic properties at ambient conditions, an equation of state was developed for unreacted AN, which compared favorably with available experimental Hugoniot data on several densities of AN.

2.3.4 Vapor Pressure of Ammonium Nitrate

Ammonium nitrate sublimates and has a noticeable vapor pressure even before irreversible decomposition starts. The solid vaporizes by dissociation into ammonia and nitric acid. The vapor pressure of AN was measured using a transpiration–transference method [138]. A known volume of dry gas was passed slowly over heated (353–513 K [80–240 °C]) 30-g samples of AN and then through a condensation trap for durations of 1 to 120 h. The weight gain of the cold trap was identical to the weight loss of the sample, indicating that no gaseous decomposition products had formed

and escaped as a gas. The maximum weight loss was 15% during 40 min at 513 K (240 °C). The vapor pressure for the different phases of AN is illustrated in Figure 16. The green lines are the phase boundaries, and the Roman numerals designate the phase prevalent in this temperature range.

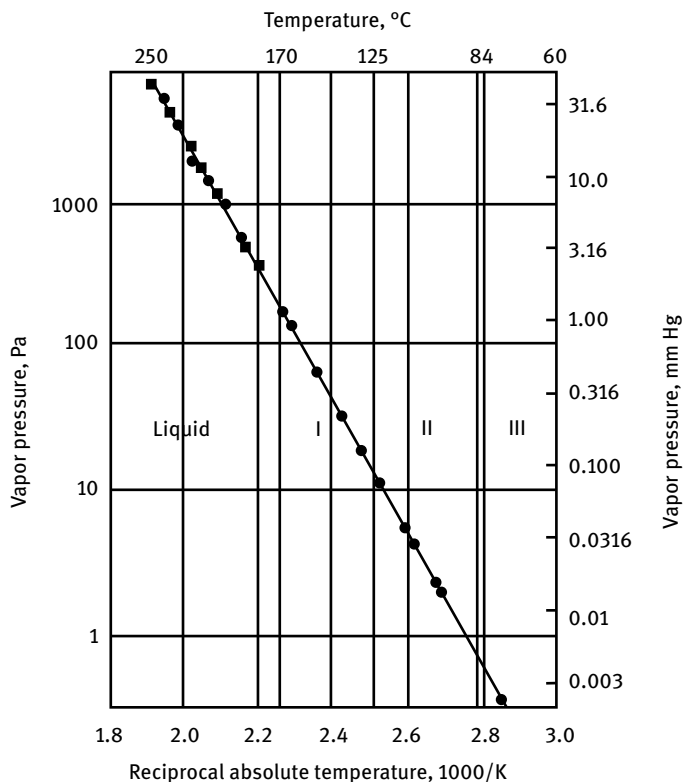


Figure 16: Vapor pressure of ammonium nitrate. (Reprinted and modified from [138], with permission from © 1962 American Chemical Society; permission conveyed through RightsLink.)

The vapor pressure of the solid and the liquid can be expressed by the following equations

$$\text{Solid} \quad \log p = 10.708 - \frac{4670}{T}$$

$$\text{Liquid} \quad \log p = 9.981 - \frac{4360}{T}$$

where p is the pressure in mmHg and T is the temperature in kelvin. The heats of vaporization calculated from the slopes are 178.6 and 166.9 kJ/mol (42.7 and 39.9 kcal/mol), respectively, for the solid and the melt.

It is difficult to measure the vapor pressure and dissociation pressure of AN due to incipient decomposition at temperatures where the vapor pressure and dissociation pressure become measurable [139].

Nevertheless, the dissociation pressure and enthalpy of liquid ammonium nitrate have been measured for the temperature range from 463 to 543 K (190–270 °C) [140]. From these data (Table 9), the free energy and entropy were calculated for the liquid and for the solid at 298 K (25 °C).

Table 9: Dissociation pressure of liquid ammonium nitrate.

Temperature		Dissociation pressure	
K	°C	Pa	mm Hg
461	188	432	3.25
478	205	991	7.46
489	216	1535	11.55
496	223	2100	15.80
510	237	3588	27.0
522	249	5448	41.0

Melting point 189.6 °C = 462.7 K

Data source: [140]

When plotting $\ln p$ vs. $1/T$, the average value of $d(\ln p)/d(1/T)$ corresponds to a heat of vaporization of 166.5 kJ/mol (39.8 kcal/mol), which is in approximate agreement with the values of 161.1–163.6 kJ/mol (38.5–39.1 kcal/mol) calculated from thermal data for this temperature range. The heat capacity of molten AN is 161 J K⁻¹ mol⁻¹ (38.5 cal °C⁻¹ mol⁻¹). The enthalpy of molten AN at the melting point (442.7 K [169.6 °C]) is 34.1 kJ/mol (8.15 kcal/mol) above that of solid AN (phase IV) at 298 K (that includes sensible heat for heating the solid to 442.7 K [169.6 °C]). In confirming the results of other investigations, the data indicated that the vapor of AN is completely dissociated into NH₃ and HNO₃ in the range of temperatures investigated.

Aerosol sampling by several groups indicates the presence of solid AN particles in the atmosphere. Long lifetime and long-range transport of these particles are predicted regardless of ammonia and nitric acid vapor concentrations. In support of atmospheric pollution studies in which AN aerosols contribute to nitrogen transport, microscopic anhydrous AN particles were levitated in a vacuum at 298 K (25 °C), and size and mass changes of the evaporating particles were monitored continuously *in situ* using light scattering and gravity balancing [141]. Fresh solid particles evaporated at a rate proportional to $1/r$, where r is an equivalent radius. Beyond 4 h, the rate was a constant $-0.06 \text{ \AA/s}$. These rates were consistent with those predicted from thermodynamics.

The total vapor pressure and vapor molecular weight of AN were determined by a torsion-effusion method, and vapor composition was determined by effusion-beam MS [142]. Total vapor pressures of AN were measured by using two effusion cells with different orifice diameters over the pressure range of 10^{-6} to 10^{-3} kPa, between 313 and 360 K. The equilibrium vapor-pressure equation was extrapolated from measurements with different orifice Knudsen cells, P1 and P2 cells:

$$\log P_T = (10.400 \pm 0.0002) - (4783.16 \pm 0.07)/T$$

where P_T is the pressure at temperature T in kPa and T is the temperature in kelvin. The molecular weights of AN vapor were measured as 48.7 g/mol for P1 cells and 50.7 g/mol for P2 cell, both of which are much less than the theoretical molecular weight of AN (80.04 g/mol). This significant difference in molecular weight suggests that there is some disproportionation of AN in the vapor phase. Mass spectroscopic analysis revealed that NH_4NO_3 decomposes to NH_3 and HNO_3 , but none of the expected N_2 , O_2 , and H_2O decomposition products were found during vaporization. The partial pressures of the three vapor-phase species (NH_4NO_3 , NH_3 , and HNO_3) that were evolved during vaporization of NH_4NO_3 sample were determined as $P_{\text{NH}_4\text{NO}_3}/P_T = 0.1490$, $P_{\text{NH}_3}/P_T = 0.2911$, and $P_{\text{HNO}_3}/P_T = 0.5599$.

The sublimation pressures of $\text{NH}_4\text{NO}_3(\text{g})$ over the range 321–360 K were derived from the total pressures measured by a torsion-effusion method and the NH_4NO_3 partial pressure [143].

The vapor pressure of AN was measured at 373–433 K (100–160 °C) using an isothermal thermogravimetric weight loss method and compared to that of guanidinium nitrate and urea nitrate [144]. The Clapeyron equation for urea nitrate vapor pressure is

$$\ln P = 35.141 - 12690/T$$

where P is the pressure in Pa and T is the temperature in kelvin. For a temperature of 298 K, this equation gives a vapor pressure of 5.98×10^{-4} Pa = 4.49×10^{-6} mm Hg. From the slope of this equation, an enthalpy of sublimation was calculated as 106 kJ/mol.

2.3.5 Solubility of Ammonium Nitrate

2.3.5.1 Solubility of Ammonium Nitrate in Water

Ammonium nitrate is quite soluble in water. This makes it easy to clean processing equipment that was used for grinding or coating AN, and it also would be easy to demilitarize AN-based propellant grains by extracting the oxidizer with water. The solubility of AN in water is summarized in Table 10.

Table 10: Solubility of ammonium nitrate in water

Temperature		AN concentration, mass-%	Phase
K	°C		
279.3	6.2	59.7	III (metastable)
290	16.9	64.64	
297.6	24.5	68.03	
305	31.9	71.05	
307.4	34.3	71.84	III (stable)
311.2	38.1	73.8	
316.8	43.7	75.71	
324.6	51.5	78.04	
331.5	58.4	80.24	
344.5	71.4	83.06	
354.5	81.4	86.56	
356.9	83.8	87.11	
358.7	85.6	87.84	II
363.5	90.4	88.99	
366.8	93.7	89.7	
368.1	95	89.96	
372.1	99	91.24	
373.2	100.1	91.1	
385.1	112	93.76	
393.9	120.8	95.23	
395.1	122	95.61	
406.1	133	96.8	I
408.9	135.8	97.14	
419.1	146	97.99	
430.1	157	98.95	
443.1	170	100	

Data source: [136]

2.3.5.2 Solubility of Ammonium Nitrate in Liquid Ammonia

Ammonium nitrate dissolves readily in liquid ammonia, forming a liquid that exists at room temperature with a vapor pressure only slightly above atmospheric pressure. Such solutions are called Divers' solution N. Similar solutions with even lower vapor pressures are formed with ammonium thiocyanate. Solutions of AN in liquid ammonia are potentially very cheap and very clean monopropellants, but they are difficult to ignite and sustain (*Encyclopedia of Monopropellants*). The vapor pressure of a saturated solution reaches atmospheric pressure at room temperature (293 K [20 °C]). It is therefore relatively easy to handle Divers' solution N in glassware in the laboratory. The

solubility of AN in liquid ammonia is summarized in Table 11 (based on data from two different sources, covering different temperature ranges). The freezing-point diagram of the AN/NH₃ system does not show any evidence for the formation of ammoniates with discrete AN:NH₃ ratios.

Table 11: Solubility of ammonium nitrate in liquid ammonia.

Temperature		Concentration		Temperature		Concentration
K	°C	Mol-% AN	Mass-% AN	K	°C	g AN/100 mL solution
~441	~168	100	100	239.1	−34	77.9
382.9	109.8	74.2	93.1	238.9	−34.2	77.4
367.1	94	67.3	90.6	236.5	−36.6	77
341.9	68.8	53.8	84.6	232.3	−40.8	75.1
309	35.9	47	80.6	229.1	−44	73.5
306.4	33.3	45.9	79.9	228.1	−45	73.4
273.1	0	38.3	74.5	226.6	−46.5	72.6
262.6	−10.5	36.9	73.3	222.5	−50.6	70.1
243.1	−30	32.3	69.2			
228.6	−44.5	13.9	43.1			
213.1	−60	6.25	23.9			
~193	~−80	0	0			

Data source: [136]

2.3.5.3 Solubility of Ammonium Nitrate in Nitric Acid

Ammonium nitrate is reported to be appreciably soluble in aqueous and concentrated nitric acid; solutions of 50 mass-% AN in anhydrous nitric acid are commonly used in the manufacturing of explosives. Heat is evolved when AN is dissolved in 99.6% HNO₃, but heat is absorbed if AN is dissolved in water. Dissolving AN in HNO₃ would lower the vapor pressure and freezing point of the acid but would not improve its oxygen content.

The solubilities of AN (and alkali metal nitrates) in HNO₃ at 273–303 K (0–30 °C), the vapor pressures of these solutions at 273–288 K (0–15°), and their densities, electrical conductivities, and viscosities at 298 K (25 °C) were measured [145].

The phase diagram of the system AN/HNO₃ is shown in Figure 17. Ammonium nitrate forms 1:1 and 1:2 adducts with HNO₃. The 1:2 adduct is evident from a distinct peritectic in the phase diagram. Ammonium nitrate crystallized from a solution in fuming nitric acid forms prismatic needles of NH₄NO₃•2HNO₃ that melt at 302–303 K (29–30 °C) or NH₄NO₃•HNO₃ that crystallizes in the shape of leaflets or plates that melt at about 285 K (12 °C).

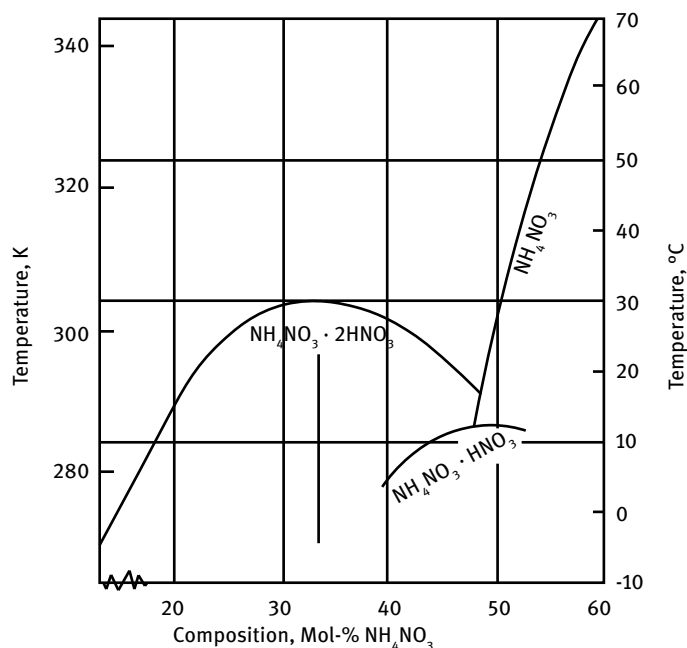


Figure 17: Phase diagram of the system ammonium nitrate/nitric acid. (Reproduced and modified from [136])

2.3.5.4 Solubility of Ammonium Nitrate in Organic Solvents

If sufficient AN could be dissolved in organic solvents, this would make very economical potential monopropellants. Ammonium nitrate is soluble to a modest extent in the lower alcohols and amines but not enough to make a full-fledged monopropellant.

The solubility of AN in methanol is better than in ethanol. At 291.6 K (18.5°C), 100 g methanol will dissolve 16.3 g AN, and at 293.6 K (20.5°C) it will dissolve 17.1 g AN. At 293.6 K (20.5°C), ethanol will dissolve only 3.8 g AN. At 353 K (80°C), absolute ethanol will dissolve 10.5 g AN per 100 g solvent. The solubility can be improved by adding a little water.

2.3.6 Hygroscopicity of Ammonium Nitrate

One of the main disadvantages of AN for use in rocket propellants is its hygroscopicity [146]. Ammonium nitrate left open in the air will soon absorb moisture and become deliquescent. Cycles in ambient humidity and temperature will cause it to cake. Various additives and coatings have been tested to reduce hygroscopicity and prevent caking of AN during storage.

Samples of 40-mesh AN and 100-mesh AN stabilized with 10% KN were exposed to controlled-humidity atmospheres in a desiccator for 5 d and weighed at the end of

the tests [147]. There was no measurable weight gain below 51% relative humidity, but beginning weight gain was noted at 52% relative humidity. KN-stabilized AN absorbed more moisture than pure AN. At 75% relative humidity, AN absorbed 4.8% moisture after 5 d, and KN-stabilized AN absorbed 10% moisture after 5 d.

Eight different samples of AN were tested for hygroscopicity at relative humidity levels of 60, 70, 80, and 90% and between 301 and 303 K (28 and 30 °C), including a sample of chemically pure reagent-grade AN, four commercial-grade samples that met military specifications, and three samples with phase-stabilizing additives [148]. Most of the samples of AN were coated, some were manufactured by a process producing prills, and clay coatings were applied in two cases. The results indicated that the AN that contained the least amount of impurities or additives was also the least hygroscopic.

Two types of tests were used to characterize the moisture sensitivity of AN. One test, a static test, consisted of Petri dishes filled with 5-g AN samples that were placed in desiccators kept at constant humidity and 303 K and were weighed periodically. In the other test, a dynamic test, a flow of moisture-conditioned air was continuously passed over AN samples for 2 h. The advantage of the dynamic method was that the samples could be weighed continuously, without opening a desiccator and disturbing the equilibrium conditions. Supplementary data were obtained by drying the moist samples at 373 K in dry air to constant weight and determining the rate at which water was removed. In a static test, reagent-grade AN gained 14.4% weight in 60% relative humidity, 51.8 in 80% relative humidity, and 67 in 90% relative humidity after 160 h. In a dynamic test, specification-grade AN gained 6% weight in 90% relative humidity after 2 h.

Other hygroscopicity results are summarized in Table 12. The weight gain of AN stored in thin layers at 22.2 °C (72 °F) at different relative humidities is summarized in Table 13.

The vapor pressure of a saturated solution of AN in water is 1.236 kPa (9.3 mm Hg) at 293 K and is 1.54 kPa (11.6 mm Hg) at 298 K, corresponding to relative humidities of 66 and 61%, respectively.

Table 12: Hygroscopicity of analytical reagent-grade ammonium nitrate.

Relative humidity, %	Weight gain, mg/g 24 h	Equilibrium
31	0.8	0.5
48	0.8	0.5
52	0.7	1.0
65	131.6	—

Humidity tests at room temperature in a static desiccator with constant-humidity solution

Table 13: Hygroscopicity of ammonium nitrate.

Exposure, days	2	3	6	1	7	8
Relative humidity, %	Weight gain, %					
52	0.2	0.2	0.2	0.2	0.2	0.2
76	26.1	29.1	69.1	14.1	74.1	78.4
90	62	84	133	32	145	156

Data source: [149]

2.3.7 Thermal Conductivity of Ammonium Nitrate

The thermal conductivity of solid AN is $0.205 \text{ kcal m}^{-1} \text{ h}^{-1} \text{ }^{\circ}\text{C}^{-1}$, which is equivalent to $0.1375 \text{ BTU ft}^{-1} \text{ h}^{-1} \text{ }^{\circ}\text{F}^{-1}$.

2.3.8 Optical Properties of Ammonium Nitrate

2.3.8.1 IR Spectra of Ammonium Nitrate

Vibrational spectroscopy of the ammonium ion in crystals is important for analyzing oxidizers for contaminants, for identifying AN residues at accidental explosion sites, and for explaining some of the phase changes that occur while ramping up or down the storage temperature of the crystals. IR spectroscopy is also used in studying the decomposition of AN and the effectiveness of catalysts and stabilizers in accelerating or retarding the decomposition of AN. Therefore, it is important to have good IR spectra of the undecomposed, pure ammonium nitrate.

Hydrogen bonding and motions of the ammonium ion in crystals are two aspects that have been studied with some success using IR, Raman, and nuclear magnetic resonance (NMR) spectroscopy. These characteristics of the ammonium ion are of exceptional importance in the case of AN since they are believed to play a key role in determining the structures of the five crystalline modifications that occur at atmospheric pressure and in the transitions between these phases. At high temperatures, NH_4^+ and NO_3^- ions are supposed to undergo nearly free rotation, and the phase transitions are associated with the freezing and thawing of the rotational degrees of freedom. Unlike the phase transitions of CsNO_3 and RbNO_3 , transitions of NH_4NO_3 are accompanied by more drastic changes in the IR spectrum. The changes in the IR spectra can be followed while going from the highly ordered phase V to phase I (where the ions rotate freely) through the intermediate phases. Some IR absorption bands disappear, and others start to show up. The symmetries and structures of all these phases can be modeled theoretically and determined using supplementary methods (XRD, NMR, XPS). The four modes of NH_4^+ oscillations are commonly described as $\nu_1'(\text{A}_1)$, $\nu_2'(\text{E})$, $\nu_3'(\text{T})$, and $\nu_4'(\text{T})$, corresponding to symmetric stretching, symmetric deformation, asymmetric stretching, and asymmetric deformation modes, respectively. Vibrational coupling may occur between factor-group modes that originate in the in-

ternal vibrations of dissimilar ions, specifically between modes of the same symmetry derived from the $\nu_3(\text{NO}_3)$ and $\nu_4'(\text{NH}_4)$ vibrations. Certain vibrational assignments initially proposed for AN were in error.

The IR spectra of solid crystalline films of AN were measured at temperatures ranging between the melting point (442 K [169 °C]) and liquid air temperature (83 K [−190 °C]) [150]. Four different spectra were obtained that were shown to belong to phase I, II, IV, and (very probably) VII. The existence of phase VII has been disputed by other investigators. Phases III and V were not encountered under the conditions of this experiment. Only the transitions $\text{I} \leftrightarrow \text{II}$ (398 K [125 °C]), $\text{II} \leftrightarrow \text{IV}$ (323 K [50 °C]), and $\text{IV} \leftrightarrow \text{VII}$ (213 K [−60 °C]) were observed in the IR spectra. A spectrum measured at 83 K (−190 °C) after rapid cooling was assigned to a mixture of phases IV and VII. The symmetry properties of the different phases are reflected in their IR spectra.

Phase transitions of NH_4NO_3 (V-IV-III-II-I) have been studied by IR spectroscopy with the material sublimed onto KRS-5 ATR crystals [151] (Figure 18). At that time, this was the best set of IR spectra for AN in all its five phases.

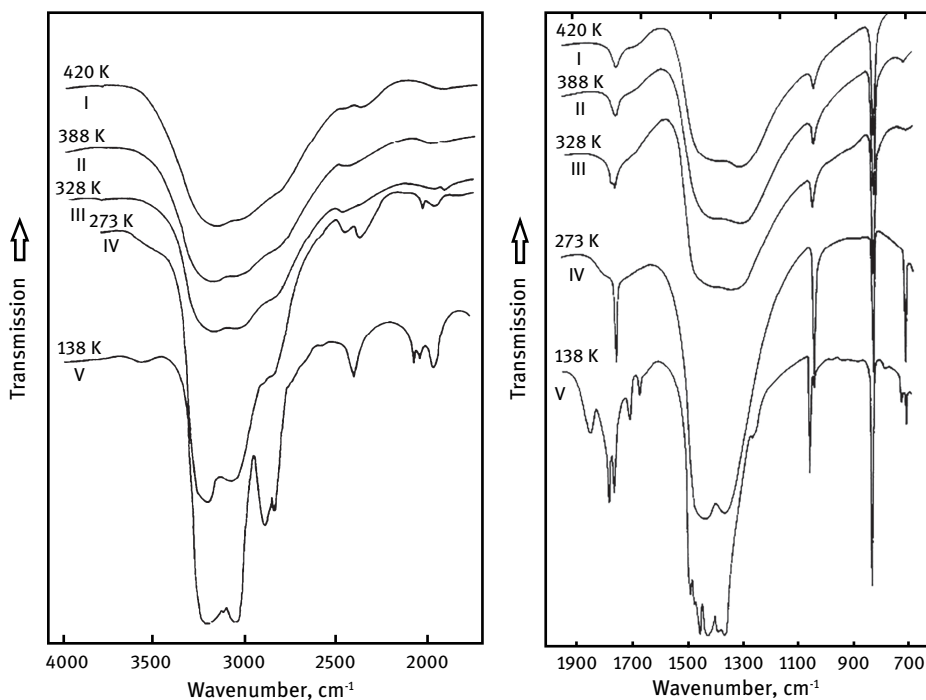


Figure 18: IR spectra of the five phases of AN in the range 2000–4000 and 700–2000 cm^{-1} .

(Reprinted and modified from [151], with permission from © 1979 Elsevier, permission conveyed through RightsLink.)

Infrared spectra of NH_4NO_3 , $\text{NH}_4^{15}\text{NO}_3$, and ND_4NO_3 were measured as nujol mulls, and the assignments of some vibrational bands of ammonium nitrate were tabulated as shown in Table 14; amendments were suggested to some previous work of other authors on this subject [152]. In dry samples, transformation of AN proceeds directly from phase IV to phase II at a temperature of about 325 K.

Table 14: Assignment of absorptions in the 1300–2600 cm^{-1} region of the IR spectrum of phase V of ammonium nitrate.

Fernandes, Ganguly, and Rao 1979 [151]		Kearley, Kettle, and Oxtan 1980 [152]			
Assignment	Frequency, cm ⁻¹	Assignment	Frequency, cm ⁻¹		
Compound	NH ₄ NO ₃		NH ₄ NO ₃	NH ₄ ¹⁵ NO ₃	ND ₄ NO ₃
ν ₃ + ν ₄	2105	ν ₂ + ν ₆	2105	2106	—
	2075		2078	2074	—
	2000	ν ₃ + ν ₄	2015	2005	^a
ν ₁ + ν ₂	1845	ν ₄ + ν ₆	1850	1843	—
ν ₁ + ν ₄	1780	ν ₁ + ν ₄	1780	1780	1779
			1761	1761	1760
	1705	ν ₂	1709	1711	—
ν ₂	1670	ν ₂	1672	1672	—
ν ₄	1490				
	1475				
2ν ₄	1460	ν ₄ , ν ₃			
	1425				
	1390				

^aNot observed due to low-frequency wing of N–D stretching absorption

Infrared spectra showing the symmetric stretching vibration band γ_1 of the nitrate ion (although it is symmetrical, it is rendered weakly IR-active by the crystal field) were recorded for sample pressures up to 6 kbar at temperatures ranging between room temperature and liquid nitrogen temperature, and a pressure–temperature phase diagram for the λ -transition of AN was obtained by this method [153]. The spectra at low temperatures and low pressures were due to mixtures of phase IV and phase VII.

The near-IR spectrum of AN displayed a doublet located at 1569 and 1642 nm due to the first overtone of symmetric and anti-symmetric NH_4 stretching vibrations ($2\nu_s\text{NH}_4$, $2\nu_a\text{NH}_4$), as well as a wide doublet located at 2031 and 2133 nm due to the first combination region, i.e., the combination of NH_4 stretching and NH_4 bending modes ($\nu\text{NH}_4 + \delta\text{NH}_4$). An additional band located at 1270 nm, whose vibrational assignment is unclear, was observed in the near-IR spectrum of AN [154].

2.3.8.2 Raman Spectra of Ammonium Nitrate

Isotope substitution allows us to assign molecular vibrations in AN crystals. The vibrations and Raman lines are different for the deuterated AN and are different for some of the polymorphic phases. The laser Raman spectra of NH_4NO_3 and ND_4NO_3 were measured between 210 and 320 K, and it was shown that the phase transition $\text{V} \rightarrow \text{IV}$ is probably a λ -transition that occurs gradually between 210 and 256 K with an abrupt change at 256 K [155]. The λ -transition is due to rotational disorder of ammonium ions, as shown by the localized disorder mode at 172 cm^{-1} . The spectrum of phase IV showed clear evidence of T and L components of the nitrate ion asymmetric stretch, but this is inconsistent with the assigned space group *Pmmn*. It was attempted to explain this by way of a thermally induced $\text{IV} \rightarrow \text{III}$ transition.

The temperature dependence of the low-frequency Raman spectrum of AN in its solid phases IV, II, and I and also in its melt was measured, and librational modes were observed in phases IV and II but disappeared in both phase I and the melt [156]. The results indicated that the NO_3 group is almost freely rotating in the solid phase I.

Raman spectra of NH_4NO_3 and ND_4NO_3 were studied from 250 to 420 K [157]. The results showed that there are four phases separated by first-order transitions. No evidence of the previously reported phase II' was observed. In phase I, the high-temperature phase, the NH_4^+ groups are in a free rotation and the nitrate groups are likely in random reorientation among 12 equivalent positions. In phase II, the NH_4^+ groups are in rapid random reorientation under the local force field of S_4 symmetry. The nitrate groups are in hindered rotation but are disordered, with one of the O—N bonds directed in one sense or the other along the *c*-axis. In phase III, the absence of the librational mode indicated that the NH_4^+ groups are in nearly free rotation, but the rotational motion is restricted by the local force field of C_3 symmetry. The nitrate groups are probably ordered as suggested by the well-polarized character of the modes associated with the nitrate groups. In phase IV, the nitrate groups are ordered with their molecular planes perpendicular to the *b*-axis. The NH_4^+ groups are in orientational disorder but may undergo hindered rotations.

Extending this work to lower temperatures, Raman spectra of NH_4NO_3 and ND_4NO_3 were recorded from room temperature down to 11K [158]. A sluggish transition from phase IV to phase V was clearly observed, but no evidence was found for another low-temperature phase. Large splitting of the ν_3 mode indicated that the inter-ionic interaction between NH_4^+ and NO_3^- is rather strong in both phases.

Polarized Raman spectra of single crystals of AN were observed for the room-temperature phase $\text{NH}_4\text{NO}_3(\text{IV})$ [159]. The spectra in the low-frequency lattice vibration region as well as in the internal vibration region were well interpreted based on a *D2h13* structure. Raman spectra of powdered samples were measured at various temperatures covering the entire range of phases I–V. A characteristic feature in the Raman spectrum could be identified for each phase. An abrupt spectral change occurred in the phase transition, indicating a first-order transition. The splitting of Ag and B1g

components of ν_3 (asymmetric stretching mode of NO_3^- ion) in NH_4NO_3 was quite large due to the strong inter-ionic interaction between NH_4^+ and NO_3^- ions.

The Raman spectra of phase III ammonium nitrate and isotopomeric materials showed that $\delta(\text{NH}_2)$ and $\nu(\text{N}-\text{O})$ vibrations are coupled together throughout the lattice [160]. This observation may be relevant to both the phase changes of AN and its detonation properties.

See also [161, 162]. Raman spectra provided spectroscopic evidence for a phase II-like intermediate during the course of the $\text{IV} \rightarrow \text{III}$ phase transition in ammonium nitrate, [163] but other investigators dispute its existence.

The temperature dependence of the Raman spectra of AN in the lattice-mode region below 200 cm^{-1} was measured at high temperatures through the tetragonal II to cubic I phase transition at 398 K [164]. As the $\text{II} \rightarrow \text{I}$ transition was approached, a pronounced softening of the librational mode was observed as well as a broadening of the line width.

Low-temperature Raman spectra of phase V AN were used to interpret the crystal structure and hydrogen bonding in the crystal [165]. The phase transition $\text{V} \rightarrow \text{orthorhombic IV}$ was observed over a 100-K range below the established transition temperature of 255 K. The phase transition may be due to a change in hydrogen bonding and gradual reorientation of NO_3^- ions in the crystal lattice. It was shown that there is heteroionic vibrational coupling between NH_4^+ and NO_3^- at 1400 cm^{-1} . Assignments of Raman bands to internal (intramolecular) and external (lattice movements) modes of vibration could be made by using isotope effects when substituting ^{14}N with ^{15}N and ^1H with ^2D .

2.3.8.3 Refractive Index of Ammonium Nitrate

The room-temperature refractive indices of AN were measured in 1933, and very little work has been done since then to extend measurements to other phases. The birefringence of these modifications is very high, with that of phase III being somewhat lower than that of the others. The index of refraction of AN is 1.413 at the Na_D line and 1.611 at the wavelength 587.6 nm of the He line.

2.3.9 Electrical Properties of Ammonium Nitrate

2.3.9.1 Electrical Conductivity of Ammonium Nitrate

The electrical conductivity of dehydrated AN pellets, partially fused in the cold, was measured at 1–600 bars and 355–442 K (82–169 °C) [166]. In this temperature range, AN exists in two different crystalline forms. Measurements were made under decreasing and then increasing temperatures. A hysteresis loop was observed that was related to the slow structural transformation. At 378.1 K (105 °C), the molar volume of formation of defects, ΔV_F , was calculated to be of the order of 26 cm^3 . The molar volume, V_m , was 47 cm^3 . As long as the ratio $\Delta V_\text{F}/V_\text{m}$ was <1 , the salt contained mainly Frenkel defects.

2.3.9.2 Dielectric Constant of Ammonium Nitrate

A pyroelectric, dielectric, and differential thermal analysis of the high-temperature phase transition II-I of AN polycrystalline samples was carried out in the temperature range 383–438 K (110–165 °C) [167]. The pyroelectric current showed a very strange behavior with temperature in which the pyrocurrent started in the positive direction, decreased during the increase of temperature, and then reversed its direction after passing through a zero value. The dielectric constant, dielectric loss, and resistivity measurements indicated that this phase transition is due to order–disorder phenomena in which a strong lattice–electric dipole interaction takes place. Thermal analyses (DTA and TGA) were also used to obtain the thermodynamic and kinetic data of this transition. This analysis showed that the heat of transition is 4.35 kJ/mol (1.04 kcal/mol) and the strain energy is $E_s = 2272 \text{ J/mol}$ (543 cal/mol).

2.3.10 Magnetic Properties of Ammonium Nitrate

2.3.10.1 Nuclear Magnetic Resonance Spectra of Ammonium Nitrate

Studies of the line width of proton magnetic resonance in solid NH_4NO_3 indicated that the NH_4^+ ions have rotational and translational freedom. Similar results were obtained for the deuterated analog ND_4NO_3 . Because the spin relaxation mechanisms of protons and deuterons are different, measurements of the two compounds may give more information about the mobility of the ions.

Measurements of the spin-lattice relaxation time T_1 of protons in solid NH_4NO_3 between 192 and 308 K gave additional information on the temperature threshold when the rotations are thawing [168]. Additional NMR pulse experiments performed under applied hydrostatic pressures between 1 and 680 atm bracket the regime of free rotation. The intramolecular rotation of groups within molecules seemed to be insensitive to pressures within this range, and the rotation of entire molecules in the solid state is pressure dependent in varying degrees. The observed pressure coefficients of T_1 in AN and other solids were related to the thermal expansion coefficient of the lattice by a simple model that postulated a localized lattice expansion as an important step in the reorientation process.

Hovi, Järvinen, and Pyykkö measured the deuteron magnetic resonance line-widths in ND_4NO_3 between 100 and 403 K [169]. They obtained values of 255, 308.5, 366, and 400.5 K with a maximum uncertainty of $\pm 2 \text{ K}$ for the transformation temperatures of $\text{V} \rightarrow \text{IV}$, $\text{IV} \rightarrow \text{III}$, $\text{III} \rightarrow \text{II}$, and $\text{II} \rightarrow \text{I}$ phase transformations, respectively.

The spin-lattice relaxation times T_1 for protons and deuterons in polycrystalline NH_4NO_3 and ND_4NO_3 at temperatures between 80 and 430 K were measured using the NMR pulse method [170]. From the measured values of T_1 , the activation energies for the reorientation motions of NH_4^+ and ND_4^+ ions below 200 K were calculated to be $8.67 \pm 0.46 \text{ kJ/mol}$ ($2.07 \pm 0.11 \text{ kcal/mol}$) and $10.72 \pm 0.96 \text{ kJ/mol}$ ($2.56 \pm 0.23 \text{ kcal/mol}$),

respectively. The quadrupole coupling constant $2Qq/h$ of the deuteron in ND_4^+ ion was 194 ± 30 kc/s.

Measurements of the proton spin-lattice relaxation times (T_1 , $T_{1\rho}$) have been made to study the translational and reorientational motions of the ammonium ions in AN crystals in several solid phases [171]. At the plastic-to-brittle phase transition at 398 K, the correlation time for translational diffusion of the NH_4^+ ion increased by more than three orders of magnitude. The self-diffusion constants for NH_4^+ in phases II and I obtained from these correlation times were in close agreement with the diffusion constants reported from electrical conductivity measurements in phases II and I.

The five solid phases of AN and transitions between these phases were studied using solid-state ^{15}N magnetic angle spinning (MAS) and static NMR [172, 173]. The $IV \leftrightarrow III$ conversion temperature, often given as 295 K (32°C), can vary depending on the moisture content and thermal history of the sample. Other transitions can also exhibit hysteresis between heating and cooling.

The temperature dependences of the ^{14}N nuclear quadrupole resonance frequencies of NH_4NO_3 in phases II, III, IV, and V were measured with the help of the 1H - ^{14}N nuclear quadrupole double-resonance technique [174]. The experimental results supported the proposed crystal structures and levels of disorder and mobility in the various crystallographic phases.

^{14}N MAS NMR spectroscopy and the associated ^{14}N quadrupole coupling data can be used for characterizing phase transitions between two solid phases. For AN, the transition between the phases IV and III at about 35°C and the phases themselves were studied by ^{14}N MAS NMR using NH_4^+ as well as the NO_3^- ion as probes [175]. Frictional heating caused the samples to warm up. The ^{14}N quadrupole coupling constants and asymmetry parameters for both the NH_4^+ and NO_3^- ion determined from these spectra showed large changes upon transition between the two phases. Also, the transition exhibited the effect of hysteresis with a deviation of about 10°C for the transition temperature. ^{14}N MAS NMR is a useful tool for characterizing phase transitions of nitrogen compounds from ^{14}N quadrupole coupling data.

The main components of industrial explosives that are sometimes diverted for illicit actions are TNT and AN. Nuclear quadrupole resonance (NQR) can be used for the detection of AN and TNT [176]. It is difficult to attenuate outside interference signals under conditions of an industrial environment.

2.3.11 Crystal Structure of Ammonium Nitrate

Most of the work dealing with the molecular structure of AN is related to the phase changes that AN undergoes at various temperatures. Each time AN changes to a different phase, so does its molecular structure. The molecular structure of AN has been determined experimentally using XRD, neutron diffraction, IR spectroscopy, and Raman spectroscopy. The measurements have been complemented by theoretical modeling using computational chemistry.

Initially, the crystal structures of all five phases (for the hydrogenous form) were studied using XRD, but only phase IV [177], phase II [178], and phase I [179] had been completely determined by neutron diffraction methods.

The crystal structure parameters and crystallographic assignments of the various phases of AN are summarized in Table 15.

Table 15: Phase-dependent crystal structure properties of ammonium nitrate crystals.

Phase	Crystal structure	Space group	Temperature, K	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	<i>Z</i>	References
I	Cubic		403	4.36			1	[66]
I	Cubic	<i>Pm</i> $\bar{3}$ <i>m</i>		4.37			1	[75]
I	Cubic	<i>Pm</i> $\bar{3}$ <i>m</i>	398–442	4.3655	4.3655	4.3655	1	[175, 180]
II	Tetragonal		363	5.712		4.924	2	[66]
II	Tetragonal	<i>P</i> $\bar{4}$ <i>2</i> ₁ <i>m</i>		5.7193		4.9326	2	[178]
III	Orthorhombic		323	7.197	7.716	5.845	4	[66]
III	Orthorhombic	<i>Pnma</i>		7.7184	5.8447	7.1624	4	[181]
IV	Orthorhombic		296	5.756	5.452	4.931		[66]
IV	Orthorhombic	<i>Pmmn</i>		5.7574	5.4394	4.9298	2	[178]
IV	Orthorhombic			5.745	5.438	4.942	2	[177]
V	Orthorhombic	<i>Pccn</i>		7.9804	8.0027	9.8099	8	[182]
V	Orthorhombic			7.8850	7.9202	9.7953	8	[183]
V	Tetragonal		255	7.925		9.820		[66]

Phase I Properties

The high-temperature phase I of pure AN is stable above 398 K and, just before melting, is a plastic phase with a cubic structure having rotational disorder of the nitrate groups [184]. The lattice parameter of the phase I cubic structure with space group *Pm* $\bar{3}$ *m* is *a* = 0.437 nm and *Z* = 1 [75].

X-ray diffuse scattering measurements due to the orientational disorder of NO₃[−] ions in the cubic phase of AN showed that the observed disk-like diffuse maxima are explained by a 12-orientation model [180]. The local order slightly deviates from what is expected from an idea of the atomic packing. The configurational entropy was calculated from five crystal parameters, and the result was not incompatible with the calorimetric measurement results.

Phase II Properties

The tetragonal structure (*P* $\bar{4}$ *2*₁*m*) of phase II was reported to be stable between 357 and 398 K [185, 186]. The lattice parameters of phase II are *a* = 0.57193(1) nm and *c* = 0.49326(1) nm, *Z* = 2 [178].

Phase III Properties

The crystal structure of phase III is orthorhombic and is stable between 305.3 and 357 K. The space group is *Pnma*, with $a = 0.77184(1)$ nm, $b = 0.58447(1)$ nm, and $c = 0.71624(1)$ nm, $Z = 4$, based on a neutron diffraction study [181].

The crystal structure of stabilized AN phase III at room temperature was examined by neutron diffraction using a single crystal containing 5% KNO_3 in solid-solution form [187]. The space group is *Pnma*, with $a = 7.6772$, $b = 5.8208$, $c = 7.1396$ Å, $Z = 4$. The ammonium ions are thermally disordered into two orientations, displaced by an angle of approximately 42° about an axis parallel to the c axis.

Phase IV Properties

Phase IV is stable between 255 and 305 K, and the structure is orthorhombic [64] and [177], with space group *Pmmn* with $a = 0.57574(1)$ nm, $b = 0.54394(1)$ nm, and $c = 0.49298(1)$ nm, $Z = 2$.

Phase V Properties

The structure of phase V was initially reported as tetragonal ($P4_2$) [188] but was later redetermined to be orthorhombic with a space group of *Pccn* by [182]. Phase V is an orthorhombic structure and is stable below 257 K with $a = 0.79804(1)$ nm, $b = 0.80027(1)$ nm, and $c = 0.98099(1)$ nm, $Z = 8$ at 233 K. Other investigators [183] measured $a = 0.78850(2)$ nm, $b = 0.79202(2)$ nm, and $c = 0.97953(2)$ nm, $Z = 8$ at 78 K.

A neutron diffraction study showed that phase V with orthorhombic structure was stable down to at least 5 K [189].

2.3.11.1 Phase Transitions

The phase transitions can be visualized by conducting a temperature-resolved series of XRD scans in which samples are heated or cooled stepwise, measuring the XRD patterns after each temperature step [190–194]. The curves for the elementary cell parameters of the different phases as a function of temperature exhibit crystal lattice details and elucidate expansion and transition mechanisms. They are used for the calculation of the volume changes during the transitions and the volumetric and linear expansion coefficients. Figure 19 illustrates a series of temperature-resolved XRD patterns. This method is particularly useful for evaluating the effectiveness of phase-stabilizing additives to AN.

Dry AN did not show a transition into phase III, but moist AN did [195]. The IV $\rightarrow$ III transition occurs through expansion of IV, where adjacent (001) layers shift in opposite directions. The shift is strongest for the tilted NO_3^- group.

Using energy-dispersive XRD for studying AN phase change between phase II and phase I, it was noted that the II/I phase transition is continuous [196].

Several series of diffraction patterns were measured with dry powdered AN from 323 to 333 K (50–60 °C) on heating and from 323 to 313 K (50–40 °C) on cooling [197]. The variations of lattice constants allow one to observe the phase transitions. On heat-

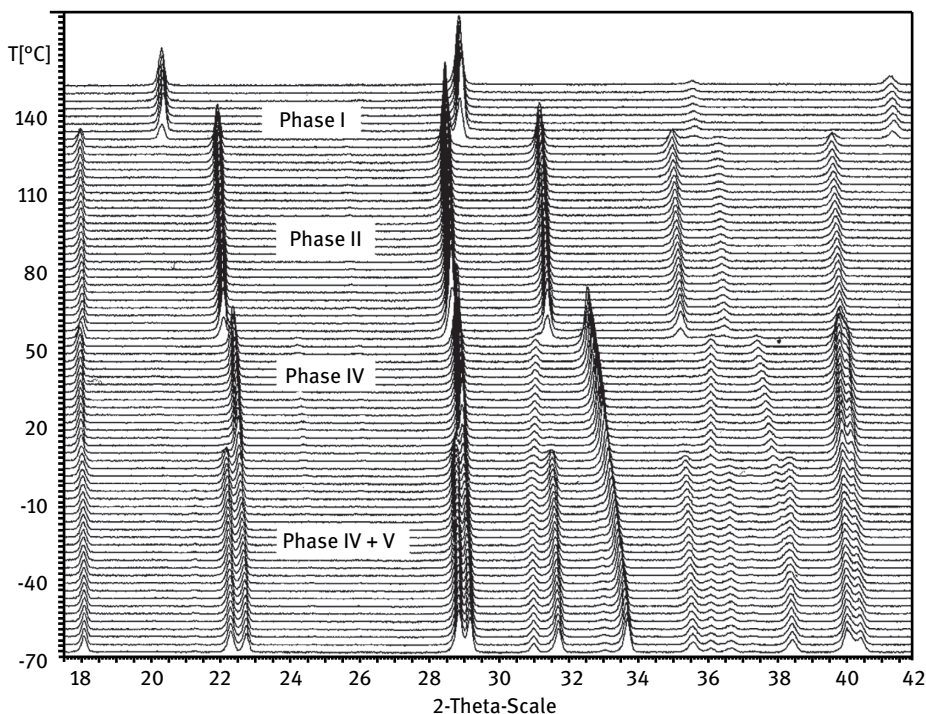


Figure 19: Series of AN XRD patterns measured after stepwise heating from -70 to $+150$ °C.

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ing, the phase transition IV/II occurs between 325 and 329 K (52 and 56 °C). In this temperature interval, both phases co-exist. On cooling, simultaneous transitions II/IV and II/V occur, with phase V slowly transforming into phase IV.

The phase transition IV/II of AN was investigated using XRD [198]. All phase transitions are very sensitive to moisture, and only a few XRD and energy-dispersive X-ray analysis (EDAX) phase-change experiments have been performed with absolutely dry samples, except in a series of experiments at the Fraunhofer Institute for Chemical Technology (ICT) in Germany [199]. A series of XRD spectra were measured in 2 °C intervals while ammonium nitrate was cycled between 203 and 353 K (-70 and $+80$ °C) or 203 and 423 K (-70 and $+150$ °C). On cooling from 423 K, the phase transitions I/II/IV/V and, on heating, the same transitions in reverse order occurred as expected. After the sample was heated to 353 K, phase II changed simultaneously into the phases IV and V below 323 K. Further cooling to 203 K changed the portion still existing in phase IV into phase V. During the succeeding heating cycle, an incomplete transition V/IV was followed by the transitions IV/II and V/II.

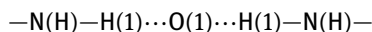
2.3.11.2 Pressure Effects on Molecular Structure

The effects of compression on phase IV AN were calculated at pressures up to 600 GPa [200]. Over this pressure range, the crystal volume was compressed by 71% of the equilibrium volume. Anisotropic behavior was observed when calculating the lattice parameters a , b , and c at different pressures. Compressibility effects were similar for the a and c direction, but the compressibility in the b direction was much higher. This can be explained by the fact that there are relatively strong $\text{NH}\cdots\text{O}$ bonds in the ac plane and weaker $\text{H}\cdots\text{O}$ bonds in the b direction.

2.3.11.3 Experimental Study of Molecular Structure of Ammonium Nitrate

Experimental methods for the study of the molecular structure of AN include XRD, neutron diffraction, IR spectroscopy, and Raman spectroscopy. Most publications deal with more than one phase of AN, but with increasing specialization some publications deal with only one phase transition or with a particular phase that is stable in a given temperature range.

The crystal structure of room-temperature phase IV has been determined by neutron diffraction. The crystal consists of hydrogen-bonded chains



parallel to the a axis. The chains are linked by somewhat weaker hydrogen bonds $\text{H}(2)\cdots\text{O}(1)$ to form sheets perpendicular to the c axis. Adjacent sheets are held together by van der Waals forces. The NO_3^- ions are distorted from the trigonal symmetry. The NH_4^+ ions are bound with two short ($\text{H}(2)\cdots\text{O}(1)$ distance = 0.205 nm) and two longer ($\text{H}(2)\cdots\text{O}(1)$ distance = 0.216 nm) hydrogen bonds. The tetragonal phase V belongs to the space group $P4_2$ with $Z = 8$. It seems to be the most ordered phase of AN.

Ammonium nitrate was temperature-cycled in consecutive steps in a high-temperature device mounted on an X-ray goniometer [201]. Diffraction patterns were measured at each temperature, using a Si-Li detector together with a multi-channel analyzer. The results strongly supported the existence of a phase II'. They showed that the phase change IV/III goes via a transition state similar to or consistent with phase II'.

The instrument developed at ICT in Germany allows the observation of the phase transitions of dry AN with XRD under cyclic thermal loading [202, 203]. The capabilities of this new instrument were demonstrated on the examples of AN phase changes. AN was subjected to two different temperature cycles: **(1)** $20 \rightarrow 150 \rightarrow -70 \rightarrow 150^\circ\text{C}$ and **(2)** $20 \rightarrow 80 \rightarrow -70 \rightarrow 80^\circ\text{C}$. Crystal structure changes were registered by continuously recording the XRD patterns. Several different phase-change paths were observed: For temperature cycling between -70 and 150°C , the sequence of phase conditions is $\text{IV}(20^\circ\text{C}) \rightarrow \text{II} \rightarrow \text{I}(150^\circ\text{C}) \rightarrow \text{II} \rightarrow \text{IV} \rightarrow \text{V}(-70^\circ\text{C}) \rightarrow \text{IV} \rightarrow \text{II} \rightarrow \text{I}(150^\circ\text{C})$. If the upper temperature limit is lowered to 353 K (80°C), the expected phase sequence $\text{IV}(20^\circ\text{C}) \rightarrow \text{II}(80^\circ\text{C}) \rightarrow \text{V}+\text{IV} \rightarrow \text{V}(-70^\circ\text{C}) \rightarrow \text{V}+\text{IV} \rightarrow \text{II}(80^\circ\text{C})$ differs from the expected path. See also [204].

One of the methods to verify experimental and theoretical molecular structure results is isotope substitution and comparison of the isotope-substituted molecule to the natural molecule. In the case of AN, isotope substitution studies have mostly been done by substitution of hydrogen with deuterium. The neutron powder diffraction data of cubic ND_4NO_3 cannot distinguish between the two best orientation models put forward for rigid NO_3 [179].

The structure of ND_4NO_3 phase V was determined by neutron powder diffraction [183]. The IR spectra of the ^1H and ^2H ammonium salt are quite different. Substitution of the ^{14}N with ^{15}N has only minor effects. However, N-isotope and O-isotope substitution has been used to resolve questions about the origin of the N-atoms in the formation of N_2O by decomposition of AN [205, 206]. The results showed that the decomposition of AN to give N_2O proceeds practically entirely by a bond formation between the two nitrogen atoms of the two different groups present, not by the interaction of similar groups. It has been found that small amounts of water were necessary to initiate the decomposition of AN. $^{15}\text{NH}_4\text{NO}_3$ has been found to yield exclusively the isomer $^{15}\text{N}^{14}\text{NO}$.

2.3.11.4 Thermal Analysis of Phase Changes of Ammonium Nitrate

Many studies of the thermal effects during phase changes in AN have been combined with other methods, such as XRD or spectral analysis of the different phases. Here we summarize publications that have relied on thermal analysis (DTA, DSC) alone to obtain information on phase changes in AN. These methods are used to study solid state phase changes that may be endothermic or exothermic. These methods are also used to study the effectiveness of stabilizing additives.

A modified DTA technique was employed for a study of the various transformations in deuterated AN [207]. The equilibrium temperatures in the transformations $\text{IV} \leftrightarrow \text{III}$, $\text{III} \leftrightarrow \text{II}$, and $\text{II} \leftrightarrow \text{I}$ were observed as 302.8, 361.52 ± 0.06 , and 400.58 ± 0.04 K, respectively. The melting point of ND_4NO_3 was found to be 1.2 K higher than that of NH_4NO_3 due to the isotope effect. In the $\text{I} \leftrightarrow \text{II}$ transformation, thermal hysteresis was not observed as indicated earlier by others in the case of NH_4NO_3 . Superheating of modification II was not found to take place at the transformation $\text{II} \rightarrow \text{I}$, while supercooling of modification I was observed at the transformation $\text{I} \rightarrow \text{II}$. Considerable superheating and supercooling proved characteristic of the III and II phases at the $\text{II} \leftrightarrow \text{III}$ transformation. Small thermal hysteresis was observed during this transformation. The $\text{III} \leftrightarrow \text{IV}$ transformation was also found to be associated with small thermal hysteresis. Modifications III and IV of ND_4NO_3 supercooled by 0.7 and 0.5 K, respectively. Consideration of the effect of deuteration on the Gibbs function of various modifications of AN indicated that the interaction of the NH_4^+ group with the lattice seemed to be strongest in modification III.

The transformation from phase IV to some other phases occurs in more than one step below 324 K (51 °C) and is accompanied by endothermic peaks if the sample is

heated after prolonged storage at room temperature or after slow cooling [208]. Removal of moisture shifts the transition temperature closer to 324 K (51 °C). Foreign materials, crystal defects, and thermal treatment history influence the transition from phase IV to phase II or III. There may be metastable phases that delay or smudge the clean transition from one phase to the other.

In addition to measuring the temperature at which the phase transitions occur, it is also important to know the enthalpy changes occurring at each step (Section 2.3.12.3).

Ammonium nitrate solid-phase transition paths between phases IV, III, and II were analyzed by XRD and DSC [209]. The analysis of the XRD and DSC measurements proved that the different phase transition paths are of structural origin.

2.3.11.5 Theoretical Modeling of the Molecular Structure of Ammonium Nitrate

Computational chemistry has gained acceptance to the point that some chemists consider it a replacement for experimental measurements, whereas others consider it only as a supplement to experimental studies. Every once in a while, the two methods agree.

A force field–based molecular model for the description of the III and IV phases of AN was used to illustrate the development of molecular modeling techniques for energetic materials [210]. In addition to describing the lattice forces, the model also correctly predicted the dominance of (200) faces in crystals grown at low supersaturation.

Interatomic potentials were derived for ammonium and nitrate molecular ions in AN crystals, using empirical fitting to known properties of ammonium halides and alkali nitrates, and were used to calculate crystal and lattice properties of AN, which were then compared with available experimental data [211]. The potentials were then used to model the low-temperature phase (phase V) of AN.

Plane-wave *ab initio* calculations based on density function theory and a pseudopotential method were used to investigate the structural and electronic properties of phases V, IV, III, and II of AN crystals [200]. The optimizations of the crystal structures were done with full relaxation of the atomic positions and lattice parameters under the experimentally determined crystal symmetries. For phases V, IV, and II, the predicted crystal structures were found in good agreement with those determined experimentally by neutron diffraction data, but for phase III the differences between the experimental and calculated values were more significant. The thermal expansion coefficients indicated anisotropic behavior with large expansions along the *a* and *b* axes and a very small one along the *c* axis.

Molecular dynamics simulations were used to calculate a predicted melting point and examine some aspects of high-temperature solid-state phase transitions of AN crystals [212]. Simulations at various temperatures were performed for phase II AN.

The melting point of AN was predicted from calculations on this crystal structure, with voids introduced to eliminate superheating effects. The melting temperature was predicted by calculating the density and the nitrogen–nitrogen radial distribution functions as functions of temperature. The melting point was predicted to be in the range 445 ± 10 K, in excellent agreement with the experimental value of 442 K. The computed temperature dependencies of the density, diffusion, and viscosity coefficient for the molten liquid were in good agreement with experiments. The ammonium ions in the phase II structure are rotationally disordered at 400 K. At higher temperatures beginning at 530 K, the nitrate ions are essentially rotationally unhindered.

It is difficult to obtain sharp XRD Bragg peaks for nanocrystalline or amorphous energetic materials that usually give only diffuse halo patterns. Use of nano-AN would be a good method to increase the burning rates of AN-based propellants, but it is difficult to characterize the crystal structure of the small particles that contain only a few unit cells. The use of total scattering, in which both Bragg and diffuse components of the scattering are analyzed together, is a possibility for the study of this kind of problem, shown with AN as an example [213]. Theoretical-pair distribution functions of AN were calculated and compared with the experimental-pair distribution functions. The interpretation of the experimental-pair distribution functions may be similar to the Rietveld method.

Ab initio molecular dynamics simulations of the phase transitions and structural properties of AN at a pressure range of 5–60 GPa and temperature range of 250–400 K predicted two new phases: One corresponds to the experimentally observed phase IV', and the other was named AN-X [214]. The lattice strains play a significant role in the formation and stabilization of phase IV', providing an explanation for experimental observation of phase IV–IV' transition that appears only under non-hydrostatic pressure. Twelve O atoms neighboring the NH (N atom in ammonium cation) atom were selected as the reference system to clearly display the tangled rotation of the ammonium cation.

A first-principles evolutionary crystal structure search found a new crystal phase of AN [215, 216]. The calculated Raman spectra of this new phase were consistent with the experimental Raman spectrum that contained two peaks previously associated with a pressure-induced phase transition. The phase transition is predicted to occur at a pressure of 17 GPa, while the new phase was calculated to be lower in free energy than phase IV of AN (AN-IV) above a pressure of 10.83 GPa. The new phase has a monoclinic unit cell with the $P2_1/m$ space group symmetry (AN- $P2_1/m$). This new phase is similar to AN-IV except the ammonium molecules are oriented differently relative to the nitrate molecules. The calculated Raman spectrum of both AN- $P2_1/m$ and AN-IV as a function of pressure showed good agreement with experimental data up to 33 GPa.

2.3.11.6 Crystal Structure of Ammonium Nitrate Solid Solutions and Mixtures

A significant amount of effort has been devoted to modifying the crystal structure of AN by co-crystallizing or co-melting additives that prevent the large density change associated with phase transitions. One of the best examined additives is potassium nitrate [112, 217].

2.3.11.7 Crystal Deformation of Ammonium Nitrate

The plasticity and cold-flow extrusion behavior of AN extruded from a pressurized chamber through an orifice varies substantially with the phase transitions in different temperature regimes.

The flow stress of AN in an extrusion die indicated phase transformations, which were automatically recorded as breaks on the curves of extrusion pressures. Extrusions were made in a 39-kN press at a rate of displacement of the piston of 1 mm/min, with automatic recording of the pressure [218, 219]. Comparison of the data for AN with information on the plasticity of other substances showed that substances in the metastable state have a plasticity exceeding several times the plasticity of the stable forms. The plasticity of the separate modifications could be evaluated by comparing the flow stresses at various temperatures and pressures under isothermal and shifting temperature conditions. In the vicinity of the transition point, the plasticity of phase III $\gamma\text{-NH}_4\text{NO}_3$ is approximately 3.6 times greater than that of phase IV $\beta\text{-NH}_4\text{NO}_3$. At each phase transition, the ions in the crystal lattice have greater mobility while they are jostling for a new spatial arrangement, and the crystal is more deformable and extrudable.

2.3.12 Thermodynamic Properties of Ammonium Nitrate

2.3.12.1 Heat Capacity of Ammonium Nitrate

The heat capacity and the heat of fusion are needed for the design of industrial processes in which AN is melted either to be prilled or to be decomposed in the production of N_2O . The heat capacity of solid AN varies considerably depending on the phase composition of the sample. The values reported in the literature during the past 140 years vary considerably. Therefore, it was a welcome step when Dellien in 1982 reexamined and summarized literature values from eight different sources, summarized in Table 16, and derived a new set of data from his own DSC experiments, including studies on the effects of moisture and thermal history of the samples [220].

The heat capacities of AN were measured between 15 and 410 K for the stable and metastable phases by use of adiabatic-type and conduction-type calorimeters [222]. The phase transformations between stable phases, i.e., $\text{V} \leftrightarrow \text{IV}$, $\text{IV} \leftrightarrow \text{III}$, $\text{III} \leftrightarrow \text{II}$, and $\text{II} \leftrightarrow \text{I}$ and the metastable transition between phase IV and II, were all found to be of first-order type. The direct transition between V and II, which was realized only for a sample treated with a minute amount of surface active agent, was ascertained

Table 16: Heat capacity of ammonium nitrate.

Temperature range, °C	Phase	$C_p, \text{J g}^{-1} \text{ } ^\circ\text{C}^{-1}$	References
0–+31 avg.	IV	1.70	
31–83.5 avg.	III	1.49	
82.5–124 avg.	II	1.78	
–15–+15 avg.	IV	1.65	
–79––20 avg.	V	1.47	
–190–+20 avg.	?	1.28	
0.5–20.1 avg.	IV	1.66	
–76.1–0	V	1.58	
–20	V	2.00	
125–170 avg.	I	2.38	[139]
170–270 avg.	Liquid	2.01	[139]
40	III	1.50	
65	III	1.59	
114	II	1.88	
189	Liquid	1.96	
25	IV	1.73	[221]

Literature data from various sources, as reported by [220]

to be a higher-order type. Heat and entropy of transition of five types of transitions were determined, and these results showed that the heat capacity data by Stephenson et al. [223] at low-temperature region are much more reliable than the values by Eichenauer [224]. The possibility of the existence of a seventh phase below 156K has been discussed, but this has been questioned by other investigators.

The heat capacity of AN and phase-stabilized AN with potassium nitrate, copper oxide, and nickel oxide was determined using a differential scanning calorimeter calibrated with sapphire and benzoic acid standards [225]. Heat capacity data were then compared with literature results, and those for the phase-stabilized AN were compared with earlier DSC results.

2.3.12.2 Enthalpy of Formation of Ammonium Nitrate

To obtain accurate data for the enthalpy of formation of crystalline AN by combustion calorimetry, one must make sure that corrections for the possible occurrence of undetected by-products of incomplete combustion are applied. The exact states of the respective samples of AN at the time of combustion must be totally in phase IV, and adsorbed water must be eliminated before the pellet is ignited.

The standard enthalpy of formation of AN in its stable reference state at 298.15K was derived from measurements of the energy of combustion of samples of hydrocarbon oil or polyethylene sheet in the presence of AN [221]. Under the conditions chosen, AN decomposed to $\text{N}_2(\text{G})$, $\text{O}_2(\text{G})$, and $\text{H}_2\text{O}(\text{L})$; the only significant by-product found was $\text{HNO}_3 \cdot n\text{H}_2\text{O}$. Special care was devoted to preparation of the NH_4NO_3 sam-

ple in its stable state (crystalline form IV), free of water. Combination of the resulting value of Δt_{H_0} with recent data on the enthalpies of solution and dilution of $\text{NH}_4\text{NO}_3(\text{cr, IV})$, together with key values from the CODATA compilation, gave $\Delta H_f^\circ(\text{NO}_3^-, \text{aq}) = -(206.81 \pm 0.41)\text{kJ/mol}$. The enthalpy of formation of crystalline AN in the phase IV condition was found from combustion calorimetric data with a hydrocarbon oil or polyethylene foil as $\Delta H_f^{298}(\text{NH}_4\text{NO}_3, \text{cr, IV}) = -(365.61 \pm 0.32)\text{kJ/mol}$.

The generally accepted tabulated value of ΔH_f^{298} of $\text{NH}_4\text{NO}_3(\text{c})$ is $-365.7 \pm 2.9\text{kJ/mol}$ ($-87.4 \pm 0.7\text{kcal/mol}$). See also [226].

The PEP data list shows ΔH_f^{298} AN as $-1090\text{cal/g} = -87.247\text{kcal/mol} = -365.04\text{kJ/mol}$ [227]. The molecular mass of AN is 80.043g/mol . This number is needed for conversion from mass-specific numbers to molar units and vice versa. Table 17 is a summary of published enthalpy-of-formation data for AN in its phase that is stable at 298 K.

Table 17: Standard enthalpy-of-formation data for ammonium nitrate.

Phase	Enthalpy of formation ΔH_f^{298} , SI units		Enthalpy of formation ΔH_f^{298} , other units		References
	kJ/mol	kJ/kg	kcal/mol	cal/g	
IV	-365.04	-4560	-87.247	-1090	[227]
	-365.6	-4567.0	-87.367	-1091.5	[228]
	-365.61 ± 0.32	-4567.7	-87.383	-1091.7	[221]

2.3.12.3 Enthalpy of Phase Changes of Ammonium Nitrate

The phase changes of AN are endothermic and exothermic and are reversible, depending on the direction in which the temperature change is taking place. Upon cooling, generally only one transition is observed, at 321 K (48°C). The enthalpies of phase changes rhombic to rhombohedral ($\text{III} \rightarrow \text{II}$) and β -rhombic to α -rhombic ($\text{IV} \rightarrow \text{III}$) vary substantially depending on sample history. Literature data vary widely. The $\text{II} \rightarrow \text{I}$ transition is well reproducible both as to size and temperature ($399\text{--}400\text{K}$ [$126\text{--}127^\circ\text{C}$]). One of the first multi-phase solids to be examined with newly developed DSC instrumentation in 1964 was AN [229].

In trying to consolidate sometimes contradictory data, Dellien [220] compiled the enthalpies of phase changes from numerous literature sources along with the heat capacity data and compared them with his own experimental results from DSC measurements. The results are summarized in Table 18.

The results of Stephenson, Bentz, and Stevenson [223] and Nagatani et al. [222] are in good agreement with each other with regard to both heat capacity and transition enthalpies. Their data were obtained using reliable experimental techniques.

Table 18: Enthalpy of phase changes of ammonium nitrate.

Phase transition	Temperature		Enthalpy of transition		References
	K	°C	kJ/mol	J/g	
V ↔ IV	256	−17.15	0.464	5.80	[223]
			0.473 ± 0.006	5.91 ± 0.08	[222]
IV ↔ III	305.4	+32.25	1.715 ± 0.0016	21.43 ± 0.02	[223]
			1.700 ± 0.009	21.24 ± 0.12	[222]
	315	41.8	1.337	16.7	[229]
IV → II	326	53	1.889 ± 0.08	23.6 ± 1.0 (avg. of 9 runs)	[220]
III ↔ II	357	84	1.350 ± 0.015	16.87 ± 0.19	[222]
	353	80	1.337	16.7	[229]
			1321	16.5	[220]
II ↔ I	399	126	4.435 ± 0.030	55.41 ± 0.38	[222]
	398	125	4.154	51.9	[229]
	399	126	4.594 ± 0.104	57.4 ± 1.3 (avg. of 17 runs)	[220]

2.3.12.4 Enthalpy of Fusion of Ammonium Nitrate

Any engineer who is tasked with designing a process that involves molten AN (prilling, nitrous oxide production) must have accurate data for the enthalpy of fusion (the heat of melting). The enthalpy of fusion is usually reported in the literature as the enthalpy of transition from phase I to the liquid phase, assuming that the solid crystals remained in the phase I regime long enough to equilibrate with the environment just prior to melting. The enthalpy of fusion of solid AN starting at room temperature (heating rapidly without allowing time for phase changes) would have to include the enthalpies of three solid–solid phase changes taking place above 298 K before the AN melts.

Enthalpy-of-fusion data reported in various literature sources are compiled in Table 19.

Table 19: Enthalpy of fusion of ammonium nitrate phase I.

Melting temperature		Enthalpy of fusion		Method	References
°C	K	kJ/mol	J/g		
170	443	6.363	79.5	DSC	[229]
169.3	442.45	6.403	80.0	Cryoscopy	[230]
		6.195 ± 0.264	77.4 ± 3.3	DSC, avg. of 13 runs	[220]

2.3.12.5 Enthalpy of Sublimation of Ammonium Nitrate

From the measured molecular weight of vapor over $\text{NH}_4\text{NO}_3(\text{c})$ by the simultaneous torsion-effusion/mass-loss method, the partial pressure of $\text{NH}_4\text{NO}_3(\text{g})$ was evaluated over the range 321–360 K [143]. The presence of the gaseous nitrate was verified by effusion-beam mass spectrometry (MS). Third-law calculations of the sublimation enthalpy of AN were made with estimated molecular constants, yielding an enthalpy of sublimation of $\Delta H_{298}^{\circ}(\text{subl}) = 87.4 \pm 8.3 \text{ kJ/mol}$ ($20.9 \pm 2 \text{ kcal/mol}$), as compared to a less reliable value of $97.07 \pm 12.55 \text{ kJ/mol}$ ($23.2 \pm 3 \text{ kcal/mol}$) derived from application of the second law of thermodynamics. If one trusts the third-law value, a first estimate for the enthalpy of formation of gaseous AN was $\Delta H_{298}^{\text{f}} \text{NH}_4\text{NO}_3(\text{G}) - 278.2 \pm 8.8 \text{ kJ/mol}$ ($-66.5 \pm 2.1 \text{ kcal/mol}$) when combined with the known $\Delta H_{298}^{\text{f}}$ value of crystalline NH_4NO_3 ($\Delta H_{298}^{\text{f}} \text{NH}_4\text{NO}_3(\text{C}) = -365.68 \pm 2.93 \text{ kJ/mol} = -87.4 \pm 0.7 \text{ kcal/mol}$). A later revision changed this to a different number, $\Delta H_{298}^{\text{fo}} \text{NH}_4\text{NO}_3(\text{G}) = -258.6 \pm 20.9 \text{ kJ/mol} = -61.8 \pm 5 \text{ kcal/mol}$ [231].

2.3.12.6 Enthalpy of Dissociation of Ammonium Nitrate

The standard free energy of dissociation of NH_4NO_3 (C, IV) to $\text{NH}_3(\text{G})$ and $\text{HNO}_3(\text{G})$ is $93.4 \pm 0.3 \text{ kJ/mol}$ [232]. Over the temperature range for which the crystalline phase IV is stable (-17 to 32°C), the temperature dependence of the dissociation constant is given to within $\pm 12\%$ by

$$\ln K_p = 118.87 - 24084/T - 6.025 \ln T$$

where T is the temperature in kelvin. For particles with radii less than $0.1 \mu\text{m}$, the Kelvin effect has a substantial effect on the vapor pressure and dissociation constant. However, particle size has little effect on the deliquescence point.

2.3.12.7 Enthalpy of Solution of Ammonium Nitrate

Enthalpy of Formation of Ammonium Nitrate Solutions

The difference between the enthalpy of formation of solid AN and the enthalpy of formation of AN solutions is the enthalpy of dissolution.

The heat of solution of AN for infinite dilution in water is $\Delta H_{\text{sol}}(\text{NH}_4\text{NO}_3, \text{cr, IV}, 4\text{H}_2\text{O}) = 25.544 \pm 30 \text{ kJ/mol}$ at 298.15 K , [233]. This heat of solution agreed well with data reported earlier where they had been reported as $\Delta H_{\text{sol}}(\text{NH}_4\text{NO}_3, \text{cr, IV}, 4\text{H}_2\text{O}) = 25.41 \text{ kJ/mol}$ [234]. The integral heat of solution forming a saturated solution at room temperature is about 16 kJ/mol . See also [226].

Table 20 gives the enthalpy of dissolution of AN in water compared with that of other high-energy oxidizers [235]. All of these salts cool off when dissolved in water, a fact that is used to advantage with AN in two-component instant ice packs for first aid for sports injuries.

Table 20: Standard enthalpy of dissolution of AN in water compared with that of other oxidizers.

Compound	Standard enthalpy of formation, kJ/mol		Enthalpy of dissolution, kJ/mol
	Crystalline solid	In solution at infinite dilution	
NH ₃ OHNO ₃	-366.5	-344.8	+22.5
NH ₄ NO ₃	-365.4	-339.9	+25.3
N ₂ H ₅ NO ₃	-246.9	-215.1	+31.8

Data source: [235]

Ammonium nitrate is reported to be appreciably soluble in aqueous and concentrated nitric acid; solutions of 50 mass-% AN in anhydrous nitric acid are commonly used in the manufacturing of explosives. Heat is evolved when AN is dissolved in 99.6% HNO₃, but heat is absorbed if AN is dissolved in water. The partial molal heat of solution of AN in HNO₃ is -27.2 kJ/mol (-6.5 kcal/mol) [236]. This heat of solution represents the heat evolved when a mol of the salt is dissolved in an infinitely large amount of the acid to form an infinitely dilute solution. At low concentrations, up to 0.15 mol AN/mol of HNO₃, the heat of solution is nearly proportional to the salt concentration (Table 21). Above 0.3 mol AN/mol HNO₃, it levels off at 20.9 kJ/mol (5 kcal/mol) of AN added. The solution process is thermoneutral if the HNO₃:H₂O molar ratio is about 1:1. In an ideal solution without thermal effects, the heat of solution is the same as the heat of fusion. In each case, the energy required to destroy the crystal lattice of the AN crystals is the same.

Table 21: Heat of solution of ammonium nitrate in anhydrous nitric acid.

Molality (298 K)	ΔH	
	kJ/mol	kcal/mol
0.2	-27.8	-6.65
1.0	-23.9	-5.72
1.5	-22.2	-5.30
2.3	-19.7	-4.70

Data source: [236]

2.3.12.8 Entropy of Ammonium Nitrate

The best value for the absolute entropy of AN at 298 K may be taken as 150.6 J mol⁻¹ K⁻¹ (36.0 cal mol⁻¹ °C⁻¹) [139]. The entropy of AN (phase IV) at 298.16 K was calculated as 151.08 J mol⁻¹ K⁻¹ (36.11 ± 0.05 cal °C⁻¹ mol⁻¹) [223].

2.4 Chemical Properties of Ammonium Nitrate

2.4.1 Stabilizer Additives to Prevent Phase Changes of Ammonium Nitrate

A significant amount of effort has been devoted to the search for stabilizing additives that will prevent the bothersome phase changes of AN, in particular the phase IV $\leftrightarrow$ phase III transition occurring at just above room temperature. Not all additives are equally effective for all phase changes. Some additives are effective only for shifting or eliminating one of the phase changes while the others remain unaffected. Phase-stabilized AN is known under the abbreviation PSAN.

At first we were not quite sure whether the chapter on stabilizing additives to prevent phase changes of AN should be placed under “Physical Properties” or “Chemical Properties.” There are no chemical reactions involved with the stabilizing mechanism. But because so many different chemicals have been evaluated, it felt appropriate to place this chapter under “Chemical Properties” instead of “Physical Properties.”

Three types of methods have been used to “stabilize” AN against phase transitions. One technique is to add dehydrating agents that remove the water that catalyzes the III $\leftrightarrow$ IV phase transition. The other methods use solid solution effects to alter the AN crystal lattice and its transition temperature. One approach is to use compounds that have identical orthorhombic crystal lattices and easily intersperse with AN. Phase stabilization is more effective if a solid solution and eutectic are formed. But there are exceptions: Although 5-aminotetrazole and AN form a solid solution and a eutectic, phase stabilization of AN is not achieved.

Efforts to stabilize AN against phase IV $\leftrightarrow$ phase III transitions have included combining it with additives such as potassium nitrate, zinc oxide, magnesium oxide, copper oxide, nickel oxide, potassium fluoride, potassium hexafluoroaluminate, and nickel oxide, as well as certain lithium, calcium, barium, and aluminum salts and other metal salts of the nitrate anion. Furthermore, organic compounds such as urea, ethylene diamine dinitrate, diethylene triaminetrinitrate, guanidinium nitrate, silicates, and melamine have also been investigated as AN stabilizers. None has proven entirely satisfactory. For instance, with regard to potassium nitrate, at least about 9 mass-%, generally about 10–15 mass-%, must be introduced into the AN crystal lattice to prevent transitions up to about 393 K (121°C). Crystal stability is achieved in many propellant compositions only at the expense of increased pressure exponents, reduced energy performance, reduced density, and increased smoke, all of which make the use of potassium nitrate undesirable as a phase stabilizer. Ammonium nitrate stabilized with CuO or with about 3 mass-% NiO has been reported to show little tendency to cake. However, such CuO- and NiO-containing compositions prevent environmental hazards, sacrifice energetic performance, and prevent aging and processing problems in energetic formulations.

Magnesium nitrate, potassium nitrate, potassium carbonate, ammonium dihydrogen phosphate, ammonium sulfate, and zinc nitrate were evaluated as stabilizing

agents for AN prills (fertilizer grade AN), but the stabilizers actually used were kept proprietary [237].

Most of AN is used as fertilizer, often in mixture with other fertilizers. Some of the fertilizer additives (ammonium sulfate, urea, calcium nitrate) to AN have beneficial side effects in that they also shift the phase-transition temperatures [238].

The kinetic constants and the enthalpy of phase transitions $\text{II} \leftrightarrow \text{I}$ of AN with and without addition of ammonium sulfate, magnesium nitrate, or ammonium polyphosphate were measured by DTA, and subsequently the samples were heated to incipient decomposition [239, 240]. See also [241].

In temperature regions with coexisting phases, Rietveld refinement has been used for quantitative phase analysis. The method yields lattice parameters and atom positions as well as intramolecular and intermolecular distances [190, 242]. The obtained data determined unambiguously the stability ranges and thermal expansion of the phases. They showed that the stability of the room temperature phase IV and that of phase II is extended to lower temperatures by adding the copper compound.

The solid-state reaction of AN and copper(II) oxide proceeds through an intermediate stage in the form of a solid solution of a diamminocopper(II) complex in the AN lattice, subsequently resulting in the formation of diamminocopper(II) dinitrate [243]. The crystallographic and kinetic aspects of the solid-state reaction of AN and copper(II) oxide were studied by *in situ* time- and temperature-resolved XRD. The kinetic profiles of the reaction were fitted by a nucleation and growth model. The rate of the reaction was found to increase as the dopant concentration decreased. The reaction resulted in an expansion of the tetragonal lattice of the AN along the base, resulting in a plausible pseudo-tetragonal-like structure.

Diammino copper (II) complexes were incorporated into the AN lattice to improve the phase behavior. The thermal expansion and the phase transitions of AN with diammino copper ("CuPSAN") contents corresponding to 7% CuO were measured with temperature-resolved XRD while the samples were heated in accordance with the temperature cycling programs 20/100/−70/100 and 20/143/−70/20 °C [244, 245]. A series of measurements were performed, while the samples were heated with the temperature cycling programs 20/100/−70/100 and 20/143/−70/20 °C. The series were evaluated by Rietveld refinement, yielding thermal expansion curves of the phases, which were identified by the known diffraction patterns. In temperature regions with coexisting phases, Rietveld refinement was used for quantitative phase composition analysis. The obtained data identified unambiguously the stability ranges and thermal expansion of the phases. It was shown that the stability of the room-temperature phase IV and of phase II can be extended to lower temperatures by selecting the correct stabilizer additives. Compared to pure AN, the elementary cell of phase V of CuPSAN approached a tetragonal structure like phase II.

A welcome side effect of the addition of stabilizers to AN is reduced hygroscopicity. However, moisture absorption remains a problem because water reduces the stabilizing effect of nickel oxide and other stabilizers.

2.4.1.1 Methods for Evaluation of Stabilizer Additives to Prevent Phase Changes of Ammonium Nitrate

The following methods are used for the study of phase changes occurring in AN either with or without the addition of phase stabilizers:

- Differential thermal analysis (DTA)
- Differential scanning calorimetry (DSC)
- Accelerating rate calorimetry (ARC)
- Dilatometry
- X-ray diffraction (XRD)

Dilatometric Measurement of Volume Changes

The effectiveness of stabilizing, anti-swelling additives can be measured in a dilatometer after repeated temperature cycling. A specially built dilatometer was filled with stabilized or unstabilized AN and topped off with mercury. The rise of the Hg column in a glass capillary during stepwise heating from 293 to 316 K (20 to 38 °C) gave a good indication of the effectiveness of the stabilizing agents. Results of tests on ten samples were reported [246].

Dilatometric investigations of natural and phase-stabilized AN have shown the beneficial effect of adding stabilizers [247–249].

A combination method of dilatometry and thermal analysis gives multiple answers when applied to phase changes occurring in AN [250]. With the aid of this apparatus it is possible to measure the temperature, the change in weight, and the dilatation of the sample, as well as the rate of the changes in enthalpy and weight and the velocity of dilatation (shrinking or swelling).

The swelling of propellant grains prepared with insufficiently stabilized AN, unstabilized AN, and PSAN is quite obvious when comparing the three cylindrical propellant samples in Figure 20 that went through a series of temperature cycling.



Figure 20: Example of swelling of ammonium nitrate-based propellant grains as a result of temperature cycling. *Left:* Cycled urea-stabilized AN; *Center:* Cycled AN propellant; *Right:* Cycled PSAN (ZnO-stabilized) propellant. (Reproduced with permission from Wickman Spacecraft Propulsion Company at <http://www.wickmanspacecraft.com/psan-i.html>; last accessed 12/22/2018)

Visual Examination Under the Microscope

Phase transitions $IV \leftrightarrow II$, $IV \leftrightarrow V$, and $II \leftrightarrow V$ of AN were examined through a polarizing microscope by using thin single crystals of various orientations [251]. In the transition $II \rightarrow IV$, a single crystal split itself into two kinds of crystals, in which the direction of the c -axis was common but the a - and b -axes were interchanged. A composite pattern appeared that was characteristic of the orientation of the initial crystal. The crystal composites had boundaries of $\{110\}$ planes, which may be twinning planes. The new phase grows in a specified direction in the mother crystal in conformity with a minimum strain postulate. The $IV \leftrightarrow V$ transitions were very similar to the $IV \leftrightarrow II$ transitions except for the appearance on occasion of a faint light/dark pattern of phase V. This pattern was probably due to the formation of micro twins. The $II \leftrightarrow V$ transitions occurred as a second-order transition in minute crystals within a temperature range of about 317 to 314 K (44 to 41 °C). The transformation was detected only by the same light/dark pattern of phase V in some crystals as in the case of the $IV \rightarrow V$ transition.

Quantitative conoscopy was used as a method to determine an optical orientation angle $2V\gamma = 86^\circ 15' (+)$ for the orthorhombic phase III and an angle $2V\alpha = 36^\circ 30' (-)$ for the orthorhombic phase IV [96]. Measuring the change in the optic axial angle allows one to monitor the transition from IV into II or II' as a function of time and temperature. At 349 K (76 °C), it took 50–100 d to stabilize the angle at 82° . The change occurred over an intermediate, metastable phase II' that persisted for the first 50 d and then underwent a secondary stabilization that took another 100–150 d to complete. The curve had a discontinuity at 50 d (refer to Figure 2, page 213, of de Saenz et al. [96]). The intermediate phase II' was obtained by annealing crystals in the stability range of phase III, resulting in crystals of tetragonal or lower symmetry. After some time, the crystals turned biaxial by annealing. Many discussions were carried on in the literature about the rather peculiar behavior of AN phase transitions. To a considerable amount, the speed and the extent of phase change depends on the history of samples with “memory.” The existence of nuclei of one phase persisting, after the transition, in the other phase (e.g., nuclei of III in IV) is part of this ongoing discussion.

Goniometric measurements were performed with similar results [252].

One of the plainly visible effects of phase changes during repeated temperature cycling of AN is that solid crystals or prills break apart into smaller particles and end up as a powder. The method of using particle-size analysis to examine the route of a phase transformation in a crystal slurry was tested, and results for the $IV \rightarrow III$ transition in aqueous slurries of AN crystals illustrated the viability of this technique [98].

Single crystals of phase IV AN shaped (ground or split) into thin foils show unusual elasticity in that they can be bent to nearly 180° without breaking. It was suggested that this elasticity of AN makes it difficult to comminute it by grinding and that grinding would best be done at lower temperatures at which the material is more brittle.

2.4.1.2 Inorganic Stabilizer Additives to Prevent Phase Changes of Ammonium Nitrate

Most of the stabilizing additives are nitrates of other cations. Some of the additives are ammonium salts with anions other than nitrate.

Metal Nitrate Additives

The most thoroughly investigated phase-stabilizing additive for AN is potassium nitrate, KNO_3 , abbreviated KN. Potassium nitrate has the advantage that it is less hygroscopic than AN, is readily available, is an oxidizer in its own right, and requires only 4–10 mass-% KN to achieve a noticeable improvement in either shifting or totally eliminating one of the phase changes.

The occurrence of a “metastable” transition at 323 K (50 °C) between modifications IV $\rightarrow$ II is associated with special drying of the sample or its immersion in a non-solvent. Prompt occurrence of the transition IV $\rightarrow$ III at 305 K (32 °C) would thus appear to depend on the presence of an aqueous phase. A surface film of saturated solution carried by the hygroscopic salt is most often responsible for its ready transition.

Potassium nitrate in solid solution in the AN modifications alters their temperature ranges of stability [102]. At 256 K (–16 °C), a 30% addition renders phase III completely stable, whereas phase IV becomes unstable with more than 8% of the added salt. Between these limits, equilibrium mixtures of III and IV can exist. However, with 10% or less of KNO_3 in suitable preparations, stabilization of phase III between 253 and 333 K (–20 and 60 °C) may be obtained, and claims have been made that as little as 1% KNO_3 is effective in phase stabilization. Stabilized AN has been made by mechanically mixing, co-crystallizing, or fusing a finely divided potassium salt with ammonium nitrate.

X-ray powder diagrams showed that solid solution formation by physical grinding takes place more easily between KNO_3 and phase III AN than phase IV AN [109]. The transition point is at 305.4 K (32.3 °C). Solid solution formation can take place by ion migration in the solid state and is accelerated by heating the mix to 323 K (50 °C). Mixed crystals containing 19.29% KNO_3 were crystallized from a saturated aqueous solution of 80 parts AN and 20 parts KNO_3 between 368 and 358 K (95 and 85 °C). The crystals turned out to be of the modification III of NH_4NO_3 , acicular, four faces of the (110) form, with interfacial angles nearly 86 and 94° and the angle between (110) and [110] faces being 94°. The refractive indices in the three different directions are $\alpha = 1.46$, $\beta = 1.54$, $\gamma = 1.60$.

It was suggested that surface solid solutions rich in KNO_3 would prevent surface nucleation with phase IV [253].

Ammonium nitrate was fused with 1 to 10% of $\text{Ce}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ or $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, and the phase-change retardation was evaluated by doing dilatometric, TGA, and XRD analyses [254]. The additives were not very effective.

A solid solution of AN containing 15 mass-% KN was obtained from the ternary system NH_4NO_3 - KNO_3 - H_2O [255]. The mixed crystals prepared by crystallization un-

der metastable condition were acicular with well-developed faces, while under unstable conditions, referred to as spinodal decomposition, rounded crystals could be obtained. It was found that the sphericity of the crystals was largely dependent on the interaction of hydrodynamics and growth of higher-ordered species of clusters in the system. To evaluate the AN (phase III) as an ingredient for explosive compositions, several formulations with such binders as TNT, acrylate elastomers, and silicone prepolymers were prepared and temperature-cycled. Dimensional stabilities of these compositions were confirmed with a thermal cycle test, dilatometer, and thermal and thermomechanical analyzer.

Modification of the room-temperature phase transition (IV $\rightarrow$ III) of AN has been attempted using a variety of potassium salts, including KNO_3 , KF, KCl, KI, K_2CO_3 , K_2SO_4 , KSCN, and $\text{K}_2\text{Cr}_2\text{O}_7$ [256]. No phase transition was observed when AN containing 1–2% by mass of these potassium salts was heated from room temperature (25 °C) upward in DTA and DSC scans, but the linear expansion due to phase transition was still observable in thermomechanical analysis (TMA) measurements. Complete arrest of the linear expansion could be achieved only when a higher concentration of the additive was used. Addition of potassium dichromate modified the phase as well as the decomposition pattern of AN.

Magnesium nitrate is not a desirable additive to AN, but the phase transitions in the AN/ $\text{Mg}(\text{NO}_3)_2$ system nevertheless have been mapped [257]. See also [114, 258].

Aluminum ion stabilizes phase IV of AN [259]. The objective of this work was to improve the stability of phase IV of AN by adding Al^{3+} cations to counteract the negative influence of contaminant cations such as Mg^{2+} . AN was doped, and NH_4^+ cations were replaced by Al^{3+} and Mg^{2+} by melting or co-crystallizing from aqueous solutions with $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The amount of additives was limited to 5 mass-%. XRD spectra at low temperatures confirmed the positive effect of Al^{3+} cations on the stability of phase IV of AN and the negative action of Mg^{2+} cations.

Dried samples of AN containing 1, 3, or 5 mol-% KNO_3 , RbNO_3 , or CsNO_3 were investigated with temperature-resolved XRD [260]. The samples were cycled repeatedly with two temperature programs from 203 to 373 K (–70 to 100 °C) and 203 to 423 K (–70 to 150 °C), respectively. DSC measurements were made for comparison. KNO_3 extended the stability range of phase III. The supercooling observed with the II $\rightarrow$ III and III $\rightarrow$ IV transitions was so severe that the phases III and IV could be skipped and the material changed directly from phase II to IV and III to V. RbNO_3 -doped AN behaved like moist AN. Phase III appeared on heating but was skipped on cooling, when the sample had been heated to 423 K. CsNO_3 stabilized phase II and V. No strong hysteresis or supercooling could be observed with CsNO_3 -stabilized AN.

The effects of KNO_3 on the phase transitions of solid AN were examined using *in situ* microscopic Raman spectroscopy [261]. Both the transition path and transition temperature of AN single particles (40–700 μm) depend on the KNO_3 mass percentage and the particle size. With the addition of KNO_3 , the IV $\rightarrow$ II transition, which appears at 325 K (52 °C) for pure AN, is replaced by the IV $\rightarrow$ III transition. The KNO_3 mass

percentage required for this change in the transition path increased with decreasing particle size, and the transition temperature decreased with increasing KNO_3 percentage. At a relatively high KNO_3 content ($\geq 7.4\%$), the $\text{KNO}_3/\text{NH}_4\text{NO}_3$ mixture underwent the IV $\rightarrow$ III transition under ambient temperatures, or even crystallized directly in phase III from droplets with a further increase in the mass percentage of KNO_3 .

Another phase-change stabilizer investigated is a mixture of potassium nitrate and disodium tetrahydrogen nitrilotris-(methylenephosphonate) [262].

Three-component inorganic additives can exert a synergistic effect, lowering the transition energy in AN phase changes. The additives were introduced into AN by isothermal co-crystallization from aqueous solutions. Phase stability in the system constituted by AN, potassium dichromate, and alkaline-earth metal (Mg, Ca, Sr) nitrates was measured by DTA at a heating rate of $3^\circ\text{C}/\text{min}$ [263]. The best results were obtained with mixtures containing magnesium nitrate, such as $\text{KNO}_3/\text{Mg}(\text{NO}_3)_2$ and $\text{KNO}_3/\text{K}_2\text{Cr}_2\text{O}_7/\text{Mg}(\text{NO}_3)_2$ [264]. It was expected that introduction of the additive(s) via isothermal crystallization from an aqueous solution would eliminate the IV $\rightarrow$ III phase transition and diminish to the maximum possible extent the activation energy of the thermal decomposition of AN. Introduction of magnesium nitrate leads to an increase in the activation energy of the decomposition of modified AN by 25 kJ/mol as compared with the pure substance (126 kJ/mol), and introduction of potassium nitrate and potassium dichromate leads to a decrease in E_a by 13 and 10 kJ/mol , respectively. For an addition of 4% total stabilizer, the optimal composition of a three-component stabilizer was as follows (mass fraction): $\text{Mg}(\text{NO}_3)_2$ 0.47, KNO_3 0.14, $\text{K}_2\text{Cr}_2\text{O}_7$ 0.39, or $\text{Mg}(\text{NO}_3)_2$ 0.44, KClO_4 0.21, $\text{K}_2\text{Cr}_2\text{O}_7$ 0.35.

Basic copper nitrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2]$ in combination with AN has been investigated to improve the performance of gas-generating agents. In order to better understand the thermal behavior and stability of $\text{AN}/[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2]$ mixtures, samples prepared by two kinds of methods, with and without heat treatment, were analyzed using XRD to investigate the composition of samples, and DSC and TGA-DTAMS were used to investigate the thermal behavior and evolved gases [265]. It was found that $[\text{Cu}(\text{NH}_3)_2](\text{NO}_3)_2$ was formed in the sample with thermal treatment. The samples with and without heating exhibited different decomposition behavior. The residual AN and the amount of $[\text{Cu}(\text{NH}_3)_2](\text{NO}_3)_2$ in the mixture may affect the decomposition behavior.

KNO_3 -stabilized AN intended to be used in solid gas generants has been coated with organic polymers to reduce its hygroscopicity [266]. The thermal stability of coated AN/KN is not much different from uncoated stabilized AN/KN [267–269].

Dinitramide Additives

A deviation from the historical trend to use nitrates of different cations to interrupt the regularity of the AN crystal lattice is the application of metal dinitramidates (also ADN) and the dinitramide anion as stabilizers [270, 271]. This not only stabilizes the AN but it also improves its performance as a rocket propellant oxidizer. Ammonium nitrate is

phase-stabilized against phase IV $\leftrightarrow$ phase III transitions and the undesired volume changes associated with that phase change by the inclusion of an effective amount of at least one metal dinitramide salt having the formula $M[N(NO_2)_2]_n$ wherein M is a metal cation and n is 1, 2, or 3. Metals claimed in the patent include a good part of the periodic table of elements, in particular lithium, cerium, potassium, zinc, and lanthanide elements.

Another application of potassium dinitramide (KDN) would be as a stabilizer for AN. While KNO_3 has been used for decades as a stabilizer for AN in solid-propellant and gas-generant formulations, the disadvantage of KNO_3 is that it reduces the performance of AN as a rocket propellant. KDN, however, more than compensates for the performance loss due to the introduction of the potassium [272, 273].

AN phase transitions leading to volume change can be overcome by the use of phase stabilizers. Unfortunately, most of the phase stabilizers used to prepare PSAN are non-energetic, and the overall energy content of the formulation is reduced to some extent. Using KDN as a stabilizing additive makes a PSAN with improved energy content. A DSC study of KDN/AN compositions evaluated KDN concentrations in the range of 0.2 to 5% (by weight). PSAN samples containing 0.2, 0.5, 1, 3, and 5% KDN were prepared, and their thermal properties were examined using DSC. The results showed that at concentrations above 3%, KDN has a good phase-stabilization effect on AN [274, 275]. An overlay of the DSC curves with increasing KDN additions (Figure 21) shows the complete disappearance of the phase transition at 327 K (54 °C).

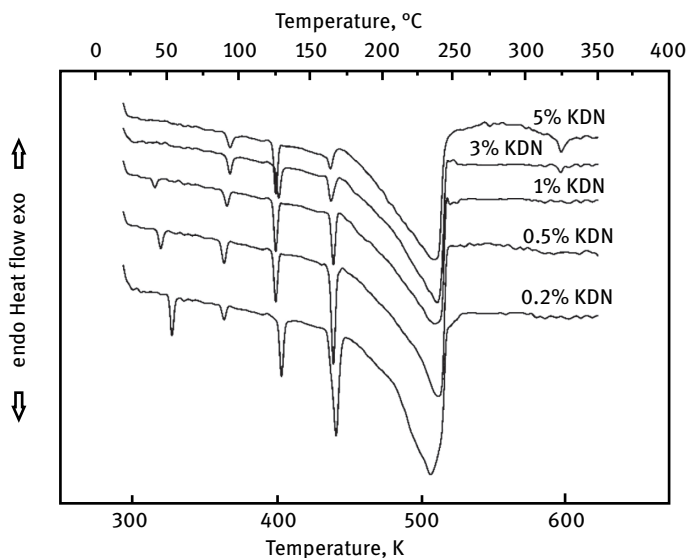


Figure 21: Overlay of DSC curves of AN with increasing KDN additions. (Reprinted and modified from [274], with permission granted by Dr. Santhosh 8 February 2021.)

In ADN-AN mixtures with different mol ratios that were analyzed using DSC, the maximum melting endotherm was obtained for a mixture with mol fraction $\chi_{\text{ADN}} = 0.71$, demonstrating that the eutectic point (marked with E in Figure 22) is close to this value [276].

Binary ADN/AN phase diagram calculations were performed using a basic model based on ideal ionic liquid and pure non-miscible solid phases, and they were compared to the experimental-phase diagram determined by DSC analyses of 24 prepared ADN/AN compositions [277]. Both oxidants have their ammonium $[\text{NH}_4^+]$ cations in common and possess anions composed of nothing other than oxygen and nitrogen atoms. These results were then compared to estimated binary phase diagrams of AP/ADN and AP/AN systems. Table 22 summarizes the enthalpy of fusion and melting points of the pure compounds used as input data for this study. The estimated eutectic point of the AN/ADN mixture is at 328.0 K (54.9°C) for a predicted mol fraction of ADN $\chi_{\text{ADN}} = 0.43$, but the experimental eutectic was more at $\chi_{\text{ADN}} = 0.6$.

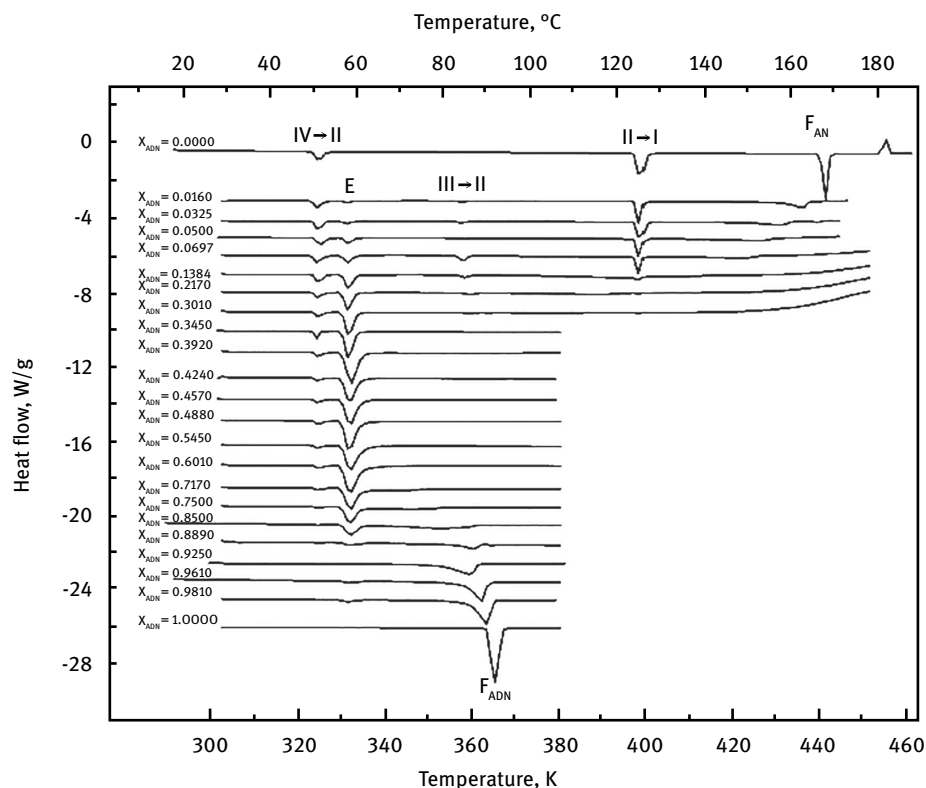


Figure 22: DSC thermograms of AN/ADN mixtures with increasing ADN concentrations at a heating rate of 2°C/min (Reprinted and modified from [277] with permission from Dr. X. Secordel 26 May 2020.)

Table 22: Enthalpy of fusion and melting points of AN, ADN, and AP.

	ΔH_{fus}		T_{fus}	
	kJ/mol	kcal/mol	K	°C
AN	6.11	1.46	442.7	169.6
ADN	17.62	4.21	366.0	92.9
AP	29.30	7.00	513.1	240

Data source: [277]

As shown in Figure 22, from $\chi_{\text{ADN}} = 0.00$ at the top thermogram, two clear endothermic peaks appear close to 325 and 399 K (52 and 126 °C), corresponding to the IV $\rightarrow$ II and II $\rightarrow$ I solid-solid transitions, respectively [277]. The II $\rightarrow$ I transition peak integrated intensity decreases progressively with the increasing amount of ADN (top to bottom) and vanishes for $\chi_{\text{ADN}} = 0.217$. The new peak (E) close to 333 K (60 °C) is typical of the eutectic transition at constant temperature.

A very detailed review of various methods and additives for phase stabilization of AN included additional data on the effectiveness of KDN as a stabilizing additive [278]. With the addition of only 5% KDN, AN can be phase stabilized, and the KDN addition to AN crystals increased the energy capacity of AN significantly. The phase transition of AN at 330.79 K (57.64 °C) was completely removed by the addition of 3% of KDN. For AN/KDN propellant systems, a maximum of 30% KDN can be added to AN. The reason for this limitation lies in the decomposition mechanism of KDN.

Metal Ammino Complexes as Additives

Ammino complexes of Ni, Cu, or Zn stabilize phase IV, while KNO_3 stabilizes phase III.

Cobalt(II)hexammino nitrate is one of the several ammino complexes evaluated as stabilizers for AN [279]. Ammino complexes of Co(II), Ni(II), and Zn were claimed and patented as stabilizers [280]. The metals are added to molten AN in the form of hydroxides or carbonate [281, 282]. The additives are melted with AN, and the melt is sprayed into a prilling tower to obtain spherical particles. NiO and ZnO were also claimed as stabilizers. In another approach, copper(II) oxide or nickel oxide is melted with one-tenth of the AN to be treated while bubbling ammonia through the melt at 383–443 K (110–170 °C) to form the ammino complexes, followed by adding the remaining nine-tenths of the AN to the melt and prilling [283].

AN samples stabilized with copper(II) diammino and copper(II) tetrammino complexes were stored for 4–5 years and re-analyzed using DTA and dilatometry [248]. Samples stabilized with copper(II) diammino complexes showed little or no tendency to agglomeration, and DTA did not reveal any III/IV phase changes below 323 K (50 °C). Copper(II) tetrammino complexes were equally effective. The effectiveness of either additive depends on the moisture content of the samples.

The volume increase due to the phase transition $\text{IV} \leftrightarrow \text{III}$ of AN at 305 K (32 °C) is reduced by incorporating the diammino complexes of nickel, copper, or zinc into the lattice, as shown by dilatometric measurements [249]. The transition temperatures are raised above 323 K (50 °C) by the nickel and copper ammino complexes. The zinc complex is less effective, depending on the water content of the samples.

Ammonium nitrate doped with copper diammino dinitrate and stored for 10 years was reinvestigated by DTA and TMA [284]. The phase transitions $\text{IV} \leftrightarrow \text{II}$ and $\text{IV} \leftrightarrow \text{III}$, which are of concern for the practical use, still occur above 323 K (50 °C), but they are less likely to take place during storage in a military underground magazine that rarely gets that warm. Despite moisture contents between 0.4 and 1.4%, no caking was observed.

Zinc diammino nitrate in AN can be formed by melting a 1:3 mixture of ZnO and AN, removing the water of reaction by purging with a dry gas, adjusting the ammonia balance by bubbling ammonia through the melt, and adding the product to molten AN to obtain a final composition with about 1–4 wt-% Zn [285]. Propellants prepared with this type of PSAN did not suffer swelling when temperature cycled. However, in wet PSAN, the zinc diammino complex may hydrolyze and lose ammonia and form an AN-insoluble hydroxide.

NH_4NO_3 , $\text{NH}_4\text{NO}_3/\text{KNO}_3$, $\text{NH}_4\text{NO}_3/\text{CsNO}_3$, and NH_4NO_3 with nickel(II) diammino nitrate, copper(II) diammino nitrate, and zinc diammino nitrate were investigated using XRD for an unambiguous determination of their phase properties [286]. The samples were cycled stepwise with a temperature program from 298 to 373 K (20 to 100 °C), cooled to 203 K (–70 °C), and heated back to 373 K (100 °C). Diffraction patterns were measured after each step every 2.5° increment. The measurements resulted in information about the phases present and their phase transitions. The ingredients are readily available for the development of propellants in bulk quantities of metric tons with particle size of 20–500 μm .

Metal Oxide Additives

The action mechanism of metal oxides is different from that of nitrates or dinitramides. Due to the acidic hydrolysis of AN, some of the metal oxides are superficially converted to nitrates and interact with the crystal lattice. In some cases, the metal oxides dissolve in molten AN if some excess ammonia is bubbled through the melt, converting the insoluble metal oxides to soluble ammino complexes. Because metal oxides are basically insoluble in AN, it is important to use finely divided metal oxides in the smallest particle size available. This is one example where nano materials promise to bring improved properties.

Most of the stabilizer work in AN has been done with copper(II) oxide, but copper(I) oxide has also been tested to see whether Cu(I) will become oxidized to Cu(II) under conditions of the AN melt [287]. This can be done by electron paramagnetic resonance measurements.

The phase changes of AN doped with small amounts of NiO or CuO have been studied using XRD and neutron diffraction at temperatures from 80 to 423 K [288]. AN with metal-oxide additives, which are believed to form complexes, exists as a solid solution. Phase IV was stable down to 140 K in the NiO-doped samples and to 210 K in the CuO-doped sample. While most previous studies looked just at the overall volume change, it has now been noted that the crystal growth (shrinkage) is not uniform in all directions of the crystal lattice. The thermal expansion of phase IV is extremely anisotropic, with the *b*-axis expanding rapidly with increasing temperature while the *a*-axis contracts slightly. At higher temperatures the doped samples transformed directly from phase IV to phase II, bypassing phase III, starting at about 328 K. Based on new data, the structure of phase II, which is disordered, was refined and has now been assigned to space group *P4/mbm*. The structure of phase III contains hydrogen-bonded chains parallel to the *b*-axis.

The stabilizing effect of ZnO was measured using temperature-programmed energy-dispersive XRD [289].

Metallurgical wastes are often used in the production of fertilizers enriched with vital essential elements, including zinc. Besides zinc oxide, they may contain iron, calcium, and magnesium oxides. Zinc oxide reacts with AN, forming water-soluble zinc nitrate hexahydrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and a less water-soluble compound, which has been characterized as complex zinc nitrate hydroxide hydrate, $\text{Zn}_5(\text{NO}_3)_2(\text{OH})_8 \cdot 2\text{H}_2\text{O}$ [290].

Rare-earth oxides, namely Y_2O_3 , Nd_2O_3 , La_2O_3 , and CeO_2 , were evaluated as phase stabilizers for AN in comparison with CuO and NiO [291]. DTA studies established the effectiveness in overcoming the problem of IV $\rightarrow$ III transition occurring at 32 °C. A new endotherm was observed for PSAN incorporating 4% rare-earth oxides in the temperature range of 55–60 °C, as reported by others for CuO-stabilized and NiO-stabilized PSAN. Incorporation of Y_2O_3 or CeO_2 can reduce the moisture susceptibility of AN. DSC data confirmed the phase stabilization of AN containing rare-earth oxides with respect to phase IV–III transition at 32 °C. XRD patterns provided evidence in support of a change in the crystal structure of AN doped with Y_2O_3 or CeO_2 , which may be the cause of their effectiveness as phase stabilizers.

Ammonium nitrate that was phase-stabilized with copper(II) diammino dinitrate was cycled between 203 and 373 K (–70 and 100 °C) in steps of 10 °C, with diffraction patterns measured after each step [292, 293]. The measured XRD series were used for phase identification and for Rietveld analysis, which provided the elementary cell parameters and quantitative phase analysis for temperature regions with coexisting phases. Expansion coefficients were calculated from the elementary cell dimensional data. During cycling, the phases II and IV were observed exclusively. Phase IV changed on heating into phase II, which on cooling reconverted into phase IV. With a CuO concentration of 3 mass-% the transitions were complete, whereas with 5 and 7 mass-% CuO, only partial reconversion was observed into phase IV at essentially

lowered transition temperatures, with parts of the sample remaining until 203 K (-70°C) in phase II or the similar phase V, which are not easily distinguishable.

Copper phase-stabilized AN (Cu-PSAN) was prepared by the incorporation of copper(II) oxide into the AN crystal lattice by a melt process. The phase transitions of AN and dimensional changes occurring during this phase-stabilization process, and crystallographic aspects of the solid-state reaction between AN and CuO and thermal behavior of phase-stabilized AN were measured. It was found that solid-state reactions occurred by an intermediate solid solution formation [294]. Lattice parameters and unit cell volume as a function of temperature were derived from XRD patterns. They showed a non-linear and anisotropic behavior with increasing temperature, such as lattice expansion along the *b*-axis and contraction along the *a*- and *c*-axes. The unit cell volume increased with temperature.

Earlier PSAN-based propellant formulations used a PSAN containing 3.5% nickel oxide. Unfortunately, after some promising formulations had been developed, NiO was identified as a potential carcinogen. All subsequent formulations have contained 3% zinc oxide PSAN instead of 3.5% NiO PSAN.

Anatase-brookite mixed-phase TiO_2 nanoparticles ($\sim 10\text{ nm}$) were used as catalyst to enhance the reactivity of AN [295]. The activation energies required for the decomposition reactions, computed by differential and non-linear integral isoconversional methods, were used to compare the catalytic activity. Presumably, the removal of NH_3 and H_2O , known inhibitors of AN decomposition reaction due to the surface reactions on the active surface of TiO_2 , changes the decomposition pathway and thereby the reactivity.

CuO has been used as a stabilizer for AN [296]. A DSC thermogram of CuO-stabilized AN is shown in Figure 23. This thermogram should be compared to that of pure AN under identical conditions, shown in Figure 24. When comparing the two thermograms, it is obvious that several of the phase changes were suppressed by adding CuO.

An analysis of the thermal decomposition mechanism of AN and copper(II) oxide (CuO) mixtures using DSC and evolved gas analysis based on TGA-DTA-MS was carried out, and decomposition behavior was observed using a hot stage with a camera containing a charged-coupled device [297]. DSC results showed that the AN/CuO mixture had a higher exothermic onset temperature than pure AN and that CuO did not promote the decomposition of AN. From TGA-DTA-MS results, the endothermic reaction of AN/CuO mixture started after the AN melting point of 442 K and resulted in the evolution of H_2O . At approximately 500 K or above, the AN/CuO mixture generated significant quantities of N_2 and H_2O , and an exothermic reaction began to offset the endothermic processes. Above 510 K, the AN/CuO mixture began to evolve NO_2 . Around 493 K, molten AN/CuO changed to a deep blue color because of the presence of a copper(II) amine complex.

Ammonium nitrate was co-crystallized along with copper(II) oxide, titanium dioxide, or lithium fluoride as candidate stabilizers, and thermal kinetic constants for the

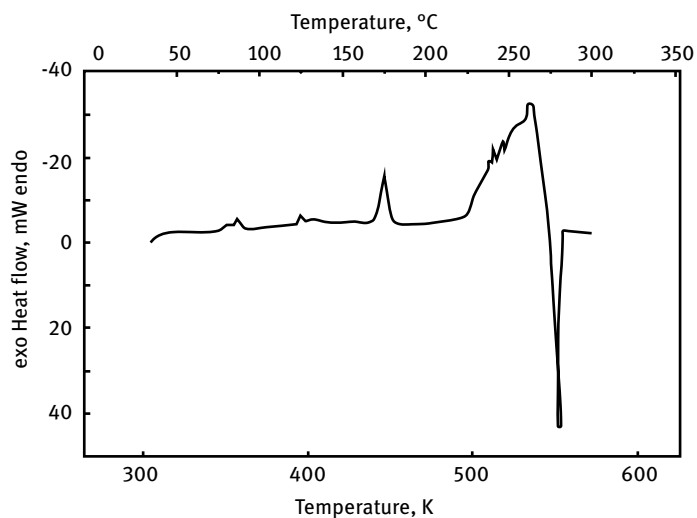


Figure 23: DSC thermogram of phase-stabilized AN with CuO. (Reprinted and modified from [296], by permission of the publisher Taylor Francis Ltd, <http://www.tandfonline.com>).

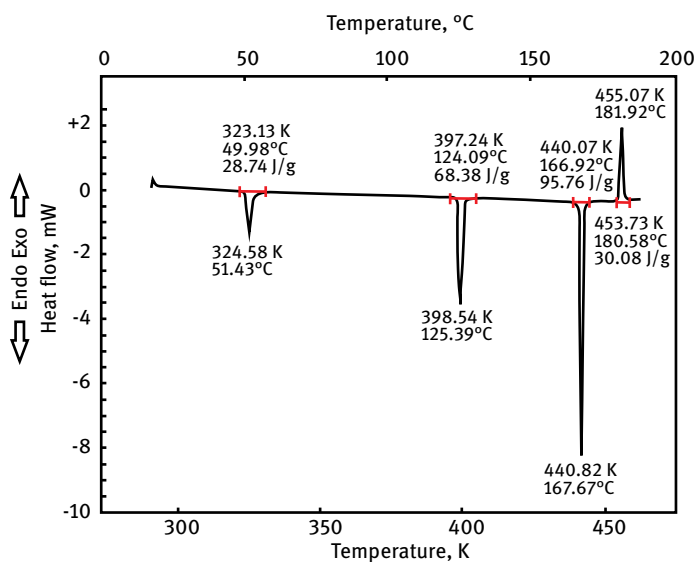


Figure 24: DSC thermogram of pure ammonium nitrate. (Reprinted and modified from [277] with permission from Dr. X. Secordel 26 May 2020.)

decomposition reactions of the samples were calculated by model-free and model-fitting methods [298]. The results of the model-fitting method showed that the decomposition mechanism for all samples was a contracting cylinder mechanism. The phase behavior of the obtained samples was evaluated by DSC, and structural properties were determined by XRD. The results indicated that copper oxide modifies the phase-transition behavior and can catalyze AN decomposition, whereas LiF inhibits AN decomposition.

Titanium dioxide (TiO_2) nanocatalyst with an average particle size of 10 nm was synthesized by a sol-gel method using titanium alkoxide as precursor, and the catalytic effect of TiO_2 nanocatalysts on the solid-state thermal decomposition reaction of AN and non-aluminized AN/hydroxyl-terminated polybutadiene (HTPB) propellant was evaluated [299]. To quantify the effectiveness of the TiO_2 nanocatalyst, the thermal decomposition kinetic constants for the catalytic and non-catalytic decomposition of AN and AN propellant samples were computed and compared by using a non-linear integral isoconversional method. The catalytic influence of TiO_2 was evident from the lowering of the activation energy for the catalyzed decomposition reactions. Apparently, the TiO_2 nanocatalysts provide Lewis acid and/or active metal sites, facilitating the removal of AN dissociation products NH_3 and HNO_3 and thereby enhancing the rate of decomposition.

Potassium Fluoride Stabilizer

A PSAN mixed crystal structure can be produced by the addition of potassium fluoride (KF) [300, 301]. Thus, the undesirable abrupt expansion and contraction of AN in the temperature range of use in rocket motor propellants and explosives is eliminated. The stabilized AN is made by the addition of between 3 and 5% and preferably about 3.5 mass-% KF to the AN by a non-hazardous aqueous solution method. The aqueous solution method is safer than the melting method described in prior art patents. Propellants made with AN containing only 2% KF were not effectively stabilized, but an Omax-601-type compression-molded propellant formulation containing AN stabilized with 3.5% KF and also containing Milori blue (ferric ferro ammonium ferrocyanide) and bonded with HTPB suffered only 0.87% volume change after 30 temperature cycles, whereas a grain prepared with unstabilized AN had swollen by 3.2%.

Samples of AN containing 4 mass-% KF were investigated during cycling the material between 203 and 353 K (−70 and 80 °C) [302–304]. The incorporation of 2–4% KF into the AN lattice extended the stability range of phase III to lower temperatures. The results differed in dry and humid samples. In dry samples, phase III changed directly into phase V on cooling at temperatures between 263 and 208 K (−10 and −65 °C). The transitions were not complete in dry samples. In humid samples, the transition into phase V was complete and occurred at higher temperatures between 278 and 263 K (5 and −10 °C). In this case, phase IV could not be excluded reliably. It was suggested that the differences can be explained by a retarded nucleation of phase V in the dry

samples. On heating, the transition V $\rightarrow$ IV occurred in all samples at temperatures slightly above 273 K (0 °C), followed by the transition IV $\rightarrow$ III at 303–308 K (30–35 °C). Due to the extended stability range of phase III, a direct transition V $\rightarrow$ III could then be observed in the dry samples.

Thermal analysis by DSC of crystallized AN prepared from an aqueous solution containing 1 mass-% KF and heated from room temperature to 573 K (300 °C) showed the disappearance of the phase transformation that normally appears at 305 K (32 °C) [305]. Phase changes appeared only at 364.7, 395.9, and 435.9 K (91.6, 122.76, and 162.82 °C), even after the AN was stored under natural conditions for 75 d or was exposed to heating at elevated temperature and cooling to room temperature several times. Potassium fluoride also accelerated the thermal decomposition of AN.

Other Inorganic Stabilizing Additives

The main objective for stabilizing additives is to prevent or suppress the unwanted phase changes. Other additives may delay the thermal decomposition of AN [306].

Significant improvement in the dimensional stability of AN was achieved using 0.05 mass-% FeSO₄ [307]. After being subjected to 23 temperature cycles, an AN sample containing 1% FeSO₄ did not show any volume change, whereas an unstabilized sample had swollen by 50% of its original volume.

The use of ammonium sulfate (AS) as a stabilizer may not be the best choice for AN as a rocket propellant, but it would be very convenient for stabilizing AN that is to be used as a fertilizer, since AN/AS mixtures are commonly used as fertilizers anyway. Based on DTA and XRD investigations of the changes induced in the phase transitions of AN by the addition of AS (and water) and by repeated heating and cooling cycles going through the NH₄NO₃(IV) $\leftrightarrow$ NH₄NO₃(III) phase transition point, AS is not a very effective stabilizer [308].

A variety of potassium salts have been tested in an effort to prevent or at least shift the IV $\leftrightarrow$ III phase transformation of AN [256]. The salts tested include KF, KCl, KI, KNO₃, K₂CO₃, K₂SO₄, KSCN, and K₂Cr₂O₇, typically in concentrations of 1–2 mass-% in AN. KF was a better stabilizer than KNO₃. The samples were analyzed by DSC, DTA, dilatometer, and XRD. DSC and DTA thermograms did not show any phase-change endo/exotherms, but the linear expansion due to phase transition was still observable in the dilatometer. That undesirable phase change could be avoided only if a higher concentration of the additive was used. In thermal cycling experiments in which the samples were cycled between 193 and 373 K (–80 to 100 °C), the phase change could be suppressed only with fairly high additive concentrations (6–8%). Potassium dichromate showed a dual effect: It modified the phase transition and changed the thermal stability of AN. An unstabilized AN pellet would typically expand in the dilatometer by 6.6% linearly when heated from room temperature to 403 K (130 °C).

Stabilized AN was prepared by adding more than 20 different inorganic additives at a dosage of ~1 mass-%, and the effects of these additives on AN polymorphs were studied using DSC [309]. The results showed that potassium salts prevented the tran-

sition of IV $\rightarrow$ III effectively; oxide, $\text{Cu}(\text{NO}_3)_2$, $(\text{NH}_4)_2\text{SO}_4$, and MgSO_4 prevented the transition of III $\rightarrow$ II; and the composite of KCl and ZnO prevented both transitions of IV $\rightarrow$ III and III $\rightarrow$ II simultaneously. The effects of inorganic additives on AN phase transition are the co-active results of such factors as anion and cation radius and their matching, ion substitution, the formation of solid solutions, solubility, charge distribution, and ion stereo structure.

2.4.1.3 Organic Stabilizer Additives to Prevent Phase Changes of Ammonium Nitrate

The addition of 0.03–1 mass-% urea to dry AN can reduce its rate of decomposition at 473 and 498 K (200 and 225 °C) [310–312]. The same results were obtained by adding urea to a 60–70% AN solution and co-crystallizing before drying. The pH of a 10% solution of a sample taken from NH_4NO_3 heated for 1 h at 473 K was 3.15; after 0.5 h at 498 K, it was 2.09 due to increasing acid formation. The corresponding values of the pH of stabilized NH_4NO_3 containing 0.1–1 mass-% urea were 6.55–6.6. Urea and NH_4NO_3 stabilized each other only at small urea additions because the addition of 2–5 mass-% urea lowered the stability of the system. This was attributed to the instability of urea itself. The pH of samples taken from AN/urea mixtures containing 1.0 mass-% urea and kept at 498 K (225 °C) and dissolved in water increased during the first 5 min and then remained constant, whereas that of a control experiment, without an inhibitor, continued to decrease. Besides urea, the best inhibitor was Zn, the activity of which has been ascribed to the complex $[\text{Zn}(\text{NH}_3)_4](\text{NO}_3)_2$.

The substance *n*-octadecylamine, $\text{C}_{18}\text{H}_{37}\text{NH}_2$, has a retarding effect on the IV $\rightarrow$ II and IV $\rightarrow$ V phase transitions and wet sintering of AN [313].

Aliphatic amines influence the kinetics of the IV $\leftrightarrow$ III polymorphic transformation of AN [314]. Surfactants influence the kinetics of the IV $\leftrightarrow$ III polymorphic transformation of AN [315].

AN phase stabilization is typically accomplished by introducing another substance into the AN crystal structure. Salts containing ions larger or smaller than either ammonium or nitrate ions have been used. Because the U.S. military has decided not to use nickel or copper phase-stabilizing agents, the Air Force Research Laboratory has been looking for alternative materials for phase-stabilizing AN for use in solid propellants [316, 317]. Use of *N,N,N',N'*-tetramethyl-hexane-1,6-diamine appears to solve many AN problems such as phase changes, propellant grain growth during temperature cycling, moisture interference during curing, and caking in environments of 50% relative humidity. Interference of propellant cure using isocyanate curatives commonly occurs due to moisture content in the AN. Coating of AN particles with tetramethylhexane diamine was accomplished by bubbling nitrogen through the diamine and carrying the vapor through a bed of AN particles supported by a glass filter element. The AN particles had been carefully dried and screened, providing an initial free-flowing powder. Ammonia evolution was tracked by a Nicolet Impact 400 Fourier transform spectrometer. When ammonia evolution became undetectable, the coated AN was found to have increased in weight by

1.03%. The vapor pressure of the tetramethylhexamine was low, and the rate of mass transport was slow. Since the amount of tetramethyl hexane diamine needed to halt the ammonia replacement process was fairly large, the layer of tetramethylhexane diamine dinitrate salt was much thicker than a unimolecular layer. This indicated that some migration of material at the particle surfaces occurred during the diamine treatment of AN. DSC scanning of the tetramethylhexane diamine-coated AN provided a surprise: The typical 325 K (52°C) phase IV to phase II crystal transition was moved to about 344 K (71°C). Absence of the 325 K (52°C) phase change for the elevated-temperature-coated AN attested to completeness of AN particle coating. In another experiment, AN was coated at temperatures above 325 K (52°C). Elevated-temperature-coated AN particles did not exhibit caking activity over a 16-month period in a controlled 50% relative humidity environment. Free-flowing powder stored long term at 50% humidity demonstrated that the tetramethyl hexane diamine coating process totally eliminated AN phase III.

Some organic additives have a stabilizing effect on AN crystal phase changes that is indicated by decreasing the thermal effect of crystal transformation as measured by DSC [318]. These additives, including sawdust, cotton fiber, phosphonic acid, potassium chloride, and potassium bichromate, inhibited or shifted the phase change, but they also accelerated the thermal decomposition of AN at higher temperatures, lowered the exothermic temperature, and caused the energy release to occur more abruptly.

Ammonium nitrate that is intended to be used as an oxidizer in airbag inflator gas generants cannot be stabilized with KNO_3 because the gas generant would then no longer be smokeless. Also, sulfur-containing or halogen-containing stabilizers had to be eliminated for toxicity reasons. The search for stabilizers was therefore extended to organic compounds as stabilizers for AN [319, 320].

A polyvinylpyrrolidone (PVP)-AN glass provides both phase and thermal stabilization of AN [321]. PVP is capable of separating AN into its ions through an ion-dipole interaction. The ions remain separated below the glass transition temperature (T_g) of PVP (~433 K [~160°C]), which is confirmed by the disappearance of the solid-solid phase transitions associated with AN. Above the T_g , AN ions recombine, giving rise to a fast exothermic reaction suitable for rocket propellants. The material was then characterized by DSC, TGA, and FTIR.

The phase stabilization of AN with minor additions of organic substances with crystallographic parameters close to those of AN has been studied [322]. In order to restrain or prevent AN phase transitions, six types of polymers were added to AN, and the effects of polymers on AN phase transitions were studied using DSC [323]. The results showed that sodium *p*-ethylenebenzenesulfonate-acrylic acid polymer had little effect on AN phase transitions, whereas sodium *p*-ethylenebenzenesulfonate-dodecyl acrylate polymer prevented the transition of IV $\rightarrow$ III effectively. In addition, sodium *p*-ethylenebenzenesulfonate polymer, dodecyl acrylate, sodium *p*-ethylenebenzenesulfonate-*N,N*-dimethyldiallyl ammonium chloride polymer,

and sodium *p*-ethylenebenzenesulfonate-dodecyl acrylate-*N,N*-dimethyldiallyl ammonium chloride polymer effectively prevented the III $\rightarrow$ II transition. The mechanism of polymer phase stabilization of AN may be that polymers strengthen the hydrogen-bond network and impede the free rotation of NO_3^- .

The effect of the potassium salt of polyacrylic acid on phase stabilization of AN was tested using DSC and XRD [324]. The results showed that when the amount of the additive was more than 2.0%, it could prevent IV $\rightarrow$ III phase transitions of AN and raise the III $\rightarrow$ II phase-transition temperature to 110 °C. There are two effects when the potassium salt of polyacrylic acid is used as phase stabilizer: one is the replacement of ammonium ions in AN by potassium cations, and the other is a thin polymer coating on the surface.

DSC results showed that organic compounds and potassium salts of organic compounds can have an effect on the phase-transition behavior of AN [325]. The samples were further analyzed using IR and XRD spectra. The influence of additives on the phase transition of AN may occur through the polar groups that are involved in intermolecular interactions of orbital and electrostatic types that form new hydrogen bonds. AN existed in only one phase in the temperature range from 303 to 373 K (30 to 100 °C) when a potassium salt of organic compounds was added. However, with organic compounds, the III $\rightarrow$ II phase transition was changed. Compacted samples of AN containing potassium salts of organic compounds exhibited better stability than AN containing organic compounds to multiple cyclic changes within a temperature range.

The addition of amino acids to AN changes the temperatures of the solid-state phase transitions [326]. AN was combined with various amino acids in equimolar ratios; the phase transitions of the resulting mixtures were studied using DSC, *in situ* Raman spectroscopy, and XRD; and the predicted stabilities of various molecular structures were assessed via quantum calculations. DSC and Raman results indicated that *l*-glycine and *l*-alanine inhibited the solid-state phase transitions of AN. Both XRD and calculation results suggest that AN reacts with these amino acids to form nitrate salts and that clusters are also generated by interactions between these compounds.

2.4.2 Additives to Improve Thermal Stability of Ammonium Nitrate

Urea has been added to AN to prevent phase changes and to improve thermal stability. Urea/AN mixtures are also used as fertilizers.

The thermal decomposition temperature and surface morphology of AN/urea samples were investigated using DSC and SEM [327]. The results indicated that urea can substantially increase the thermal stability of AN (the largest exothermic peak was shifted by more than 100 °C) and reduce its thermal sensitivity.

The thermal stability and thermal decomposition behavior of AN and its mixtures with 1–20% of ammonium dihydrogen phosphate (ADP) were investigated using DSC-TGA, DSC-TGA-quadrupole mass spectroscopy, and TGA-FTIR [328]. Experimental re-

sults showed that the AN-ADP mixtures had higher onset of decomposition temperatures, narrower reaction temperature ranges, and lower enthalpy values than pure AN. Onset temperatures for AN-ADP mixtures with 1, 5, 10, 15 and 20 mass-% ADP were 539.4, 539.9, 541.0, 543.3, and 544.6 K (266.3, 266.8, 267.9, 270.2, and 271.5°C), respectively. The main evolved decomposition gases of pure AN were NH_3 , H_2O , NO , N_2O , NO_2 , and HNO_3 , while the major gaseous products of the AN mixture with ADP were NH_3 , H_2O , NO , N_2O , and NO_2 . A proposed decomposition mechanism of an AN-ADP mixture and the inhibition mechanism of ADP was discussed. It was concluded that ADP is an effective inhibitor for AN and that its thermal stability can be improved by this method.

2.4.3 Reactions of Ammonium Nitrate

One of the most important reactions of AN is its thermal decomposition, either that of AN by itself or AN in mixtures with combustible binders in various solid propellants and gas generants.

One of the first reactions in the thermal decomposition of AN may be a proton transfer, a reaction that reverses its formation from ammonia and nitric acid. This reaction can be studied either experimentally by analyzing intermediates of the decomposition reaction or it can be modeled using modern methods of computational chemistry.

Aqueous solutions of AN are acidic and quite corrosive. Similarly, moist AN in metallized composite propellant formulations may react with the metal during storage [329]. Metallized AN propellants must be kept perfectly dry to prevent such reactions.

2.4.3.1 Reactions of Ammonium Nitrate with Organic Compounds

Reactions of AN with organic compounds most often lead to ignition and total destruction of the organics by combustion. This reaction is the reason for the popularity of AN as an oxidizer in solid propellants, gas generants, and explosives. Ammonium nitrate was combined with nitrate esters as early as the 1870s when Nobel incorporated AN in dynamites. In World Wars I and II, both sides added AN to their conventional organic explosives when supplies ran low. Usually this involved mixtures of AN with TNT (“amatols”), but this decreased the explosive potential. At the beginning of the insensitive munitions/low-vulnerability ammunition effort in the 1990s, in an effort to formulate more insensitive explosives, the military began adding AN to traditional organic explosives. At the same time, the commercial producers of AN blasting agents began to add surplus military explosives to their formulations to improve performance.

The first step in most reactions of AN with organic compounds is dissociation of AN into ammonia and nitric acid. Kinetic regularities of the heat release during the interaction of some organic compounds with AN were measured using DSC [330]. Despite the fact that many AN-based explosive or propellant formulations contain

a combination of two or more energetic species, mechanistic thermal stability studies of such combinations were lacking.

Pyroxylin is a partially nitrated cellulose used in lacquers and coatings. Collodion is a solution of pyroxylin in ether or ethyl acetate. The kinetics of heat release during the thermal decomposition of a mixture of AN and pyroxylin were studied to elucidate the mechanism of this process [331]. The temperature dependence of the constants in the kinetic equations gave the activation energies. The influence exerted by addition of diphenylamine on the rate of heat release in AN/pyroxylin mixtures was analyzed.

The kinetics, mechanisms, and rates of thermolysis of mixtures of AN with polynitro compounds depend on the type of nitro compound involved. Examples tested included bis(2,2,2-trinitroethyl) succinate, tetrakis(2,2,2-trinitroethyl) orthocarbonate, and technical-grade trinitrotoluene [332]. Mixtures of AN and TNT are widely used as castable explosives (amatols).

When the thermal stability of mixtures of AN with a variety of organic explosives was examined over the temperature range 443–593 K (170–320 °C), it was found that nitrate esters pentaerythritol tetranitrate (PETN) and nitrocellulose, the nitramines RDX and HMX, and the nitroarenes TNT and trinitroaniline destabilized AN [333, 334]. Ammonium nitrate, or its decomposition products, destabilized the organic explosives to varying degrees. All the organic explosives examined destabilized AN. The extent of destabilization was roughly in line with their own thermal stability. For RDX and PETN, the destabilization was only slight. Surprisingly, over the temperature range examined (489–553 K [216–280 °C]), AN and TNT had similar thermal stabilities, although at the lower temperatures TNT appeared to decompose slightly more slowly than AN. Based on DSC thermograms of AN, TNT, and their 1:1 mixture, when AN and TNT were mixed in a one-to-one ratio, the stability of both was adversely affected. In fact, with the exception of TATB, the presence of any of the monomolecular explosives, TNT, trinitroaniline (TNA), RDX, and PETN, increased the rate of AN decomposition. When AN was mixed one-to-one with either TNA, RDX, or PETN, there was a single exothermic DSC maximum at a temperature lower than that of neat AN. The mixture of AN with TNT exhibited two exothermic maxima. The first, with an exothermic maximum at a lower temperature than that of neat AN, was assumed to represent the AN decomposition, while the higher temperature exotherm was assumed to result primarily from TNT decomposition. When mixed one-to-one with AN, all three nitroarenes, TNT, TNA, and TATB, showed significant destabilization. PETN, a nitrate ester, most dramatically destabilized AN; the rate constant of AN mixture with PETN at 489 K (216 °C) was over 300 times faster than that of neat AN. RDX, a nitramine, was second in its ability to destabilize AN; the 489 K (216 °C) rate constant of AN decomposition was 30 times faster in the AN/RDX mixture than in a neat AN melt. Trinitroaniline and trinitrotoluene accelerated the decomposition of AN by roughly a factor of three, while TATB had little effect. Over the temperature range examined (473–553 K [200–280 °C]), AN was found to be less thermally stable in admixture with nitroarenes. The decomposition of all nitroarenes

was catalyzed by nitric acid, and the decomposition of TNT was found to be catalyzed by ammonia.

PSAN was prepared by incorporating copper(II) diammino dinitrate in the AN crystal lattice. A study of the effect of RDX on the thermal decomposition of PSAN showed that decomposition temperatures of PSAN and RDX were almost in the same temperature range [335]. The synergetic effect of the interaction between PSAN and RDX resulted in a net exothermic reaction of PSAN. The kinetic and thermodynamic parameters of the exothermic decomposition of a 1:1 mixture of AN and RDX were then computed from the DSC data. For heating rates from 2 to 15°C/min, the peak temperatures ranged from 222 to 248 °C. The activation energy was ~158 kJ/mol, and the pre-exponential factor was 1.23×10^{14} to $1.42 \times 10^{14} \text{ s}^{-1}$.

Ammonium nitrate crystals have a high affinity for trimethylamine and other alkylamine vapors in the air and may absorb amine vapors during storage, becoming more sensitive in the process [336].

2.4.4 Theoretical and Computational Studies of Ammonium Nitrate Decomposition Reactions

Quantum chemistry studies of proton transfer in gas-phase AN decomposition predict that a stable molecular form is the hydrogen-bonded $\text{H}_3\text{N} \cdots \text{HONO}_2$ neutral pair [337]. The most energetically favorable gas-phase reaction of nitric acid and ammonia in the absence of a solvent results in proton exchange, not proton transfer from acid to base.

Proton transfer reactions in vapor-phase ammonia–nitric acid clusters containing up to four component units were modeled, and the energy levels were calculated [338]. In a single AN unit, proton transfer between the nitric acid and ammonia unit does not occur, but the two molecules are strongly hydrogen-bonded. In a dimer cluster of two adjacent AN formula units $[\text{NH}_3\text{HNO}_3]_2$, proton transfer does occur, and the components are stabilized by ionic interactions. Ammonium nitrate solvated with a single ammonia $[\text{NH}_3\text{HNO}_3] \cdot \text{NH}_3$ or nitric acid $[\text{NH}_3\text{HNO}_3] \cdot \text{HNO}_3$ was also studied. The structure of clusters differed from that of free molecules. Using population analysis, the total electrostatic interaction between the components of each cluster was calculated. The binding energy of the neutral pair form was 46 kJ/mol (11 kcal/mol) greater than the $[\text{NH}_4^+] \cdots [\text{NO}_3^-]$ ion pair. It was argued that the magnitude of the total electrostatic interactions within the cluster determines whether proton transfer and ion formation will take place. Binding energies alone do not give a reliable indication of the likelihood of the occurrence of proton transfer. See also [339].

The decomposition mechanism of AN in the gas phase was characterized by means of complete basis set method calculations [340]. Five reaction channels were identified, leading to the formation of products (N_2 , H_2O , O_2 , OH , HNO , NO_3^-) found by experimental chemical analysis. The mechanism well explained the chemical hazard of AN, which is related to the exothermicity of the lowest decomposition channels. Furthermore, the high barrier to overcome in the rate-determining step

well explained the fact that the reaction is not usually spontaneous and requires a significant external stimulus for its onset. An accurate density functional theory benchmark study was then conducted to determine the most suitable exchange-correlation functional to accurately describe the reaction profile both in terms of structures and thermochemistry.

2.4.5 Analytical Methods for Ammonium Nitrate

Quality control of AN is extremely important because there are many commercial grades of AN available on the market, but few are suitable for use in propellants.

For an assay of AN, ammonium can be determined by quantitative distillation of ammonia in a Kjeldahl apparatus. Nitrate can be determined by quantitative reduction with ferrous ammonium sulfate. An alternative volumetric procedure was also investigated for assay based on the reduction of nitrate by titanous ion. However, this reduction was shown to be non-stoichiometric [341]. See also [342].

2.4.5.1 Military Specifications for Ammonium Nitrate

It appears that the military relies on commercial sources if it needs ANFO for bulk blasting jobs, such as in simulations of nuclear blasts using non-nuclear explosives. The quality control of AN procured for the U.S. government is assured by a series of military specifications (Table 23). Surprisingly, this specification also limits the amount of allowable boric acid (0.14 ± 0.03 mass-%). It is not known where the boric acid comes from and why it is detrimental to the intended use of AN.

Table 23: Military specifications for ammonium nitrate.

Designation	Title	Date	Pages
JAN-A-175	Ammonium Nitrate	30 May 1945	12
MIL-A-50460A (MU)	Ammonium Nitrate, Prilled (For Use in Ammunition)	15 Sep 1973	24
MIL-A-175C	Ammonium Nitrate, Technical, Canceled, superseded by A-A-59476	11 Aug 1983	14
MIL-A-50460A(AR)Notice 1	Ammonium Nitrate, Prilled (For Use in Ammunition)	13 Jul 1989	1
A-A-59476	Ammonium Nitrate, Technical. Superseding MIL-A-175C (11 Aug 1983)	26 Apr 2000	3
A-A-59476, Notice 1	Ammonium Nitrate, Technical	15 May 2006	1

2.4.5.2 Moisture Content of Ammonium Nitrate

The maximum moisture content of AN intended for use in explosives allowed in military specifications is 0.15 mass-%. The recommended method for the analysis of moisture in AN is the American Society for Testing and Materials method E203-64, which

uses the Karl Fischer reagent containing pyridine, sulfur dioxide, methanol, and iodine.

A procedure for determining the water content of NiO PSAN using the Karl Fisher direct titration technique has been optimized [343]. The parameters investigated included possible side reactions, dissolution time, pH, and temperature. However, although accurate, straightforward, and simple, the method routinely used for AP was yielding non-reproducible results for PSAN, despite the fact that it is reportedly used for AN. A dependable procedure had to be developed to assess the moisture content of AN with the necessary degree of confidence. Recording the amount of water titrated against time revealed fading end points (i.e., extended time required to complete titration). Long titration times could have three causes: side reactions that produce water or consume iodine, a working pH outside the optimum range, or slow water release by PSAN while the titration is in progress. Other factors possibly affecting water determination results were the presence of nickel oxide, the mode of dissolution of the sample, the pH, and the temperature of the solution. See also [344].

2.4.5.3 Detection of Hidden Ammonium Nitrate

Detection of AN in improvised explosive devices (IEDs) is a major security issue for military and civil defense agencies. The vapor pressure of AN at room temperature is very low, and the vapors are difficult to detect with portable instrumentation.

A search for a system for the detection of AN in vehicles by remote nuclear quadrupole resonance (NQR) that depends on the penetration of radiofrequency (RF) magnetic fields inside certain metal enclosures, including full-scale vehicles, led to the design of a high-Q resonant probe [345]. The probe was shaped not only for optimal penetration of RF magnetic fields into vehicles but also for optimal rejection of RF interference and ease of shielding. A full-scale technical demonstrator was designed and built, and it successfully demonstrated the ability to generate and detect NQR signals from AN concealed within the trunk (boot) of a car and in the loading bay of a (metal-sided) van.

To detect and characterize the low-volatility components emanating from AN in IEDs, a sample of AN was sealed inside a stainless steel chamber while a laminar flow of air swept the headspace vapor components into a water impinger or cold trap for pre-concentration and subsequent analysis by ion chromatography [346]. Both collection methods were found to be 100% efficient for collecting nitric acid vapor, whereas the collection efficiency for ammonia was dependent upon the collection method and, for the water-impinging method, additionally upon the vapor concentration, humidity, and flow rate. Cold-trapping efficiency for ammonia was only 4% across all parameters studied. Water impinging was more efficient (20–70% recovery), but the efficiency varied according to each of the aforementioned variables. The characteristics of an AN vapor generated from a solid sample were found to vary as the sample approached equilibrium inside the chamber. Initially, large quantities of ammo-

nia were observed, but as a steady state was achieved within the laminar flow and a dynamic equilibrium established, the ratio of ammonia to nitric acid in the effluent vapor dropped, although never becoming equimolar. The ratio was strongly dependent upon humidity.

Known concentrations of AN were uniformly deposited onto commercially available surface-enhanced Raman scattering (SERS) substrates using a drop-on-demand inkjet printing system, and the phase changes observed after the deposition of AN under several solvent conditions were investigated [347]. Characteristics of the collected SERS spectra of AN demonstrated that knowledge of the exact nature of the AN samples deposited will result in improved ability to accurately and reliably “train” hazard-detection systems.

2.4.6 Thermal Stability and Decomposition of Ammonium Nitrate

The decomposition of AN does not follow a single reaction with a reproducible set of reaction products, but rather it follows a group of competitive reactions, the relative contribution of each depending on the rate of venting reaction products and operating under isothermal or adiabatic conditions. Table 24 is a list of possible decompositions with their energy output/input. The combustion reaction of AN with polyethylene is shown for comparison. The combustion reaction, of course, is much more energetic than the monopropellant decomposition.

Table 24: Decomposition reactions of ammonium nitrate.

Number	Reaction	ΔH , MJ/kg
1	$\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$	-0.73
2	$\text{NH}_4\text{NO}_3 \rightleftharpoons \text{NH}_3 + \text{HNO}_3$	+2.00
3	$2\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2 + 2\text{NO} + 4\text{H}_2\text{O}$	-0.35
4	$4\text{NH}_4\text{NO}_3 \rightarrow 3\text{N}_2 + 2\text{NO}_2 + 8\text{H}_2\text{O}$	-1.16
5	$5\text{NH}_4\text{NO}_3 \rightarrow 4\text{N}_2 + 2\text{HNO}_3 + 9\text{H}_2\text{O}$	-1.54
6	$2\text{NH}_4\text{NO}_3 \rightarrow 2\text{N}_2 + \text{O}_2 + 4\text{H}_2\text{O}$	-1.47
7	$\text{NH}_4\text{NO}_3 + \text{CH}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{CO}_2$	-3.80

Data source: [61]

The effect of sample mass on the kinetics of the non-isothermal mass-loss process of molten AN was investigated using TGA-DTG [348]. The apparent Arrhenius parameters were shown to decrease with increasing sample mass. Using the conventional method of kinetic calculation, it was shown that the sample-mass-dependent variation in the apparent pre-exponential factor resulted from the use of fractional reaction in the kinetic expression. The value of the apparent activation energy varied

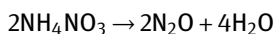
consequently to compensate the sample-mass-dependent change in the apparent pre-exponential factor on the regime of the mutual dependence of the Arrhenius parameters. This is known as the kinetic compensation effect. The more-specific Arrhenius parameters that are independent of sample mass were obtained by using the specific pre-exponential factor that is independent of sample mass, instead of the apparent pre-exponential factor.

A method to produce phase-modified AN (PMAN) by means of habit modification was investigated using potassium ferrocyanide [349]. The thermal stability and moisture absorption characteristics of PMAN were evaluated, and the energy of activation of decomposition reaction of AN, PMAN, and an admixture of AN-potassium ferrocyanide trihydrate were computed with non-linear integral isoconversional methods and used to measure their thermal stability. The moisture absorption characteristics were determined at 53 and 62% relative humidity, and the cyclic DSC analysis, a combination of non-isothermal and isothermal, was used to trace the phase behavior of the PMAN, indicating that PMAN and AN have comparable properties, suggesting similar processing and handling conditions.

The thermal and phase-change behaviors of PSAN films in a polymer matrix were characterized using neutron reflectometry and ellipsometry [350]. These techniques are highly sensitive to small changes in composition and density that occur during phase transitions. PSAN films were generally stable up to 433 K (160 °C), although small material loss may occur between 333 and 373 K (60 and 100 °C), which was attributed to solvent interactions with the PSAN. Crystallization of AN from super-saturated polymer is most common at thicker regions of the film, suggesting a critical nucleation thickness for the AN that can be avoided by making very thin films.

2.4.6.1 Slow Controlled Decomposition of Solid Ammonium Nitrate

The initial step of AN decomposition is melting. The next process is a reversible sublimation due to the measurable vapor pressure of AN, but without noticeable decomposition (Section 2.3.4). The species in the vapor phase are free ammonia and nitric acid. Chemical decomposition of AN leads to a mixture of nitrous oxide and water:



In addition to study of the slow thermal decomposition of AN using TGA, DTA, and DSC, a combination of these methods with simultaneous XRD offers insight into the phase changes and crystal transformations taking place in the AN crystals immediately prior to decomposition.

The rate of decomposition of AN was determined by the increased pressure when heated in a vacuum (10 mm Hg) at 443–473 K (170–200 °C) [351, 352]. Plots of mass loss/pressure increase vs. time indicated that AN decomposes autocatalytic at all temperatures. At 443 K (170 °C) the decrease in mass started after 3.5 h, whereas at 453, 463, and 473 K (180, 190, and 200 °C), it occurred after 2 h, 50 min, and 20 min, respectively.

As the temperature increased, the heterolytic decomposition increased and the share of homolytic decomposition decreased, resulting in a stoppage of the autocatalytic process. The autocatalytic process was probably due to HNO_3 , NO_2 , and H_2O formed during decomposition and remaining in the condensed phase. NO_2 was detected only in the gaseous products of decomposition at or above 458 K (185 °C).

The rate of decomposition of molten AN in a closed system at different mass/volume ratios ($[1-80] \times 10^{-3} \text{ g/cm}^3$) and at temperatures of 453–533 K (180–260 °C) was determined by measuring the changes in specific volume and vapor pressure with time [353]. At lower temperatures and greater mass/volume ratio, the reaction was self-accelerating, whereas at higher temperatures and smaller mass/volume ratios it was either first order or decelerating, with irregular behavior in between. The results were explained by postulating that dissolved reaction products, probably HNO_3 and H_2O , the solubility of which decrease with increasing temperature or decreasing mass/volume ratios, may accelerate the decomposition.

Most AN decomposition studies have used IR or MS to analyze the gaseous decomposition products, but some of the products are IR-inactive and cannot be detected by IR. A complete gas analysis is possible by repetitive and time-resolved gas chromatography [354]. The thermal decomposition of AN and associated mixtures in the range 443–473 K (170–200 °C) was studied by measuring the rate of evolution of nitrous oxide using a flow system in conjunction with gas chromatography, enabling measurements to be made at temperatures of practical importance not covered in previous investigations. The rate constant calculated from the data for pure AN was compared with the values obtained by other researchers. The effects of several metal ions, water, or monoammonium phosphate on the decomposition rate were studied by this method, but no clear pattern emerged from the results.

During DSC examination of the same AN samples, the salt undergoes the transformations $\text{IV} \rightarrow \text{III}$ and $\text{IV} \rightarrow \text{II}$ in parallel, then undergoes the crystal transformations $\text{III} \rightarrow \text{II} \rightarrow \text{I}$, and finally melts [355]. The investigation conditions and the transformation history of the samples do not influence the crystal transformations during thermal analysis very much.

Simultaneous thermal and gravimetric analysis (DSC-TGA) with heating rates from 2.5 to 20 K/min was used for the thermal characterization of PSAN containing 1.0% of NiO and 0.5% of Petro (an anti-caking agent) as additives [356]. The main features of the thermal behavior of PSAN, i.e., two phase transitions, melting, and decomposition, were quite reproducible. Non-isothermal kinetic analysis was then used to estimate the Arrhenius parameters of the decomposition process by applying both a single-curve method and two isoconversional methods to the TGA data. Under the conditions of this study, the activation energy was $81.4 \pm 3.5 \text{ kJ/mol}$ and the pre-exponential factor was $(5.63 \pm 0.01) \times 10^5 \text{ s}^{-1}$. These data accurately described the process over a wide range of the kinetic analysis.

Major accidents involving overheating of large quantities of packaged AN or ANFO have occurred. To study these events on a smaller scale, convenient laboratory quantities to investigate thermal decomposition properties are generally less than 1 kg. In order to provide information applicable to real-life situations, any laboratory study must use techniques that minimize heat losses from the samples to their environment. Two laboratory-scale calorimeters providing an adiabatic environment were used to study the slow decomposition of AN: an accelerating rate calorimeter and an adiabatic Dewar calorimeter [357]. Experiments were performed on pure and packaged AN and ANFO. The effects of sample mass, atmosphere, and formulation on the resulting onset temperatures were measured. The results from the two techniques were compared, and a method to extrapolate these results to large-scale inventories was proposed.

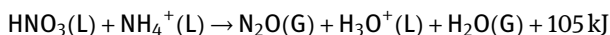
See also [296, 358, 359]. Figure 24 shows a baseline DSC thermogram of dry, pure AN. This thermogram was the baseline for a study on the effect of ADN on AN stabilization [277].

Pressure TGA-DTA was used to study the thermal decomposition of AN under open and non-isothermal conditions as functions of the sample size, heating rate, flow rate of purge gas, shape of sample pans, and pressure [360]. The thermal decomposition was simulated using a physicochemical model. The thermal decomposition of AN consisted of a chemical reaction and a thermal dissociation process. The model considered thermal dissociation as a first-order diffusion model and succeeded in reproducing the experimental results.

The thermal properties of AN were studied using pressure differential scanning calorimetry (PDSC), and evolved gases were analyzed by combining PDSC with FTIR and mass spectrometry [361]. PDSC results showed that AN undergoes an exothermic reaction above 0.3 MPa, and this exothermic reaction offsets the endothermic reaction of AN as the ambient pressure is increased. Evolved-gas analyses demonstrated that AN decomposition generates N_2O and H_2O during the exotherm and generates NO_2 throughout the endotherm. The heat flow associated with the thermal decomposition of AN was simulated, assuming that the decomposition rate of AN is given by

$$-dC_{AN}/dt = 10^{9.4} \exp(-126000/RT) C_{NH_4^+} \times C_{HNO_3},$$

that the heat of reaction is 105 kJ as per the reaction equation



and that $C_{NH_4^+}$ and C_{HNO_3} are constant due to chemical equilibrium. The heat-flow curves calculated in this manner were in good agreement with experimental DSC curves obtained at 1.1 MPa.

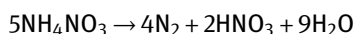
2.4.6.2 Effect of Moisture on Slow Controlled Decomposition of Solid Ammonium Nitrate

^{15}N - and ^{18}O -isotope substitution has been used to resolve questions about the origin of the N-atoms in the formation of N_2O by decomposition of AN [206]. As part of this investigation about the possible participation of H_2O in the decomposition reactions of AN, a sample of AN was very carefully dried to remove all traces of moisture by heating it to 423 K (150 °C) and evacuating it overnight in hard vacuum from a mercury diffusion pump. All AN had sublimed to the cool section of the tube above the furnace. The sample bulb was disconnected from the pump and connected to a pressure gauge. The furnace was raised to surround the AN, and the temperature was raised slowly to 573 K (300 °C). The result was very surprising: There was no decomposition detectable manometrically for more than an hour. The experiment was interrupted, and the sample was allowed to cool off. A small amount of water vapor was admitted to the system, and heating was resumed. This time the decomposition started at 453 K (180 °C). This experiment was reproducible using a fresh sample of AN.

In a parallel experiment, the admission of dry N_2O to the bone-dry AN had no effect, and it neither aided nor retarded the decomposition of AN. In order to answer the question of whether H_2O participates in the AN decomposition reaction, the bone-dry AN was moistened with H_2O containing 1.5% H_2^{18}O and decomposed above 453 K (180 °C). The $^{18}\text{O}/^{16}\text{O}$ ratio of the N_2O thus formed was the same as that with normal water (within 0.3% error limit), indicating that water does not participate in AN decomposition.

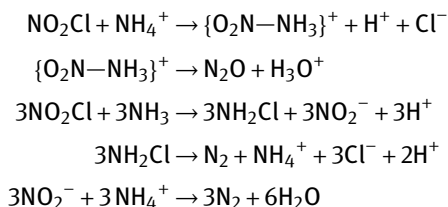
It was attempted to determine the influence of a great number of successive rhombic $\rightarrow$ monoclinic, monoclinic $\rightarrow$ trigonal, and trigonal $\rightarrow$ cubic crystal transformations on the AN crystal transformation energies [362]. The energies of prilled AN crystal transformations from rhombic into monoclinic, from monoclinic into trigonal and from trigonal into cubic were observed as functions of the number of previous crystal transformations (5, 10, 15, 20, 35, 50 rhombic $\rightarrow$ monoclinic transitions) and the moisture content (0.01–1.21 mass-% H_2O).

During the production of AN, the process water is evaporated, leaving supersaturated and superheated solutions behind. Under these conditions, just prior to allowing the hot product to crystallize, there may be incipient decomposition of AN that would contaminate the product and may be a process hazard. The decomposition of aqueous AN at elevated temperatures and pressures was examined as a function of chloride, nitrate, and total acidity [363]. Catalysis requiring both chloride and acid was observed in solutions containing 20 mass-% AN at 453 K (180 °C). Nitrous oxide and dinitrogen were generated in a 4:1 ratio below 0.2M $[\text{H}^+]$. Dinitrogen formation correlated with the production of additional acidity by the reaction



The second-order dependence of the decomposition reaction on $[\text{H}^+]$ is consistent with the reversible formation of NO_2^+ . Incorporation of ^{18}O into the N_2O product, as well as

the inverse deuterium isotope effect, supported this conclusion. A novel mechanism based on the intermediacy of NO_2Cl was proposed for the chloride catalysis and contrasted with the radical-based pathways operational in molten AN decompositions. Isotope-labeling experiments using $^{15}\text{NH}_4\text{NO}_3$ led to the formation of ^{15}NNO -labeled nitrous oxide and the dinitrogen products $^{15}\text{N}^{15}\text{N}$ and $^{14}\text{N}^{15}\text{N}$ in a 1 : 3 ratio. Decomposition of $\text{NH}_4^{15}\text{NO}_3$ produced only $^{14}\text{N}^{15}\text{NO}$ and $^{14}\text{N}^{15}\text{N}$. This agreed with the following reaction sequences:



These results bear on the industrial production of AN and suggest conditions under which industrial nitrous oxide emissions might have an impact on the global N_2O budget.

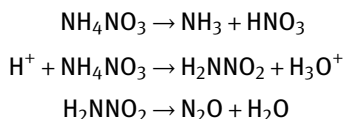
2.4.6.3 Effect of Ammonia on Slow Controlled Decomposition of Solid Ammonium Nitrate

Similar to the detailed studies on the effect of ammonia in retarding the decomposition of AP (Volume 1, *Encyclopedia of Oxidizers*, chapter “Perchlorate Oxidizers”), detailed experiments have shown that the decomposition of AN is likewise retarded in the presence of excess ammonia. A study of the effect of the partial pressure of gaseous ammonia on DTA and TGA thermograms of AN showed variations of the thermal effect and decomposition rate [364]. These data constitute a basis for analysis of the factors that determine the decomposition and equilibrium of exothermic and endothermic processes.

2.4.6.4 Effect of Acidity on Slow Controlled Decomposition of Solid Ammonium Nitrate

In order to study the effect of acid catalysis on the thermal decomposition of AN, weighed samples of AN were placed into carefully dried Pyrex tubes that were then evacuated and sealed [365, 366]. The sealed tubes were immersed for varying lengths of time in a thermostatted oil bath at 488 or 503 K. At the end of the test period, the tubes were quickly cooled to room temperature, frozen in LN_2 , and broken under water, and their contents were rinsed into a beaker for titration of free acid and ammonium ion before and after the addition of formaldehyde. Other AN samples were doped with a known amount of HNO_3 before the vials were sealed. The molar ratio of AN : HNO_3 was varied between 625 and 6900. The acid addition caused accelerated AN decomposition. On the other hand, tests with varying ullage volumes showed that

ammonia retards the AN decomposition. A mechanism involving the intermediate formation of nitramide was proposed for the AN decomposition:



The surface-to-volume ratio also affected the rate of AN decomposition. If additional surface was added in the form of glass wool, the rate of AN decomposition was reduced because the decomposition of HNO_3 was heterogeneously catalyzed by the added surface, and formation of NO_2 was observed.

The decomposition of molten AN was investigated manometrically at 473 K (200 °C) [367]. HNO_3 accumulated as the reaction proceeded, and its concentration increased with temperature and with the degree of filling of the reaction vessel. The decomposition rate increased in the presence of added HNO_3 , particularly when it was highly concentrated. Small amounts of H_2O also accelerated the initial decomposition, but large amounts of H_2O inhibited the rate of decomposition.

Because the first AN dissociation product to decompose is nitric acid, the effect of nitric oxide and nitrogen dioxide on AN decomposition had to be investigated by adding NO and/or NO_2 to the decomposition chamber [368]. The effect of the partial pressures of NO and/or NO_2 in the gas phase at 0–0.1 MPa on the profile of DTA and TGA curves for AN, on its rate of decomposition (from 388 to 548 K), and on nitric acid concentration in the condensed phase have been investigated. Both compounds were found to increase the isothermal decomposition rate and to lower the temperature of initiation. The results of these studies have led to the conclusion that as the factors causing an increase in the concentration of both compounds in ammonium nitrate increase, the possibility of autoignition or explosion also increases.

In the presence of traces of concentrated sulfuric acid, the self-accelerating decomposition temperature (SADT) of AN is lowered substantially [369]. This is important when assessing the stability of AN/ammonium sulfate mixtures often used as fertilizers. The explosion in Oppau, Germany, involved such a mixture.

The heat release during decomposition of pure AN and its mixtures with inorganic acids was analyzed in a heat flux calorimeter model C80 [370]. The results showed that mixtures of AN with acids are more unstable than pure AN. The AN decomposition reaction is catalyzed by acids. The calculated SADTs of AN mixtures with acid are much lower than those of pure AN. In continuation of this work, the influence of HCl on AN decomposition was studied using the same C80 calorimeter [371]. The data were analyzed to show the different decomposition reactions of AN and its mixtures with HCl. The SADTs of AN and its mixtures with HCl in 25-kg standard packages based on the thermal explosion theory were calculated and compared. The results showed that AN decomposition can be catalyzed by HCl and that the activation energy of AN with HCl is smaller than that of pure AN. See also [372].

2.4.6.5 Effect of Additives on Thermal Decomposition of Ammonium Nitrate

The kinetics of the thermal decomposition reaction of analytically pure AN, commercially pure AN, and mixtures of analytically pure AN and NaNO_3 have been investigated by means of non-isothermal DSC and TGA at various heating rates of 2, 4, 6, and 8 K/min [373]. The results showed that the decomposition reaction rate in the conversion degree range of $0.0 < \alpha < 0.4$ for AN is controlled by nucleation and growth, and the mechanism function is an Avrami-Erofeev equation with $n = 2/3$. The decomposition process of the mixture in the conversion degree range of $0.0 < \alpha < 0.4$ is classified as a one-dimensional phase-boundary reaction and the mechanism function is the contracting sphere (volume) equation with $n = 1/3$. The kinetic equations of analytically pure AN and the mixture are

$$\frac{d\alpha}{dT} = 109.43(1 - \alpha)[- \ln(1 - \alpha)]^{\frac{1}{3}} \exp\left(-1.319 \times \frac{10^4}{T}\right)$$

and

$$\frac{d\alpha}{df} = 109.4(1 - \alpha)^{\frac{2}{3}} \exp\left(-1.566 \times \frac{10^4}{T}\right)$$

respectively, indicating that NaNO_3 addition can improve the thermal stability of AN.

A DSC study of the effect of RDX or HMX on the thermal decomposition of PSAN showed that the decomposition temperatures of PSAN and RDX are almost in the same temperature range [374, 375]. The decomposition of PSAN was endothermic and that of RDX was exothermic, while that of a 1:1 mixture of the two was exothermic with a net heat release in excess of that of the individual reactions, which was attributed to a combustion reaction among the decomposition products of PSAN and RDX. Though HMX decomposed at a higher temperature, in presence of molten PSAN a substantial portion of it decomposed at a lower temperature along with PSAN with a net excess heat release, again due to a combustion reaction.

Mixtures of AN and guanidinium nitrate have improved thermal stability [376]. The kinetics of heat release in thermal decomposition of guanidinium and ammonium nitrates and their mixtures in the liquid phase in a calorimeter were investigated. The temperatures and ΔH values of melting of the initial salts and their eutectic mixture were determined.

Runaway reactions present a serious threat to the chemical process industry and surrounding communities. Such reactions occur time and time again, often with devastating consequences. The root causes associated with AN explosions during storage and the effects of different types of fertilizer additives on AN thermal decomposition need to be studied. A reactive systems screening tool (RSST) has been used for reactivity evaluation and to better understand the mechanisms that result in explosion hazards [377]. The results are reported as onset of exotherm temperature, rate of temperature and pressure rise, and maximum temperature. The runaway behavior of AN

has been studied as a solid and as a solution in water. The effects of additives such as sodium sulfate (Na_2SO_4) and potassium chloride (KCl) have also been studied. The results showed that the presence of Na_2SO_4 can increase the onset temperature of AN decomposition, thus acting as an AN thermal decomposition inhibitor, while KCl tends to decrease the onset temperature, thus acting as an AN thermal decomposition sensitizer.

Potassium chloride is not a likely contaminant of AN, and contact of AN with KCl would be possible in potassium (sylvite) mines where ANFO is used as a blasting agent. KCl might also be part of fertilizer mixtures. The thermal decomposition of AN and KCl mixtures was investigated using DSC, and the evolved gas was analyzed using TGA with MS and pressurized DSC coupled with MS (TG-DTA-MS and PDSC-MS) [378]. DSC measurements of AN/KCl mixtures in sealed and sealed-separated sample pans showed a sharp exothermic decomposition and lower onset temperature than pure AN, whereas AN/KCl in an open pan exhibited an endothermic reaction. In the sealed-separated pan, a separator with a pinhole divided the KCl and AN physically, and only the evolved gas could interact with both AN and KCl. TG-DTA-MS results showed that HCl gas was evolved from AN/KCl, which indicated that the reaction of KCl with HNO_3 dissociated from AN formed HCl, with subsequent destabilization of AN. However, the TG-DTA-MS results did not indicate the violent exothermic reaction due to using an open pan and ordinary pressure conditions. PDSC-MS was used to observe a sequence of two exothermic reactions of AN/KCl and to analyze the evolved gases from the reactions. A violent first exothermic reaction was accompanied by a large amount of N_2 and N_2O evolution without H_2O , and a second exothermic reaction was accompanied by evolution of H_2O , N_2O , and other gases. It was concluded that AN reacts with KCl to produce Cl radicals via HCl and NO_2Cl , and the Cl radical triggers a radical chain reaction of AN.

Spray-dried AN particles were prepared from AN, potassium nitrate as a phase stabilizer, and a polymer (e.g., polyvinyl alcohol, carboxymethylcellulose salt, and styrene-butadiene latex) for moisture proofing [267]. The crystal transformation behavior of AN/ KNO_3 /polymer particles was investigated using DSC and TGA. The results confirmed that AN can be phase-stabilized by the addition of KNO_3 . Carboxymethylcellulose ammonium salt and polyvinyl alcohol, which were both added as polymer components for moisture proofing, also acted as phase stabilizers to retard AN crystal transformations. The thermal stability of the AN/ KNO_3 /polymer crystals was enhanced by the thermal properties of the polymer components [268].

Ammonium nitrate has been modified with non-explosive additives to prevent its use in illegitimate, clandestine bomb making. The thermal stability of normal AN and anti-explosive additive-treated AN (AEAN) was examined using ARC, and apparent activation energy and pre-exponential factor were calculated [379, 380].

2.4.6.6 Effects of Particle Size and Porosity on Decomposition of Ammonium Nitrate

For many propellant formulations, similar to what is being done for AP, it would be desirable to use finely ground AN to increase the burning rate. The decomposition of AN may depend on the particle size.

According to DSC measurements, AN samples with particle sizes between 0.062 and 2 mm have different structural phase transition paths in the temperature range 298–373 K (25–100 °C) [381]. Samples with particle sizes of about 2 mm underwent the transition path IV → III → II, whereas those with particle size near 0.06 mm were more likely to undergo the transition path IV → II.

Ammonium sulfate and AN aerosols can be found in polluted atmospheres and contribute to energy balance and contaminant transport. For this reason, the effect of particle size on AN decomposition and phase changes has been examined by atmospheric chemistry investigators.

The bulk density of porous (“expanded”) AN is typically 0.35–0.6 g/cm³. The thermal stability of expanded AN was examined using TGA and DSC and was found to be the same as that of solid, non-porous AN [382].

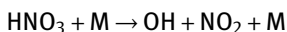
2.4.6.7 Effects of Pressure on Slow Controlled Decomposition of Solid Ammonium Nitrate

If AN is decomposed at high pressure (either externally applied gas pressure or self-decomposition in a closed volume under the pressure of its decomposition products), the rate of decomposition and composition of its decomposition products can be quite different.

In order to study the decomposition of AN under pressure developed by its own decomposition products, samples of absolutely dry AN were sealed in glass capillary tubes and immersed in a molten metal bath for varying lengths of time. The capillaries were quenched, and the gas evolved was captured and analyzed [383, 384].

The kinetics of AN thermal decomposition were studied with DTA in the pressure range from atmospheric pressure to 1.0 GPa [385]. The decomposition under pressure was shown to obey a zero-order equation, with a constant proportional to the initial free HNO₃ concentration in the sample. The structural transitions in AN were found to affect its exothermic interaction with boron. The volume increase on melting of AN is 0.072 cm³/g.

If AN is heated at low pressures, it may sublime and dissociate before it decomposes. The thermal decomposition of AN in the gas phase has been studied at 423–456 K by pyrolysis/MS under low-pressure conditions using a reactor coated with boric acid [386, 387]. The sublimation of AN at 423 K was proposed to produce equal amounts of NH₃ and HNO₃, followed by the decomposition of HNO₃ according to



(where M = third-body and reactor surface). The absolute yields of N₂, N₂O, H₂O, and NH₃, which can be unambiguously measured and quantitatively calibrated under con-

stant pressure, were kinetically modeled using a detailed [H,N,O]-mechanism established earlier for the simulation of $\text{NH}_3 + \text{NO}_2$ reactions and ADN decomposition reactions. Since the homogeneous decomposition reaction of HNO_3 itself was found to be too slow to account for the consumption of reactants and the formation of products, the investigators also introduced the heterogeneous decomposition of HNO_3 in their kinetic modeling. The heterogeneous decomposition rate of HNO_3 was determined by varying its rate to match the modeled result to the measured concentrations of NH_3 and H_2O . The rate could be represented by

$$k_{2b} = 7.91 \times 10^7 \exp(-12600/T) \text{ s}^{-1},$$

which appeared to be consistent with those reported by others for HNO_3 decomposition in glass reactors at higher temperatures.

2.4.6.8 Effect of Contaminants on Decomposition of Ammonium Nitrate

A comparison of two grades of commercial AN showed that a product made in the United States contained ~1% of a hydrocarbon and 5% kaolin to confer free-running properties of the granules, but a product obtained from the United Kingdom was nearly pure AN and was considered safer under normal conditions of storage and transport [388].

The location of the maximum of the exotherm peak of AN decomposition in a DTA ($543 \text{ K} = 270^\circ\text{C}$) was not affected by addition of 5 mol-% NaF, NaI, NaBr, or $(\text{NH}_4)_2\text{SO}_4$, but the ΔT peak height increased somewhat [389]. The exotherm maxed out at a much lower temperature ($455 \text{ K} [182^\circ\text{C}]$) if 5 mol-% $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ was added to the AN. NaCl and NH_4Cl had in-between effects, but chlorides are the most likely contaminants in AN.

The decomposition of AN containing 1% NH_4Cl was examined by heating the samples at $473 \text{ K} (200^\circ\text{C})$, removing small samples periodically and dissolving them in water, and plotting the pH of 10% solutions vs. time [390]. The decomposition of AN is a complex autocatalytic reaction, consisting of (1) hydrolysis of nitrate, (2) thermal decomposition of resulting HNO_3 , and (3) reaction of chloride with NO_2 , giving NO_3^- , NO, and free chlorine. Free chlorine is an activator, as it oxidizes NH_3 , and some reactions can be explained by free radical formation of some of the intermediates.

Chloride and various transition metal ions, notably chromium and copper, exhibit an unexpectedly large synergistic effect in the catalysis of the thermal decomposition of AN [391]. In the case of copper(II) and chloride, a proposed mechanism involves the operation of redox cycles in which reactions occur by electron transfer in chloro-bridged activated states. NH_4^+ and NH_3 are oxidized to NH_3^+ and NH_2 , and NH_2Cl is produced by reaction of NH_2 . The original copper(II) catalysts are then regenerated through oxidation by NO_2^+ and NO^+ . The proposed mechanism for chromium catalysis depends on the participation of dichromate in a fused-salt acid-base reaction with nitrate in which nitronium and chromate ions are formed. Any metal capable of forming chloro complexes of reasonable stability in two oxidation states differing by one

electron unit makes a good catalyst. Chromium is a special case in which oxo complexes are believed to be involved. An attempt was made to correlate synergistic catalytic activity with chloride ion with various other properties of the metal ions, such as stability constants of complexes, ionization and oxidation potentials, and ionic and atomic radii. All chromium species added to the decomposing acidic AN melts immediately assumed the characteristic orange color of dichromate. This color persisted throughout the course of the reaction.

The activation energy and frequency factor of the thermal decomposition of AN/ammonium chloride mixtures were determined volumetrically by catching the gases formed during decomposition and ramping up the temperature with a linear temperature profile heating rate [392, 393]. Small amounts of chloride ions lowered the thermal stability of AN markedly.

The rate of disappearance of ammonium ion in chloride-catalyzed nitric acid mixtures at 373 K (100 °C) can be expressed by the rate equation

$$d[\text{NH}_4^+]/dt = -k[\text{H}^+]^n[\text{NO}_3^-]^o[\text{Cl}^-]^p[\text{NH}_4^+],$$

where $k = (2.430 \pm 0.186) \times 10^{-7} \text{ s}^{-1}$, $n = 2.426 \pm 0.034$, $o = 3.096 \pm 0.039$, and $p = 1.295 \pm 0.035$ [394]. Fluoride and bromide had no catalytic activity.

A study of the effect of adding 0.5–1 mass-% of ammonium molybdate $(\text{NH}_4)_2\text{MoO}_4$, boric acid H_3BO_3 , zinc sulfate ZnSO_4 , magnesium sulfate MgSO_4 , iron(II) sulfate FeSO_4 , copper(II) sulfate CuSO_4 , cobalt(II) sulfate CoSO_4 , or manganese(II) sulfate MnSO_4 on the thermal stability of AN at 493 and 513 K (200 and 220 °C) showed that FeSO_4 and CuSO_4 catalyzed AN decomposition and MgSO_4 retarded it [395].

An examination of the mechanism of AN thermal decomposition in the temperature regime of 573–673 K (300–400 °C) showed that the first step in fused NH_4NO_3 decomposition is dissociation into NH_3 and HNO_3 [396]. At temperatures below 573 K (300 °C), its further decomposition was said to be governed by the rate at which nitronium ion is formed from nitric acid. As a result, the decomposition rate is sensitive to exogenous water, ammonia, and nitric acid. Above 513 K (340 °C), the sensitivity of the decomposition to these additives was substantially less. It was proposed that a free-radical decomposition mechanism is dominant in this temperature regime and that the rate-controlling step is homolysis of nitric acid to form nitronium and hydroxyl radical, the rate being the same for the liquid and vapor-phase reaction.

Much of the work on the effect of contaminants on the thermal stability of AN and AN formulations was done for the use of AN in ANFO blasting agents, but the rocket propellant and gas generant applications will benefit from the results of this work, and this is why we reference it here. The effects of various anions on the thermal stability of AN/fuel oil and an AN emulsion were examined using DSC and conventional methods [397, 398]. It was found that salts of weak acids, due to their basicity, stabilized these formulations. The added stability was enough to counteract the influence of ferric or ferrous salts, frequent contaminants that normally enhance decomposi-

tion. Ammonium cation, the salt of a weak base, slightly destabilized the AN compositions. Sodium and calcium nitrates, where both anions and cations were salts of strong acids and strong bases, respectively, did not appear to affect thermal stability.

On 21 September 2001, about 300–400 tons of AN exploded at the Grande Paroisse (AZF) fertilizer plant in Toulouse, France. The explosion killed 31 people and injured over 200. An internal investigation by Grande Paroisse's parent company, Atofina, has focused on three possible causes:

- (1) scattering of metal fragments on the fertilizer storage facility by a plant explosion
- (2) anomalies in the paperwork
- (3) contamination of AN by other chemicals produced at the site

One of the other chemicals produced at the site was the sodium salt of dichloroisocyanurate (sodium 3,5-dichloro-2,4,6-trioxo-1,3,5-triazinan-1-ide, sodium troclosene, DCCNa), a chemical that is often used as a disinfectant for swimming pools and as a biocide, industrial deodorant, and detergent. In an effort to find a cause of the accident, DCCNa was added to AN at concentrations of 0.01, 0.03, 0.1, 0.5, and 1 mass-% [399]. A heat flux calorimeter and an accelerating rate calorimeter were used to analyze the thermal decomposition of AN and its contaminated mixtures. The results showed that the initial decomposition temperature of the mixture decreased markedly compared to that of pure AN. It was suspected that DCCNa catalyzes the decomposition of AN through key steps, including the synergism between HNO_3 and Cl_2 . However, the results of the BAM 50/60 steel tube detonability test did not show a distinct effect of added DCCNa on the detonation behavior of AN.

In a similar study, the thermal hazards of mixtures of AN and the sodium salt of dichloroisocyanuric acid were investigated using DSC, ARC, TGA, simultaneous TG-DTA-FTIR-MS, heat flow calorimetry (HFC), and isothermal nanocalorimetry [400]. The sensitivity of the mixtures to impact, friction, and electrostatic discharge (ESD) was also determined using standard sensitivity test methods. ARC experiments on a 2-g sample of AN/DCCNa mixtures in humid air revealed an onset temperature for exothermic thermal decomposition as low as 310 K (37 °C). Isothermal nanocalorimetry experiments revealed three overlapping exothermic peaks that resulted in a total energy release of 0.4 kJ/g over the course of 13 d at 298 K (25 °C). Simultaneous TG-DTA with FTIR and MS detectors identified the reaction products as CO_2 , HCl , N_2 , N_2O , NO_2 , and Cl_2 . The results from this study suggested that accidental mixing of bulk quantities of these materials would pose a considerable hazard and should be avoided.

Prilled commercial fertilizer-grade AN is often coated with limestone or dolomite powder as an anti-caking agent. Thermal decomposition of AN and its coated prills was studied using combined TGA-DTA-FTIR under dynamic heating conditions up to 1173 K (900 °C) at a heating rate of 10 °C/min [401]. The amount of additives used was 5, 10, or 20 mass-% or was based on the mol ratio of $\text{AN}/(\text{CaO}, \text{MgO}) = 2:1$ in the blends. The results of analyses of the gaseous compounds evolved during thermal treatment of neat AN indicated some differences in the decomposition of AN in air and in N_2 .

During the thermal treatment of AN blends with CaCO_3 , MgCO_3 , natural limestone, and dolomite samples, the decomposition of AN proceeded through a completely different mechanism depending on the origin and the content of additives, partially or completely, through the formation of $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$.

Additional runs at 2, 5, and 20 °C/min in a stream of dry air were made for calculation of kinetic parameters [54]. The results of TGA-DTA-FTIR and the variation of the value of activation energy along the conversion parameter α indicated the complex character of the decomposition of neat AN as well as of the interactions occurring during thermal decomposition of AN prills coated with limestone or dolomite powder.

Moist AN is acidic, and AN stored in steel containers is likely to contain corrosion products in the form of iron(III) nitrate $\text{Fe}(\text{NO}_3)_3$. The influence of iron(III) nitrate on the thermal stability of AN was measured with ARC and constant temperature calorimetry [402, 403]. It was shown that iron(III) nitrate catalyzes AN decomposition; it will decrease the onset of decomposition exotherm temperature of AN by 60 °C. The catalytic effects of iron(III) nitrate on AN decomposition as measured by ARC or constant temperature thermal decomposition are the same. Based on ARC data, the activation energy and pre-exponential factor were $f(\alpha) = 1 - \alpha$, $E_a = 195.41 \text{ kJ/mol}$ and $A = 2.08 \times 10^{19} \text{ s}^{-1}$. The experiments showed that once the iron ions fuse into the AN, thermal stability will decrease remarkably. The kinetics of AN decomposition can be used to calculate the critical temperatures for AN decomposition with and without the presence of iron(III) nitrate, based on the Frank-Kamenetskii model of thermal runaway explosions.

As part of an ongoing investigation into a cause of the AN explosion in Toulouse, France, in September 2001 and in continuation of earlier compatibility studies of AN with the sodium salt of dichloroisocyanuric acid, a detailed theoretical study was performed to better understand the involved mechanisms, considering the reaction between AN and the sodium salt of dichloroisocyanuric acid (SDIC) [404, 405]. The gas-phase decomposition mechanism of the mixture was investigated and fully characterized by means of density functional theory calculations. Beyond the complete characterization, in terms of intermediate structures and energies of the decomposition pathways, the results pointed toward the role of water in catalyzing the decomposition reaction, through a significant decrease of the activation energy of the rate-determining step. These results, in qualitative agreement with calorimetric experiments, confirmed the instability of the AN + SDIC wet mixture and the incompatibility mechanism between these two chemicals.

In another study of the Toulouse explosion, several chloride salts, including ammonium chloride, barium chloride, calcium chloride, sodium chloride, and potassium chloride, were added to AN at concentrations of 0.05, 0.1, 0.5, 1, and 2%, respectively, and DSC and a heat flux calorimeter with high sensitivity were used to measure the decomposition of AN and its mixtures with these impurities [406]. All of the results demonstrated that the addition of a small amount of chloride caused a significant decrease in the initial decomposition onset temperature of AN by nearly 100 °C and an

increase of heat release from the reaction. The intensity of the decomposition of AN with and without added impurities was also examined by a modified pressure vessel test (MCPVT) in which the rate of pressure rise of AN in the presence of chlorides in the MCPVT was a multiple of that of pure AN. However, in the BAM 50/60 steel tube test, no detonation was observed for either pure AN or contaminated AN under the test conditions.

The effects of inhibitors, confinement, and heating rate on AN thermal decomposition were studied in the presence of different types of additives, including sodium bicarbonate, potassium carbonate, and ammonium sulfate at two concentrations, 2.8 and 12.5 mass-%, using an RSST [407]. The results showed that the three salts are good inhibitors for AN. The effect of confinement was tested by observing AN decomposition under five different initial pressures, varying from ambient pressure to 1.29 MPa gauge (187 psig). It was concluded that confinement aggravates explosive decomposition. The effect of heating rate was studied by heating AN under two heating rates of 0.25 and 2°C/min. The slower the heating rate, the lower the onset of exotherm temperature detected.

Properly selected calcium and magnesium carbonates (fertilizer additives) may increase the thermal stability of AN [408]. The influence of the carbonate mineral type and composition on phase transitions and the decomposition process of fertilizer-grade AN was measured using DTA and TGA coupled with MS. The results showed that too high a level of carbonate reactivity can cause problems during the production of fertilizer, reducing the effectiveness of the filler in a final product.

The kinetic parameters of AN/KCl thermal decomposition over a range of KCl mass fractions were experimentally measured using an advanced reactive chemical screening tool [409]. Based on experimental findings and past literature review, an AN/KCl decomposition mechanism was proposed, proceeding along four separate pathways: **(1)** a direct AN main decomposition pathway, **(2)** an indirect AN main decomposition pathway via chlorine radical, **(3)** a direct pure AN side decomposition pathway, and **(4)** an indirect AN side decomposition pathway via chlorine radical. KCl addition not only accelerated the AN decomposition but also increased the reaction heat release. See also [410–412].

2.4.6.9 Effect of Catalysts on Slow Controlled Decomposition of Ammonium Nitrate

There is hardly any decomposition in solid AN below the melting point. Most investigations of the effect of additives and stabilizers on the rate of AN decomposition have therefore worked with molten AN.

An excellent summary of the effect of catalysts on the decomposition of AN is a dissertation by Franco from 1968 [413]. Considering the early date of this work, it has an amazing amount of detail and a good discussion of the state of knowledge of AN decomposition kinetics at that time.

Ions of many transition metals, most of all chromium salts, catalyze the decomposition of AN in small quantities and at moderate temperatures below its melting point.

The catalytic activity and the overall rate of decomposition accelerates once the AN has melted. Metals investigated include Mn, Co, and Cu cations [414]. Chromium ions are a very good catalyst, particularly if they are soluble in molten AN [415, 416]. The effect of chromium compounds on the kinetics of decomposition of liquid AN has been studied in the temperature range 460–520 K [417]. Chromium compounds soluble in liquid AN were found to be very effective catalysts. For low concentrations of catalyst, the principal products of decomposition were N_2 , N_2O , H_2O , and HNO_3 . The catalyzed decomposition, like the uncatalyzed decomposition, is inhibited by NH_3 and H_2O and promoted by HNO_3 . Low concentrations of chromium catalyst can produce easily detected changes in the course and rate of decomposition, and higher concentrations can result in an explosive rate of reaction. The metals studied for lowering the thermal stability of AN are the same ones that are also good candidates for burning-rate enhancing additives for AN in solid propellants.

Metal Oxide Catalysts for AN Decomposition

Metal oxides of copper, nickel, and cobalt react with molten AN to form ammino complexes that catalyze the decomposition of AN synergistically [418]. At the same time, and at lower temperatures, some metal ammino complexes stabilize AN by shifting the temperatures at which troublesome phase transitions occur.

The solid-state reaction of AN and copper oxide was studied by the use of energy-dispersive and angle-dispersive XRD [419]. It was shown that the reaction takes place within the temperature interval 383–423 K (110–150 °C) and consists of two steps. The product of these consecutive reactions is the diammino copper complex. The relative concentrations of the species involved were determined by summing up different X-ray spectra. The resulting curves were analyzed by a computer program to obtain the kinetic constants of these reactions.

Copper(II) and zinc chromates intended as catalysts for AN decomposition can be prepared by co-precipitation and calcination. Copper(II) and zinc chromates were prepared by this method, and their catalytic activities for AN thermal decomposition were determined at 487 K (214 °C) [420]. The experimental kinetic data were interpreted in terms of a quantum cluster model calculation of the interaction of the spinel crystal structure with NH_4NO_3 and NH_3 . The activity of the spinel structure depends on the ratio of cation donor–acceptor properties and the capacity of the cations to participate in the electron density redistribution associated with the interaction with NH_4NO_3 or NH_3 .

The introduction of aluminum cations into $Cu_{1-x}Zn_xCr_{2-y}Al_yO_4$ catalysts drastically lowered their catalytic activity for AN decomposition [421]. The negative influence of aluminum cations on the catalytic properties of these catalysts was explained by quantum chemical computational analysis of the interaction between spinel clusters and AN. An increase of the presence of aluminum cations hinders the decomposition of AN because it increases the strength of proton bonding to the NH_4 group and

inhibits the first stage of decomposition of ammonium salts, which depends on proton transfer to the acid rest.

The effects of metal oxides, organic metal salts, energetic binders, and HNIW (CL-20) on the thermal decomposition of AN were studied using DSC and TGA-DTG [422]. Results showed that catalysts lower the endothermic decomposition temperature of AN to a certain extent, and energetic additives accelerate the exothermic decomposition process of AN.

Nanocomposites (nano-CuO and CuFe_2O_4) were characterized by powder XRD, transmission electron microscope, and XPS, and the catalytic performance of nano-CuO and CuFe_2O_4 on the thermal decomposition of AN was investigated using TGA/DSC and TGA/MS [423]. The results of TGA/DSC experiments indicated that nanocomposites catalyzed thermal decomposition of AN, especially copper oxide/graphene oxide. Copper iron oxide did not have a synergistic effect. The activation energy of AN mixture was calculated, and the initial onset temperature, peak temperature, and activation energy were significantly decreased. Nitrous oxide formed at a very low temperature, as observed by mass spectra. Two stages of thermal decomposition of AN catalyzed by copper oxide/graphene oxide were first observed with TGA/MS.

Metalorganic Catalysts for AN Decomposition

Ferrocene and similar metalorganic complexes are widely used as burning-rate catalysts for composite propellant and are effective catalysts for the decomposition of AN and AP, even in the absence of an organic binder. Similar catalytic effects are observed with metal complexes of 1,4,8,11-tetraaza[14]annulenes. The effect of various metal complex catalysts of tetraaza-(14)-anurene = tetraaza[14]annulene on the thermal decomposition of AN, AP, and a solid propellant containing AP as an oxidizer was studied using thermal analysis and burning-rate measurements. [424]. A metal complex that had iron or vanadium as the central metallic ion showed high activity during the thermal decomposition of AN. This activity was accelerated when chloride and perchlorate ions were present with iron or vanadium ions. Iron and vanadium catalysts also had high activity during the thermal decomposition of AP.

Supported PGM Catalysts for AN Decomposition

Methods for removing nitrates from natural and drinking waters include the catalytic decomposition of AN solutions on supported platinum group metal catalysts. This method may also be used for cleaning rinse waters from AN processing equipment before releasing the waste stream to surface waters or sewers. Supported platinum group metal catalysts for wet decomposition of AN were investigated in order to develop the catalysts, which can convert both ammonium ion and nitrate ion selectively to N_2 and H_2O under mild conditions, and to investigate the possible reaction pathways for simultaneous decomposition of ammonium and nitrate [425]. Pt/active car-

bon catalysts turned out to be the most active among the several catalysts examined; 2 mass-% Pt/active carbon decomposed AN effectively under 0.5 MPa of air at 453 K, showing a conversion of 99% or higher and N_2 selectivity of 95% or higher. N_2O was the main by-product with a selectivity of 5% or lower. Hardly any NO_2^- , NO, or NO_2 was observed. A series of experiments using isotope-labeled AN revealed that simultaneous removal of ammonium ion and nitrate ion did not take place via independent reactions of the two ions but rather via the equimolecular reaction between the two, and wet air oxidation of ammonium ion competed with the reaction of ammonium ion with nitrate ion. N_2O was the major intermediate of the reaction for all the reactions studied.

2.4.6.10 Inhibitors for the Decomposition of Ammonium Nitrate

Premature decomposition of AN during its manufacturing detracts from the nitrogen content, the fertilizer value, and the purity of the resulting product. It would be desirable to identify compounds (“anti-catalysts”) that would retard the thermal decomposition of AN under its manufacturing conditions. The rate of decomposition of AN at 498 K (225 °C) was investigated by determining the weight loss, the composition of the residue, and the change in pH for pure AN and simple mixtures containing AN and an additive [426]. The decomposition rate of pure AN climbed during the first 2 h until it reached 5.5% weight loss per hour of the original sample weight. The rate then dropped to about 2.5%/h. The pH of the salt decreased from 5.2 to 3.5 during the first 2 h of heating and then remained constant. The increase in acidity resulted in a corresponding increase in the rate of decomposition. Several amphoteric and basic oxides were added in an attempt to control pH. Alkali metal and ammonium bromides and iodides proved to be effective inhibitors when added in concentrations as low as 0.5%.

2.4.6.11 Slow Controlled Decomposition of Molten Ammonium Nitrate

Molten AN is self-decomposing, but the reaction may easily run away and result in an explosion. The differences in the reactions taking place in the vapor phase and in the condensed phase are difficult to explain under practical conditions. It is obvious that the mechanism depends on temperature and pressure. Most investigations were conducted only for a narrow pressure range; a few reports exist on the effect of pressure on the phase changes and decomposition processes.

Raman spectra of AN above its melting point of 443 K and decomposition temperature of 533 exhibited a strong peak at 1043 cm^{-1} , assigned to the ν_1 vibrational stretching mode of the NO_3^- group, and a 710 cm^{-1} peak attributed to the δ_4 bending mode of the NO_3^- group, whereas no peak was observed at approximately 940 cm^{-1} due to the $O'-NO_2$ stretching mode of HNO_3 [427]. Chemical equilibrium calculations based on the reaction $NO_3^- + NH_4^+ \rightleftharpoons HNO_3 + NH_3$ demonstrated that the concentration of HNO_3 gradually increases with temperature, although the HNO_3 to NO_3^- ratio

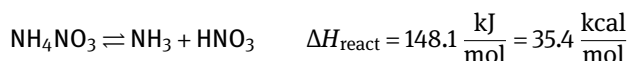
was still only approximately 0.0034, even at 533 K. Thus, molten AN was found to contain primarily NO_3^- and only a minor amount of liquid HNO_3 over the temperature range analyzed. The heat flow associated with condensed-phase decomposition was simulated based on the assumption that the decomposition rate of AN is given by

$$-dC_{\text{AN}}/dt = 10^{9.4} \exp(-125520/RT) C_{\text{NH}_4} + C_{\text{HNO}_3}$$

and that C_{NH_4} and C_{HNO_3} are constant due to chemical equilibrium. The heat-flow curves thus calculated were in good agreement with the experimental DSC data acquired at 5.1 MPa.

2.4.6.12 Mechanism and Reaction Sequences for Decomposition of Ammonium Nitrate

There are several reaction sequences depending on the temperature and pressure at which the reaction is allowed to proceed and the presence or absence of additives [139]. At temperatures just above its melting point, AN initially dissociates in reversal of its formation from ammonia and nitric acid, and it may sublime and recondense in colder parts of the system. This initiating step is a proton-transfer reaction:



Ammonia and nitric acid can be identified above 453 K (180 °C) in the gas phase during rapid-scan FTIR thermal profiling [428]. At higher temperatures, between 483 and 563 K (210 and 290 °C), the slow irreversible decomposition would lead to a mixture of nitrous oxide and water:



This is actually one of several methods for the production of nitrous oxide. This is a dangerous reaction, and, unfortunately, several factories performing this reaction have blown up. This is a first-order reaction, and the activation energy is about 159 kJ/mol (38 kcal/mol) [429]. Side reactions make the interpretation of kinetic measurements more difficult [430].

The rapid pyrolysis chemistry of thin films of AN and ADN at temperatures approximating a burning surface was studied using T-jump/FTIR spectroscopy [431]. It is quite valuable to study these two oxidizers next to each other using the same equipment because AN is one of the intermediate decomposition products of ADN. The sequence of appearance and amounts of each gas product combined with the net endothermicity and exothermicity of the process at each point in time gave the necessary information to develop multi-step reaction schemes. The decomposition of the condensed phase of AN is net endothermic up to at least 3.33 MPa (33 atm). Although

dissociative sublimation and the formation of N_2O and H_2O dominate the overall process, the superposition of two additional reactions is needed to account for all of the products observed from AN. The spectra and thermal responses are consistent with the assumption that the reaction of NH_3 with NO_2 is the major source of heat released during the decomposition of AN above 3.33 MPa (33 atm).

Based on the species detected in the mass spectrogram of a dynamic flow reactor, the following equations were proposed to describe the decomposition of AN (Table 25; [432]).

Table 25: Balanced equations for decomposition reactions of AN.

Equa- tion no.	Balanced equation	Enthalpy of reaction, kJ/mol	Entropy of reaction, $\text{J mol}^{-1} \text{K}^{-1}$	Adia- batic temp, °C
1	$2\text{NH}_4\text{NO}_3(\text{S}) \rightarrow \text{O}_2(\text{G}) + 4\text{H}_2\text{O}(\text{G}) + 2\text{N}_2(\text{G})$	-118.1	521	970
2	$\text{NH}_4\text{NO}_3(\text{S}) \rightarrow 2\text{N}_2\text{O}(\text{G}) + 2\text{H}_2\text{O}(\text{G})$	-36.5	446	345
3	$2\text{NH}_4\text{NO}_3(\text{S}) \rightarrow 2\text{NO}(\text{G}) + 4\text{H}_2\text{O}(\text{G}) + \text{N}_2(\text{G})$	-26.8	533	261
4	$2\text{NH}_4\text{NO}_3(\text{S}) \rightarrow \text{NO}_2(\text{G}) + 4\text{H}_2\text{O}(\text{G}) + 1.5\text{N}_2(\text{G})$	-100.9	490	848
5	$1.5\text{NH}_4\text{NO}_3(\text{S}) \rightarrow \text{HNO}_2(\text{G}) + 2.5\text{H}_2\text{O}(\text{G}) + \text{N}_2(\text{G})$	-89.8	461	754
6	$2.5\text{NH}_4\text{NO}_3(\text{S}) \rightarrow \text{HNO}_3(\text{G}) + 4.5\text{H}_2\text{O}(\text{G}) + 2\text{N}_2(\text{G})$	-123.3	257	989
7	$\text{NH}_4\text{NO}_3(\text{S}) \rightarrow \text{HNO}_3(\text{G}) + \text{NH}_3(\text{G})$	+185.5	94	

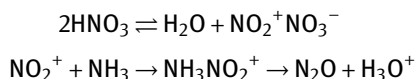
Data source: [432]

The results can be compared to those obtained for hydroxylammonium nitrate and ammonium dinitramide decomposition. In both cases, nitric acid formation competes with oxygen formation. Based on equilibrium calculations using HSC Gibbs, nitric acid is a very stable intermediate kinetic product up to about 523 K (250 °C). Above 573 K (300 °C), HNO_3 decomposes into H_2O and NO_2 .

An excellent summary of the role of additives in the combustion of AN was published by Sinditskii et al. [433] in 2007. Another study evaluated processes that take place in the condensed phase during combustion of AN. The AN decomposition begins with a proton transfer, with the formation of NH_3 and HNO_3 dissolved in the condensed phase. This is followed by thermal decomposition of nitric acid. It was shown by direct experiments that the rate of HNO_3 consumption was higher in the presence of NH_4^+ ions than the thermal decomposition of pure nitric acid [434, 435]. The increase in the HNO_3 consumption rate was directly proportional to the NH_4^+ concentration. It was assumed that the kinetics of this reaction could be described by interaction of NH_4^+ ions not only with HNO_3 molecules but also with N_2O_5 molecules. N_2O_5 is the anhydride of nitric acid but is not very stable.

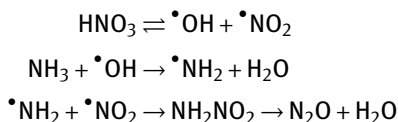
Known amounts of water, ammonia, or nitric acid were added in various combinations to a stream of entraining helium gas to determine their effects on the rate of AN decomposition in the molten state [436, 437]. Water and ammonia inhibited the re-

action, and nitric acid catalyzed it. The water effect reported here is contrary to other observations that carefully dried AN does not decompose below 573 K (300 °C).

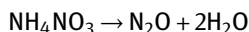


This sequence explains the observable behavior of liquid-phase AN decomposition very well: Acidic species increase the rate of AN decomposition dramatically, whereas bases such as ammonia and water retard decomposition. For a high-dipole environment, as in a solvent of molten AN, the existence of an ionic structure such as $\text{NO}_2^+ \text{NO}_3^-$ is quite acceptable, although its covalent but less stable isomer N_2O_5 also plays a role in the overall process of AN decomposition. See also [438].

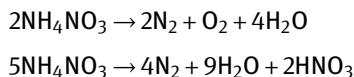
At higher and higher temperatures, the ionic mechanism of AN decomposition is replaced by reactions involving free radicals, with homolysis of nitric acid being the rate-controlling step:



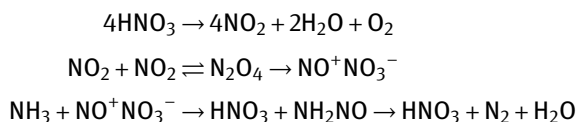
The end result of AN decomposition is the same for both modes of decomposition:



Parallel to the main decomposition reaction, several side reactions can take place:



Intermediate steps in these reactions involve the following reactions:



N-isotope and O-isotope substitution has been used to resolve questions about the origin of the N-atoms in the formation of N_2O by decomposition of AN [206]. The decomposition products of $^{15}\text{NH}_4\text{NO}_3$ were analyzed for isotope effects both during the course of the reaction and at complete decomposition. An authentic sample of $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ was prepared that contained ^{15}N exclusively in the end position, characterized by IR spectra, and was used for comparison to N_2O samples obtained in the course of this study. It was found that small amounts of water are necessary to initiate the decomposition of AN. $^{15}\text{NH}_4\text{NO}_3$ has been found to yield exclusively the

isomer $^{15}\text{N}^{14}\text{NO}$. Some inferences can be drawn from this observation regarding the mechanism of the reaction. Oxygen and nitrogen isotope effects accompanying the decomposition have been compared to results obtained with material of “natural” isotopic composition. Satisfactory agreement was found between the experimental results and theoretical calculations. Other species that have been hypothesized as intermediates in AN decomposition include nitrosamine $\text{ON}-\text{NH}_2$, nitramine $\text{O}_2\text{N}-\text{NH}_2$, and hyponitrous acid $\text{HO}-\text{N}=\text{N}-\text{OH}$.

There are several experimental techniques for investigating the rate of decomposition of AN and the strand burning of AN. All require exact knowledge of the temperature of the bulk sample, the flame front, and the decomposition products. It is important to use thermocouples made from materials that do not catalyze the decomposition of AN and do not catalyze the combustion of NH_3 in HNO_3 . The validity of some published temperature-measurement data has been questioned because of alleged catalytic thermocouple-sample interactions.

The onset of thermal decomposition and the rate of heat evolution during storage of bulk AN are greatly affected by the type and quantity of contaminants commonly found in industrial grades of AN [439]. In the wake of the Texas City (1947) and Toulouse (2001) disasters and other explosive events, the effect of impurities on the rate of AN decomposition has been thoroughly investigated.

An experimental and modeling study was aimed at a better understanding of the impact of the operating conditions on the interplay between AN decomposition pathways and their coupling with gas-phase chemistry and the role of operating conditions on AN thermal decomposition [440]. A condensed-phase semi-detailed kinetic mechanism was developed and validated against new data and reported data from other groups. This mechanism was coupled to a gas-phase mechanism, making it possible to quantify the contributions of condensed-phase and gas-phase reaction pathways to AN thermal decomposition at different heating rates. At typical burning surface temperatures (523 K [350 °C]), gas-phase reactions involving nitramide and nitric acid play a significant role.

A series of TGA experiments with AN was conducted with four different heating rates to obtain the accurate kinetic parameters of AN thermal decomposition in air [441]. The activation energies of AN pyrolysis were calculated by different isoconversional methods. The value of E_{act} was stable near 93 kJ/mol in the conversion range of $\alpha = 0.1 - 0.96$, which means the reaction obeying the single-stage character of the irreversible process can be represented by model-free approaches. The expression of the optimal kinetic mechanism model for four heating rates was

$$f(\alpha) = \alpha^{-0.0259}(1 - \alpha)^{0.0617}$$

2.4.6.13 Effect of Pressure on Decomposition of Ammonium Nitrate

An accelerating rate calorimeter was used to study the decomposition of AN under 0.1–3 MPa helium pressure [442]. Gas chromatography and MS analysis of the gaseous

products indicated that the decomposition proceeds by the same mechanistic pathway up to 3 MPa applied pressure. Kinetic fitting of the ARC data was done using the BatchCAD package. There was good agreement between the predicted and experimental values. For the first time, independent Arrhenius parameters for two parallel reactions for AN decomposition were reported, with different E_a and A values in the two kinetic equations.

The influence of pressure on phase transitions, melting, and thermal decomposition characteristics of pure AN was measured using PDSC under ambient pressure conditions and up to a maximum pressure of 6.868 MPa (68 atm) [87]. A sample of four DSC thermograms for four different pressures was already shown in Figure 2. The temperatures of the onset of decomposition were distinctly shifted with increasing pressure (Table 26). At the highest pressure, the decomposition created a strong exotherm, starting at 583 K (310 °C) and peaking at 586.6 K (313.5 °C).

Table 26: Effect of pressure on onset of decomposition temperature of ammonium nitrate.

Sample no.	Pressure		Decomposition onset temperature	
	MPa	atm	K	°C
1.	0.101	1	481.75	208.6
2.	1.379	13.61	487.44	214.29
3.	2.068	20.41	584.99	311.84
4.	2.757	27.21	541.69	268.54
5.	4.136	40.82	532.25	259.10
6.	5.514	54.42	546.46	273.31
7.	6.893	68.03	583.30	310.15

Data source: [87]

2.4.6.14 Kinetics of Decomposition of Ammonium Nitrate

The decomposition kinetics of liquid AN can be described by a first-order equation of autocatalysis. The temperature dependence of the rate constants is as follows:

$$k_1 = 10^{14.4} \exp(-23754/T), \quad \text{s}^{-1}$$

$$k_2 = 10^{7.3} \exp(-5736/T), \quad \text{s}^{-1}$$

The decomposition at temperatures near 473 K (200 °C) has often seemed to show variable induction periods and capricious variations in rate. It has been reported, for example, that completely dry AN does not decompose below 473 K (200 °C). On the other hand, there are clear indications that water inhibits the decomposition. In view of conclusions made by some investigators [384] about ionic and radical mechanisms of AN decomposition, it was proposed that k_1 describes the radical decomposition pathway,

with an activation energy corresponding to $\text{HO}-\text{NO}_2$ bond scission, and k_2 describes the low-temperature ionic pathway of decomposition. In these experiments, the rates of decomposition of AN in the liquid and vapor states were measured at temperatures up to 673 K (400 °C). Samples of absolutely dry AN were sealed in glass capillary tubes and immersed in a molten metal bath for varying lengths of time. The capillaries were quenched, and the gas evolved was captured and analyzed. The liquid remaining after complete decomposition was analyzed using ion chromatography. Nitrate ion was the only anion found. The quantity of nitric acid was determined by electrical conductivity. The data were fitted into Arrhenius plots and indicated that an ionic mechanism predominating at temperatures below 563 K (290 °C) is overtaken by a homolytic mechanism at higher temperatures. The low-temperature activation energy of 118 kJ/mol is somewhat lower than other reported values. With higher operating temperatures, the activation energy increased to 193 kJ/mol, which is nearly equal to the N—O bond energy in HNO_3 and the enthalpy of reaction for homolysis of HNO_3 into $\cdot\text{OH}$ and $\cdot\text{NO}_2$. Water and NH_3 strongly inhibit the ionic reaction at low temperature, but the effect diminishes at high temperature. Based on experiments with ND_4NO_3 , there is no primary H/D kinetic isotope effect. The primary reaction pathways predict that there should be no H/D kinetic isotope effect, but other schemes might involve abstraction of hydrogen from ammonia in the rate-determining step. The rate of decomposition of NH_4NO_3 and ND_4NO_3 was measured at 613 K (340 °C), and an isotope effect of 1.2 was found. This may have been due to secondary dissociation of $\text{DO}-\text{NO}_2$. The reaction rates of liquid and vapor were nearly the same at high temperature.

The introduction of Cl^- ions into AN increases both the initial rate of decomposition (k_1) and the rate of self-acceleration (k_2), with the latter growing much faster than the former (Section 2.4.6.8). Thus, the introduction of only 0.5% Cl^- leads to a 5-fold increase in k_1 and a 30-fold increase in k_2 at 473 K (200 °C). The greater increase in the degree of self-acceleration results in reduction of the activation energy of the leading combustion reaction of catalyzed AN.

Estimates based on fitting data to single-step kinetic models tend to be misleading, especially when these estimates are obtained from non-isothermal measurements. As an alternative, one may use model-free isoconversional methods that allow for reliably estimating the activation energy as a function of the extent of conversion. Both model-fitting and model-free computational techniques were applied to the thermal conversion of AN under isothermal and non-isothermal conditions as measured by TGA [443]. The model-fitting method to the isothermal data demonstrated that both solid-phase and liquid-phase kinetics are characterized by a single activation energy of 90 kJ/mol. In parallel, a model-free isoconversional method was applied to isothermal and non-isothermal data and yielded an almost identical activation energy, which is essentially independent of the extent of conversion. In both phases, the process can be described by the activation energy of ~ 90 kJ/mol and by a pre-exponential factor of around 10^9 min^{-1} . These kinetic characteristics are assigned to the process of dissociative sublimation/vaporization.

The thermal gasification of AN demonstrates similar kinetics in the solid and liquid phases. The Arrhenius plot of the gasification of AN is shown in Figure 25.

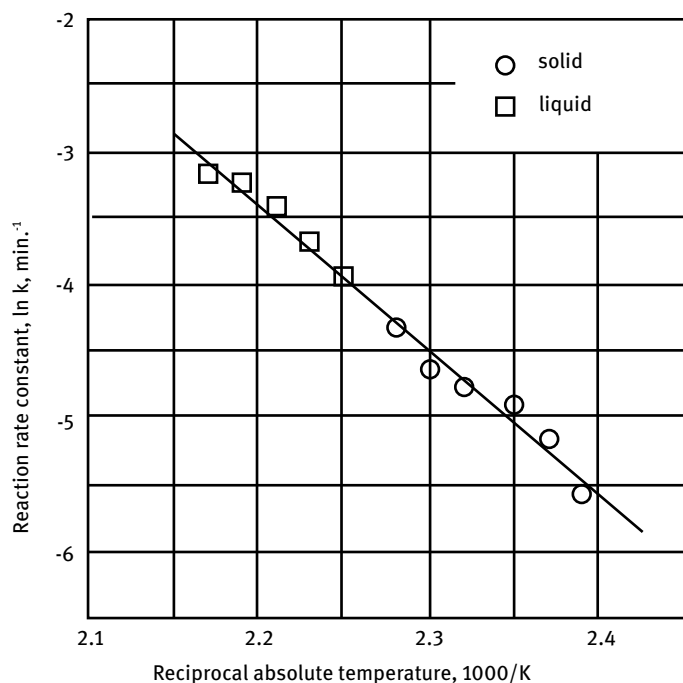


Figure 25: Arrhenius plot for the isothermal gasification of solid and liquid AN. (Reprinted and modified from [443], with permission from © 2001 American Chemical Society; permission conveyed through RightsLink.)

The majority of AN decomposition studies worked with molten AN. There are only a few studies that worked at higher heat fluxes such that solid AN would immediately transition to the vapor phase. The rate of AN decomposition also depends on the composition of the atmosphere surrounding the reacting sample. The decomposition takes different routes if the decomposition products are trapped near the sample (static) or if they are purged away by a stream of inert gas (dynamic).

Making use of labeled nitrogen in the AN decomposition reaction, it has been shown that the principal decomposition product N_2O is formed from NH_4^+ and NO_3^- ions (one atom of nitrogen from each ion). This led some investigators to postulate direct bimolecular interaction of the NH_4^+ and NO_3^- ions or molecular decomposition of NH_4NO_3 into the end products. Certain investigators emphasize the important role of the nitric acid formed during the thermal decomposition of AN. In this case, the acceleration of decomposition is associated with interaction of the NO_2^+ ions and the NH_4NO_3 entering the reaction.

The decomposition of AN is carried out on an industrial scale for the production of nitrous oxide. This is a very hazardous operation, and several factories have been destroyed by explosions in the process. To reduce the explosion hazard, it has been attempted to dilute the AN melt with other fused salts in which the AN dissolves [444].

2.4.6.15 Fast Controlled Decomposition of Ammonium Nitrate

Ammonium nitrate as oxidizer in a solid propellant or gas generant decomposes rapidly as soon as the flame front has worked its way to the oxidizer granules. The fast decomposition of AN obeys different kinetics than the slow decomposition of AN. One of the common methods to study fast decomposition is to place the AN crystals on a platinum ribbon and pass an electric current through the ribbon so that it glows like a light bulb filament. Diagnostics can then be done on the volatilized products by absorption spectroscopy or mass spectrometry.

Fast thermolysis studies of AN and its mixtures with Mg or activated charcoal have been carried out using an FTIR/temperature profiling technique [445]. When subjected to rapid heating (about 80 °C/s), AN sublimed/decomposed at around 573 K (300 °C). Sublimation dominated at ambient pressures. The IR-active products of decomposition were NH_3 , NO_2 , N_2O , and H_2O . One of the first steps of reaction is most likely a proton transfer leading to NH_3 and the decomposition products of HNO_3 . The decomposition of AN was significantly enhanced when AN was mixed with Mg powder or charcoal, and it may occur at temperatures as low as 408 K (135 °C). Whereas NH_3 was the major product of decomposition of AN/Mg mixtures, no NH_3 was observed from AN/C mixtures. The different behavior of AN in these mixtures may be the result of reactions of AN with Mg or C.

Sputtering of condensed-phase AN at the inlet to a mass spectrometer yields many positive and negative cluster ion series derived from different ionic cores [446]. The cluster cores are surrounded by varying numbers of AN monomer units, such as $[(\text{NH}_4\text{NO}_3)_n\text{NO}_3]^-$, $n \geq 3$ or $[(\text{NH}_4\text{NO}_3)_n\text{NH}_4]^+$. Collision-induced dissociation of mass-selected cluster ions suggests that the first two members of the negative series, $n = 1$ and $n = 2$, are not detected because they rearrange and lose one or more ammonia molecules. NH_4NO_3 is strongly hydrogen bonded, but $[(\text{NH}_4\text{NO}_3)\text{NO}_3]^-$ has no hydrogen bonds. This is consistent with this ion rearranging by loss of NH_3 to form the strongly hydrogen-bonded ion $[\text{H}(\text{NO}_3)_2]^-$.

Rapid Decomposition of Gasified Ammonium Nitrate

Experiments were conducted in which the surface of solid AN was heated at such a high rate of heat input that the surface gasified at a rate much higher than the bulk decomposition rate [447]. Under these conditions, the surface gasification proceeded by a mechanism that was characterized by a small activation energy (29.3 kJ/mol = 7 kcal/mol) and produced essentially only HNO_3 and NH_3 as the primary products. There may actually be some surface superheating beyond the equilibrium condition.

The experimental linear pyrolysis rates of AN strands between 452 and 573 K (180 and 300 °C) can be expressed in good approximation by the equation

$$B = 120 \exp(-7100/RT_s)$$

where B is the regression rate in cm/s, T_s is the surface temperature in kelvin, and R is the gas constant. The linear pyrolysis of AN is a very endothermic event. Figure 26 shows the linear pyrolysis rate of AN (on a logarithmic scale) as a function of the reciprocal surface temperature.

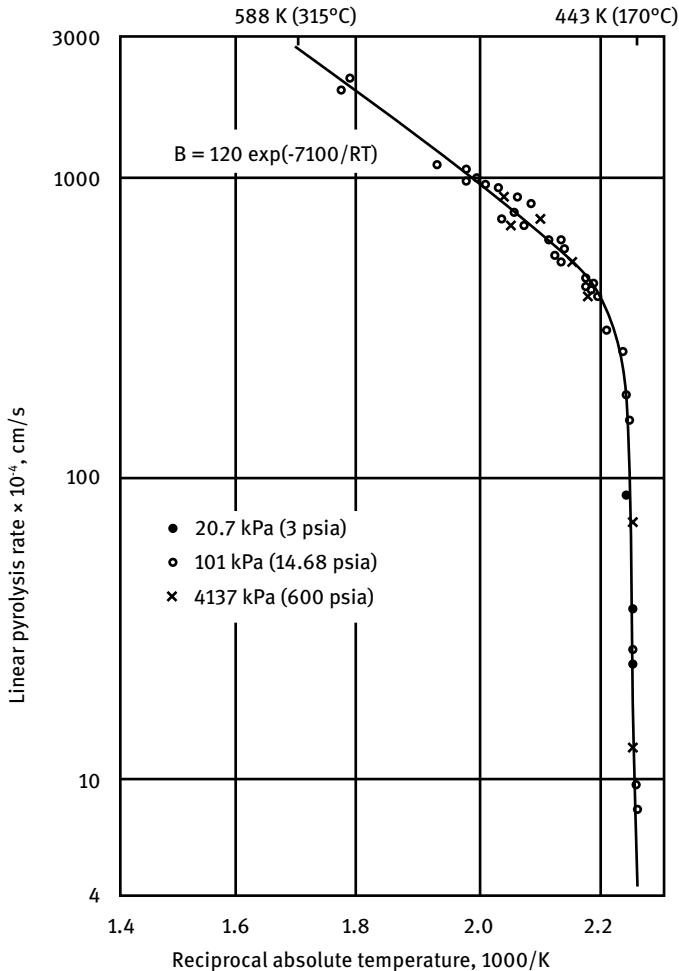


Figure 26: Linear pyrolysis rate of AN as a function of the reciprocal surface temperature. (Republished and modified from [447], with permission of American Institute of Aeronautics Astronautics; permission conveyed through Copyright Clearance Center, Inc.)

Below 453 K (180 °C) the pyrolysis rate dropped sharply and became essentially independent of temperature. It was suggested that this drop is related to melting process rather than a sublimation process. One of the less volatile species that remains adsorbed to the melting AN is nitric acid. The heat of vaporization of HNO_3 is of the same magnitude as the energy of activation for rapid pyrolysis of AN, suggesting that the desorption of HNO_3 is the rate-controlling step. The heat of fusion of AN is 6.1 kJ/mol (1.460 kcal/mol) and is less likely to be rate controlling.

Investigators developing a model for the combustion of AN composite propellants pointed to the leading role of AN gas-phase reactions [447–449] and postulated that AN gasifies first at about 600 K by an endothermic reaction to form ammonia and nitric acid. These gaseous products then undergo exothermic redox reactions near the surface to establish a flame front of about 1250 K, which radiates and conveys heat that drives the gasification of AN and pyrolysis of the binder.

In contrast to that, it was postulated by Kondrikov et al. (1998) [450] that the leading reaction in combustion of AN-based compositions takes place mostly in the condensed phase up to pressures of the order of hundreds of atmospheres. They studied the critical burning conditions of three categories of AN-based compositions: neat AN with minor additives to lower the pressure deflagration limit, a composition based on AN/TNT 80/20 mixtures, and materials containing RDX or liquid nitric esters. It was shown that combustion of almost all the substances studied can be characterized by steady burning rates and dependence of the burning rates on pressure, but at the same time it is connected with the very low levels of burning stability at lower pressures: The pressure deflagration limit and the critical diameter of burning in the majority of cases were much higher than the corresponding values observed for the standard double base and composite propellants as well as for the variety of nitro compounds investigated earlier.

Mass spectrometry and IR spectrophotometry are the two prime fast-response methods used to analyze transient phenomena occurring on the surface of decomposing energetic materials. These methods can be applied to oxidizers by themselves, to formulated solid propellants, or to slabs of oxidizer sandwiched between two layers of fuel binder. The methods for rapid heating in either case can be a laser pyrolysis or thin-film sample heating on a rapidly heated metal ribbon (T-jump/FTIR spectroscopy).

A different chemical mechanism of combustion of AN-based composites has been offered, in which the main reason for the inability of AN and mixtures to burn at low pressures was supposed to be the presence of a large amount of water in the reaction layer as a product of AN decomposition, which of course extinguished combustion by decreasing reaction rate and surface temperature [451]. The role of catalysts in this combustion mechanism is to enhance the rate of AN decomposition, which, in turn, results in water removal from the reaction mixture. On the other hand, combustion of water-impregnated AN-based explosives showed that the presence of 15–22% water in the compositions did not hinder sustained burning.

2.5 Strand-Burning Rates of Ammonium Nitrate

Strand burning of AN by itself (without addition of binders or combustibles) was studied to better understand the mechanism of AN combustion and to study the effect of burning-rate modifying additives without interference by combusting fuels. However, according to Glazkova [452], neat AN does not burn in glass tubes of large diameter (30 mm), not even at 100 MPa. In other studies [433, 453, 454], AN in the molten state was found to be incapable of burning in tubes with a 7-mm diameter at atmospheric pressure. Results at pressures up to 20–30 MPa indicated that the leading reaction of combustion of AN doped with additives proceeds in the condensed phase. An addition of small amounts of some catalytic mineral substances to AN is required to burn AN without a fuel, but the role of additives in the combustion mechanism is difficult to explain. It is known that the addition of chlorides results in a decrease in AN stability, shifting the temperature of the onset of exotherm from 599 to 519 K (326 to 246 °C) for a mixture with 5% KCl. One proposed mechanism of additive action is to promote heat generation in the condensed phase, which stabilizes combustion and raises decomposition rate. The AN flame consists of separate flame zones and remains at some distance off of the surface at pressures below 20 MPa. This distance decreases with increased pressure, and the flame settles onto the surface at 20–25 MPa (i.e., when the burning rate vs. pressure curve also undergoes a break). It is interesting to compare the peculiar behavior of AN deflagration with that of other ammonium salt oxidizers, such as ADN and AP [455]. Based on numerous thermocouple-aided experimental studies on the combustion of different energetic oxidizers, it has been shown that a material in the condensed phase can be heated up to its boiling point or, in the case of salts, to their dissociation temperatures. In contrast to the gas-phase model, the condensed-phase model has an energy limitation. Since in condensed-phase reactions the burning rate increases at the expense of surface temperature increase with pressure, there can be a situation when the heat effect of energetic material decomposition is no longer sufficient for warming-up the substance to the surface temperature. This induces an instability of combustion and burning-rate oscillations [456, 457]. See also [458, 459].

2.5.1 Additives for Strand Burning of Ammonium Nitrate

Because the strand-burning rate of AN by itself and in combination with fuels in solid propellants is relatively slow (in comparison to those of AP propellants), a significant amount of effort has been devoted to find additives to increase the burning rate for AN [460]. Ideally, such additives should not only increase the burning rate but also eliminate the nasty phase transitions of AN at the same time.

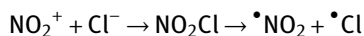
Pellets of cast instead of tamped or pressed AN/HN and HN were used in a study of surface temperatures of burning solid propellants. The HN and HN-AN eutectics were used as model substances because the melt surface gives a well-defined surface

temperature. Both 32 mol-% AN/68 mol-% HN (melting point 316 K) and HN castings had to be catalyzed with 1.5 mass-% Cr_2O_3 catalyst, which was mixed in at temperatures a few degrees above the melting point before the cylinders were allowed to solidify in glass tubes as molds. A series of thermocouples was embedded in the cast grain, which recorded the passing of the combustion front. The temperature would level off while the melted zone was passing through. Burn rates of 0.25–0.78 cm/s at 0.68–5.35 MPa were typical for catalyzed AN-HN, whereas catalyzed HN would burn much faster, 1.2 cm/s at 41 bar. The average surface temperature of burning AN-HN was 580 K vs. 468 K for HN by itself.

The effects of additives on the rate of deflagration of AN and AP were summarized in a book by Glazkova [461]. The effect of catalysts such as 4.9% NaCl and NH_4Cl can be enhanced further by addition of promoters [462]. Some promoters can enhance the burning-rate-increasing effect of catalysts by a factor of 1.5–3.

An excellent summary of the role of additives in the combustion of AN was published by Sinditskii and co-authors [433, 453, 463]. It was determined that the surface temperature of AN is controlled by the dissociation reaction of the salt occurring at the surface. Results obtained from experimental analysis have indicated that the leading reaction of combustion of AN doped with additives proceeds in the condensed phase up to pressures of 20–30 MPa. It is surprising that many inorganic mineral additives to AN increased the rate and completeness of burning of both the pure salt and reactive oxidizer/fuel compositions. Thus, an addition of 7 mass-% of sodium chloride to AN makes sustained burning possible at and above 1.2 MPa (Figure 27). The particle size of the additives was less than 100 μm . Additives of other chlorides of alkaline and alkaline-earth metals had a similar effect. Generally, the curve of burning rate (r_b) vs. pressure (p) demonstrated a break (change of slope) at 20–25 MPa, with a strong pressure influence on the burning rate before the break (the pressure exponent, $n = 0.9 - 0.95$) and a weaker dependence above it ($n = 0.5 - 0.6$).

Many investigators have attempted to explain the effect of halide ion addition on AN burning. It is known that the addition of chlorides results in a decrease in AN stability, shifting the onset of AN exotherm from 599 K (326 °C) to 519 K (246 °C) for a mixture containing 5% KCl and 95% AN [464]. The mechanism of influence of halide ions is not completely understood. Many researchers, e.g., Rubtsov et al. [465], have pointed to a synergism in the action of HNO_3 and Cl^- and tried to explain the presence of an induction period observed by Colvin et al. [466]. They suggested that the key reaction in the catalysis of AN decomposition by chloride ions involves the intermediate formation of nitryl chloride:



Atomic chlorine, a free radical, is a very reactive species and may participate in several critical decomposition steps. The rate-controlling step of these processes could be the hydrogen atom abstraction from ammonia under the action of a chlorine atom. The subsequent reactions of $\bullet\text{NH}_2$ radical with NO_2 and NO proceed quickly. This mecha-

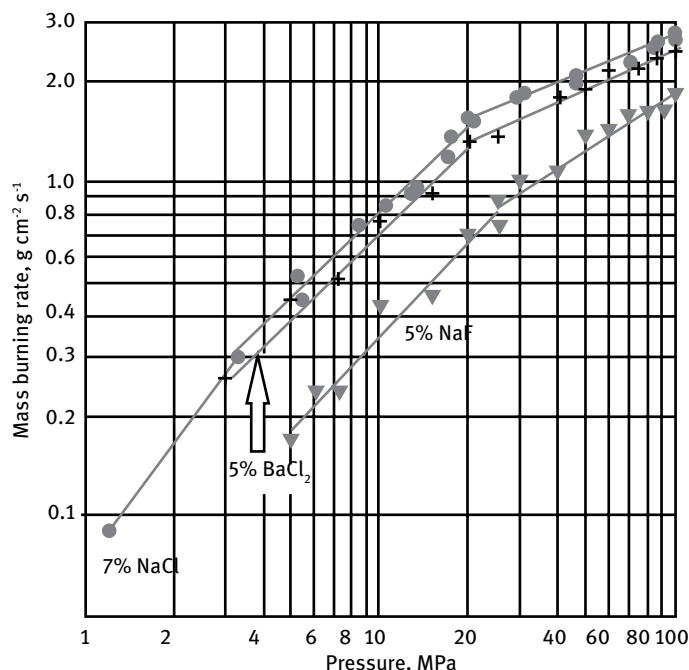


Figure 27: Pressure dependence of the burning rate of AN with addition of 7% NaCl (● circles), 8.5% BaCl₂ (+ crosses), or 5% NaF (▼ triangles). (Reprinted and modified from [433], with permission from © 2007 Begell House, Inc.)

nism casts some doubt on a conclusion made by Brower et al. that formation of NO₂⁺ is the rate-limiting step in the ionic mechanism of AN decomposition. Other halides, bromides and iodides, act in a similar way. In contrast to chlorides, bromides, and iodides, the fluorides inhibit AN decomposition rather than catalyze it. Another intermediate postulated in the chloride-catalyzed decomposition of AN is chloramine ClNH₂.

Amatol is a mixture of AN and TNT and burns more readily than AN by itself. The effect of partial substitution of AN in amatol 80/20 by alkali metal salts on the strand-burning rates of amatol was measured at high pressures [467]. There are two ways of retarding the chemical reactions involved in the combustion of AN and its mixtures: One is the addition of compounds that readily release ammonia, thus shifting the AN dissociation equilibrium to the left. The other is the addition of reducing agents, which sequester the HNO₃ and thus slow down the oxidation of NH₃. In 7-mm plexiglass tubes, the amatol mass consumption rate at 145–1000 atm can be expressed by the equation

$$U_b = -0.58 + 0.00554P$$

where U_b is the mass consumption rate in $\text{g cm}^{-2} \text{s}^{-1}$ and P is the pressure in atm. Addition of ammonium oxalate or iron oxalate decreased the burning rate, while sodium oxalate or potassium oxalate increased the burning rate. Potassium fluoride increased the burning rate even more significantly.

There will be substantially more information on the effect of burning-rate modifying additives in AN/binder solid propellant compositions in future volumes of the *Encyclopedia of Rocket Propellants*, and a brief introductory discussion is given in the following section.

2.5.2 Combustion of Ammonium Nitrate in Rocket Propellants

There are numerous publications on the combustion of AN in rocket propellants and gas generants. Here we have discussed some related papers in which the emphasis is on the kinetics of AN decomposition as an oxygen source and on the effects of AN particle size and additives on the burning rates of such propellants.

The combustion of AN and energetic mixtures containing AN were examined based on combustion and deflagration chemical and thermal decomposition mechanisms and compared to results obtained with AP in similar experiments [468]. The main features of AN thermal decomposition compared with AP decomposition are as follows: **(1)** The salt decomposes in the liquid phase during combustion, **(2)** the concentration of acid formed in the liquid phase, as a result of dissociation equilibrium, is greater because HNO_3 is a weaker acid than HClO_4 , **(3)** the volatility of NH_4NO_3 is higher and the temperature of the burning surface is lower, and **(4)** the oxidizing ability of AN decomposition products is weaker than that of AP. The combustion of AN-based propellant compositions can be explained in terms of the mechanism in which the decomposition in the condensed phase plays a major role, with additional influence exerted by gas-phase reactions. Similar observations have been made with other ammonium salts and are characteristic for most ammonium salts (including hydrazinium nitrate).

Excellent summaries of decomposition kinetics of AN and other oxidizers and energetic materials in the combustion wave were compiled by Sinditskii and co-authors [469, 470]. Experimental data on burning rates and surface temperatures have allowed us to derive unique information on the decomposition kinetics of energetic materials at high temperatures, provided that combustion of these materials occurs in the condensed phase. Kinetic parameters of the leading reaction on combustion of AN were compared to those of three other solid rocket propellant oxidizers: AP, ADN, and HNF, as well as six energetic fillers.

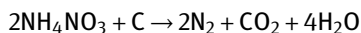
The surface temperature in the combustion wave of AN, as well as in ADN, HNF, and AP, is controlled by a dissociation process similar to that postulated for other onium salts [471].

2.5.3 Combustion of Activated Charcoal in Ammonium Nitrate

Activated charcoal (AC) is not a typical rocket fuel, but the combination of AN and AC would make a potential rocket propellant or explosive, and carbon black is very cheap. Charcoal has very simple combustion mechanics and creates only two combustion products. Surprisingly, activated charcoal has a very strong catalytic effect on the decomposition of AN. This may be different from the effect of graphite, which is sometimes added as an opacifier or applied as a coating to make the surface of solid propellant grains electrically conductive to prevent buildup of electrostatic charges.

We are not quite sure if we should list carbon black (CB) as a combustible additive or as a catalyst. The true designation of a catalyst is that it is not consumed in the reaction, but carbon black is altered in the decomposition of AN and eventually consumed once the mixture ignites. Therefore, we list carbon black as an additive and not as a catalyst.

In the presence of carbon black, the decomposition rate of solid AN in the temperature range 343–423 K (70–150 °C) was shown to increase by more than seven orders of magnitude [472]. At relatively low temperatures, the process proceeded by a two-stage mechanism, with corresponding acceleration at each stage. At elevated temperatures, the first stage was absent, and the reaction went directly into high gear. The decomposition rate was proportional to the amount of carbon black in the mixture. The activation energy for the decomposition (≈ 125 kJ/mol = ≈ 30 kcal/mol) did not vary during transformation. Water decelerated the process. For a water content of 4–5%, an intermediate maximum of the deceleration was observed. The main gaseous decomposition product was N_2 . In a stoichiometric mixture, carbon black is oxidized to CO_2 :



The strong increase in the rate of thermal decomposition of AN under the action of carbon black is probably due to the fact that HNO_3 formed in this reaction is rapidly reduced by carbon black to HNO_2 and its anhydride N_2O_3 , which are, in turn, active nitrosation agents with respect to NH_3 and NH_4^+ , enhancing their transformation to N_2 . The ordinary thermal decomposition of HNO_3 , as shown by its kinetics, cannot yield the necessary rates even at the highest possible concentrations of the acid corresponding to the achievable depth of AN conversion in a mixture with CB.

Raman spectroscopic analysis, DSC, TG-DTA-IR, TG-MS, and flash pyrolysis MS were carried out to study the influence of the physical properties of different types of carbon on the thermal decomposition behavior of AN/carbon mixtures [473]. As seen in DSC thermograms, AN mixed with activated carbon or carbon nanotubes exhibited violent reactions after the melting of AN, while AN mixed with graphite or fullerene showed only mild exothermic peaks, the same as for pure AN. Diamonds were not tested for lack of free samples. From the TG-IR results, CO_2 formation was more pronounced for AN and activated carbon and for AN and carbon nanotube mixtures than for other mixtures. It was concluded that AN mixed with carbon of low crystallinity showed violent reactions after melting, while AN mixed with carbon of

high crystallinity showed the same behavior as pure AN. The thermal decomposition behavior of AN/carbon mixtures was not influenced by the crystallinity of carbon when flash-heated rapidly and instantaneously. Ammonium nitrate mixed with carbon, such as graphite, did not burn below 7 MPa. Compositions with more than stoichiometric amounts of activated carbon had higher burning rates. The burning rate of AN/AC mixed with CuO as a combustion catalyst deteriorated faster than if additive-free [474].

In order to obtain a better understanding of combustion and ignition properties of AN or PSAN and activated carbon (AC) mixtures, friction sensitivity tests, thermal analysis, and 200-mL closed-vessel combustion tests were carried out, and the influence of the mixture ratio on the combustion and ignition properties of various AN/AC mixtures was investigated [475–478]. In the differential scanning calorimeter, AN mixed with more than 4 mass-% of AC mixtures showed a violent exotherm after the melting of AN, and some of the mixtures exploded. In the 200-mL closed-vessel test, the maximum rate of pressure rise was observed at a higher AN concentration than the stoichiometric composition.

The effects of copper(II) oxide on the thermal decomposition of AN mixtures and the thermal characteristics of AN, carbon, and CuO mixtures were measured using simultaneous DSC and TGA-DTA connected with IR spectroscopy and MS [479]. In the TGA-DTA results for AN/AC/CuO and AN/CB/CuO mixtures in an open cell, an exotherm was observed at approximately 483 and 503 K (210 and 230 °C), respectively. In addition, the IR and mass spectra of the gases produced from the AN/AC/CuO and AN/CB/CuO mixtures indicated the presence of CO₂. These results suggest that the effect of CuO on the oxidation of different types of carbon depends on the chemical reactivity of the carbon, which is derived from its physical properties.

A thermal analysis using DSC of the decomposition of AN with activated charcoal (carbonized rice husks) or dextran showed a tendency of lowering of the activation energy of the oxidizer in the presence of dextran [480]. The calculated activation energies were in the range of 65–82 kJ/mol. The combustion wave behavior was studied in a windowed high-pressure chamber and recorded by a high-speed camera.

2.6 Safe Handling of Ammonium Nitrate

2.6.1 Materials for Construction, Compatibility, and Corrosion of Ammonium Nitrate

2.6.1.1 Compatibility of AN with the Environment

Ammonium nitrate comes in contact with the environment in packaging materials, shipping containers, mixing equipment, and rocket/gas generator combustion chambers prior to ignition. These conditions are relatively easy to control, and materials are selected that are known to be compatible.

For AN used in blasting agents, the downhole conditions are less well known or predictable and may involve minerals that AN is not compatible with. A frequent

mineral encountered in coal seams or rock quarries is pyrite. Pyrite is not likely to be encountered in rocket propellants, but we include these data here nevertheless. The effect of pyrite on AN decomposition had to be studied to prevent premature ignition of ANFO pumped into drill holes. The reaction of AN with pyrite was studied using a simultaneous differential scanning calorimeter and thermogravimetric analyzer (TGA/DSC) [481, 482]. When a mixture of pyrite and AN is heated at a constant heating rate from room temperature to 1073 K, two exothermic reactions occur at about 473 and 723 K, respectively. The first exothermic reaction is considered to take place between AN and pyrite, where NO, NH₃, SO₂, and N₂O gases are produced. The second exothermic reaction is due to the oxidation of the remaining pyrite by atmospheric oxygen. Based on the quantitative analysis of the gaseous and solid products of the reaction, a new overall reaction was proposed at the first exothermic peak of interest, which is thermodynamically favorable. The results have significant implications for the understanding of the stability of AN-based industrial blasting agents in reactive mining grounds containing pyritic minerals. The activation energy and the pre-exponential factor of AN decomposition were determined to be 102.6 kJ/mol and $4.55 \times 10^7 \text{ s}^{-1}$ without the presence of pyrite and 101.8 kJ/mol and $2.57 \times 10^9 \text{ s}^{-1}$ with the presence of pyrite. The kinetics of AN decomposition was then used to calculate the critical temperatures for AN decomposition with and without the presence of pyrite, based on the Frank-Kamenetskii model of thermal explosion. It was shown that the presence of pyrite reduces the temperature for, and accelerates the rate of, decomposition of AN, causing dangerous premature detonation of the explosives.

2.7 Transportation, Storage, and Disposal of Ammonium Nitrate

2.7.1 Transportation of Ammonium Nitrate

There are two main grades of AN, fertilizer grade (FGAN) and technical grade (TGAN). The two are chemically identical. TGAN formulations are more porous than FGAN to facilitate the absorption of fuel for use in explosives (e.g., ANFO). As the name suggests, fertilizer grade is the type that is used for fertilizer application in agriculture, most commonly in prill/granule form. Transportation of AN with not more than 0.2% combustible substances (including any organic substance calculated as carbon, to the exclusion of any other added substance) is covered by 49 CFR § 172.101 with label code 5.1 Oxidizer, UN1942.

2.7.2 Storage of Ammonium Nitrate

Under the recommendations issued by the National Fire Protection Association (NFPA) Code for the Storage of Liquid and Solid Oxidizers [483], AN was ranked along with all other inorganic nitrates as a Class 1 oxidizer, which is the oxidizer class with the lowest hazard rating. As such, the requirements (number and spacing of

sprinklers, separation from nearest important structure, non-combustible materials of construction for storage buildings and storage bins) had to be met only for storing more than 1814 kg (4000 lb_m) of AN in one location. To anybody who remembers the extent of damage caused by the Texas City and Toulouse disasters, this seems to be a very lenient classification of the potential hazards of AN storage. In the most recent revision of NFPA 400, Hazardous Materials Code, the Technical Committee classified AN as a Class 2 oxidizer. The burning rate of technical-grade AN prill falls within the Class 2 oxidizer criteria in Annex G of NFPA 400 (2016) [484].

The Occupational Safety and Health Administration (OSHA) standard at 29 CFR 1910.109(i) contains requirements for AN stored in the form of crystals, flakes, grains, or prills [485].

2.7.3 Accident History of Ammonium Nitrate Explosions

The conditions under which the decomposition of AN can transition into a deflagration and then into a detonation were thoroughly investigated in the wake of several disasters, most prominently the explosion of two shiploads of AN in Texas City, Texas, on 16 April 1947. About 2500 tons of AN packed in paper bags were in the cargo hold of the vessel *SS Grandcamp* when it first smoldered and then exploded, killing more than 500 people and injuring 4000 more. A second explosion occurred 20 h later involving 900 tons of AN in the cargo hold of the *High Flyer*, which was moored next to the *Grandcamp*, but that explosion caused only one more fatality [486]. The news of the explosion at Texas City had barely spread around the world when a similar explosion aboard the *SS Ocean Liberty* shook the harbor of Brest, France, on 28 July 1947. In view of such destructive behavior, who would want to use AN as a rocket propellant?

Even in mixtures of AN with ammonium sulfate (AS), which is a fertilizer mixture, AN is still detonable, as an industrial accident in Oppau, Germany, in 1921 showed when people foolishly tried to loosen a chunk of caked AN/48.5% AS by setting off an explosive charge in a silo, which had been done several times before without any ill effects. The entire silo containing 4500 tons of the fertilizer exploded, killing 561 people, injuring 2000 people, flattening the chemical factory, and causing destruction for miles around [487–489]. The crater at the location of the former storage silo was 100 m in diameter and 19 m deep (Figure 28). Similar explosions have occurred at numerous other industrial installations (Table 27).

Process safety, as well as the safe storage and transportation of AN, has been a topic of increasing interest in the last few decades. The increased interest in improving the safety of AN operations has been driven largely by a series of explosion catastrophes that have occurred in the United States and the rest of the world. A review of past incidents and disasters to look for common causes and lessons to be learned is an



Figure 28: Aftermath of the explosion of an ammonium nitrate/ammonium sulfate mixture at Oppau, Germany, in 1921. (Photo courtesy of Stadtarchiv Ludwigshafen, Fotosammlung Nr. 23639)

essential component to any process safety and loss prevention program. Although analyzing the causes of an accident cannot prevent that accident from occurring, learning from it can help prevent future incidents. A review of major incidents involving AN in the last century was done to identify common causes and lessons that can be learned in the hope of preventing future disasters [490]. Ammonium nitrate has been involved in dozens of major incidents in the last century. Of those, 12 incidents were selected and reviewed, and lessons from these incidents have been shared with the rest of us. Although propellant manufacturing sites do not involve the same quantities of AN as in the fertilizer industry, the storage of raw ingredients nevertheless must meet all safety criteria, including setback requirements from the nearest occupied buildings and the property boundary.

At Terra Industries in Port Neal, Iowa, on 13 December 1994, an AN manufacturing unit exploded. Four employees were killed, and 18 were hospitalized. A total of 5700 tons of anhydrous ammonia and 25000 gallons of nitric acid were released. Resi-

Table 27: Summary of ammonium nitrate explosions.

Year	Location	Material involved	Consequences
1920	Stolberg, Germany	AN, all, induced by blasting	Civil explosion
1921	Kriewald, Silesia (now Knurow, Poland)	AN, all, induced by blasting, 25 t AN	19 dead, 23 injured
1921	Oppau, Germany	AN, all, induced by blasting, 4500/750 t AN + AS	561 dead, 1991 injured
1942	Tessenderlo, Belgium	150 t AN + AS, same as in Oppau	100 dead
1947	Texas City (× 2), Texas, USA	2300/962 t AN, fire → explosion	450 dead, 4000 injured
1947	Brest, France	3300 t AN, fire → explosion	21 dead
1953	Black Sea, USSR	4000 t AN, fire → explosion	
1964	Japan	2200 t AN, fire → explosion	
2001	Toulouse, France	300–400 t AN	31 dead, 200 injured
2013	West, Texas, USA	30 t AN	15 dead, 200 injured
2015	Tianjin, China	AN	165 dead, 798 injured, 8 missing
2020	Beirut, Lebanon	AN, fire → explosion	207 dead, 7500 injured

dents were evacuated from the surrounding area, and ammonia plumes were detected several miles away.

In West, Texas, on 17 April 2013, a chemical storage and distribution facility caught fire, followed by the explosion of around 30 tons of AN while the emergency responders were trying to extinguish the fire, leading to 15 fatalities and numerous buildings, businesses, and homes being destroyed or damaged. Authors of one publication investigated the root causes of the incident, presented a simplified consequence analysis, and discussed how the current regulations could be modified to prevent or minimize future losses [491]. See also [492–494].

2.8 Safety Properties of Ammonium Nitrate

For the sake of reproducibility and to be able to compare results obtained at different laboratories, safety properties of AN have been determined based on pure AN. However, that is not the grade of purity that is representative for the bulk of AN used in industry for propellants and explosives. Many of the real-life safety properties for industrial-grade AN may be quite different from what was measured in an academic laboratory using reagent-grade AN.

2.8.1 Explosive and Fire Hazards of Ammonium Nitrate

Until the Oppau disaster in Germany in 1921, AN was not considered an explosive in the absence of fuels. In the wake of this disaster, numerous investigations have been carried out to better characterize AN as an energetic material.

The likelihood of accidental explosions of AN is increased by the porosity created by repeated cycling though the 32°C IV ↔ III phase-transition temperature. The explosion sensitivity can be reduced by incorporating some potassium nitrate in the AN during crystallization (which also shifts unwanted phase changes) [495].

A study was directed toward determining conditions under which AN will explode when heated [496]: 2.26-kg (5-lb) charges of pure or fertilizer-grade AN were packed into bombs consisting of seamless steel tubes that were closed at one end and had vents measuring up to 19 mm (0.74 in) in diameter at the other. These bombs were wired for electric heating at rates up to about 1700 W. The fertilizer-grade AN came from the same suppliers that had supplied the ships in the Texas City disaster and had 0.7% of a wax coating and 3% clay as anticaking additive. Possible spontaneous heating of AN was investigated by placing about 20 thermocouples in the holds of a Liberty-type ship during the loading of some 8000 tons of AN fertilizer and making temperature records during the voyage, which occurred in the heat of summer between Louisiana and the Panama Canal Zone.

Deflagration-to-detonation transitions of molten AN can occur at any time, depending on the mode of confinement and the surface-to-volume ratio of the container [497, 498].

2.8.2 Drop-Weight Sensitivity of Ammonium Nitrate

Solid AN will explode in the drop-weight impact-sensitivity apparatus only at the upper limit of capability of most machines. Molten AN is much more sensitive and is easy to initiate by impact (Table 28). In the Picatinny Arsenal apparatus with a 2-kg weight, the 50% point was reported as 79 cm (31 in) for chemically pure AN and 74–81 cm (29–32 in) for AN coated with about 1% wax. For comparison, tests conducted

Table 28: Drop-weight impact sensitivity of ammonium nitrate at various temperatures.

Temperature		50% positive impact tests, inches			
K	°C	AN, chemically pure		AN, wax-coated	
298	25	78.7	31	76.2	30
373	100	68.6	27	55.9	22
423	150	68.6	27	58.4	23
448	175	30.5	12	30–32	12–13

Picatinny Arsenal apparatus, 2 kg weight
Data source: [499]

at the same time with Picatinny apparatus for standard explosives gave 43 cm (17 in) for Explosive D (ammonium picrate), 30.5–38 cm (12–15 in) for TNT, 20 cm (8 in) for tetryl, and 10 cm (4 in) for lead azide. In the U.S. Bureau of Mines apparatus with a 2-kg weight, no reaction was observed for chemically pure or wax-coated AN. The test at 448 K (175°C) showed that AN in the molten condition is much more sensitive than the solid material.

Mixtures of AN with metal powders are quite sensitive to shock. The shock sensitivity decreased in the order $\text{Ti} > \text{Sn} > \text{Al} > \text{Mg} > \text{Zn} > \text{Pb} > \text{Fe} > \text{Sb} > \text{Cu}$ [500]. For comparison, the autoignition temperature decreased in the order $\text{Zn} > \text{Mg} > \text{Pb} > \text{Fe} > \text{Cu} > \text{Ti} > \text{Sn} > \text{Sb} > \text{Al}$.

The sensitivity of AN can be modified by adding anti-explosion agents to reduce its impact sensitivity. Six different additives – ZnO , urea, Na_2HPO_4 , camphor, $\text{Mg}_2(\text{OH})_2\text{CO}_3$, and Na_2CO_3 – were mixed with AN and tested [501]. The impact-sensitivity test results of these mixtures at a drop height of 65 cm with a 10-kg drop hammer showed that in comparison with pure AN without additive, when 5% of a $\text{ZnO}/\text{Na}_2\text{HPO}_4/\text{Mg}_2(\text{OH})_2\text{CO}_3 = 33/34/33$ mixture was added to the system, the impact sensitivity could be decreased from 88 to 24% positive tests, and the impact sensitivity also declined with the decrease of hardness and density of modified AN.

Similar to what is observed with AP, the particle size of modified AN has a pronounced effect on its mechanical sensitivity [502].

In a round-robin test of AN drop-weight sensitivity performed by four different laboratories with the type 12 drop-weight sensitivity apparatus with a 2.5-kg weight, the average values for DH_{50} impact sensitivities were 156 cm for 120-grit sandpaper and 82 cm for 180-grit sandpaper [72]. One lab tested AN both dried and not dried using 180-grit sandpaper and found the material to be completely insensitive up to the limit of their equipment. Another lab using 180-grit sandpaper found the sensitivity to be much like what others had found for 120-grit sandpaper, with an average DH_{50} value of 201 ± 29 cm. A third lab tested a double-dried material and found the average DH_{50} value to be 60.5 ± 2.5 cm. The variations may be due to different relative humidities in the laboratory air. RDX and PETN were tested on the same equipment for comparison and calibration.

2.8.3 Cap Sensitivity of Ammonium Nitrate

Porous AN with uniform porosity of carefully controlled void fraction, average pore size, and pore size distribution can become cap sensitive, either as AN by itself [57, 503–505] or AN with fuel oil imbibed into the porosity. This material is often called “expanded ammonium nitrate.” This is similar to sensitizing liquid explosives by including microballoons. The collapse of voids under conditions of sudden adiabatic compression causes hot spots that aid the propagation of low-velocity detonation.

The bulk density of expanded AN is typically $0.35\text{--}0.6\text{ g/cm}^3$. At a density of 0.35 or 0.6 g/cm^3 , the material is no longer cap sensitive [506].

The sensitivity of commercial grades of AN can change after it leaves its manufacturing site and is exposed to various changes and multiple cycles of temperature and humidity during transport and storage, depending on the weather [507]. Contaminants can either catalyze or inhibit the detonability of AN [508].

2.8.4 Card-Gap Sensitivity of Ammonium Nitrate

The distances over which sympathetic detonation of AN and ANFO might be expected were measured in large-scale gap tests using two types of ANFO donor charges in three sizes with AN, both at ambient and elevated temperatures, and ANFO acceptor charges [509]. The up-and-down experimental design was chosen to determine the 50% initiation point. The acceptor charges were instrumented to indicate initiation and to determine detonation velocity. Required separation distances between donor and acceptor were found to be larger than anticipated, both for the AN and the ANFO. With ANFO acceptors and a 16-gauge steel-faced donor, one initiation (positive test) occurred at a separation of 636 in = 53 feet or nearly 16 charge diameters. With AN by itself, initiation occurred at 4–5.5 charge diameters.

Liquid molten AN at 453 K (180 °C) was less sensitive in the card-gap test, with 1.5-in charge diameter in steel pipe than hot prilled AN heated to just below the melting point [510]. In these tests, the pressure was ~20 kbars and the detonation velocity was ~2000 m/s. Additional tests were conducted with heavy and with light confinement and with charge diameters of 7, 10, 15, 20, and 30 cm (3, 4, 6, 8, and 12 in). In a series of tests with 4-in samples with light confinement and a 320-g tetryl booster with incrementally increased initial sample temperature, prilled AN started to become detonable at 398–413 K (125–140 °C). Because AN and urea are both used as fertilizer and are often mixed and stored together or alternately shipped in shared transportation and storage containers, the card-gap testing included mixtures of AN and urea. The card-gap sensitivity of a 20% urea/80% AN mixture was positive at 2.3 in, showing a narrow range of detonability and a sharp maximum when the go/no-go boundary was plotted in a card gap vs. composition diagram.

The conditions under which AN can be brought to a state of sustained detonation by incidental and explosive derived shocks were determined, especially under conditions of fire exposure [511, 512]. The results indicated that the shock sensitivity of molten AN increased exponentially from 493 to 533 K (220 to 260 °C), at which point the shock sensitivity approached that of nitroglycerine-based dynamites. Subsequently, critical parameters for low-amplitude shock initiation of molten AN and AN fertilizer solutions were determined in a series of experiments [513].

Ammonium nitrate has been modified with non-explosive additives to prevent its use in illegitimate, clandestine bomb making. The thermal stability of normal AN and anti-explosive additive-treated AN (AEAN) was examined using accelerating rate calorimetry, and apparent activation energy and pre-exponential factor were calculated. The cap sensitivity of ANFO made with normal AN and with AEAN was com-

pared in field tests. AEAN/FO did not detonate. The elimination of AEAN explosive characteristic was assumed to be due to the improvement of its thermal stability [379, 380].

2.8.5 Friction Sensitivity of Ammonium Nitrate

Pure AN by itself is not friction sensitive. In the BAM friction sensitivity tester, no reaction was detected at the upper limit load of the machine at up to 353 N pistil load.

The friction sensitivity of AN/fuel oil or AN/paraffin mixtures culminates at 0.75–1.5% hydrocarbon. This is below the stoichiometric ratio where one would expect maximum sensitivity. This has been explained by the hydrocarbon sensitizing the AN at low concentrations but lubricating the mixture at higher concentrations. AN/hydrocarbon mixtures are still much less sensitive than corresponding AP/hydrocarbon mixtures.

In a round-robin test of AN friction sensitivity performed by four different laboratories with the BAM friction apparatus, all participants found AN to be insensitive to friction at the maximum load of the machine (353 N = 37 kg_f) [72]. RDX and PETN were tested on the same equipment for comparison and calibration.

2.8.6 Electrostatic Discharge Sensitivity of Ammonium Nitrate

There was concern that AN dust formed during pulverizing, pouring, pneumatic feeding, or mixing of AN may carry electrostatic charges that might accumulate and cause accidental ignition. The electrostatic charge buildup of modified AN dust, based on a continuous mixing operation of modified AN explosive, was simulated, and the electrostatic charge in the pneumatic airflow transportation process was measured [514]. Experimental data indicated that although the gas–solid concentration and the discharge voltage were quite high, AN did not ignite. The results showed that the electrostatic spark sensitivity of modified AN was E_{50} 2074 mJ, and the minimum electrostatic ignition energy was 1104 mJ. It was concluded that the modified AN dust was resistant to electrostatic discharges in the pneumatic airflow transportation process.

In a round-robin test of AN electrostatic discharge sensitivity performed by four different laboratories with custom-built apparatus, 20 negatives out of 20 tests were achieved at 0.12–0.32 J, but incipient reaction occurred with discharges of 0.31–0.85 J [72].

2.8.7 Bullet-Impact Sensitivity of Ammonium Nitrate

Fertilizer storage adjacent to areas open for public hunting may be subject to unintended stray bullets. In other instances, fragments from one exploding AN container may hit an adjacent container in a case of fratricide. The projectile-impact sensitivity of AN was tested in a T-shaped test fixture holding 2 kg of AN where the projectile first had to penetrate a 1/8-in-thick aluminum front plate [510]. The results demon-

strated that AN, as hot prills or liquid, could be initiated to an apparent detonation by bullet impact if the bullet had sufficient velocity. In the temperature range of 373–413 K (100–140 °C), the prills were initiated, and it was possible to obtain 50% velocities under elevated temperature conditions. Projectile velocity was varied from 800 to 3500 m/s, and the velocities at which half of the tests resulted in explosions were 1000–1500 m/s. See also [515].

2.8.8 Cook-off and Bonfire Tests with Ammonium Nitrate

Several incidents have occurred in which AN that was involved in a fire exploded. The specific hazardous properties are determined by the physical properties (particle size, porosity, density), chemical properties (stabilizers, moisture), and environmental factors (confinement, contamination, temperature, and pressure) of AN [516]. Molten AN is somewhat unique among explosive compounds in that its density can be varied by either raising or lowering the temperature in the fluid, especially at temperatures higher than 483 K (210 °C). Confinement and/or contamination appear to be important parameters for causing an AN explosion by the action of heat alone.

In addition to studying the possibility of AN explosions initiated by simple burning, the initiation of detonation by shocks derived from nearby gas explosions or from projectile impact was investigated as a function of temperature and charge diameter [510]. The burning of raw or contaminated AN under pressure did not lead to explosions. No transition from burning to detonation was experienced in burning AN. The critical diameter for detonation of fertilizer-grade AN was quite small when the AN was preheated to temperatures just below its melting point. Transitions from burning to detonation were observed in AN intimately mixed with fuels such as polyethylene, paper, or fuel oil when these materials were contained in vessels with restricted vents. AN by itself was heated in 4-ft-diameter vessels with various orifice sizes ranging in diameter from 1/8 in to 3/4 in. In many cases the sample decomposed for 100–150 ms with little pressure increase, but then the rapid pressure increase would burst the vessel. It was concluded that the initiation of detonation in AN from fire exposure in normal storage and during transportation accidents is unlikely. A flashover explosion in an adjacent compartment where pyrolysis gases from pyrolyzed solid combustibles accumulate and then ignite and explode may be strong enough to initiate the hot AN. Because AN and urea are both used as fertilizer and are often stored together or alternately shipped and stored in shared containers, the bonfire testing included mixtures of AN and urea.

A modified vented pipe test was used to study the cook-off behavior of AN prills, AN suspensions in water, and AN emulsions, with the samples filled to three-quarters full in a steel container with an array of thermocouples and heated from below with a propane burner [517]. The apparatus would typically hold 28 kg AN. Pure AN decomposed without venting or explosion in the modified vented pipe test.

Self-sustaining decomposition (SSD) of AN and AN fertilizer blends is often a pre-stage to explosion. Based on the consequence analysis of SSD, early detection of decomposition in storage warehouses and proper temperature control in the manufacturing process is important [63]. SSD and oxidizing properties were found in AN/KN compositions where the K3 phase exists. It was assumed that potassium nitrate forms a solid matrix in which AN can decompose. A high bulk density is of key importance for detonation resistance.

Ammonium nitrate under fire exposure is a well-established explosion hazard and has been responsible for some of the greatest industrial accidents to date. The investigative literature on AN thermolysis is reviewed in [518]. Morphology, decomposition pathways, and the shock sensitivity of AN are influenced by elevated temperatures and heating rates. However, researchers have never been able to induce explosion in pure AN under controlled conditions by heat alone. Here, other factors play an important part. Of these, confinement stands out as a key determinant. Elevated pressure increases gas–solid-phase interactions under decomposition, promoting exothermic behavior, even for pure AN. This is an important feature to consider if bulk amounts of AN are subjected to fire. Due to the endothermic behavior of AN dissociation, however, AN is in most cases a relatively stable compound even when heated. Strictly defined conditions are necessary for achievement of deflagration-to-detonation transitions or just deflagration alone [497]. Heat exposure is the most obvious, generic, and critical cause of explosion in any fire-related AN explosion.

2.9 Explosive Performance of Ammonium Nitrate

Ever since the Texas City disaster in 1947, the detonability of AN by itself and of AN with various contaminants and additives has undergone thorough examination. For the rocket propellant chemist, the main concern is the accidental detonability of AN while it is being made, stored, shipped, or processed into rocket propellants, and a later concern is the bulk detonation properties of AN-based rocket propellants and gas generants in the field under various conditions of energetic stimuli. See also [519].

2.9.1 Detonation Velocity of Ammonium Nitrate Detonations

The detonation velocity of AN detonations is mostly of academic interest, but it also relates to the detonation velocity of AN-based blasting agents such as ANFO. There is no relationship between the detonation velocity of AN in explosives and the strand-burning velocity of AN in rocket propellants. Nevertheless, some of the information on detonation of AN is presented here because it may help to explain AN accidents.

A reactive force-field parametrization initially developed for nitramine/TATB explosives was optimized to reproduce electronic structure calculations for dissociation barriers, heats of formation, and crystal structure properties of AN phases [520]. With

this tool, the isothermal pressure-volume curve and the unreacted principal Hugoniot states of AN were predicted. The predicted isothermal pressure-volume curve for phase IV solid AN agreed with electronic structure calculations and experimental data within 10% for the considered range of compression. The predicted unreacted principal Hugoniot states were approximately 17% stiffer than experimental measurements. A simulated thermal decomposition during heating to 2500 K agreed with experimental findings.

2.9.2 Detonation Velocity of Ammonium Nitrate/Fuel-Mixture Detonations

There are hundreds of patents on ANFO-type explosives, which we do not include in our collection. We are interested only in AN/fuel mixtures that can potentially be used as rocket propellants. A mixture of AN with hydrocarbons (ANFO explosive) does not burn (slow strand burn) below at least 40 MPa, whereas addition of 4% charcoal results in a mixture capable of strand burning at 1.7 MPa. The effect of organic fuels (guanidinium nitrate, mannitol, sorbitol, PETN) on detonation parameters of AN mixtures has been measured [521].

2.9.3 Critical Density of Ammonium Nitrate Detonations

Explosives can be classified into two types: For compounds of the first type, which includes high explosives (TNT, RDX, and others), the detonation velocity (D) increases linearly with an increase in density (ρ). Explosives of the second type are characterized by **non**-monotonic dependence $D = f(\rho)$. The detonation velocity for those substances first increases with density and then passes through a maximum, and then detonation fails to propagate past a certain distance from the booster. These explosives of the second type are referred to as *non-ideal* explosives and include individual chemical compounds (AN, AP, ADN, nitroguanidine, and HN) and many explosive compositions of the oxidant/fuel type. The reasons for such a behavior of $D = f(\rho)$ for individual explosives and explosive compositions are different [522].

2.9.3.1 Critical Density of Ammonium Nitrate/Solid Fuel–Mixture Detonations

We are interested only in the accidental detonation behavior of AN-based rocket propellants and gas generants that were not supposed to be detonable as designed but that may become detonable if not properly formulated or if they are exposed to extreme stimuli or have deteriorated during aging. The detonability of mixtures of AN with liquid fuels (such as ANFO, which is for a different business) will be discussed but only in passing.

Ammonium nitrate in mixtures with urea makes a very good garden fertilizer. The effect of urea on the detonation characteristics of AN was investigated [327]. The thermal sensitivity and shock sensitivity of the samples were examined using the Koenen test and the UN gap test. It turned out that 50AN-50urea mixtures can still produce

a steady detonation in the UN gap test. Addition of less than 50% urea cannot reduce the ability of AN to propagate a detonation.

2.9.3.2 Critical Diameter of Ammonium Nitrate Detonations

The detonation of technical-grade AN at the density $\rho = 0.666 \text{ g/cm}^3$ confined in PVC and steel tubes was studied experimentally [523]. The results showed that the detonation is self-sustained and steady in steel tubes with diameters as small as 12 mm. Critical detonation diameter lies between 8 and 12 mm in 2-mm-thick steel tubes and between 55 and 81 mm in PVC tubes. These values are indicative of a strong detonation sensitivity of this product. The results are dependent on the packing density of the material. Figure 29 shows the critical diameter of unconfined prilled AN as a function of the packing density [524].

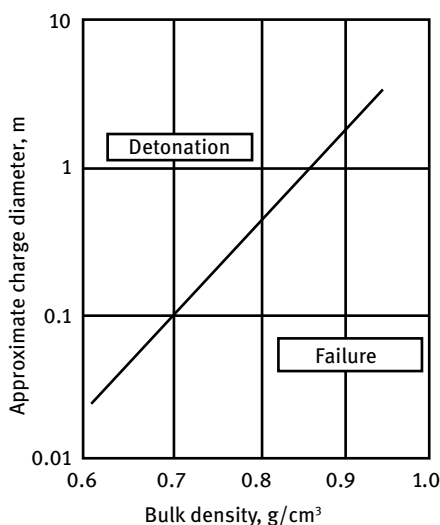


Figure 29: Critical diameter of unconfined AN as a function of packing density. (Reproduced and modified from [524].)

Critical Diameter of Ammonium Nitrate/Solid Fuel–Mixture Detonations

In order to obtain a better understanding of detonation properties of AN and activated carbon (AC) mixtures, a series of steel tube tests with several different diameters was carried out for various compositions of powdered AN and AC mixtures, and the influence of the charge diameter on the detonation velocity was investigated [525]. The test results indicated that the detonation velocity increased with the increase of the charge diameter (as expected). The experimentally observed values were far below the theoretically predicted values made by the thermohydrodynamic CHEETAH code, and they showed so-called non-ideal detonation. When extrapolating the detonation velocity of stoichiometric compositions to infinite diameter samples, the numbers showed good agreement with the theoretical values. Mixtures of AN with AC and

Al were extensively used as military and commercial explosives under the designation “ammonal.”

2.9.4 Explosive Yield of Ammonium Nitrate

The explosive yield of AN by itself is not very good. Most explosive applications will use mixtures of AN with combustible organics (fuel oil, wax, sawdust) to improve the explosive yield. The Trauzl lead block indentation of dry AN by itself can be as high as $180\text{ cm}^3/10\text{ g}$. Lead block indentation tests of commercial-grade AN fertilizer samples were conducted before and after normal and accelerated aging and temperature cycling [526].

A 10-g charge of AN in a Trauzl lead block can be detonated completely by a No. 8 blasting cap, but detonation was not complete with a No. 6 cap, and with smaller caps no detonation occurred. The Trauzl block cavity volume increase was about 165 cm^3 .

2.9.5 Velocity and Critical Diameter of Ammonium Nitrate Detonations

Detonation velocities ranged from 1200 to 1900 m/s when AN was loaded at density of $0.65\text{--}1.0\text{ g/cm}^3$ in wrought-iron tubes having diameters of 2.5–10 cm and the charges were detonated by means of boosters consisting of 50–300 g of tetryl or picric acid (PA). Detonations of AN were observed only when the charge diameter (“limit charge diameter”) was greater than 80–100 mm (Table 29). When heavy confinement casings, such as concrete, were used, or when explosions were under water, the limit charge diameter decreased to 30–40 mm [527].

Table 29: Detonation velocity of ammonium nitrate at room temperature.

Density g/cm ³	Charge diameter mm	Confinement	Initiation charge No. 8 cap plus:	Detonation velocity m/s
0.69	50	Steel tube	100 g PA	1230
0.84	25	Steel tube	50 g tetryl	1310
0.83	26	Steel tube	60 g tetryl	1470
0.79	80	Steel tube	100 g PA	1530
0.88	80	Steel tube	100 g PA	1550
0.84	100	Steel tube	200 g PA	1820
0.64	100	Steel tube	100 g PA	1920

Data source: [527, 528]

A later investigation [529] measured the detonation velocity of pure AN (as well as of its mixtures with TNT and with Composition B) as a function of charge diameter. A hand-tamped charge of AN in paper tubing with a diameter of 12.72 cm failed to detonate. Average rates in larger-diameter paper tubes were as listed in Table 30. In a different test,

rates of detonation of pure AN packed in steel tubes at an approximate packing density of 0.96 g/cm^3 were 2570 m/s in 12.7-cm (5-in)–inner-diameter (ID) tubes and 1681 m/s in 10-cm (4-in)–ID tubes, but there was failure to propagate in 7.5-cm (3-in)–ID tubes. The rate of detonation of AN increases with increasing diameter of the charge, and if the diameter is great enough, unconfined AN can detonate, but then the rate decreases with increased distance from the initiator and the process eventually “fizzles out.”

Table 30: Detonation velocity of ammonium nitrate in large-diameter charges.

Charge diameter cm	Detonation velocity m/s
16.0	1300
19.99	1500
25.4	1750
35.7	2150
40.4	2360
46.0	2760

Data source: [529]

It has been known for many years that AN, even when free from combustible material, can detonate. This is not surprising, since the products of decomposition must be entirely gaseous and have substantially less energy of formation than the original substance. For example, if the nitrogen is not oxidized, the energy released at constant volume, with water in the vapor phase, is 1590 J/g (380 cal/g) or 8.7 kcal per mol of gas. This is rather low compared with typical values for explosives, which lie in the range of $20\text{--}50 \text{ kcal/mol}$ gas. One might expect the substance to detonate with difficulty and only under good confinement. For normal AN at bulk densities around 1 g/cm^3 , cartridge diameters of many inches or heavy metal tubes are necessary to achieve detonation, and even then the measured speeds are much lower than the maximum values calculated for products $\text{N}_2 + 2\text{H}_2\text{O} + \frac{1}{2}\text{O}_2$. This has led some authors to conclude that an equilibrium involving oxides of nitrogen is more appropriate and that the release of energy is of the order of 962 J/g (230 cal/g) [530].

Detonation velocity and pressure of low-density prilled AN was measured in steel tubes of varying diameters and wall thicknesses [531]. Tube diameter had a much more pronounced effect on detonability than the confinement. The detonation velocity and pressure extrapolated to infinite diameter were 3.85 km/s and 3.2 GPa , respectively, which were in agreement with predicted ideal detonation parameters from the TIGER computer code.

2.10 Toxicity of Ammonium Nitrate

2.10.1 Oral Toxicity of Ammonium Nitrate

For most people, the highest probability of daily nitrate exposure is through its natural occurrence in vegetables, particularly beets, celery, lettuce, parsley, broccoli, carrots, radishes, rhubarb, spinach, melons, and turnip greens. These vegetables accumulate nitrates, including AN because of its natural occurrence and agricultural application as a fertilizer.

Another potential source of nitrate is drinking water. Drinking water coming from private wells, particularly in agricultural areas, can be contaminated with higher levels of nitrates, primarily from fertilizer runoff, animal manure, and human sewage from septic tanks. Tolerable nitrate levels are regulated in public water supplies. The U.S. Environmental Protection Agency has established a limit of 1 ppm for nitrite and 10 mg/L for nitrate. See also [532].

2.11 Ammonium Nitrate–Based Rocket Propellants

Formulations and processing of AN-based rocket propellants will be described in detail in planned future volumes of the *Encyclopedia of Rocket Propellants*. Here we only summarize the properties and applications of AN as an oxidizer.

One of the first summary publications on AN as a rocket propellant has now been declassified [533]. This is a real classic, but some of the problems with AN first recognized in 1954 persist to this date.

As of 1994, a commercial source for propulsion-grade AN (PROGRAN), a stabilized, controlled-particle-size AN suitable for the formulation of propellants and gas generants, was available at Nobel Explosives Co. in the United Kingdom [534].

Ammonium nitrate promises to be an environmentally-friendly oxidizer in gas generators and propellants. Ammonium perchlorate, which is the workhorse oxidizer in composite propellants, may need to be replaced because of its environmental and human health issues. In this context, AN is regarded as an alternative to AP because it is readily available and its combustion products are environmentally friendly and chlorine free. However, AN has its own inherent drawbacks, such as hygroscopicity, room-temperature phase transition, and low burning rate. Several aspects of polymorphism, phase stabilization, thermal decomposition, hygroscopicity, specific impulse, and burn-rate modification of AN have been reviewed, and ways to overcome the inherent weakness of AN as a propellant oxidizer to formulate more effective and less hazardous gas generant and propellant compositions were pointed out [535].

2.11.1 Ammonium Nitrate–Based Gas Generants

A continuing problem with all gas generant and propellant formulations based on AN is the prevention of AN phase changes. Incorporating AN into a binder matrix has very little effect on phase changes of AN and does not prevent them. Other additives, typically added to or co-crystallized with the AN before mixing it with a binder, are required to prevent swelling of the grains and delamination of the oxidizer–polymer bond as a result of temperature cycling. A substantial amount of experimental effort has gone into the development of AN-based gas generants for a variety of military and commercial applications. While the ready availability of AN and its low flame temperature make it attractive as a gas generant ingredient, the problems with unavoidable or only partially preventable phase changes have delayed their application.

2.11.2 Ammonium Nitrate–Based Explosives

Until the Oppau disaster in 1921, AN was not considered an explosive. Commercial AN-based explosives will contain a sensitizing agent (fuel, fuel oil, high explosive) to make it cap sensitive or at least booster sensitive as a blasting agent. Another method to sensitize AN is to make it highly porous (“self-sensitized”).

There are several thousand patents on AN-based explosives and blasting agents. Many of the patents are so similar to each other that one really wonders how they could wiggle their way through the patent office’s system without being rejected by the examiner or challenged by a competitor with earlier priority.

This book is about rocket propellants and not about explosives. In a few cases, explosives-derived know-how has come back to benefit propellant applications of AN, and that is why a few typical AN-based explosives and blasting agents are included here. The propellant formulator must know the limits between an energetic rocket propellant and an explosive. The propellant formulator must understand the explosive properties of AN/fuel mixtures before he or she can intelligently formulate an AN-based propellant. Propellant formulators often walk a fine line between making a good propellant and making a poor explosive. In some cases, the line may shift if large-scale energetic events are involved and the effect of the scale factor is forgotten. See also [536].

2.11.2.1 Porous Ammonium Nitrate–Based Explosives

Porous (“expanded”) AN can be made by rapid crystallization from supersaturated solutions (Section 2.2.3.2). Additional porosity is often added to AN-based blasting agents, slurries, and emulsions in the form of glass or plastic microballoons.

2.11.2.2 Ammonium Nitrate/Fuel Oil Explosives

There are hundreds of patents on ANFO-type explosives, which we do not include in our collection. We are interested only in AN/fuel mixtures that can potentially be used

as rocket propellants. A few studies on explosions of AN in mixtures with organics (mostly fuel oil) are included here because similar hazardous situations may occur during the mixing of AN-based propellants or gas generants in large-batch mixers. The test methods used to establish the safety of ANFO mixtures can also be used to measure the sensitivity of AN-based gas generants and propellants.

One report summarized results of tests on the sensitivity of various experimental explosive systems using AN as the oxidizing agent [537]. The sensitivity survey included drop-weight and friction testing and sensitivity to initiation by projectile impact and a No. 8 blasting cap. It was found that certain types of AN prills can result in cap-sensitive mixtures when combined with No. 2 diesel fuel (FO). Prilled AN mixed with nitromethane also resulted in cap-sensitive mixtures. Mixtures of prilled AN and neat 1-nitropropane and 2-nitropropane were not cap sensitive, and the use of powdered or grained aluminum in ANFO did not adversely affect the sensitivity, except possibly to increase its sensitivity to friction.

2.11.2.3 Ammonium Nitrate-Nitroalkane Explosives

Instead of using hydrocarbons with a high oxygen demand, explosives with a lower AN content can be formulated by replacing the alkanes with nitroalkanes, which bring some oxygen of their own and do not totally depend on AN as the oxidizer. Some of these nitroalkanes, such as nitromethane, may even be detonable on their own without the assistance of AN. AN/nitroalkane explosives may even be cap sensitive, thus eliminating the need for a booster charge in quarry-style or seismic exploration operations [538, 539]. The preferred mass ratio of AN to nitroethane is 80 : 20. A mixture containing 50.5% AN, 30% nitromethane, 10% H₂O, 5% urea, 2% microballoons, 2% nitrocellulose, and 0.5% guar gum had a detonation velocity of 5867 m/s in 3-in-diameter charges and 4663 m/s in 2-in-diameter charges. It did not crystallize at temperatures down to 285 K (12 °C), but it required a booster of at least 10 g of C-4 [540].

2.11.2.4 Ammonium Nitrate-Water-Gel Explosives

Another widely used category of AN-based explosives consists of those using AN mixtures with other alkali metal nitrates or alkaline earth-metal nitrates, with just enough water added to facilitate mixing and which are then emulsified with an organic fuel and stabilized by a gelling agent. Such liquid slurries can be easily pumped into boreholes at the blasting site and are relatively safe to handle. There are hundreds of patents on water-gel explosives and slurry explosives containing AN as the main ingredient.

2.11.2.5 Eutectic Ammonium Nitrate Explosives

The objective of developing eutectic AN melt-cast explosives was to find economical replacements for TNT in bomb fill and large-scale demolition tasks. Some of the eutectics developed for explosive applications are also of interest as solid propellants.

Although eutectics do not segregate during cooling, they do not totally avoid the troublesome expansion of AN as a result of temperature cycling.

Failure diameter and impact, thermal, and shock sensitivities for eutectic mixtures of AN with various additives have been measured [541, 542]. Compatibility of the eutectics with nitroguanidine (NQ) was unusually good, as shown by very little gas evolution with storage at elevated temperatures. Performance of mixtures of AN/ammonium 3,5-dinitro-1,2,4-triazolate (ADNT) with NQ, aluminum (Al), or EDDN/KN has been determined. Measurement of the irreversible growth of pressed pellets in which 15% of the AN was replaced by KN during temperature cycling showed that some grains swelled by 11 vol-% after temperature cycling.

2.11.2.6 Ammonium Nitrate/Metal Explosives

Any combustible metal will add sufficient energy to the AN decomposition reaction to make the mixtures detonable. For industrial applications, the preferred metal would be aluminum in the form of a fine powder.

Pure AN is not treated as an explosive compound, but a slight addition of organic or inorganic combustibles makes the mixtures capable of explosion. Experimental detonation tests focused on aluminum as the most effective sensitizer. Mixtures of AN or aqueous solutions or slurries of AN with aluminum (ammonals and hydro-ammonals) were studied using an electromagnetic method of measuring the mass velocity behind the detonation wave front, detonation parameters, and the shape of detonation waves in explosive mixtures [543].

2.11.3 Gas Generator Applications Based on Decomposition of Pure Ammonium Nitrate

A gas generator has been patented that consists of a solid grain of AN containing only insufficient binder or catalyst to sustain self-decomposition [544]. Decomposition in a pressurized chamber is initiated and controlled by a movable catalyst (a nichrome metal grid impregnated with a potassium dichromate catalyst) on a control rod that can be moved in and out of the proximity of the AN grain. The catalyst would be preheated by an electric heater to get the reaction started, or it might still be hot from a previous operation. This device can be restarted repeatedly, and the gas output can be controlled similarly to moving boron rods in and out of a nuclear reactor. The oxidizer-rich off-gas is kept at a temperature near 673 K (400 °C) to prevent condensation and then is fed to a bipropellant rocket engine, where it is combusted with a solid, liquid, or gaseous fuel (preferably a fuel hypergolic with the hot oxidizer-rich gas) to produce thrust. Lithium hydride in polyethylene would be one hypergolic fuel option. The device can be used for an astronaut hand-held maneuvering unit.

2.12 Ammonium Nitrite

Ammonium nitrite, NH_4NO_2 , CAS RN 13446-48-5, is the less oxygen-rich relative of AN, but it is much more reactive than AN. Ammonium nitrite occurs naturally in large quantities, but only in small concentrations, wherever ammonia-oxidizing bacteria are at work. Small quantities of ammonium nitrite may occur as contaminants in AN and adversely influence its thermal stability. Ammonium nitrite is not an oxidizer to use but rather an oxidizer to avoid in rocket propellants. The tolerable amount of ammonium nitrite in AN for propellant and explosive applications is limited by military specifications. Ammonium nitrite may also be an intermediate in the thermal decomposition of AN. For this reason, some information on ammonium nitrite is included in this book.

2.12.1 Physical Properties of Ammonium Nitrite

Nitrous acid (HONO) exists in *cis* and *trans* isomer modifications, and ammonium salts of the two acids have different properties, in particular different IR spectra [545].

The heat capacity of ammonium nitrite was measured between 13 and 310 K with an adiabatic calorimeter [546]. Two phase transitions were found at 181.3 and 276.5 K. The heat of formation of ammonium nitrite is -272 kJ/mol (-65 kcal/mol). The density of ammonium nitrite is 1.69 g/cm^3 .

2.12.2 Chemical Properties of Ammonium Nitrite

Ammonia is a weak base, and nitrous acid is a weak acid. The salt formed from the two compounds dissociates readily. Ammonium nitrite is highly unstable, both in a dry state and in concentrated aqueous solutions. When such solutions are used industrially for production of caprolactam, they are normally stored at a pH of 8–9 and a temperature of 278 K (5°C) or less. Ammonium nitrite decomposes in solution in the presence of acid or catalytic transition metal (e.g., chromium) ions. The military specifications for AN do not allow any detectable amount of ammonium nitrite in AN that is intended for use in explosives or propellants.

2.12.2.1 Thermal Decomposition of Ammonium Nitrite

A 0.25-g sample of NH_4NO_2 was decomposed completely after 2 min at 358–363 K ($85\text{--}90^\circ\text{C}$) or 9 min at 328–333 K ($55\text{--}60^\circ\text{C}$). Another sample of NH_4NO_2 was decomposed to 10% at room temperature after 6 weeks. Similar decomposition behavior is observed with hydrazinium nitrite and hydroxylammonium nitrite [547]. Ammonium dinitramide is substantially more stable than ammonium nitrite [548, 549].

2.12.2.2 Strand Burning of Ammonium Nitrite

Pressed samples of ammonium nitrite of 7-mm diameter are capable of burning even at subatmospheric pressure near 0.55 atm, while uncatalyzed AN will not burn at all at

atmospheric pressure [550, 551]. Similar to the relationship of the burning rates of ammonium chlorate and perchlorate, ammonium nitrite burns faster than AN containing a combustion catalyst (Figure 30).

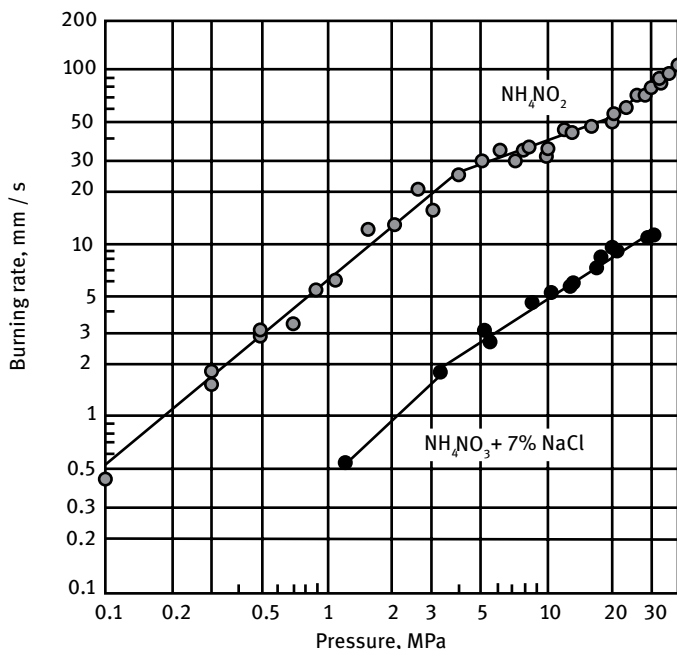


Figure 30: Comparison of strand-burning rates of ammonium nitrite and ammonium nitrate. (Reproduced and modified from [551]; Cent. Eur. J. Energ. Mater.; licensed under Creative Commons <https://creativecommons.org/licenses/by-nc-nd/4.0/>.)

The strand-burning rate of NH_4NO_2 can be described by a straight line with two breaks: $r_b = 5.97p^{1.05}$ at pressure 0.1–4 MPa, $r_b = 13.62p^{0.44}$ at 4–20 MPa, and $r_b = 2.57p^{1.01}$ at 20–40 MPa. The thermal stability of ammonium nitrite is less than that of AN. Its autoignition temperature is 362–363 K (89–90 °C). If one plots experimental points of the burning rate vs. the initial temperature at atmospheric pressure, the results match those predicted for a condensed-phase reaction and not those for a gas-phase reaction. The surface temperature (dissociation temperature) of burning NH_4NO_2 at atmospheric pressure is 440 K (167 °C), which is significantly less than the surface temperature of burning AN (580 K). The decomposition rate of NH_4NO_2 is almost five orders of magnitude higher than the rate of the rate-determining reaction of NH_4NO_3 combustion.

2.12.3 Handling-Safety Properties of Ammonium Nitrite

There are no industrial uses for ammonium nitrite. Only a few laboratories have ever had to prepare this substance for scientific studies. Solid ammonium nitrite is an explosive substance, and its preparation should be attempted only in properly equipped laboratories. It is sensitive to mechanical shock, friction, and rapid heating. The hazard properties and the critical diameter for propagation of detonations have been determined [552, 553].

The effect of traces of chromium compounds on the decomposition of ammonium nitrite solutions was studied under isothermic and non-isothermic conditions [554, 555]. It was found that such compounds catalyze the decomposition of ammonium nitrite more intensely than HCl. This led to the conclusion that contamination by even small amounts of such contaminants should be carefully avoided in industrial work with ammonium nitrite solutions in order to minimize the danger of explosive decomposition.

3 Metal Nitrates

3.1 Alkali Metal Nitrates

Although potassium nitrate is the oldest rocket propellant oxidizer, dating back almost a millennium to the early Chinese experiments with black powder, very little is written now about this chemical. There is ample information about potassium nitrate and the other alkali metal nitrates in other readily available sources, including handbooks, websites, and encyclopedias, so we can cut our discussion of this oxidizer

Table 31: Physical properties of alkali metal nitrates.

Compound name	Formula	Molecular mass g/mol	Total oxygen content, mass-% O	Available oxygen, mass-% O	Melting point		Density at °C g/cm ³	Enthalpy of formation	
			mass-% O	mass-% O	K	°C		kJ/mol	kcal/mol
Lithium nitrate	LiNO ₃	68.94	69.62	58.02	525	252	2.38 (25°)	-482.4	-115.3
Sodium nitrate	NaNO ₃	84.99	56.47	47.06	585	312	2.257	-424.7	-101.5
Potassium nitrate	KNO ₃	101.10	47.47	39.56	607	334	2.109 (16.0°)	-492.5	-117.7
For comparison:									
Ammonium nitrate	NH ₄ NO ₃	80.04	59.97	19.99	442.7	169.6	1.725 (25°)	-367.9 -365.6	-87.93

short. Potassium nitrate is used as a stabilizer for AN and is used in igniter mixtures, the most frequently used being potassium nitrate and boron with a shellac binder. Potassium nitrate and black powder are used in many display and safe-and-sane fireworks articles. The physical properties of alkali metal nitrates are summarized in Table 31. A few other nitrates are listed for comparison.

3.2 Alkaline Earth-Metal Nitrates

The physical properties of alkaline earth-metal nitrates are summarized in Table 32. A few other nitrates are listed for comparison. Most of these metal nitrates crystallize with two, four, or six molecules of water in the sphere of hydration, but for their use in pyrotechnic formulations they have to be used in the anhydrous state. In the anhydrous state, the salts are quite hygroscopic. Most alkaline earth-metal nitrates begin to decompose when heated, even before they melt.

Table 32: Physical properties of alkaline earth-metal nitrates.

Compound name	Formula	Molecular mass	Total oxygen content,	Available oxygen,	Melting point		Density at °C	Enthalpy of formation	
		g/mol	mass-% O	mass-% O					
Mag- nesium nitrate	Mg(NO ₃) ₂	148.32	64.72	54.0	—	—	—	−791	−188.97
Calcium nitrate	Ca(NO ₃) ₂	164.088	58.50	48.8	834	561	2.504	−938	−224.28
Stron- tium nitrate	Sr(NO ₃) ₂	211.63	45.36	37.9	843	570	2.986	−978	−233.8
Barium nitrate	Ba(NO ₃) ₂	261.337	36.73	30.7	865	592	3.24	−768	−183.6

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Nitric Oxide

1 General Comments about Nitrogen Oxides

Nitrogen commonly forms several different oxides with oxygen, depending on the state of oxidation of the central atom, nitrogen. The state of oxidation of nitrogen can be +1, +2, +3, +4, +5, or +6. This chapter is on nitric oxide, NO. Nitric oxide is one of the thermodynamically unstable oxides and has a tendency to decompose to dinitrogen and dioxygen.

Oxygen is the third most abundant element in the Universe after hydrogen and helium. Wherever it is available in the presence of nitrogen and exposed to cosmic radiation, one must assume that nitrogen oxides may form and condense in colder parts of the system. Therefore, nitrogen oxides, including nitric oxide, are expected to be present in the solid phase in giant gas planets and “icy” grain mantles of comets and interplanetary particles.

Coverage of nitrogen oxides had to be spread out over seven chapters because a single chapter devoted to the topic would have been unwieldy and made it more difficult for readers to find information on a specific compound; in addition, such an approach would have made it difficult to arrange 30 chapters among 5 subvolumes in such a way that each subvolume was about the same size. Briefer chapters made our task much easier. The other six chapters in this series are titled “Nitrogen Oxides,” “Nitrous Oxide,” “Dinitrogen Trioxide,” “Nitrogen Dioxide,” “Dinitrogen Tetroxide,” and “Dinitrogen Pentoxide.”

2 Nitric Oxide

Nitric oxide, NO, also called nitrogen(II) oxide, nitrogen monoxide, mononitrogen monoxide, and CAS RN [10102-43-9], is a colorless gas. As soon as it comes into contact with air (or oxygen) it becomes oxidized (autoxidized) to nitrogen dioxide, NO₂, a dark red gas, which makes a potential NO leak more visible and causes the gas to be more toxic if inhaled.

Nitric oxide, NO, is a free radical similar to NO₂ and is an important intermediate in the chemical industry. Nitric oxide is a byproduct of hot combustion processes in air, as in automobile and jet engines and fossil fuel power plants, and is produced naturally in electrical discharges of lightning in thunderstorms. In most cases, it autoxidizes in air in the presence of excess oxygen and converts to nitrogen dioxide as soon as it has cooled off. It is an essential part of the nitrogen cycle on Earth.

It is unlikely that nitric oxide, in particular liquid nitric oxide, will ever be used as a rocket propellant because of its explosion hazard. However, nitric oxide is needed for the preparation of mixed oxides of nitrogen and so must be included here in this

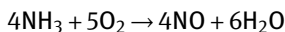
book on rocket propellants, even if it is rarely handled in its pure state. Exothermic nitric oxide decomposition has been used to create hot gases with a chemical composition similar to that of hot air for studies of ablation in simulating atmospheric reentry of space capsules in a high-temperature wind tunnel [1]. It was in the preparation for one of those experiments that a tank with liquid nitric oxide exploded and caused substantial damage. This accident triggered a series of safety investigations. Nitrous oxide had been evaluated for the same application. Nitric oxide has been used as a chemical laser propellant, and this book contains information on many other energetic chemicals that are of interest for chemical lasers as well as rocket propellants.

Nitric oxide is an intermediate in the production of dinitrogen tetroxide and nitric acid, widely used rocket propellant oxidizers. Nitric oxide and other oxides of nitrogen derived from it are important atmospheric pollutants and play a key role in atmospheric nitrogen chemistry relating to smog formation and ozone destruction. Therefore, the kinetics of NO formation and decomposition under the influence of a wide range of energy sources (heat, UV radiation, electron bombardment, gamma radiation, atomic oxygen collisions) have been extensively investigated. Some of these atmospheric chemistry studies contain information that is also useful for the handling and purity control of nitric oxide to be converted to rocket propellant. The main mechanism of abiotic atmospheric nitrogen fixation, converting dinitrogen to a form that can be digested by all plants (even those without nitrogen-fixing *azotobacter* bacteria in their root nodules) is through nitric oxide formed in lightning strikes.

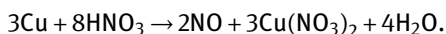
Nitric oxide is one of the few chemicals that has an entire journal title and a society dedicated to its chemistry, mostly for its role as a signaling chemical in nerve conduction. *Nitric Oxide* (ISSN 1089-8603) is a peer-reviewed scientific journal of the Nitric Oxide Society. The journal covers the broad field of nitric oxide research and includes basic and clinical topics such as cell biology, molecular biology, biochemistry, immunology, pathology, genetics, physiology, pharmacology, and disease processes. Nitric oxide is a vasodilator, and well-known blood-pressure-lowering pharmaceuticals such as nitroglycerin and amyl nitrite are precursors to nitric oxide in the bloodstream.

3 Preparation of Nitric Oxide

The predominant method for the production of nitric oxide is the catalytic combustion of ammonia over a platinum gauze (Ostwald process):



but under the conditions of this process, the nitric oxide is immediately oxidized with additional oxygen to form nitrogen dioxide, which is then absorbed in water to form nitric acid. For the preparation of small amounts of NO in the laboratory, a convenient method is the reaction of copper shavings with nitric acid:



It sometimes helps to purify the NO before converting it to NO₂ [2]. This report also describes methods for the detection and measurement of residual impurities in the final products.

4 Physical Properties of Nitric Oxide

4.1 Freezing Point and Phase Behavior of Nitric Oxide

Table 1 gives a summary of various freezing point (melting point) and boiling point data reported for nitric oxide in the literature.

Table 1: Freezing point (melting point) and boiling point of nitric oxide.

Property	Temperature		Author	Year
	K	°C		
Melting point	109.49	−163.66	Johnston and Giauque [3]	1929
	109.88	−163.27	Goldschmidt [4]	1923
Boiling point	121.36	−151.79	Johnston and Giauque [3]	1929
	121.87	−151.28	Goldschmidt [4]	1923

The triple point temperature of nitric oxide is at 109.49 ± 0.05 K, and the triple point pressure is 16.438 ± 0.004 cm Hg.

4.1.1 Phase Behavior at Very High Pressures

At pressures above 1.5 GPa, NO undergoes a disproportionation reaction, leading to N₂O and N₂O₄. At even higher pressures, many nitrogen oxides transform to a remarkably stable isomer, nitrosonium nitrate NO⁺NO₃[−]. It was not possible to extend thermal conductivity measurement beyond 13.76 MPa (2000 psia) because of incipient disproportionation of NO into NO₂ and N₂.

The chemistry of nitric oxide under static high-pressure conditions has been studied using diamond anvil cells and spectroscopic methods [5, 6]. Pressurized samples that were warmed rapidly to room temperature underwent facile disproportionation to form N₂O, N₂O₃, N₂O₄, and NO⁺NO₃[−]. Nitric oxide maintained at 80 K was observed to react at ca. 2.5 GPa to form N₂O and NO⁺NO₃[−]. The complex chemistry of nitric oxide is best explained in terms of two competing primary reaction mechanisms: **(1)** direct formation of N₂ and O₂ and **(2)** disproportionation to form N₂O and NO⁺NO₃[−]. The disproportionation reaction, which is favored under higher-temperature conditions, releases two-thirds of the total energy content and is believed to be important in the early chemistry accompanying shock-initiated detonation of nitric oxide.

4.2 Density of Nitric Oxide

The density of gaseous nitric oxide at 298 K is 1.3402 g/L, and the density of liquid nitric oxide at 123 K (−150.2 °C) is 1.269 g/mL. The density of frozen nitric oxide at 78 K is 1.556 g/cm³ [7].

4.3 Compressibility of Gaseous Nitric Oxide

The virial coefficients B of the equation of state

$$PV = RT + BP$$

were determined for nitric oxide and nitrous oxide [8]. The virial coefficient B of nitric oxide in the temperature range 121 to 307 K as a function of temperature and pressure can be expressed by the equation

$$B = 20 + 5881.5/T - 5.7639 \times 10^6/T^2 + 8.4301 \times 10^{10}/T^4 - 9.2783 \times 10^{14}/T^6$$

where B is the virial coefficient in cm³/mol, and T is the temperature in kelvin. Later examination by other investigators showed that the Johnston and Weimer [8] values for N₂O were consistently too low and for NO the values were consistently too high. Vapor density and compressibility measurements of NO at high pressures and temperatures near the boiling point were performed in an effort to determine whether NO associates to a dimer under those conditions. PVT measurements alone were not able to conclusively answer that question. The unusually steep rise in the heat capacity curve of liquid nitric oxide indicated that dissociation of the polymerized molecules was proceeding rapidly in the liquid phase just below the boiling point. This made it unlikely (although not impossible) that any appreciable trace of association remained in the gas phase because of the much lower concentration of the molecules in the latter.

4.4 Vapor Pressure of Nitric Oxide

The sublimation vapor pressure of frozen nitric oxide in a range between 65 K = −208 °C = 0.5 μm Hg and 95 K = −178 °C = 10 mm Hg pressure can be expressed by the following equation:

$$\log P = -(877.2/T) + 10.2368$$

where P is the vapor pressure in mm Hg, and T is the temperature in kelvin [9].

The vapor pressure of frozen nitric oxide can be calculated from the following equation [3]:

$$\log p = -867/T + 0.00076T + 9.05125$$

where p is the pressure in cm Hg (intl.) and T is the temperature in kelvin, and for liquid nitric oxide:

$$\log p = -776/T - 0.002364T + 8.562128$$

where again p is the pressure in cm Hg (intl.) and T is the temperature in kelvin. See also [8].

4.5 Viscosity of Nitric Oxide

The viscosities of gaseous nitric oxide (372–1015 K) and gaseous nitrous oxide (372–733 K) were measured using a capillary-flow viscometer in comparative mode, calibrating the instrument with nitrogen gas [10]. Smoothed viscosity data for nitric oxide are shown in Table 2.

Table 2: Smoothed dynamic viscosity data for gaseous nitric oxide.

Temperature K	Dynamic viscosity		
	mPa s	$\mu\text{N s m}^{-2}$	μPs
400	0.02405	24.05	240.5
500	0.02855	28.55	285.5
600	0.03266	32.66	326.6
700	0.03644	36.44	364.4
800	0.03996	39.96	399.6
900	0.04326	43.26	432.6
1000	0.04637	46.37	463.7

Data source: [10]

The viscosity of gaseous nitric oxide as a function of temperature can be expressed by the equation

$$\eta = \frac{aT^{1/2}}{1 + b/T + c/T^2}$$

where η is the viscosity in $\mu\text{N s m}^{-2}$, T is the temperature in kelvin, and a , b , and c are constants: $a = 1.740 \mu\text{N s m}^{-2} \text{ K}^{-1/2}$, $b = 191.9 \text{ K}$, and $c = -5276 \text{ K}^2$. See also [11].

4.6 Surface Tension of Nitric Oxide

An application of the corresponding states principle to the surface tension of nitric oxide can provide an interpretation of the unique surface tension behavior of NO: the

surface tension decreases when the temperature increases, as expected, but it does so at a substantially higher rate than is usually observed with other substances [12].

The surface tension of three binary liquid mixtures of NO with Kr, CH₄, and C₂H₄ was determined in the temperature range 102 to 119 K, depending on the ability of the molecules of one component to associate with each other [13]. The surface tension of liquid nitrous oxide as a function of temperature can be expressed by the equation

$$\eta = 69.72 - 0.3840 T$$

where η is the surface tension in mN/m, and T is the temperature in kelvin. This work also contained the surface tensions of the pure compounds (Table 3). Mixtures of NO with hydrocarbons would probably be detonable, but nowhere do the authors alert the reader to this potential hazard. It seems the apparatus was still in one piece at the time they finished their surface tension measurements. See also [14].

Table 3: Surface tension of liquid nitric oxide.

Temperature, K	Surface tension, mN/m
112.6	26.51
113.0	26.33
113.5	26.12
114.1	25.88
115.0	25.61
116.0	25.14
117.4	24.55
118.7	24.12
120.1	23.64
121.0	23.28

Data source: [13]

4.7 Velocity of Sound in Nitric Oxide

The velocity of sound in gaseous $\text{N}_2\text{O}_2 \rightleftharpoons 2\text{NO}$ was determined at various temperatures [15]. The velocity of sound data obtained were used to calculate the mol fractions of N_2O_2 and NO in the $\text{N}_2\text{O}_2 \rightleftharpoons 2\text{NO}$ mixtures. From these data the equilibrium constants of dimerization were calculated for the system at various temperatures and compared to the literature. The $\text{N}_2\text{O}_2 \rightleftharpoons 2\text{NO}$ system was studied at approximately 270 K (3 °C). With a tube length of 0.986 m and a travel time of 6.14 ms (for twice the distance of the tube), the velocity in $\text{N}_2\text{O}_2 \rightleftharpoons 2\text{NO}$ was determined to be 321.2 m/s. At this temperature, it was determined that the system was 95% monomeric NO. At a pressure of 22.3 Pa (168.0 mm Hg), the K_p was determined to be 3.99 atm.

4.8 Thermal Conductivity of Gaseous Nitric Oxide

A section in *Encyclopedia of Oxidizers*, in the chapter “Nitrous Oxide,” lists the thermal conductivities of nitric oxide at atmospheric pressure for a temperature range from 120 to 380 K in comparison to those of nitrous oxide and dioxygen, based on data from [16].

The thermal conductivity of gaseous nitric oxide was determined in an apparatus that consisted of two concentric spherical shells whose temperatures were measured while a known radial thermal flux passed between them [17]. Figure 1 illustrates the effect of pressure and temperature on the thermal conductivity of nitric oxide. It was not possible to extend the data measurement beyond 6.88 MPa (1000 psia) at 444 K (171.1 °C = 340 °F) or 13.76 MPa (2000 psia) at 277.6 K (4.44 °C = 40 °F) because of incipient disproportionation of NO into NO₂ and N₂.

The thermal conductivity of liquid nitric oxide at its normal boiling point was estimated to be 0.176 W m⁻¹ K⁻¹ (4.2×10^{-4} cal s⁻¹ cm⁻¹ °C⁻¹) [18].

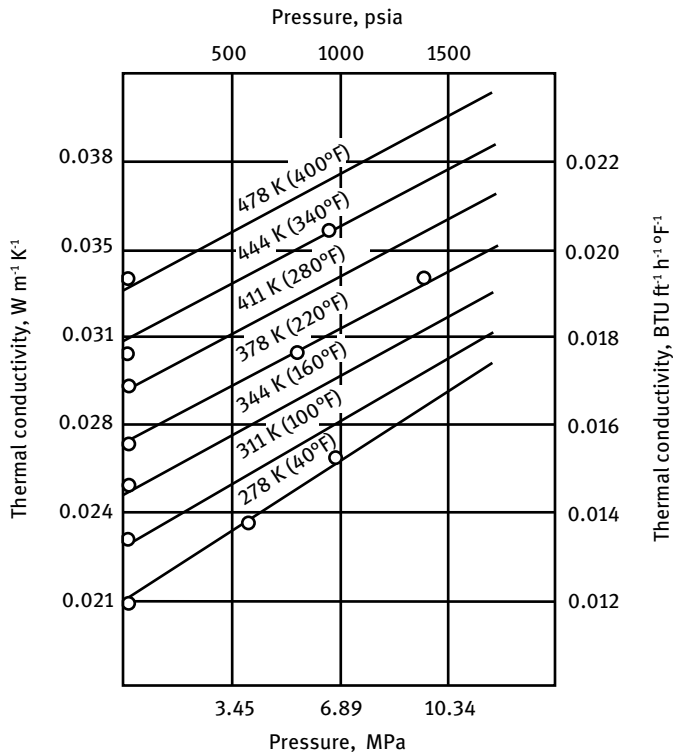


Figure 1: Effect of pressure and temperature on thermal conductivity of gaseous nitric oxide. (Reproduced and modified from [17].)

4.9 Thermodynamic Properties of Nitric Oxide

A complete set of thermodynamic data for nitric oxide can be downloaded from the NIST Chemistry WebBook web site [19]. Another set of data is available in the JANNAF tables.

4.9.1 Heat Capacity of Nitric Oxide

The heat capacity of gaseous nitric oxide as a function of temperature can be expressed by the Shomate equation

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + E/\tau^2$$

where C_p is the heat capacity in $\text{J mol}^{-1} \text{K}^{-1}$, τ is the temperature in kelvin divided by 1000: $\tau = \text{K}/1000$, and A, B, C, D, and E are constants listed in Table 4 for two different temperature ranges.

Table 4: Thermodynamic property polynomial equation coefficients for nitric oxide gas.

Temperature range, K	298–1200	1200–6000
A	23.83491	35.99169
B	12.58878	0.957170
C	−1.139011	−0.148032
D	−1.497459	0.009974
E	0.214194	−3.004088
F	83.35783	73.10787
G	237.1219	246.1619
H	90.29114	90.29114

Data source: [19]

Uncorrected, raw heat capacity data for solid and liquid nitric oxide are listed in Table 5.

4.9.2 Enthalpy of Formation of Nitric Oxide

The standard enthalpy of formation of gaseous nitric oxide is $+90.29 \text{ kJ/mol} = +21.58 \text{ kcal/mol}$ (JANAF). A positive enthalpy of formation explains the explosive potential of liquid and gaseous nitric oxide, which has been the cause of industrial accidents during isotope separation and hot gas generation for supersonic wind tunnels. The standard enthalpy of formation of gaseous nitric oxide as a function of temperature can be expressed by the equation

$$H^\circ - H^\circ_{298.15} = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{\tau} + F - H$$

Table 5: Uncorrected heat capacity data for solid and liquid nitric oxide.

Physical state	Temperature, K	Heat capacity, cal mol ⁻¹ °C ⁻¹	Heat capacity, J mol ⁻¹ K ⁻¹
Solid	15.57	0.935	3.912
	17.75	1.303	5.452
	19.51	1.59	6.653
	22.27	1.964	8.217
	25.36	2.389	9.996
	28.59	2.807	11.744
	32.08	3.274	13.698
	35.50	3.691	15.443
	39.20	4.06	16.987
	43.51	4.481	18.749
	48.16	4.895	20.481
	52.64	5.543	23.192
	57.25	5.686	23.790
	62.32	6.016	25.171
	67.90	6.392	26.744
	73.24	6.76	28.284
	78.84	7.158	29.949
	83.83	7.516	31.447
	88.96	7.795	32.614
	94.04	8.13	34.016
	98.51	8.397	35.133
	102.55	8.713	36.455
	106.39	9.033	37.794
	106.65	9.12	38.158
	108.39	9.456	39.564
Liquid	112.81	16.067	67.224
	114.01	16.362	68.459
	115.79	16.915	70.772
	117.35	17.329	72.505
	118.86	17.935	75.040
	120.56	18.667	78.103

Data source: [3]

where H° is the standard enthalpy in J mol⁻¹, τ is the temperature in kelvin divided by 1000: $\tau = K/1000$, and A, B, C, D, E, F, and H are constants listed in Table 4 for two temperature ranges. See also [20].

4.9.3 Heat of Fusion of Nitric Oxide

The heat of fusion of nitric oxide at its natural melting point (109.49 K = -163.66 °C) is 2299 ± 4 J/mol (549.5 ± 1 cal/mol) [3].

4.9.4 Heat of Evaporation of Nitric Oxide

The heat of evaporation of nitric oxide at its normal boiling point (121.36 K) is 13.776 ± 0.014 kJ/mol (3292.6 ± 3.3 cal/mol) [3].

4.9.5 Entropy of Nitric Oxide

The standard entropy of gaseous nitric oxide as a function of temperature can be expressed by the equation

$$S^\circ = A \times \ln(\tau) + B\tau + \frac{C\tau^2}{2} + \frac{D\tau^3}{3} - E/(2\tau^2) + G$$

where S° is the standard entropy in $\text{J mol}^{-1} \text{K}^{-1}$, τ is the temperature in kelvin divided by 1000: $\tau = K/1000$, and A, B, C, D, E, and G are constants listed in Table 4 for two temperature ranges. The entropy of gaseous NO at 298 K and 1 bar is $210.76 \text{ J mol}^{-1} \text{K}^{-1}$.

4.10 Molecular Properties, Structure, Dipole Moment, Molecular Orbital Calculations of Nitric Oxide

4.10.1 Molecular Structure of Nitric Oxide and Its Dimer

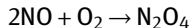
It is not commonly known that nitric oxide forms a dimer in the liquid state, dinitrogen dioxide, similar to dinitrogen tetroxide, but with a weaker association between the two molecules. The dimers of molecules that exist in monomer and dimer forms are also called homodimers. The study of the molecular structure of NO is revealing because NO is one of the simplest molecules capable of forming dimers but not larger aggregates. This compound is known to be moderately associated in the gaseous state but to be wholly dimerized in the solid and partially associated in the liquid states. The question of the dimerization of nitric oxide in the gas phase was first examined in the light of the principle of corresponding states, applied to the second virial coefficient. This dimerization is expressed in some physical properties, such as surface tension of liquid nitric oxide.

The molecular structure of NO and its dimer have been thoroughly investigated, mainly for its involvement in atmospheric pollution and natural nitrogen fixation, but also in the hope of identifying more energetic forms of NO and its oligomers that might be stable enough to be used as rocket propellants. The N_2O_2 dimer has been studied more extensively due to the discovery that NO regulates many physiological processes in the body. Some investigators have examined N_2O_2 dissociation energy while others have concentrated on the method and shape of bonding or critical point properties.

The existence of the $(\text{NO})_2$ dimer has long been invoked from anomalous Pressure-Volume-Temperature (PVT) behavior, thermodynamic properties, and second virial coefficient measurements. Its IR, Raman, UV, X-ray diffraction, and mass spectra have been observed. It was determined that N_2O_2 does in fact exist and is a very flexible molecule [21]. From the temperature dependence of the IR

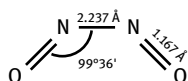
and UV intensities, obtained in liquid NO at temperatures in the range 100–140 K, the heat of dimerization was measured as -2.45 ± 0.2 kcal/mol (115–126 K) and -2.25 ± 0.1 kcal/mol (100–140 K), respectively.

It has been suggested that it is the NO dimer, N_2O_2 , that reacts with O_2 in the reaction



The dimer $(\text{NO})_2$ can also be detected at room temperature in compressed gaseous NO. From the temperature dependence of the UV absorption intensity the enthalpy change for the reaction $2\text{NO} \rightarrow (\text{NO})_2$ was calculated to be -4.48 ± 0.29 kJ/mol (-1.07 ± 0.07 kcal/mol) at 273–364 K, and the standard enthalpy of formation would be $\Delta H_f^{316} = 176.1 \pm 0.5$ kJ/mol (42.09 ± 0.11 kcal/mol) [20].

Microwave and radiofrequency spectra for $(\text{NO})_2$ using the technique of molecular beam electric resonance spectroscopy were used to determine rotational, nuclear quadrupole coupling and spin-rotation constants of the ground electronic state treated as a singlet state [22]. From these data $(\text{NO})_2$ was interpreted to have a symmetric *cis*-planar trapezoidal shaped structure with the structural parameters $r_{\text{N}-\text{N}} = 2.33(12)$ Å, $r_{\text{N}-\text{O}} = 1.15(1)$ Å, $\angle \text{NNO} = 95(5)^\circ$. The long N–N bond is the weakest bond in this molecule.



The quadrupole coupling constants of the nitrogen nuclei and the dipole moment indicated that little electron rearrangement occurs on dimer formation. The spin-rotation constants of the dimer were larger than expected; this fact can be rationalized in terms of low lying electronic states. See also [23, 24].

The origin of the long N–N bond in the C_{a2v} isomer of N_2O_2 was modeled by *ab initio* valence bond calculations [25]. The very long N–N bond in this isomer is associated mostly with the nature of the hybridization and the orientation of the lone-pair atomic orbitals on each nitrogen atom. The optimum forms of the two orbitals have a large 2s component and overlap appreciably when the N–N internuclear separation is close to that of a normal single bond. The associated strong non-bonded repulsions that exist between the nitrogen lone-pair electrons lengthen the N–N bond. At N–N distances close to the equilibrium value (2.237 Å), the orbitals that form the N–N σ bond are almost entirely 2p in character and oriented at right angles to the N–O bond axes.

One of the postulated structures for the NO dimer is isoelectronic with dicyclobutane. Based on this similarity, attempts have been made to predict the stability of $(\text{NO})_2$ by computational chemistry [26].

Density functional theory and *ab initio* quantum chemistry methods were used to predict the structures and energetics of neutral and anionic N_2O_2 species [27]. When going from a neutral NO dimer to an anionic species the N–N bond lengths were pre-

dicted to decrease drastically and the corresponding N—N frequencies would increase. The relative stabilities of the different N_2O_2^- isomers suggested an ONNO structure in a *trans* configuration to be the most stable monovalent anion. The total energy of the hyponitrite ion, $\text{N}_2\text{O}_2^{2-}$, was expected to be 2.7–2.8 eV above the total energy of N_2O_2^- .

The binding energy of the NO dimer has been measured directly using velocity-mapped ion imaging [28]. The NO dimer was photodissociated to produce NO(X) and NO(A), and the NO(A) was then non-resonantly ionized to NO^+ . The threshold for the production of NO^+ ions was measured at $44893 \pm 2 \text{ cm}^{-1}$, which corresponds to a binding energy of $696 \pm 4 \text{ cm}^{-1}$.

The continuing interest in high-energy nitrogen oxides has arisen due to their potential applications as new high energy density materials (HEDM). To be useful as potential rocket propellants, metastable species must be rather high in energy relative to their more stable isomers and to potential decomposition products (e.g., $\text{NO} + \text{NO}$, $\text{N}_2 + \text{O}_2$, $\text{N} + \text{NO}_2$, or $\text{N}_2\text{O} + \text{O}$ in the case of N_2O_2). In addition to a large thermodynamic exothermicity, these species must be kinetically stable, both adiabatically (that is, relative to an energy barrier on a singlet potential energy surface) and non-adiabatically (so that decomposition via coupling to a repulsive, e.g., triplet state is unlikely). In looking for better oxidizers, several high-energy isomers of N_2O_2 were examined, with particular emphasis on the molecular structure, fundamentals of bonding and energetics relative to decomposition products [29]. The only isomer of N_2O_2 that has been characterized experimentally is the weakly bound *cis* ONNO dimer, which lies 1–2 kcal/mol lower than $\text{NO} + \text{NO}$. Figure 2 illustrates other potential structures for the N_2O_2 molecule, some with substantially higher energy than the *cis* ONNO dimer, with the calculated energy levels below each image. Five high-energy minima were located above 2NO with relative energies (in kcal/mol) indicated below each image. The four-membered ring structure (**1**) has N—O = 1.351 Å, O—O = 1.398 Å and an N—N distance essentially identical to the N=N double bond in $\text{HN}=\text{NH}$. The 1,3-diazo-2,4-dioxal[1.1.0]-bicyclobutane structure (**5**) is a minimum on

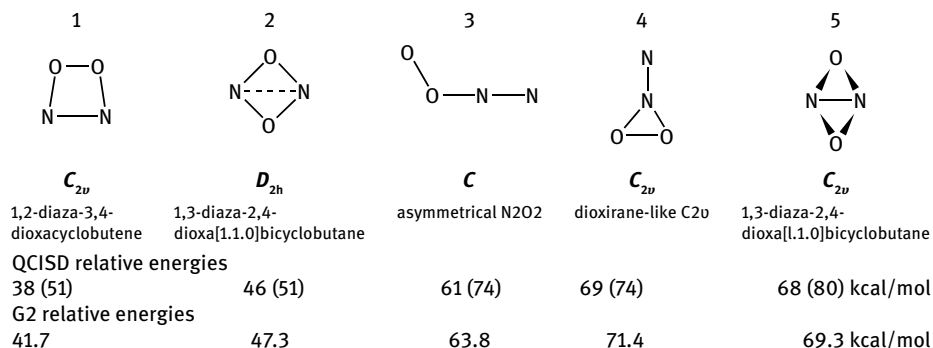


Figure 2: Potential structures and calculated energy levels for the N_2O_2 molecule. (Reproduced and modified from [29].)

the SCF potential energy surface. This C_{2v} structure possesses an N—N bond (1.322 Å) that is shorter than the N—N single bond in hydrazine (1.426 Å, H_2N-NH_2) and longer than the N=N double bond in diimide ($HN=NH$, 1.216 Å), at the same level of theory.

A tetramer of NO has been postulated and predicted by theoretical calculations, but the experimental proof is lacking. The ground-state properties of $(NO)_2$ and $(NO)_4$ have been investigated using multi-reference second-order perturbation theory (MRMP2) [30]. For the NO dimer, the MRMP2-predicted structure, binding energy (with respect to $2NO$; $D_e = 14.48 \text{ kJ/mol} = 3.46 \text{ kcal/mol}$), and dipole moment ($\mu_e = 0.169 \text{ D}$) were in excellent agreement with experimental measurements, where a range of data was shown ($D_e = 11.7\text{--}15.9 \text{ kJ/mol} = 2.8\text{--}3.8 \text{ kcal/mol}$; $\mu_e = 0.171 \text{ D}$). Probing the possibility of the presence of higher-order clusters, the stability of $(NO)_4$ was investigated and the calculation results indicated the possibility of three isomers, each resembling pairs of dimers, that were stable to dissociation to $2(NO)_2$, with the lowest-energy isomer (C_i structure) having a predicted binding energy almost identical to that of the dimer. Experimental Raman and IR data going back to 1951 were reexamined and reassigned and indicated that the best predictions of vibrational frequencies of $(NO)_2$ and $(NO)_4$ were consistent with experimental observations.

Photolysis of N_2O in an argon matrix deposited on an IR-transparent window resulted in the formation of asymmetrical N_2O_2 having the structural formula $O-O-N-N$, which has been named asymmetric dinitrogen dioxide [31]. An absorption peak at a frequency of about 1220 cm^{-1} , which falls within the region of predicted N—O stretch frequency for $asym-N_2O_2$, was present only after irradiation. See photolysis section in the chapter “Nitrous Oxide.”

IR and Raman spectroscopy are best suited as characterizing techniques for studying the $1000\text{--}2400 \text{ cm}^{-1}$ range since most N—O stretches and all but the very weak N—N stretches occur in this frequency range. Moreover, even subtle changes in molecular bonding or conformation give rise to small frequency shifts that can be detected by vibrational spectroscopy. The approximate stretching frequencies expected for N—O, N—N, and O—O bonds or different bond orders may be deduced from the data for diatomic molecules and ions. Frequencies below 1000 cm^{-1} must also be considered when a comprehensive picture of the NO and NO_2 molecular systems is desired; in fact, certain stretching frequencies, such as the ν_0 at 480 cm^{-1} in ONON and the N—N at 241 cm^{-1} in $ONNO_2$, may occur in this region. Because nitric oxide has an odd electron, its electronic ground state is $^2\Pi$, which is split about 120 cm^{-1} by spin-orbit interaction into $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ components. As a result of this small energy separation, the gas-phase IR spectrum of NO is complex [32].

4.11 Optical Properties of Nitric Oxide

The electronic and vibration spectra of nitric oxide and related nitrogen oxides are summarized here in detail because in the search for higher-energy nitrogen oxides as rocket propellants, spectroscopy is the main tool to look for elusive, short-lived species that could potentially be stabilized under suitable (e.g., cryogenic) conditions. This spectroscopy topic has been thoroughly investigated owing to the participation of NO and related oxides in atmospheric chemistry.

4.11.1 Ultraviolet Spectra of Nitric Oxide

At pressures less than 150 mm Hg the only NO absorption found down to 2200 Å was the 0–1 band of the γ system [33]. At higher pressures a strong continuous absorption setting in at about 2600 Å made observation at shorter wavelengths impossible. No discrete NO absorption was observed above 2600 Å at a pressure of 700 mm Hg, above 2500 Å at 300-mm Hg pressure, or above 2400 Å at 150-mm Hg pressure. The dimer $(\text{NO})_2$ can be detected at room temperature in compressed gaseous NO. From the temperature and pressure dependence of the UV absorption intensity (Figure 3) the enthalpy change for the reaction $2\text{NO} \rightarrow (\text{NO})_2$ and the standard enthalpy of for-

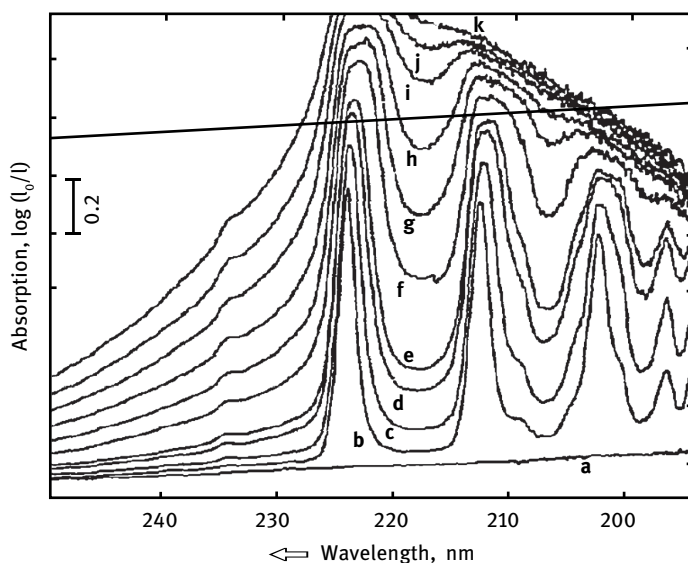


Figure 3: UV spectrum of gaseous NO and $(\text{NO})_2$ at several different pressures of NO at 298 K.

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Legend: (a) baseline; (b) 1.03 atm; (c) 1.79 atm; (d) 2.54 atm; (e) 3.2 atm; (f) 4.06 atm; (g) 4.89 atm; (h) 5.72 atm; (i) 6.48 atm; (j) 7.23 atm; (k) 7.99 atm.

mation could be obtained [20]. The effective decadic molar extinction coefficient of the dimer is $E \leq 3.6 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ at 199 nm.

The short-wavelength end of the UV spectrum of NO is the ionization limit. This process takes place in the upper atmosphere. Recombination of the dissociated species leads to fluorescence.

The absorption spectrum of liquid NO was also obtained through a 3-cm path length at 121 K (-152°C), with a tungsten filament as source [33]. A strong continuous absorption starting at 4000 Å and extending to shorter wavelengths and one at 5600 Å and extending to longer wavelengths were observed. Maximum transmission occurred at around 4600 Å. Since liquid NO is completely associated, the strong violet and red cut-offs are most likely due to N_2O_2 molecules.

The far UV continuum of nitric oxide was assigned to the dimer based on four points of experimental evidence [34]: **(1)** the intensity of the spectrum is proportional to $[\text{NO}]_2$; **(2)** the possibility that the carrier may be some other known oxide of nitrogen was eliminated; **(3)** from the temperature dependence the enthalpy change accompanying dissociation was 9.37 kJ/mol (2.24 kcal/mol) (100–140 K), in good agreement with 19.04 kJ/mol (2.4 kcal/mol) deduced from the dimer IR intensities; **(4)** approximate upper and lower limits to the dissociation constant, and the temperature dependence, were consistent with calculations based on the principle of corresponding states. The dissociation free energy of the dimer is 1.6 kcal/mol. The dimer continuum exhibits a maximum at 2050 Å.

The absorption spectrum of cold NO gas was photographed at high resolution between 1400 and 1250 Å for two isotopic species [35]. Resolved bands of the Rydberg series converging to vibrational levels of the $1\Sigma^+$ ground state of NO^+ revealed X bands up to $n = 15$ and ns-X bands up to $n = 11$, all of which showed a sharp rotational structure.

The $(\text{NO})_2 v_1 + v_5$ photodissociation spectrum at $3624\text{--}3629 \text{ cm}^{-1}$ proved that photodissociation arises from the dimer [36]. This photodissociation can be compared to $\text{HN}_3 + h\nu \rightarrow \text{NH} + \text{N}_2$, which is discussed in the same paper.

The dissociation barrier of $(\text{NO})_2$ was calculated to be 10.5 kJ/mol (2.5 kcal/mol). Dissociation barriers of this size would indicate that this molecule would not be long-lived. This molecule might be synthesized and stored in a solid-state matrix, but calculations indicated that the gas-phase lifetime of this molecule would be small [37].

4.11.2 Infrared Spectra of Nitric Oxide

4.11.2.1 Infrared Spectra of Gaseous Nitric Oxide

The wide-range IR spectrum of gaseous nitric oxide is shown in Figure 4.

The absorption spectrum of the “heavy” isotopic nitric oxide molecule $^{15}\text{N}^{18}\text{O}$ was studied in the IR region under high resolution [39]. Wavelength measurements and analyses of the 1-0 band at 5.58μ and the 2-0 band at 2.81μ yielded the molecular constants. The linear dependence of the spin-orbit coupling constant A upon the vibra-

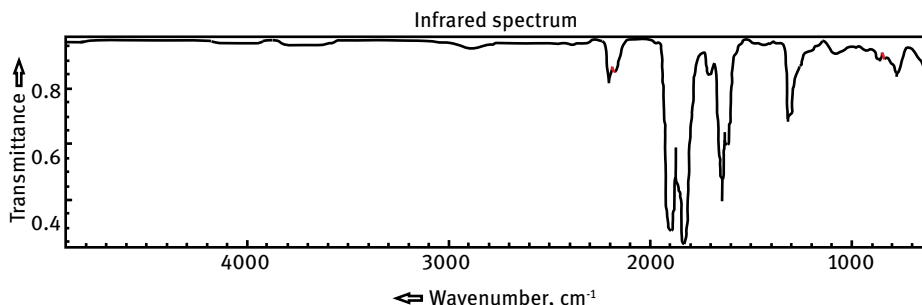


Figure 4: Wide-range IR spectrum of gaseous nitric oxide. (Reproduced and modified with permission from [38])

tional quantum number ν was similar to the results for other isotopic species of the nitric oxide molecule. An overlapping impurity band at 5.43μ was identified as the 1-0 band of $^{15}\text{N}^{16}\text{O}$. The theoretical vibrational and rotational isotopic relations were verified to within observational accuracy.

The IR spectrum of gaseous nitric oxide was examined from 4000 to 1600 cm^{-1} at temperatures between 77 and 150 K with a 3.9-m and a 6-cm path length cell [40]. Features found at 1860 and 1788 cm^{-1} exhibited a quadratic pressure dependence and were assigned to the dimer $(\text{NO})_2$. The band shape of these features indicated the presence of a *cis*- $(\text{NO})_2$ isomer. The heat of formation of $(\text{NO})_2$ from monomeric NO was estimated as $\Delta H = -10.25\text{ kJ/mol}$ (-2.45 kcal/mol).

The IR spectral absorptivity of nitric oxide gas has been measured at low resolution at temperatures ranging from 300 to 1200 K , while the optical path lengths were such that the resulting data fell in the transition to strong absorbing regions [41]. The results were correlated in terms of spectral mean (or narrow band) properties as well as wide-band properties. A total IR emissivity chart for NO was constructed using the results of the band absorptance correlation. This would be of interest where NO is an intermediate in combustion processes.

FTIR spectra of NO and NO_2 are used for the analysis of NO in mixed oxides of nitrogen (MON) [42]. The absorption peaks at 1887.5 , 1900.2 , and 1912.1 cm^{-1} were selected for the calibration curve.

4.11.2.2 Infrared Spectra of Frozen Nitric Oxide

The IR spectra of frozen nitric oxide, both in the pure state and at several dilutions trapped at liquid-helium temperatures in matrices of argon or carbon dioxide, were measured in a wavenumber range from 700 and 2000 cm^{-1} (14 to $5\mu\text{m}$) [43]. NO was found as the monomer and two forms of dimer, *cis* and *trans*; the *cis* is the more stable form. Four major bands were observed, all in the region broadly assigned to the $\text{N}=\text{O}$ stretch vibrations. In a *cis* form both the symmetric and asymmetric $\text{N}=\text{O}$ stretching

modes would be IR-active but in a *trans* form only the asymmetric mode would be. The band at 1883 cm^{-1} was assigned to the nitric oxide monomer in a CO_2 matrix. The band at 1768 cm^{-1} (in solid NO or solid CO_2) was assigned to the asymmetrical vibration in the *cis* form of the dimer $(\text{NO})_2$, the band at 1862 cm^{-1} was assigned to the symmetrical vibration in the *cis* form of the dimer $(\text{NO})_2$, and the band at 1740 cm^{-1} was assigned to the asymmetrical vibration in the *trans* form of the dimer $(\text{NO})_2$.

Matrix-isolated $(\text{NO})_2$ was obtained by rapid deposition of NO/ N_2 mixtures on an optical window at 15 K, by limited diffusion of matrix-isolated NO at low temperatures, and by photochemical production of O atoms in an N_2O environment [44]. Experiments carried out using isotope-labeled ^{15}NO and N^{18}O samples indicated that *cis* and *trans* O—N—N—O and possibly another unstable *cis* form are produced.

During a near- and far-IR study of ^{14}NO — ^{14}NO and its isotopomers, ^{14}NO — ^{15}NO and ^{15}NO — ^{15}NO , isolated in an argon matrix, IR-active fundamental vibrational modes ν_1 , ν_2 , ν_3 , ν_5 , and ν_6 for each species of the dimer could be observed, as well as overtone bands $2\nu_1$ and $2\nu_5$, and combination bands $\nu_1 + \nu_5$, $\nu_1 + \nu_6$, $\nu_5 + \nu_6$, and $\nu_4 + \nu_5$ [45]. From knowledge of the 18 available frequencies of the 3 isotopic species, force constants for the *cis*-ON—NO were then calculated. The potential energy distribution calculated for each vibration showed that the ν_2 and ν_3 modes are strongly coupled and that there is no pure N—N stretching mode.

4.11.3 Raman Spectra of Nitric Oxide

The IR and Raman spectra of liquid and solid nitric oxide were measured in an attempt to prove the existence of the $(\text{NO})_2$ dimer molecule [46]. The liquid has four strong Raman lines at 1861 , 262 , 196 , and 167 cm^{-1} , two weaker Raman lines at 1760 and 487 cm^{-1} , and two strong IR bands at 1863 and 1770 cm^{-1} . Several weaker IR bands could be tentatively assigned as combinations using the observed strong IR and Raman frequencies. The spectra were found to be due exclusively to a dimer that probably exists as a bent ONNO molecule.

The Raman spectra of $(^{14}\text{NO})_2$ and $(^{15}\text{NO})_2$ and the far-IR spectra of $(^{14}\text{NO})_2$ at 20 K were measured in order to identify the bond strengths of the dimer [47]. The band wavenumbers were assigned on the basis of a C_{2v} molecular model, and normal coordinate calculations were performed for a variety of assignments. The vibrational mode assignment that yielded the best fit was selected for further study.

Infrared and Raman spectra of polycrystalline samples of dimeric nitric oxide N_2O_2 were measured between 18 and 80 K, and several new low-frequency peaks could be observed [48]. The Raman spectrum of the liquid at 115 K was measured in an attempt to distinguish between vibration characteristics of the dimerized molecule and of the lattice.

4.12 Magnetic Properties of Nitric Oxide

Using a specially designed cryostat, the magnetic susceptibility of liquid nitric oxide was measured by both the Faraday method and the Gouy method [49]. A temperature variation of susceptibility was found corresponding to an equilibrium dissociation of feebly magnetic dimer molecules into paramagnetic monomers. Measurements of the susceptibility of liquid nitric oxide-liquid krypton mixtures were used to estimate the contribution of the $(\text{NO})_2$ molecule, which was found to be about 0.026×10^{-2} per mol of $(\text{NO})_2$. The degree of dissociation of liquid nitric oxide varied from 2.7% at 110 K to 5% at 120 K and the heat of dissociation of the dimer was found to be $15.52 \pm 0.62 \text{ kJ/mol}$ ($3710 \pm 150 \text{ cal/mol}$).

4.13 Solubility of Nitric Oxide

The solubility of NO in N_2O_4 is due to the formation of N_2O_3 . The two (three) nitrogen oxides are miscible over the entire range of compositions.

The solubility of NO in water and blood is a key property for the biological activity of this compound in nerve signal transmission and blood pressure regulation.

In all cases where the solubility of NO is investigated, one must take precautions to avoid contact with air or dissolved oxygen, which might cause the formation of NO_2 and disturb the solubility measurements.

5 Chemical Properties of Nitric Oxide

5.1 Autoxidation of Nitric Oxide

The most prominent property of nitric oxide is its autoxidation as soon as it comes into contact with air. This reaction has been the key to the historical Birkeland process for industrial production of nitric acid from air by passing air through an electric arc discharge. For a long time, this process has been a major source of urgently needed fertilizer to increase agricultural production and feed the hungry among the world's increasing population, until the Haber-Bosch process made ammonia the prevalent method of atmospheric nitrogen fixation for fertilizers. Ammonia can be used as a fertilizer or converted to nitric oxide, nitrogen dioxide, and nitric acid by air-oxidation over a platinum catalyst.

We were not quite sure whether the heading of the current section should be "Autoxidation" or just plain "Oxidation," but we decided that "Autoxidation" better described this property of nitric oxide. The autoxidation of nitric oxide plays an important role in atmospheric air pollution. Consequently, the majority of published studies describing the autoxidation of nitric oxide were done in connection with and support

of air pollution research. Considerable effort has been devoted to the removal of nitric oxide from combustion products in stationary or mobile power plants before it has a chance to escape to the atmosphere and oxidize itself to nitrogen dioxide. NO and NO_x removal from combustion products can be done by reduction or decomposition or oxidation and wet absorption in a scrubber.

Pressurant gases vented from MON storage and propellant transfer containers contain varying amounts of NO, which must be oxidized to NO₂ before they can be washed out in a scrubber before the pressurant gases can be vented to the atmosphere. In designing NO_x scrubbers at launch facilities, the rate of autoxidation of NO in the presence of additional air provided must be known.

Dinitrogen tetroxide and nitric acid and their mixtures are important storable rocket propellant oxidizers. All nitrogen in those two oxidizers has at one point or another gone through the intermediate stage of nitric oxide. This is why nitric oxide reactions are of importance for rocket propellants.

5.1.1 Kinetics of Nitric Oxide Autoxidation

The autoxidation reaction of NO takes place in polluted atmospheres and is instrumental in the formation of smog. It is also a key step in the industrial production of NO₂, N₂O₄, and HNO₃.

The thermal oxidation of nitric oxide at very low concentrations in the parts-per-million range has been investigated under simulated atmospheric conditions by long-path IR spectrophotometry [50]. At 293 K (20 °C), the reaction followed pseudo second-order kinetics with a rate constant of $(2.0 \pm 0.1) \times 10^{41.2} \text{ mol}^{-2} \text{ s}^{-1}$, defined by

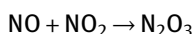
$$k = -d[\text{NO}]/dt = K[\text{NO}]^2[\text{O}_2].$$

Excess water vapor and the presence of different surfaces had no apparent effect on the order or the rate constant. Removal of nitrogen dioxide from the gas phase was attributed largely to adsorption on silicon monoxide and chromium-plated surfaces. The rate of adsorption is increased by the presence of nitric oxide and water vapor in the gas phase.

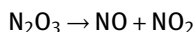
The reaction between molecular oxygen and two nitric oxide(II) molecules was modeled with high-level *ab initio* wave function computational chemistry methods, including geometry optimizations with coupled cluster and complete active space with second-order perturbation theory levels [51]. The best calculated estimate of the activation energy of this reaction was 6.47 kJ/mol.

5.1.2 Reaction of Nitric Oxide with Nitrogen Dioxide

Dinitrogen trioxide, the most important ingredient of MON, is made by the reaction of nitric oxide with nitrogen dioxide



and MON is a mixture of dinitrogen trioxide and dinitrogen tetroxide. MON is an important rocket propellant oxidizer, which is why the reaction between NO_2 and NO should be discussed here in a book on rocket propellants. It is important that MON chemical composition should not change when it is transferred from one container to another while loading a spacecraft with propellants or while pressurizing and depressurizing a propellant tank. However, the foregoing reaction is an equilibrium and the reverse reaction,



the dissociation of dinitrogen trioxide into its constituents, is just as likely to occur at higher temperatures. Each time a pressurized MON tank is vented, it preferentially loses some of the NO and the composition of the liquid phase shifts. If MON lost all its NO and N_2O_3 , the remaining oxidizer would be more corrosive and become capable of stress corrosion of titanium and stainless-steel tanks.

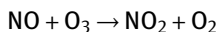
The gas-phase reaction of nitric oxide with nitrogen dioxide occurs on a global scale in the upper atmosphere, although only a trace of dinitrogen trioxide can be detected at any moment because dinitrogen trioxide exists mostly in the liquid state and not in the vapor state.

The liquid-phase reaction of nitric oxide with nitrogen dioxide (or dinitrogen tetroxide) is important to rocket propellant chemists who are about to make MON usable as a rocket propellant.

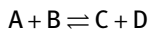
The section on absorption spectra of N_2O_3 (the chapter “Dinitrogen Trioxide”) contains more information on the reaction of nitric oxide with nitrogen dioxide and the dissociation of dinitrogen trioxide.

5.1.3 Reaction of Nitric Oxide with Ozone

The rate of reaction between nitric oxide and ozone that occurs in the ozonosphere was followed optically at 230 and 198 K (-43 and -75°C) [52]. The reaction appeared to be elementary bimolecular



and the rate constant was $k = 0.8 \times 10^{12} e^{-2500/RT} \text{ mol}^{-1} \text{ s}^{-1}$. The preexponential factor for this reaction was compared with those of six other elementary gas-phase reactions of the type



involving the oxides of nitrogen for which the energies of activation were higher. For this series of similar reactions the molecular complexity of the reactants was about constant (five or six atoms), and there appeared to be no systematic difference in pre-exponential factor between the fast and slow reactions.

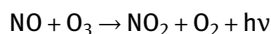
5.2 Combustion Sustained by Nitric Oxide as an Oxidizer

An attempt was made to use liquid nitric oxide as an oxidizer with non-hypergolic fuels such as kerosene JP-4 and methanol, but the poor reactivity required a very long $L^*38.4\text{ m}$ (!) engine and very long dwell times in the reaction chamber [53, 54]. It was impossible to achieve ignition with JP-4, and with methanol the engine sputtered.

5.3 Analysis of Nitric Oxide

Analytical methods are needed to determine the concentration of NO (or N_2O_3) in mixed oxides of nitrogen and in ambient air.

Nitric oxide concentration in air can be determined using a chemiluminescent reaction involving ozone: A gas sample containing nitric oxide is mixed with an excess of ozone in air. The nitric oxide reacts with the ozone to produce oxygen and nitrogen dioxide. This reaction also produces light (chemiluminescence), which can be measured with a photodetector. The amount of light produced is proportional to the amount of nitric oxide in the sample.



Other methods of analysis include electroanalysis (amperometric approach), where NO reacts with an electrode to induce a current or voltage change.

5.4 Decomposition and Thermal Stability of Nitric Oxide

Under the conditions of an electric discharge in air, nitric oxide decomposes just as fast as it forms. Only if the heated air is rapidly quenched can useful amounts of nitric oxide be obtained, as was once done on a commercial scale in the Birkeland process for making nitric acid from air.

The standard enthalpy of formation of gaseous nitric oxide is $+90.29\text{ kJ/mol}$. Note that the enthalpy of formation is positive, similar to that of nitrous oxide or other monopropellants. The decomposition of NO for removal from combustion products can be achieved thermally and/or by contact with a catalyst, preferably in the presence of a reducing gas like ammonia or hydrazine. This is the basis of industrial denox flue gas denitrification processes, also called selective catalytic reduction. The kinetics of NO and NO_x removal reactions have been investigated thoroughly and would fill a book by themselves. They have little relationship to reactions in rocket engines and are not discussed any further in this text.

5.4.1 Thermal Decomposition of Nitric Oxide

The effects of nitrogen and oxygen on the kinetics of decomposition of nitric oxide have been investigated [55]. In the temperature region in which the heterogeneous mechanism prevails (at $T < 1000$ K), the presence of nitrogen has a marked retarding influence on the reaction rate of nitric oxide due to poisoning of the surface. On the other hand, the addition of oxygen results in a marked increase in the rate of decomposition of nitric oxide over the entire temperature range studied. At high concentrations of oxygen the following empirical rate expression obtains:

$$-d[\text{NO}]/dt = k_a[\text{NO}]^2 + k_b[\text{NO}][\text{O}_2]^{1/2}$$

with an activation energy of 327 kJ/mol (78.2 kcal/mol) for the rate-determining step. The decomposition of nitric oxide is autocatalytic. On the basis of these experimental observations, a mechanism was proposed involving a chain reaction propagated by the atomic species formed in the reaction.

The thermal decomposition of pure nitric oxide and of mixtures with nitrogen or helium was studied in quartz vessels at 1170 to 1530 K [56]. Above about 1400 K, the reaction was homogeneous and cleanly second order in NO throughout the course of decomposition. A change in the surface-to-volume ratio left the rate unchanged, as did the addition of a fourfold excess of nitrogen or helium as a diluent. Above 1400 K, the activation energy was constant at 63.8 ± 0.6 kcal/mol.

The nitrogen oxide equilibrium was recalculated on the basis of the new spectroscopic value for the dissociation energy of dinitrogen [57]. Complete tables of the equilibrium composition were given in the temperature range up to 5000 K. The maximum amount of fixed nitrogen (at 1 atmosphere pressure and a nitrogen oxygen ratio as in natural air) is around 5 mol percent and occurs at a temperature of around 3500 K.

The decomposition of nitric oxide in a shock wave was studied in a shock tube in which the NO concentration was followed as a function of time behind the shock front by absorption of 1270 Å radiation, where ground vibrational states of reaction products O_2 and N_2 are essentially transparent [58]. The absorption coefficients of the species NO, O_2 , and N_2 as functions of the respective vibrational temperatures were determined by measuring the absorption by the shock-heated gas at a point in the time history corresponding to complete vibrational relaxation but before the onset of dissociation. Time history analyses were conducted on a total of 42 shock-tube runs covering a temperature range of 3000–8000 K on six mixtures of NO and air with argon.

Mixtures of NO in argon (0.01–5.0%) and NO with H_2 in argon (1% NO, 1% H_2) were passed through a ceramic flow tube reactor at temperatures between 1500 and 2100 K at atmospheric pressure [59]. A portion of the NO decomposed during its passage through the reactor. The fraction of initial NO leaving the reactor was monitored as a function of flow rate (or equivalently as a function of residence time in the reactor). The reactor temperature and gas composition were varied as experimental parameters. Five mixtures were used: 5% NO, 1% NO, 0.1% NO, 0.01% NO, and 1% NO/1% H_2 ,

all in a balance of argon. Theoretical models were developed for the chemically reacting flow and used to determine the rate constant values by parametric optimization. The rate constant for $\text{NO} + \text{O} \rightarrow \text{N} + \text{O}_2$ was found to be

$$k_2 = 1.72 \times 10^{9 \pm 0.1} T \exp(-38.64/RT)$$

in a temperature range between 1750 and 2100 K, and the rate constant for $\text{NO} + \text{H} \rightarrow \text{N} + \text{OH}$ was found to be

$$k_{10} = 1.74 \times 10^{14 \pm 0.2} \exp(-49.20/RT)$$

in a temperature range between 1750 and 2040 K. These results compared well with those of previous workers and were incorporated into least-squares curve fit analyses to yield rate constant expressions useful over a wide temperature range for both reactions.

5.4.2 Catalytic Decomposition of Nitric Oxide

It would be of interest to compare the decomposition of nitric oxide and nitrous oxide side by side in the same apparatus and with the same catalysts. If a small percentage of nitric oxide in nitrous oxide lowered the temperature above which the catalytic decomposition of nitrous oxide as a monopropellant becomes self-sustaining, this might expand the range of applications where nitrous oxide monopropellants can be used without having to preheat the catalyst. The same $\text{NO}/\text{N}_2\text{O}$ mixture could also be used as an oxidizer in hybrid or bipropellant engines.

A series of catalysts composed of barium oxide supported on magnesium oxide with Ba loadings up to 7 mol% has been studied for NO and N_2O decomposition [60]. Nitrous oxide is an intermediate in the decomposition of nitric oxide. With this particular catalyst, the rate of N_2O decomposition was much faster than that of NO decomposition. The ratio of activities may reverse for other catalysts. But it is not only the rate of decomposition but also the onset of exothermicity that would determine if NO addition to N_2O is helpful to speed up its decomposition or not.

5.4.3 Photolysis of Nitric Oxide

Nitric oxide is both formed from air and decomposed by intense UV radiation in the upper atmosphere and plays a key role in atmospheric chemistry, air pollution, and ozone destruction. The photolysis of nitric oxide and the recombination of N and O atoms are important chemical reactions in the Earth's atmosphere. Photolysis of NO and quenching of excited states may lead to more energetic oxidizers.

Electronically excited $\text{NO}(A^2\Sigma)$ was produced by irradiation with the 2144- and 2265-Å lines of a cadmium arc at NO pressures from 2.67 to 80 kPa (20 to 600 mm Hg) [61]. The products were nitrogen and nitrogen dioxide. A pressure drop accompanied the reaction equivalent to the nitrogen produced. The quantum yield of nitrogen formation was independent of irradiation time and incident intensity. These results,

when combined with radiative lifetime measurements, showed that removal of $\text{NO}(A^2\Sigma)$ occurred on nearly every collision.

At an even shorter wavelength of UV, NO was photolyzed at 1550–1650 Å using a hydrogen discharge and at 1470 and 1236 Å using xenon and krypton discharges, respectively [62]. The products at all wavelengths were N_2 and NO_2 . At 1470 Å small amounts of N_2O were detected. The quantum yield of N_2 increased over the nitric oxide pressure range 0.67–120 kPa (5–900 mm Hg) from around 0.2 to 0.5 and also with added inert gas. Quantum yields of NO_2 production and of NO decomposition increased in a similar manner, and the wavelength had no profound effect. Since 1236-Å light ionized NO, it was concluded that the recombination of NO^+ and an electron would lead to an excited molecule that decomposed, as it does at 1600 and at 1470 Å, into N and O atoms. These atoms reacted with excess NO, producing N_2 and NO_2 .

Photodissociation of NO in the middle and upper atmosphere was examined using a line-by-line approach to describe competitive absorption in the NO δ bands and O_2 Schumann-Runge bands [63]. A new analysis of O_2 absorption resulted in greater transmission of UV radiation in the Schumann-Runge (5–0) band in comparison with previous studies, leading to increased rates for photolysis of NO in the $\delta(0-0)$ band. Absorption in strong lines of the NO δ bands was shown to make a non-negligible contribution to atmospheric opacity at wavelengths that are important for NO photodissociation. Depending on variations in solar irradiance, photolysis rates at altitudes below 100 km may be smaller during a solar maximum compared to a solar minimum. Thus one must consider the effects of varying opacity by NO in the atmosphere.

Nitrous oxide, N_2O , is a natural source of stratospheric NO, where NO is formed by the photolysis of N_2O [64].

5.4.4 Microwave-Assisted Decomposition of Nitric Oxide

The decomposition of NO by a continuous or pulsed electrodeless microwave plasma discharge of NO/He or NO/Ar mixtures was studied at NO and rare-gas flow rates of 2–50 and 1000 standard cm^3/min , respectively [65]. Although a stable discharge could be maintained in a low total-pressure range of 0.13–46 kPa (1–350 mm Hg) for NO/He mixtures, stable microwave discharge could be maintained in the wide total-pressure range of 0.13–101 kPa (1–760 mm Hg) for NO/Ar mixtures at a microwave power of 200 W. The decomposition efficiency of NO was measured as a function of the microwave power and the NO flow rate in a continuous mode. Emission spectroscopic data gave information on the decomposition mechanism of NO in He and Ar discharges.

5.5 Detonability of Nitric Oxide

5.5.1 Detonability of Liquid Nitric Oxide

Nitric oxide is the simplest known molecule capable of detonation, detonating in all three phases.

At the former NASA Lewis Research Center, controlled nitric oxide decomposition in a reactor was once considered to generate hot air for high-speed supersonic wind tunnel tests, as a means of providing additional enthalpy to a heated air stream to achieve temperatures associated with flows at Mach numbers in a range of 8 to 9 [66]. The practice of storing NO in the liquid state was discontinued after one of the storage tanks with liquid NO exploded. Since storing and pumping liquid NO was preferred to handling it in the gas phase, it became necessary to characterize the detonability of NO in all three phases.

Potentially catastrophic explosions propagated in condensed-phase NO at temperatures near its normal boiling point during controlled detonation experiments [67]. At 101 and 303 kPa (1 and 3 atm) initial pressure, brisant (shattering) detonations occurred with velocities exceeding 5000 m/s and estimated peak pressures as high as 10 GPa (100000 atm). At an initial pressure of 2.32 MPa (23 atm), a less catastrophic explosion severely oxidized stainless steel and produced momentary pressure pulses estimated at 202 MPa (2000 atm). Propagation of the brisant detonations seemed to be associated with the presence of gas bubbles, either from NO vapor or from N₂ impurity. All explosion experiments were in vertical CRES 304 stainless-steel pipe, 52 mm i. d., 4 mm wall thickness, and 1220 mm length. All samples were initiated by the detonation of a 135-g RDX booster charge. A control experiment, done in the same way using liquid N₂O at 85 K, showed no evidence of oxidation or explosion. The RDX compressed solid booster charge was separated from the interior of the pipe by a sealed aluminum diaphragm. The initiation train was an Army Engineers-type electric detonator and a 22-g pellet of tetryl. The progress of explosions up the pipe was sensed by detectors shorting five horizontal pairs of parallel stainless-steel platelets inside the pipe positioned 76, 149, 294, 586, and 1168 mm above the diaphragm. A Cathode Ray Tube (CRT) oscillograph recorded the shorting events against time, to within 1 μs accuracy, as pulses on a raster display. Each station in the pipe was uniquely identified by pulse shape. Three copper-constantan thermocouples, each inside a coil of stainless-steel small-diameter tubing, were positioned inside the pipe above the 76-, 586-, and 1168-mm stations. Thermocouple data were read from a calibrated self-balancing indicating potentiometer using a reference junction in boiling nitrogen. The shorting sensors and thermocouples were held inside the pipe by stainless-steel plugs screwed into bosses leading through the pipe and cooling jacket.

Liquid nitric oxide has been distilled for a number of years to alter the ¹⁵N/¹⁴N isotope ratio in the production of ¹⁵N-labeled chemicals. An NO distillation system had been operated at Los Alamos National Lab (LANL) since 1963 with distillation units containing up to 40 kg of NO. An explosion occurred in January 1975 which involved

an estimated 50 g NO in one of the product collection traps. During the subsequent investigation, it was found that liquid NO is an extremely sensitive explosive [68]. The detonation velocity for the liquid at 115 K was estimated to be 5.62 ± 0.07 mm/ μ s and the detonation pressure as 100 kbar. The failure diameter for the liquid confined in stainless steel was between 4.6 and 3.1 mm. A high-pressure reaction, but not a detonation wave, propagated through a tube as narrow as 0.7 mm. At LANL, the failure diameter was determined by detonating the liquid in an assembly containing a series of stainless-steel tubes with the diameter decreasing in steps. Each section was either ten diameters long or 100 mm long, whichever was longer. The booster consisted of an SE-1 detonator, a 12.7-mm-long tetryl pellet and a 25-mm-diameter $\times$ 25-mm-long PBX-9404 charge with a 2.5-mm-thick stainless-steel barrier. In the first shot the inside diameters were 22.1, 18.9, 15.8, 12.6, 9.4, 6.2, 4.6, and 3.1 mm with a 1.65-mm wall thickness. No fragments were recovered from this assembly. The inside diameters in the second shot were 6.2, 4.6, 3.1, 1.6, 0.71, and 0.25 mm with wall thicknesses of 1.65, 1.65, 1.65, 0.25, 0.113, and 0.13 mm, respectively. The entire length of the 3.1-mm-diameter tube was recovered, but no fragments of the 4.6-mm-diameter tube were found. The 0.7-mm-diameter tube was ruptured.

A bullet impact sensitivity test of liquid NO showed that a violent reaction occurred in a 1.6-mm wall thickness, 76-mm outer diameter (OD) stainless-steel tube, 254 mm long filled to a depth of 100 mm with liquid NO when it was struck by a .30-cal bullet weighing 5.8 g and traveling at 451 m/s [69]. In a similar test no reaction occurred with nitromethane.

Liquid nitric oxide boiling at 121 K in a 406-mm-long steel pipe with a 26.64-mm inner diameter (ID) and 3.38-mm wall thickness, open to the atmosphere at the top and closed at the bottom with a 0.08-mm-thick Teflon membrane, when boosted with a 50-g tetryl donor, and with only the 0.08-mm Teflon as a gap, detonated at high velocity. High-velocity detonations were also obtained with attenuated shocks at 102- and 254-mm gap thicknesses. The average detonation rate of boiling NO was 5400 m/s [70]. Similar tests were conducted with non-boiling NO. See also [71–73].

Measurements of detonations of homogeneous liquid nitric oxide initially at $T = 119$ K and $\rho_0 = 1.28$ g/cm³ using plane-shock initiation in mirror-covered wedges demonstrated a detonation in preshocked material (superdetonation) that overtook the smooth input shock [74]. Its transverse irregularities continued in the unsupported detonation. The input shock ran approximately 3 mm at $u_1 = 3.8 \pm 0.2$ km/s. Behind it the fluid had $u_p = 0.89 \pm 0.02$ km/s, $p = 4.3 \pm 0.03$ GPa, and $\rho = 1.67 \pm 0.03$ g/cm³, and the superdetonation had $D^* \approx 6.9$ km/s. In 356-mm-long graphite tubes with a 25.4-mm ID, measured detonation velocity was $D = 5552 \pm 3$ m/s. Failure diameter in graphite was below 8 mm. Free-surface velocities of 1- and 2-mm aluminum flyer plates terminating the detonation axis were near 1.5 km/s approximately as predicted for Chapman-Jouguet (C-J) flow at $D_\infty = 5564$ m/s, $u_p = 1.34$ km/s impinging on aluminum.

In August 2004, the US Chemical Safety and Hazard Investigation Board (CSB) issued a case study examining the causes of a September 2003 nitric oxide leak and explosion that had occurred at a Sigma-Aldrich Corporation-owned Isotec facility, an ^{15}N isotope separation plant in Miami Township, Ohio, near Dayton [75]. The accident destroyed a 91-m (300-ft.)-tall nitric oxide distillation column, installed below ground. The explosion caused a 6-m (20-ft.)-diameter, 2.4-m (8-ft.)-deep crater and structural damage (Figure 5). If the column had been mounted above ground, the damage would have been much more severe.



Figure 5: Post-accident scene at Isotec ^{15}N isotope separation plant after explosion of nitric oxide. (From CSB case study.)

The explosion happened as company operators worked to shut down the system after a nitric oxide leak and empty the liquid NO . A large steel panel from a blast containment structure was blown off, striking a 23-metric-ton (52000-lb) carbon monoxide storage vessel. Leaking CO gas ignited and burned for more than an hour. The blast destroyed other nearby plant structures and blew out windows in the main office building about 42 m (140 ft.) from the explosion. Glass shards lacerated the hand of one employee, but no other people were injured. Small chunks of concrete and metal shards were propelled as far as 300 m (1000 ft.) and fell on adjacent property. The extensive destruction of the distillation system prevented identification of the exact cause of the nitric oxide leak and type of stimulus that triggered the explosion. The study concluded that the most likely cause was a hole that had developed somewhere along the more than 670 m (2200 ft.) of pipe in the distillation column, releasing nitric oxide liquid into the surrounding vacuum jacket. The CSB study revealed that Isotec had experienced two earlier incidents in similar distillation columns in 1995 and 1998.

Both involved piping failures that allowed nitric oxide to leak into the vacuum jacket. One involved a small explosion below ground, but no corrective action was taken in time to prevent the third, more severe, incident.

5.5.2 Detonability of Gaseous Nitric Oxide

An attempt was made at predicting the detonability of gases from theoretical considerations, and the reliability of predictions was tested against experimental data for nitric oxide or ozone. It was predicted that ozone would detonate but nitric oxide would not [76].

The method gives the length of the reaction zone, and a governing equation was obtained by combining the Rayleigh line equation, the Hugoniot equation, and reaction rate equations.

At the US Bureau of Mines, the detonability of nitric oxide was tested in the gaseous state and in the solid state (see below) [70]. Detonability experiments with gaseous NO at ambient temperature were conducted at ambient pressure (0.1 MPa) and at elevated pressures of 2.17, 2.9, and 7 MPa. Experiments at 0.1 MPa initial pressure were conducted in a closed steel vessel 178 mm in diameter and 3.66 m long. The explosive charge, together with a No. 6 electric blasting cap, was suspended at one end of the vessel, which was then evacuated and filled with NO. Propagation rates were measured at the downstream end of the vessel with pressure-sensitive switches spaced 500 mm apart. For initiators weighing 43 g or less, reaction velocities on the order of 1000 m/s were observed, but velocities in excess of 2000 m/s were observed for initiators weighing 60 g or more. The high-velocity reactions were described as detonations in the true sense, while the lower-velocity reactions were presumably unstable and were referred to as deflagrations. Initiation studies with gaseous NO were extended to 2.17 and 2.90 MPa using 82.6-mm-ID $\times$ 1.22-m-long closed steel pipes. At 2.17 MPa, the initiating charge weight corresponding to the deflagration/detonation threshold was between 2 and 20 g of pentaerythritol tetranitrate (PETN); at 2.90 MPa, the critical charge weight was between 1 and 2 g. At 7 MPa, a small detonator containing only 0.9 g PETN was sufficient to initiate a detonation that propagated at a rate of 2100 m/s.

5.5.3 Detonability of Solid Nitric Oxide

In tests at the US Bureau of Mines with frozen nitric oxide at 78 K with a charge length of 510 mm and 26.64-mm ID $\times$ 3.38-mm-wall steel pipe all samples detonated at high order with a detonation velocity of 6000 m/s when initiated by a 50-g tetryl booster [70].

Samples of solid nitric oxide (NO) weighing up to several hundred milligrams at 30 K have been shocked by detonating PETN boosters in a high-vacuum chamber [77, 78]. The products expanding from the shocked sample were identified, and the product concentrations were measured as a function of time by quadrupole mass spec-

trometry. The gases expanding from unconfined shocked solid NO contained mostly NO_2 , N_2O , and unreacted NO. Nitrogen and oxygen, the expected equilibrium products from detonating NO, were seen in somewhat smaller amounts. Confined samples gave a greater proportion of N_2 and O_2 . The products observed were similar in many respects to those obtained from NO compressed to very high pressures in a diamond anvil cell and those collected from NO shocked in a closed container.

6 Toxicity and Physiological Effects of Nitric Oxide

With nitric oxide rapidly converting to nitrogen dioxide once released into air and inhaled, the inhalation toxicity of nitric oxide would essentially be the same as that of nitrogen dioxide. During its short life span before it becomes oxidizer, nitric oxide may have clinical applications when administered by inhalation and cause selective rapid pulmonary vasodilatation in emergency cases of pulmonary hypertension. It is a selective pulmonary vasodilator effective in the management of persistent pulmonary hypertension of newborns. Inhalation of NO with air is accompanied by inevitable conversion to NO_2 [79].

Knowing that nitric oxide is very reactive, it was a surprise when it was discovered that it is a ubiquitous bioactive molecule and plays a key role in nerve signal conduction and excitement, including processes that are stimulated by sildenafil (Viagra) or similar drugs. The vasodilatory effect of NO plays a role in the achievement and maintenance of erection. Vasodilation of blood vessels supplying the *corpus cavernosum* results in more blood flowing in and, hence, erection. This is the mechanism of sildenafil (Viagra). Nitric oxide can occupy ligand positions in transition metal-hemoglobin, such as ferric and ferrous hemoproteins, similar to those occupied by oxygen or carbon monoxide. The bright red color of meat preserved with sodium nitrite-containing pickling salt can be attributed to such complexes. Food safety agencies limit the amount of nitrite allowed in pickling salt because it can lead to carcinogenic *N*-nitrosamines in the food.

Nitric oxide is biosynthesized endogenously from L-arginine, oxygen, and nicotinamide adenine dinucleotide phosphate (NADPH) by various nitric oxide synthase enzymes in the blood. Nitric oxide synthases are a family of enzymes catalyzing the production of nitric oxide from L-arginine. NO is an important cellular signaling molecule. It helps modulate vascular tone, insulin secretion, airway tone, and peristalsis and is involved in angiogenesis and neural development. Nitric oxide also serves as a neurotransmitter between nerve cells.

Nitric oxide takes part in the lowering of blood pressure following the administration of alkyl nitrites or alkyl nitrates and acts on the cardiac muscle to decrease contractility and heart rate.

Nitric oxide diffuses rapidly and isotropically through most tissues with little reaction but cannot be transported through the vasculature due to rapid destruction by

oxyhemoglobin. The rapid diffusion of nitric oxide between cells allows it to locally integrate the responses of blood vessels to turbulence, modulate synaptic plasticity in neurons, and control the oscillatory behavior of neuronal networks. Nitric oxide is not necessarily short lived and is intrinsically no more reactive than oxygen. The reactivity of nitric oxide *per se* has been greatly overestimated *in vitro* because no drain is provided to remove the nitric oxide. Nitric oxide persists in solution for several minutes in micromolar concentrations before reacting with oxygen to form much stronger oxidants like nitrogen dioxide. Nitric oxide is removed within seconds *in vivo* by reaction with oxyhemoglobin. The direct toxicity of nitric oxide is modest but is greatly enhanced by reacting with superoxide to form peroxynitrite (ONOO^-). Nitric oxide is the only biological molecule produced in high enough concentrations to outcompete superoxide dismutase for superoxide. Nitric oxide may be a mediator for inflammation. Nitric oxide will form nitrosamines with many amines. Nitrosamines are known carcinogens.

7 Applications of Nitric Oxide

As far as rocket propellants are concerned, the main application of nitric oxide is in the preparation of MON by bubbling it into N_2O_4 to make an $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ mixture that minimizes stress corrosion in titanium alloy tanks. There is no military specification for the procurement of NO, and contaminants in NO must be carefully controlled to prevent contamination of the MON produced. When the US Air Force (USAF) announced a procurement of NO in 2007, the requirement was as follows:

The Defense Energy Support Center (DESC) intends to procure on a full and open competition basis for 279 pounds of Nitric Oxide (NO), NSN 9135-01-0146-5135, with a minimum purity of 99.5% by weight. The NO product provided will conform to producer's specifications, standards and quality assurance practices and be the same NO product offered for sale in the commercial marketplace.

No specification was given as to what the remaining 0.5% were allowed to contain. There was an incident where NO was contaminated by SO_2 and nitrosyl sulfuric acid (remember the lead chamber process?) precipitated and clogged some flow passages. The problem may have arisen at a filling plant where both SO_2 cylinders and NO cylinders shared the same Compressed Gas Association (CGA) connection, CGA 660, and cross-contamination or shared cylinder use for both gases is possible.

Other applications of NO are in isotope separation for the production of $^{15}\text{N}_2$ and, to a very limited extent, use as an airway dilatant to treat acute cases of respiratory failure.

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Nitroaliphatic Compounds

1 Nitroaliphatic Compounds (Nitroalkanes)

The topic of nitro compounds had to be distributed over four chapters because it would have been a very large chapter that would have made it more difficult for readers to find information on a specific compound, and it would also have been difficult to arrange 30 chapters among five sub-volumes such that each sub-volume is about the same size. That arrangement was made easier by dealing with smaller chapter increments.

The chapter at hand, dealing with higher nitroaliphatic compounds, is the continuation of the chapter “Nitromethanes” that had to be separated and moved to its own chapter in order to facilitate an even distribution of chapters between the five sub-volumes that constitute the *Encyclopedia of Oxidizers*. The chapter “Nitromethanes” contains introductory information on the production of all nitroalkanes and contains several tables in which the properties of nitromethanes are compared to the properties of higher nitroalkanes. Therefore, if the reader does not find the desired information in the current chapter on higher nitroaliphatic compounds, it is recommended to open the chapter “Nitromethanes” and search there.

Besides nitroalkanes with more than one carbon atom, the most important aspects of the chapter at hand are nitro compounds that carry other substituents in addition to a nitro group or in addition to several nitro groups on the carbon skeleton.

2 Nitroethane

Nitroethane, $C_2H_5NO_2$, CAS RN [79-24-3] is often added to nitromethane to render it less sensitive. It is a by-product of nitromethane production. It is unlikely to be used as a monopropellant because it is so under-oxidized, with an oxygen balance of only –95.9%. However, mixtures of nitroethane with nitromethane or tetranitromethane would potentially make a more energetic propellant (if not an explosive, depending on what you want). It is (was) widely used as a solvent for coatings and paints (nitro lacquer). It may also be used as an additive to diesel fuel to improve the cetane number.

2.1 Production of Nitroethane

The four lower mononitroparaffins (nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane) are made on a large scale by oxidizing an excess of vapor-phase propane with nitric acid within a temperature range of 370–450 °C and pressure of 8–12 atmospheres. This reactant combination sounds more like a rocket propellant combination and accidental explosions can indeed occur during the process. Approx-

imately 40% of the nitric acid is converted to nitroparaffins; the remainder acts as an oxidizing agent to produce unwanted oxygenated by-products and is reduced to nitric oxide. The typical product composition is 48.2 mol-% 2-nitropropane, 22.0 mol-% nitromethane, 16.6 mol-% nitroethane, and 13.2 mol-% 1-nitropropane. Industrial grades of nitroethane contain these by-products as contaminants.

2.2 Physical Properties of Nitroethane

Several of the physical properties of nitroethane have already been included in the preceding tables, where the properties of nitromethane and nitroethane and other nitroalkanes were compared by listing them in the same table next to each other. The physical properties of nitroethane are summarized in Table 1.

Table 1: Physical properties of nitroethane.

Property	SI units	Other units			References
Molecular mass	75.07 g/mol				
Freezing point	223 K	−50 °C			[1]
Boiling point	387 K	114 °C	237 °F		[2]
Boiling point	387.22 K	114.07 °C			[1]
Vapor pressure at 293 K	2.099 kPa	15.8 mm Hg			[1]
Density	1.053 kg/dm ³	1.053 g/cm ³			[2]
	1.045 kg/dm ³	1.045 g/cm ³			
	1.0431 at 293 K	1.0431 g/cm ³ at 293 K			[3]
Refractive index n_D^{20}	1.3719				
	1.3924				[3]
Enthalpy of formation	−143.9 kJ/mol	−1917.4 kJ/kg	−34.4 kcal/mol	−458.3 cal/g	[2]
ΔH_{298}^f	−143.9 kJ/mol		−34.4 kcal/mol		[4]

The vapor pressure of nitroethane as a function of temperature was already listed in chapter “Nitromethanes” in the nitroalkane section. See also [5–7].

2.2.1 Thermodynamic Properties of Nitroethane

The enthalpies of formation of ethane and propane nitro derivatives were obtained for both the standard state and the gas phase based on experimental results and published data from other sources as tabulated in Table 2 from reference [8]. The bond dissociation energies of the ethane and propane nitro derivatives were calculated using the enthalpies of atomization and the energies of non-valent interactions of nitro

Table 2: Thermochemical characteristics of ethane and propane nitro derivatives

Compound	Physical state	Standard enthalpy of formation ΔH_f^{298}		Enthalpy of evaporation ΔH_{evap} at 298k		Vapor state enthalpy of formation ΔH_f^{298} (G)	
		kJ/mol	kcal/mol	kJ/mol	kcal/mol	kJ/mol	kcal/mol
Nitromethane	liquid	-143.9 ± 0.4	-34.4 ± 0.1	41.4 ± 0.4	9.9 ± 0.1	-102.5 ± 0.8	-24.5 ± 0.2
1,1-Dinitroethane	liquid	-149.4 ± 0.4	-35.7 ± 0.1	61.1 ± 0.4	14.6 ± 0.1	-88.3 ± 0.8	-21.1 ± 0.2
1,2-Dinitroethane	liquid	-178.2 ± 0.4	-42.6 ± 0.1	81.6 ± 0.8	19.5 ± 0.2	-96.7 ± 1.3	-23.1 ± 0.3
1,1,1-Trinitroethane	crystal	-113.0 ± 0.8	-27 ± 0.2	72.0 ± 0.4	17.2 ± 0.1	-41.0 ± 1.3	-9.8 ± 0.3
Hexanitroethane	crystal	+80.3 ± 0.4	+19.2 ± 0.1	61.9 ± 0.4	14.8 ± 0.1	+142.3 ± 0.8	+34 ± 0.2
1-Nitropropane	liquid	-167.8 ± 0.8	-40.1 ± 0.2	42.7 ± 0.4	10.2 ± 0.1	-124.3 ± 1.3	-29.7 ± 0.3
2-Nitropropane	liquid	-180.3 ± 0.4	-43.1 ± 0.1	41.0 ± 0.4	9.8 ± 0.1	-139.3 ± 0.8	-33.3 ± 0.2
1,3-Dinitropropane	liquid	-207.1 ± 0.4	-49.5 ± 0.1	71.5 ± 0.4	17.1 ± 0.1	-135.6 ± 0.8	-32.4 ± 0.2
1,1-Dinitropropane	liquid	-168.2 ± 0.4	-40.2 ± 0.1	59.4 ± 0.4	14.2 ± 0.1	-108.8 ± 0.8	-26 ± 0.2
2,2-Dinitropropane	amorphous	-191.2 ± 0.4	-45.7 ± 0.1	57.3 ± 0.4	13.7 ± 0.1	-134.3 ± 0.8	-32.1 ± 0.2
1,1,1-Trinitropropane	liquid	-120.9 ± 0.4	-28.9 ± 0.1	61.9 ± 0.4	14.8 ± 0.1	-59.0 ± 0.8	-14.1 ± 0.2
1,1,1,2,2-Pentanitropropane	crystal	-57.3 ± 0.4	-13.7 ± 0.1	77.4 ± 0.8	18.5 ± 0.2	+20.1 ± 1.3	+4.8 ± 0.3

Data source: [8]

groups, and the calculated values were compared with the kinetic data on thermal decomposition.

Based on a heat of combustion of 326.6 ± 0.3 kcal/mol determined calorimetrically, a standard heat of formation of -135 kJ/mol (-32.3 ± 0.3 kcal/mol) has been calculated for liquid nitroethane and of -96 kJ/mol (-22.9 kcal/mol) for nitroethane vapor [9]. The freezing point of nitroethane is 183.69 K and the heat of fusion is 9.85 kJ/mol (2.355 kcal/mol) [10].

2.2.2 Molecular Structure of Nitroethane

The dissociation energies of the bonds in polynitroethanes were determined from the energies of the non-valence interactions of nitro groups with each other and compared to the available thermodynamic and kinetic data [11]. The energies of the non-functional interaction of nitro groups were used to calculate the dissociation energies of bonds in nitroethyl radicals. The dissociation energy of the C–NO₂ bond in the nitroethane molecule calculated with the use of the enthalpies of formation of C₂H₅• (113.0 ± 8.4 kJ/mol = 27.0 ± 2.0 kcal/mol), •NO₂ (33.0 ± 0.4 kJ/mol = 7.9 ± 0.1 kcal/mol), and nitroethane (-102.5 ± 1.2 kJ/mol = -24.5 ± 0.3 kcal/mol) was found to be 248.5 ± 8.4 kJ/mol = 59.4 ± 2.0 kcal/mol. The activation energy of the abstraction of •NO₂, the primary step of the thermal dissociation of the nitroethane molecule, was estimated from kinetic measurements at 232.6 kJ/mol = 55.6 kcal/mol. The thermodynamic data in this 2008 publication differ slightly from data published by the same authors 2 years later. The dipole moment of nitroethane is 3.58 D, very similar to that of nitromethane, i.e., 3.54 D.

2.3 Chemical Properties of Nitroethane

The oxygen balance of nitroethane is -95.9% . This highly negative number alone already indicates that nitroethane would not be a good monopropellant by itself. It is highly oxygen deficient and must be mixed with a better oxidizer to formulate monopropellants with a decent performance and clean (soot-free) exhaust.

The term “alpha-effect” has been used to describe the high reactivity of nucleophiles possessing an unshared pair of electrons adjacent (α position) to the nucleophilic atom. The hydrogen in the α position is still quite acidic, although not as strongly as in nitromethane. The pK_a of nitroethane is only 8.46 compared to 10.18 for nitromethane.

The pK constants for conversion of nitroethane to its ion by amine neutralization of the anion were correlated by the Brønsted equations for general acid and general base catalysis [12]. The so-called α effect does not appear to be operative in the making of the C–H bond of nitroethane.

2.3.1 Thermal Decomposition of Nitroethane

2.3.1.1 Experimental Study of the Thermal Decomposition of Nitroethane

The decomposition reaction of nitroethane proceeds in principle following the same mechanism as that of nitromethane, a thoroughly studied decomposition reaction. Extrapolating from nitromethane to nitroethane and nitropropane gives some understanding of the effects of adding a methyl or an ethyl group to the carbon skeleton on the thermal stability of nitro compounds. The decomposition of nitroethane, 1-nitropropane, and 2-nitropropane was studied as a flow of 5–10% nitroalkane in nitrogen in a flow-through reactor, and the undecomposed nitro compound was captured in a cold trap at the exit of the reactor [13, 14]. The main difference is the increased formation of uncombusted pyrolysis products such as HCN, aldehydes, olefins, and the usual CO_2 and NO_x . The rate constant for the first-order decomposition of nitroethane was

$$k = 10^{10.83} \exp(-29700/RT) \text{ s}^{-1}$$

over the temperature range 593–713 K (320–440 °C). The equation matched data obtained in both static and flow systems, and was consistent with the postulated activated complex having a ring structure. In the range 763–808 K (490–535 °C), a special fast-flow system was used and gave the rate constant

$$k = 10^{17.56} \exp(-50600/RT) \text{ s}^{-1}$$

The activation energy approximated the C–N bond strength at these temperatures, and it appeared that a non-chain branched mechanism with initial fission of the C–N bond can account for the results at high temperature.

An accelerating rate calorimeter (ARC) was used to test the thermal stability of nitroethane in comparison to four solid explosives and 2-ethylhexyl nitrate (EHN) [15]. Kinetic and thermodynamic parameters were calculated and analyzed. Time to maximum rate under adiabatic conditions (TMR_{ad}) was calculated. Nitroethane was the thermally most stable material in the group of energetic materials tested. The thermal sensitivity (sensitivity is the opposite of stability) ranking of six energetic materials from high to low was EHN > pentaerythritol tetranitrate (PETN) > 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) > 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) > 2,4,6-trinitrotoluene (TNT) > nitroethane. See also [16].

2.3.1.2 Theoretical Study of the Thermal Decomposition of Nitroethane

Some decomposition pathways of nitroethane (**1**) and 2-nitropropane (**2**) were studied computationally [17]. It was found that the concerted molecular elimination pathway is the most favorable decomposition channel, but other potentially important mechanistic routes were also investigated. It was found that the elimination of HONO in both nitroalkanes proceeds through relatively high barriers of 176 and 164 kJ/mol (42.0 and 39.2 kcal/mol), respectively. These values agreed well with the activation energies predicted by others on the basis of experimental results. The enthalpies of formation of

(1) and (2) were also calculated, and it was found that the enthalpies of formation predicted in this way, i.e., -104 ± 4 kJ/mol and -142 ± 4 kJ/mol (-24.5 ± 1 kcal/mol and -34.0 ± 1 kcal/mol), were indeed accurate enough for practical purposes.

The reaction mechanism and kinetics of thermal decomposition of nitroethane were studied by density-functional theory calculations, automatic pressure-tracking adiabatic calorimeter (APTAC) measurements, and gas chromatography analysis [18]. The APTAC results were used to derive kinetic rate equation parameters, giving pre-exponential coefficient of $A = 10^{13.5 \pm 0.2}$ and $E_a = 192 \pm 2.1$ kJ/mol = 46.2 ± 0.5 kcal/mol. The decomposition process included three initial steps: concerted molecular elimination of HONO, nitro–nitrite isomerization, and rupture of the C–NO₂ bond. A detailed mechanism consisting of 23 elementary steps was proposed and compared to the experimental results. Numerical simulations of the proposed mechanism reproduced the distributions of major products over the temperature range reasonably well. It was found that the relative concentrations of NO and C₂H₄ depended on the reaction temperature. Combining theoretical and experimental studies, it was concluded that elimination of HONO is predominant at low temperatures and dissociation of C–NO₂ becomes significant at higher temperatures.

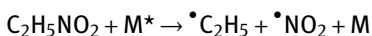
Similarly, four distinct pathways of unimolecular decomposition of nitroethylene, i.e., C–NO₂ bond breaking, nitro-to-nitrite rearrangement, 1,2-elimination reaction, and 1,1-elimination reaction, have been computationally investigated with *ab initio* methods as well as with density functional theory (DFT) methods [19]. The nitro-to-nitrite rearrangement and 1,2-elimination reactions were found to give the lowest energy decomposition pathways for this molecule, about 15 kcal/mol lower than the cleavage of the nitro group.

2.3.2 Photolysis of Nitroethane

The photolysis of nitromethane had been investigated for decades to identify reactions that might precede the initiation of nitromethane decomposition in a rocket engine by laser ignition. Similarly, the photodissociation of gaseous nitroethane at 266 nm has been studied by monitoring the NO(*X*²Π) product using a laser-induced fluorescence technique [20]. For comparison, the geometries of the nitroethane, the ethyl nitrite, and the transition state connecting the two isomeric structures were then investigated using *ab initio* methods. The photodissociation dynamics of nitroethane can be explained on the basis of experimental observations and calculation results.

2.3.3 Shock-Tube Decomposition of Nitroethane Vapor

A shockwave study of the thermal decomposition of nitroethane in excess Ar at temperatures $900 < T < 1350$ K and total concentrations of $4.5 \times 10^{-6} < [\text{Ar}] < 3 \times 10^{-4}$ mol cm⁻³ showed that C–N bond fission



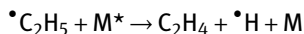
is the primary reaction step [21]. This unimolecular reaction could be observed in its transition region near the high-pressure limit. The derived rate constants were

$$k_{\infty} = 10^{15.9} \exp(-57 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$$

for the high-pressure and

$$k_0/[Ar] = 10^{18.0} \exp(-36 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for the low-pressure limit at $T \approx 1100\text{--}1200$ K. The observed concentration profiles of $\text{C}_2\text{H}_5\text{NO}_2$ and NO_2 indicated the subsequent decomposition of the ethyl radical



This reaction was found to be in the fall-off range under the given conditions.

2.4 Toxicity of Nitroethane

Nitroethane differs from nitromethane in that it exhibits anesthetic properties: stupor, narcosis, or light general anesthesia appeared in animals exposed to 30000 ppm in air for longer than 1 h or to 1000 ppm for 5 or 6 h [1].

Animal studies indicated that, regardless of the route of exposure, the liver is the organ that suffers the most severe damage from nitroethane poisoning. At necropsy, all exposed animals were found to have some liver damage; fatty infiltration was seen in a number of animals. Animals that died from nitroethane inhalation also exhibited general visceral and cerebral congestion, severe congestion of the upper respiratory tract, and pulmonary congestion with edema. Nitroethane was a relatively weak methemoglobinic poison compared to 1- or 2-nitropropane. Toxicity data for nitroethane from several sources are listed in Table 3.

Table 3: Acute effects of nitroethane toxicity.

Route	Species	Dose, mg/kg	Response
Oral	Rats	1625	LD50
Oral	Rats	1100	LD50
Oral	Mice	2150	LD50
Oral	Mice	860	LD50
Oral	Rabbits	500	LDLo
Inhalation	Rabbits	5000 ppm x 2 h	LcLo

Data source: [1]

Groups of rats were exposed in inhalation chambers to vapors of nitroethane at concentrations of 100 or 200 ppm, 7 h/d, 5 d/week for 2 years [22]. During the study, general observations were made daily and body weights were obtained weekly for the first 6 months of the study. Any rats that were found dead or sacrificed moribund during the 2-year exposure phase of the study were given a thorough gross examination and tissues were retained for microscopic analysis. After 2 years of inhalation of nitroethane, all surviving rats were sacrificed and subjected to the same thorough gross examination. Exposure of the rats to nitroethane had no pharmacologic effects nor were there any effects on mortality of rats at either level of exposure. There were no effects of exposure to nitroethane on hematology nor were there any biologically significant effects of exposure to nitroethane on clinical chemistry or on organ weights. No significant non-neoplastic or neoplastic pathology was found as a consequence of exposure of rats to nitroethane.

2.4.1 Maximum Allowable Exposure Limits for Nitroethane Vapors

The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) time-weighted average concentration (TWA) for nitroethane is 100 ppm (310 mg/m³) and the US Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) TWA is 100 ppm (310 mg/m³) for 40 h/week exposures. The NIOSH immediately dangerous to life or health (IDLH) concentration is 1000 ppm and remained unchanged from the original IDLH issued a few years earlier. The chosen IDLH was based on older observations that exposure to 5000 ppm for 2 h was lethal to one of two rabbits and to zero of two guinea pigs, and exposure to the same concentration for 3 h was fatal for two of two rabbits and to none of two guinea pigs [23].

2.5 Flammability of Nitroethane

The autoignition temperature of nitroethane in air is 688 K (779 °F). The open-cup flash point of nitroethane in air is 301 K (82 °F). Other sources gave a Tag open-cup flash point of 314 K (41 °C = 106 °F). The flammable range of nitroethane in air is 3.4–99 vol%.

2.6 Explosive Properties of Nitroethane

The section on *n*-propyl nitrate in *Encyclopedia of Oxidizers*, chapter Nitrate Esters, contains a comparison of the adiabatic compression sensitivities of nitromethane, nitroethane, and *n*-propyl nitrate [24]. Nitroethane was the least sensitive of the three liquids tested, with the energy required to initiate an explosion in 50% of the tests being the highest of the three.

Bulk nitroethane may be less detonable than other nitro compounds, but in aerosol mixtures of nitroethane mist in air, detonability is just as severe as with many other nitro compounds. A series of experiments was conducted with two different aerosol droplet diameters and the explosion pressure and temperature of the two sets of vapor–liquid mixtures of nitroethane/air at various concentrations were analyzed [25]. Similar experiments were conducted with isopropyl nitrate and/or JP-10 aerosols in air.

2.7 Applications of Nitroethane

Nitroethane is often added to nitromethane to render it less sensitive. This can only be justified if one can prove that nitroethane is less sensitive than nitromethane. Similar to nitromethane, nitroethane is widely used as a solvent for lacquers, paints, inks, coatings, and adhesives. It can be used as an additive to diesel fuels to increase power and to reduce smoke in exhaust. It is a good solvent for most nitro-organic explosives.

3 Higher ($C_{n>2}$) Mononitroalkanes

The most widely used $C_{n>2}$ nitroalkane is 2-nitropropane, $(H_3C)_2CHNO_2$, $C_3H_7NO_2$, CAS RN [79-46-9]. It is formed as a by-product during production of the lower nitroalkanes by reaction of nitric acid with propane.

3.1 Physical Properties of Higher Mononitroalkanes

Higher mononitroalkanes containing more than three carbon atoms have not been considered as rocket propellants. They are sometimes used as additives to energetic mixtures or as fuels in combination with other oxidizers. Higher nitroalkanes are less shock sensitive than nitromethane or propyl nitrate, but would give a lower specific impulse and the exhaust would be very sooty if they were used as monopropellants by themselves without any supplemental oxidizer. Properties of higher mononitroalkanes are summarized in Table 4.

Nitrobutane may form by radiolysis of tributyl phosphate/nitric acid mixtures used in the two-phase extraction of radionuclides from spent nuclear reactor fuel rods.

The heats of combustion of nitroalkanes and other organic nitrogen compounds can be extrapolated using a simple method [26] (“Upper heat of combustion” column in Table 4).

Physical and thermodynamic properties of C_1 – C_4 mono- and polynitroalkanes were determined and tabulated as shown in Table 5. The heats of combustion of the

Table 4: Physical properties of higher ($C_{n \geq 2}$) mononitroalkanes.

Compounds	Property								
	Melting point		Boiling point		Density, g/cm ³ (at ____ °C)	Index of refraction, <i>n</i> _d (at ____ °C)	Upper heat of combustion		Oxygen balance
	K	°C	K	°C			kJ/mol	kcal/mol	
Nitroethane	183	−90	387	114	1.0561 (15)	1.3901 (24.3)	1348	322.2	−95.9
1-Nitropropane	165	−108	404	131	1.003 (20)	1.4003 (24.3)	—	—	−134.7
2-Nitropropane	180	−93	393.4	120.3	1.024 (0)	1.3941 (20)	1997	477.4	−134.7
1-Nitrobutane	—	—	426	153	0.971 (20)	—	2668	637.6	−162.9
2-Nitrobutane	141	−132	413	140	0.9854 (17)	—	2653	634.0	−162.9
For comparison: Nitromethane	244.6	−28.55	374.35	101.2	1.13124 (25)	1.3818 (20)	709	169.4	−39.3

Data source: Several handbooks and [26]

Table 5: Thermodynamic properties of liquid C₁–C₄ mono- and polynitroalkanes.

Compound	Energy of combustion, ΔE_c^{298a}		Enthalpy of formation, ΔH_f^{298}		Heat of evaporation at 298K	
	kJ/mol	kcal/mol	kJ/mol	kcal/mol	kJ/mol	kcal/mol
Nitromethane	726.8	173.7	-89.0 ± 0.8	-21.28 ± 0.18	38.0 ± 0.4	9.09 ± 0.09
Nitroethane	1362.2	325.57	-140.1 ± 1.3	-33.48 ± 0.31	41.6 ± 0.4	9.94 ± 0.1
1-Nitropropane	2012.8	481.07	-167.6 ± 2.6	-40.05 ± 0.61	43.4 ± 0.4	10.37 ± 0.1
2-Nitropropane	1997.2	477.34	-183.2 ± 0.7	-43.78 ± 0.17	41.3 ± 0.4	9.88 ± 0.1
1-Nitrobutane	2665.8	637.15	-192.6 ± 1.3	-46.03 ± 0.32	48.6 ± 0.5	11.61 ± 0.12
2-Nitrobutane	2650.9	633.58	-207.6 ± 1.5	-49.61 ± 0.36	43.8 ± 0.4	10.48 ± 0.1
1,1-Dinitropropane	1871.2	447.22	-170.6 ± 1.4	-40.78 ± 0.34	62.5 ± 0.6	14.93 ± 0.15
1,3-Dinitropropane	1817.9	434.48	-223.9 ± 1.4	-53.51 ± 0.33	—	—
2,2-Dinitropropane	1854.0	443.12	-187.7 ± 2.7	-44.87 ± 0.64	—	—
Trinitromethane	469.0	112.1	77.9	18.63	—	—

Data source: [27]

^a Energy for constant-volume reaction in a combustion bomb. This is not enthalpy of combustion.

nitroparaffins have been shown to be a linear function of the oxygen balance of the molecules, and an equation was derived that relates these two variables with an average error of about 2% of the experimental values. However, the number listed for the enthalpy of formation of nitromethane in Table 5 differs substantially from more reliable and more recent data which show an enthalpy of formation of -113.1 kJ/mol for liquid nitromethane.

The heats of combustion and heats of formation of the two isomeric nitropropanes do not differ much. Based on heats of combustion of 481.8 ± 0.7 and $478.0 \pm 0.3 \text{ kcal/mol}$ determined calorimetrically, standard heats of formation of -165.3 ± 2.9 and $-180.7 \pm 1.2 \text{ kJ/mol}$ (-39.5 ± 0.7 and $-43.2 \pm 0.3 \text{ kcal/mol}$) have been calculated for 1-nitropropane and 2-nitropropane, respectively [9]. Other sources [28] gave $-45.32 \text{ kcal/100 g}$ or -168.9 kJ/mol for 1-nitropropane and $-44.69 \text{ kcal/100 g}$ or -192.8 kJ/mol for 1-nitrobutane. Additional data are shown in Table 8 (in the "Polynitroalkanes" section).

X-ray powder diffraction structural investigations of crystallized 2-nitropropane at low temperatures identified a crystalline phase, called the α phase, below 172 K [29]. This form exhibited a triclinic symmetry with the $P1$ space group, with unit cell parameters of $a = 1.0313(3) \text{ nm}$, $b = 0.5873(2) \text{ nm}$, $c = 1.6146(4) \text{ nm}$, $\alpha = 90.17(2)^\circ$, $\beta = 92.17(2)^\circ$ and $\gamma = 90.09(2)^\circ$, and $Z = 8$. At $T_t = 172 \text{ K}$, a structural transition was observed which changed to another phase, called β -phase (above T_t). This form contained four molecules per unit cell and showed $Pc2_1n$ symmetry: $a = 1.0141(3) \text{ nm}$, $b = 0.5855(2) \text{ nm}$, and $c = 0.8319(4) \text{ nm}$. The crystal structures differ in terms of the different conformations of $-\text{NO}_2$ nitro groups and in terms of the orientation of the propyl group in the unit cell.

3.2 Chemical Properties of Higher Mononitroalkanes

3.2.1 Reactions of Higher Mononitroalkanes

The hydrogen in the α position of nitropropanes is still quite acidic and can form *aci* salts, although the acidity is less than that of nitromethane. The $\text{p}K_a$ of 1-nitropropane is 8.98 and the $\text{p}K_a$ of 2-nitropropane is 7.67.

3.2.2 Thermal Decomposition of Higher Mononitroalkanes

The effect of pressure on the rates of decomposition of 2-nitropropane was measured at pressures up to 1.1 GPa [30]. The mechanisms of thermolysis were inferred from kinetic studies and product composition analysis: 2-nitropropane was less stable than nitromethane; elevated pressure accelerated its decomposition; it was believed to cyclize via the *aci*-form like nitromethane. For comparison, 2,2-dinitropropane does not have an α -hydrogen and cannot tautomerize. In earlier work it was found to have a homolytic mechanism at high pressure. Therefore, the decomposition pathways of

nitroalkanes in aprotic solvents are determined not only by the conditions but also by the availability of an α -hydrogen.

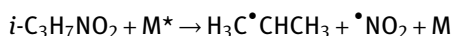
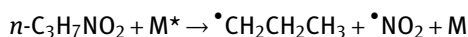
Addition of amines enhances the formation of *aci*-nitropropane. Solutions of 1- and 2-nitroalkanes were thermolyzed in the presence of amines at hydrostatic pressures up to 1.5 GPa, and their rates of decomposition were measured [31]. The probable mechanism of base-catalyzed decomposition involved a bimolecular reaction of the *aci*-nitroalkane with the nitronate ion to yield a carbonyl compound, its corresponding oxime, and a nitrite ion as the early rate-determining steps. The effects of pressure on the rates of decomposition of non-acidic nitroalkanes, i.e., 2,2-dinitropropane, and 2-methyl-2-nitropropane, were measured and used to infer the rate-controlling steps. Whereas 2,2-dinitropropane appeared to undergo rearrangement to a nitrite followed by homolysis to give acetone, NO, and NO₂, 2-methyl-2-nitropropane gave mostly isobutylene and HONO, probably via a five-membered cyclic transition state.

Nitric acid/2-nitropropane mixtures are sometimes used as a model compound to study pre-explosion reaction steps at high pressures. High-pressure Raman spectroscopy measurements on stoichiometric HNO₃/2-nitropropane mixtures in a diamond anvil cell at 0–20 GPa identified the intermediates of the first-step reactions [32]. The initiation of the chemical decomposition can be correlated with weakening of the N–O bonds in the mixture. The study of a mixture with H¹⁵NO₃ identified the origin of nitrogen formation and identified a possible chemical pathway.

Alkylamines are known to sensitize nitroalkanes to detonation. Some of this interaction may take place even in the presence of nitric acid and at high pressures [33]. High-pressure Raman spectroscopy measurements in a diamond anvil cell at 0–10 GPa on HNO₃/2-nitropropane/X (X=triethylamine, diethylamine, or water) ternary systems and HNO₃/2-nitropropane/water/Y (Y=triethylamine or diethylamine) quaternary systems showed that the presence of triethylamine, diethylamine, and/or water modifies the chemical behavior of the HNO₃/2-nitropropane model system at ambient and high pressure. At high pressure, decomposition of the HNO₃/2-nitropropane system has only been observed in the presence of triethylamine.

3.2.2.1 Shock Tube Decomposition of Nitropropane Vapor

The pyrolysis of 1- and 2-nitropropane vapor highly diluted in Ar has been studied in a shock tube at temperatures of 915 < *T* < 1200 K and total gas concentrations $7 \times 10^{-6} \text{ mol/cm}^3 < [\text{Ar}] < 1.5 \times 10^{-4} \text{ mol/cm}^3$ [34]. The reactions behind the shock waves were followed by recording light absorption-time profiles of the decomposing molecules and the produced NO₂. Under the conditions of the experiments, the primary reaction step in both cases was C–N bond fission:



The first-order rate constant k measured at concentrations of $[\text{Ar}] \approx 10^{-4} \text{ mol/cm}^3$ were:

$$n\text{-C}_3\text{H}_7\text{NO}_2 \quad k = 2.3 \times 10^{15} \exp(-55 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$$

$$i\text{-C}_3\text{H}_7\text{NO}_2 \quad k = 2.4 \times 10^{15} \exp(-54 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$$

At these concentrations the reactions are taking place near to the high-pressure limit. By varying the Ar concentrations over one order of magnitude, only a slight pressure dependence was found.

The kinetics of the thermal decomposition of 2-nitropropane vapor were investigated in a shock tube over the temperature range 970–1150 K under high dilution in argon at total pressures of 456–608 kPa (4.5–6 atm) [35]. The decay of 2-nitropropane and the production of NO_2 were followed spectrophotometrically at 276 and 405 nm, respectively. The unimolecular rate constant deduced from the loss of 2-nitropropane at the high-pressure limit was

$$k_\infty = 10^{14.55 \pm 0.13} \exp(E_{\text{act}}/RT) \text{ s}^{-1}.$$

where the activation energy is $226.8 \pm 15.9 \text{ kJ/mol}$ or $54.2 \pm 3.8 \text{ kcal/mol}$ (depending on the units used for R), T is the temperature in kelvin, and k_∞ is the rate constant in s^{-1} . The products of pyrolysis were identified and quantified by Fourier-transform infrared spectroscopy (FTIR) and gas chromatography (GC). The major products were NO , $\text{CH}_3\text{CH}=\text{CH}_2$, CO , CH_3CHO , C_2H_4 , and $(\text{CH}_3)_2\text{CO}$. The decomposition proceeded primarily through C–N bond fission, while the contribution from the five-center elimination of HONO accounted for less than 20% of the total loss of 2-nitropropane. A reaction mechanism that consisted of 81 elementary steps was proposed and accurately accounted for the overall pyrolysis process. Numerical simulations with the mechanism reproduced reasonably well the NO_2 vs. time profiles at different temperatures and the distributions of major reaction products over the temperature range studied. When the mechanism was subjected to sensitivity and principal component analysis, it was found that only 58 reactions in the mechanism are needed to faithfully reproduce the observed product distributions. The rate of pyrolysis of 2-nitropropanol appeared to be similar to that of 2-nitropropane over the temperature range studied, but had a much lower activation energy.

In a similar test, the thermal decomposition of 2,2-dinitropropane was investigated in a shock tube over the temperature range 970–1200 K under high dilution in argon at total pressures of 456–557 kPa (4.5–5.5 atm) [36].

3.2.3 Photolysis of Higher Mononitroalkanes

The one-photon, collision-free, UV (222, 249, and 308 nm) photodissociation of 2-nitropropane leads to several chemically distinct sets of products, including OH , HONO , and NO_2 [37].

3.3 Toxicity of Higher Mononitroalkanes

2-Nitropropane is a widely used volatile industrial solvent and its toxicity has been thoroughly researched. Although 2-nitropropane is not used as a rocket propellant, its toxic properties are reviewed here in detail as it has been used as a process solvent in the synthesis of other energetic compounds and in the demilitarization and extraction of nitro compounds from solid propellants and explosives. Accidental exposure of operating personnel to vapors or splashes of 2-nitropropane may occur during those operations. The toxicity, in particular the mutagenicity and carcinogenicity of 2-nitropropane, has been investigated for several decades in surprising detail, because the comparison with its less active isomer, 1-nitropropane, may explain the connection between chemical structure and toxicity or carcinogenicity, a criterion that is important for all nitro compounds, including those used as rocket propellants and explosives. 2-Nitropropane has served as a model compound for the study of the toxicity of all nitroalkanes. The questions that needed to be answered pertained to the path of metabolism that leads the toxicant to the target organ and the possible role of intermediates, such as isomerization of the $-\text{NO}_2$ group to $-\text{ONO}$, reduction to $-\text{NHOH}$, or formation of the *aci* form nitronate in alkaline medium. The answers to these questions helped to understand the toxicity of other nitro compounds, some of which are used as rocket propellants and explosives.

Unlike primary nitroalkanes, such as 1-nitropropane, the secondary nitroalkane 2-nitropropane is geno- and hepatotoxic. Nitroalkanes exist in equilibrium with alkane nitronates, particularly in alkaline media. Differences between nitroalkanes in terms of the content of nitronate tautomer at equilibrium are probably an important chemical determinant of their toxic potential [38].

A very detailed summary of the toxicity of 2-nitropropane has been published as part of an International Agency for Research on Cancer (IARC) Monograph [39].

3.3.1 Acute Inhalation Toxicity of Higher Mononitroalkanes (Animal Exposure Tests)

Additional data on the toxicity of 1-nitropropane and 2-nitropropane are available in a publication by NIOSH [1]. Table 6 and 7 are summaries of acute inhalation toxicity test results with rodents and cats.

1-Nitropropane, when administered by intra-peritoneal (IP) injection, was found to be more toxic than 2-nitropropane. The minimum dose required to kill rats within 4 h was 550 mg/kg of 1-nitropropane compared to 1100 mg/kg of 2-nitropropane. By the respiratory route, however, 1-nitropropane was clearly less toxic than 2-nitropropane. One 8-h exposure of 800 ppm 2-nitropropane caused the death of rats in 48 h, but three 8-h exposures of 800 ppm 1-nitropropane were necessary to cause death in a similar group of rats. The liver is the target organ that suffers the most severe damage from 1-nitropropane poisoning. Occupational exposure to 1-nitropropane rarely occurs with this compound alone, it is usually associated with exposure to 2-nitropropane.

Table 6: Acute toxicity of 2-nitropropane in animal tests.

Route	Species	Dose, mg/kg	Response
Oral	Rats	725 ± 160	LD50
Oral	Rats	500	LDLo
Oral	Mice	400	LD50
Oral	Rabbits	500	LDLo
Intra-peritoneal	Mice	75	LDLo
Inhalation	Rats	1513 ppm × 4.5 h	LCLo
Inhalation	Rats	3865 ppm × 1 h	LCLo
Inhalation	Rats	2773 ppm × 1 h	LCLo
Inhalation	Rats	3712 ppm × 1 h	LC50
Inhalation	Rats	400 ppm × 6 h	LC50
Inhalation	Rats	5098 ppm × 1 h	LC100
Inhalation	Rabbits	2381 ppm × 4.5 h	LCLo
Inhalation	Guinea pigs	4622 ppm × 4.5 h	LCLo
Inhalation	Cats	714 ppm × 4.5 h	LCLo

Data source: [1]

Table 7: Acute toxicity lethal concentration data for 2-nitropropane.

Species	Refer- ence	LC50 (ppm)	LCLo (ppm)	Time	Adjusted 0.5-hr LC (CF)	Derived value
Rat	[40]	400	—	6 h	1535 ppm (2.15)	92 ppm
Cat	[41]	—	714	5 h	5119 ppm (2.15)	154 ppm
Rabbit	[41]	—	2381	5 h	4324 ppm (1.6)	512 ppm
Guinea pig	[41]	—	4622	5 h	9937 ppm (2.15)	994 ppm
Cat	[41]	—	2353	1 h	2941 ppm (1.25)	294 ppm

Nitropropanes dissolve readily in fat tissue and are transported with the blood. Several publications have studied the toxicokinetics of 2-nitropropane in the body, the distribution between inhaled air and absorbed toxicant in the body, and the pathway from the lung to the tissue that suffered the most damage (i.e., the liver). Toxicokinetics of atmospheric 2-nitropropane (2-NP) were investigated in rats and rabbits [42–44]. A thermodynamic partition coefficient (body/air) was obtained from the data obtained *in vivo*. A similar value of the thermodynamic partition coefficient was calculated from the *in vitro* accumulation of atmospheric 2-NP in water and olive oil. Due to metabolism in the animals, the actual concentration at steady state was less than the former values of the thermodynamic partition coefficient, declining to 22–30 at concentrations below 10 ppm. 2-NP was found to be metabolized via two pathways: a non-saturable pathway according to first-order kinetics, which was quite similar in both sexes and all species; and a saturable pathway. The path of the toxicant in the body can be traced by using isotope-labeled nitropropane [45]. Rats were exposed by

inhalation for 6 h to 20 or 154 ppm of 2- $[^{14}\text{C}]$ nitropropane (2- $[^{14}\text{C}]$ NP) and the distribution of radioactivity in these animals was followed for 48 h. These data indicated that at least 40% of the inhaled 2- $[^{14}\text{C}]$ NP was absorbed. 2- $[^{14}\text{C}]$ NP was rapidly metabolized and eliminated, and thus had a low potential for accumulation in the rat during prolonged or repeated exposures.

Groups of rats were exposed by inhalation to vapors of 1-nitropropane at 100 ppm for 7 h/d, 5 d/week, for periods up to 21.5 months [46]. Groups of rats were killed after 1, 3, 12, and 18 months of exposure, and additional groups of exposed rats were removed from the exposure chamber after 3 and 12 months and held under non-exposure conditions for the remainder of the study. The results of gross necropsies of the animals did not disclose any adverse effects of exposure to 1-nitropropane in any of the organs or tissues. There were no histopathologic changes of the liver and, in particular, no induction of hepatocarcinoma. No effects were observed on final body weights or the weights of liver, kidney, or brain.

Groups of rats were exposed to vapors of 1-nitropropane or 2-nitropropane at concentrations of 100 ppm for 7 h/d on 4 consecutive days [47]. Livers were analyzed for enzymatic activities after 1-, 2-, and 4-day inhalation periods. Liver microsomal cytochrome P450 was depressed by 2-nitropropane but elevated following exposure to 1-nitropropane. Changes in other liver enzymes during a 4-d exposure period were observed in both of the exposed groups in comparison to control animals.

3.3.2 Chronic Inhalation Toxicity of Higher Mononitroalkanes (Animal Exposure Tests)

The effect of 2-nitropropane vapor on a number of species was tested and the animals were found to be affected in the following order of decreasing sensitivity: cats, rats, rabbits, and guinea pigs [41]. Rats, rabbits, and guinea pigs survived repeated 7-h exposures (five times weekly for 130 exposures at 328 ppm); cats (and a monkey) survived 83 ppm over the same period. The highest concentrations tolerated for 4.5 h without significant effect were 328 ppm for cats, 714 ppm for rats, 1401 ppm for rabbits, and 2381 ppm for guinea pigs. The lowest lethal concentrations for 4.5 h were 714 ppm for cats, 1513 ppm for rats, 2381 for rabbits, and 4622 for guinea pigs. Symptomatic effects resulting from sufficiently high concentrations were similar in all species and included dyspnea, cyanosis, prostration, convulsions, and coma. Pathologic changes in animals exposed to 2353 ppm were generalized vascular endothelial damage in all tissues associated with pulmonary edema and hemorrhage. No pathology was seen in rats, rabbits, or guinea pigs following repeated exposure to 328 ppm, but cats showed severe liver damage and slight to moderate degeneration of the heart and kidneys. Formation of methemoglobin and Heinz bodies in the erythrocytes occurred in proportion to the concentration and duration of exposure. Based on these results, a safe concentration of 50 ppm was recommended as the threshold limit value (TLV) for human exposure at the workplace.

The effects of 2-nitropropane administered by both intra-peritoneal injection and inhalation in the rat were investigated in France [48].

Groups of rats were exposed by inhalation to 2-nitropropane at a concentration of 25 ppm for 7 h/d, 5 d/week, over a period of 22 months [49–51]. Periodic examinations of serum chemistry, hematology, and histopathology were conducted throughout the study. All animals remaining alive were sacrificed after 22 months. No effects on serum chemistry or hematology were observed which could be attributed to exposure of the animals to 2-nitropropane. There was no methemoglobinemia and thus no apparent large release of nitrite. No malignancies or significant pathologic changes were observed in the livers of any of the rats. Focal areas of hepatic, cellular nodules were noted in 3 of 250 control animals and 13 of 249 exposed animals.

For sub-chronic exposure, two guinea pigs, two rats, and one rabbit survived exposure to 328 ppm 2-nitropropane in air 7 h/day, 5 days/week, administered over a 199-day period. Cats, however, did not survive at this concentration; one died after the third exposure period and another died after the seventeenth exposure period. 2-Nitropropane is a carcinogen: all 10 Sprague–Dawley rats exposed by inhalation to 207 ppm 2-nitropropane for 6 months developed hepatocellular carcinoma or hepatic adenoma.

In a study for NIOSH, in all 10 rats that had received 6 months of exposure to 207 ppm 2-nitropropane, multiple hepatocellular carcinomas were present [40]. These carcinomas appeared to be highly malignant. Liver weights were significantly elevated in rats exposed to 207 ppm of 2-nitropropane for 1, 3, and 6 months. No exposure-related gross or microscopic alterations were seen in any of the tissues examined for rats and rabbits exposed to 27 ppm of 2-nitropropane or in tissues of rabbits exposed to 207 ppm of 2-nitropropane. Liver neoplasms were seen in all 10 rats killed following 6 months of exposure to 207 ppm of 2-nitropropane, indicating that 2-nitropropane is a potent carcinogen in the rat.

In another study, groups of rats were exposed to 25 ppm 2-nitropropane 7 h/d, 5 d/week, for periods up to 22 months. At the end of the exposure period, no malignancies or any significant pathologic changes attributable to 2-nitropropane exposure had been observed in any tissues.

Groups of rats were exposed to 207, 200, 100, 27, or 25 ppm 2-nitropropane for up to 6 months [52]. Liver changes such as hepatocellular hypertrophy, hyperplasia, necrosis, and liver tumors occurred in rats exposed to 207 ppm. Rats exposed to 100 ppm developed liver tumors.

3.3.3 Toxicity of Higher Mononitroalkanes by Other Methods of Administration (Other than by Inhalation)

Intra-peritoneal injection (50 mg/kg) of 2-nitropropane induced lipid accumulation, centrilobular necrosis, degranulation of rough endoplasmic reticulum, proliferation of smooth endoplasmic reticulum, and mitochondrial abnormalities in rat liver 24 h

after exposure [53]. These pathological changes were accompanied by elevated serum alanine aminotransferase levels. Hepatic glutathione content increased rapidly in exposed rats. The results suggest peroxidative damage in the cells.

Depending on the mode of administration, 1-nitropropane was significantly less toxic than 2-nitropropane. The oral lethal dose 50% (LD50) in male rats was 528 mg/kg and the oral LD50 in female rats was 484 mg/kg. The cutaneous absorption and distribution of absorbed ¹⁴C-1-nitropropane in female Rhesus monkeys showed a relatively benign response [54, 55].

3.3.4 Mutagenicity of Higher Mononitroalkanes

2-Nitropropane was mutagenic in *Salmonella typhimurium* [56]. The mutagenicity of 2-nitropropane and the relative inactivity of 1-nitropropane in *Salmonella* was confirmed, and the *in vitro* DNA-modifying activity of 2-nitropropane presented evidence to suggest that the genetic activity of this nitroalkane may not be dependent on the enzymatic reduction of the —NO₂ group to the corresponding hydroxylamine [57].

A 10- and 12-fold increase of revertant numbers was observed for 2-nitropropane as tested in the preincubation assay with *S. typhimurium* strains TA 100 and TA 98 in the presence and absence of an activator [58]. In the nitroreductase-deficient strains TA 100NR and TA 98NR, 2-nitropropane was less mutagenic than in the parent strains. In human lymphocytes, the induction of a weak clastogenic effect and of sister chromatid exchanges required exogenous metabolic activation. No significant mutagenic or cytogenetic response was found with 1-nitropropane in *S. typhimurium* or human lymphocytes.

Chromosome analyses were carried out in human lymphocytes treated *in vitro* with 2-nitropropane in the presence and absence of a mammalian metabolic activation system [59]. 2-Nitropropane was weakly clastogenic in human lymphocytes. Sister chromatid exchanges (SCE) were induced at concentrations as low as 7.5 mM.

The genotoxicity of 2-nitropropane and 1-nitropropane was investigated by measuring the induction of DNA repair synthesis in rat liver cells *in vitro* and *in vivo*: 2-nitropropane strongly induced DNA repair synthesis in both cases [60]. 2-Nitropropane was genotoxic in mammalian systems *in vitro* and *in vivo*; 1-nitropropane was not active *in vitro* or *in vivo*.

The structural isomer of 2-nitropropane, 1-nitropropane, was less hepatotoxic [61] and did not show genotoxicity in *Salmonella typhimurium*. It was, however, found to be mutagenic in the V79 Chinese hamster cells assay [62] and increased unscheduled DNA synthesis in rat hepatocytes *in vitro* [63]. Genotoxicity was much weaker or undetectable in cells not pre-treated with the inducer. 1-Nitropropane was not genotoxic in the hepatoma cells, irrespective of whether the cells were pre-treated or not.

2-Nitropropane is a rat liver carcinogen, whilst the 1-isomer is non-carcinogenic in rodents. Although DNA repair tests in rat liver discriminated clearly between the carcinogenic and the non-carcinogenic isomer, uniformly negative results have been

published for the mouse bone marrow micronucleus test with both isomers [63, 64]. Both 2-nitropropane and its anionic form, propane-2-nitronate, were mutagenic, but the nitronate was the more powerful mutagen [65]; however, nitroreduction is not involved in the genotoxicity of 2-nitropropane in cultured mammalian cells [66].

3.3.5 Carcinogenicity of Higher Mononitroalkanes

Based on studies in animals, 2-nitropropane is reasonably anticipated to be a human carcinogen and is listed as an IARC group 2B carcinogen [67]. When tested under the same conditions as 2-nitropropane, 1-nitropropane was not carcinogenic in rats after oral administration [68]. Groups of 4–6-day-old rats were exposed for 3 weeks (6 h/d, 5 d/week) to 2-nitropropane vapors of 0, 25, 40, 50, 80, and 125 ppm. One week later, polychlorinated biphenyls were administered for promotion twice a week for 8 weeks. The logarithms of the numbers of pre-neoplastic liver foci were found to be linearly related to the exposure concentrations of 2-nitropropane [69].

3.3.6 Accident History of Higher Mononitroalkanes

Humans may not be able to detect 2-nitropropane by its odor, even in the presence of potentially hazardous concentrations. One report stated that humans cannot detect 2-nitropropane at 83 ppm by its odor. Another stated that 2-nitropropane cannot be detected by its odor until the concentration reached about 160 ppm. Nausea, vomiting, diarrhea, anorexia, and severe headache have been reported in workers exposed to daily concentrations of 20–45 ppm.

Reports of four fatal poisonings by inhalation of paint fumes containing 2-nitropropane followed by detailed autopsies of the victims should have alerted the authorities to the hazards of working with this solvent, yet it continued to be used [70].

Two construction workers became ill after applying an epoxy resin coating containing 2-nitropropane in the confined, poorly ventilated space of an underground concrete vault [71]. One man died 10 d later from fulminant hepatic failure. The second man recovered but had persistently elevated serum aminotransferase activity. There have not been sufficient warnings about the acute toxicity of 2-nitropropane despite repeated reports of death due to hepatic failure after exposure to the compound in confined spaces.

3.3.7 Established Exposure Limits for Higher Mononitroalkanes

The occupational exposure standard recommended by the American Conference of Governmental Industrial Hygienists (ACGIH; 1981) for 2-nitropropane was a threshold limit value time-weighted average (TLV-TWA) of 25 ppm (90 mg/m³) [72].

NIOSH considers 2-nitropropane to be a potential occupational carcinogen as defined by the OSHA carcinogen policy [73, 74].

- OSHA PEL: 25 ppm (90 mg/m³) TWA
- 1989 OSHA PEL: 10 ppm (35 mg/m³) TWA
- 1993–1994 ACGIH TLV: 10 ppm (35 mg/m³) TWA, A2

The IDLH chosen in the 1970s was based on the observation that the lowest lethal concentration for cat for a 1-h exposure was found to be 2353 ppm. The response of different species to 2-nitropropane varied considerably, but cat was the most sensitive species in this investigation [41].

The revised and currently valid IDLH for 2-nitropropane is 100 ppm, based on acute inhalation toxicity data in animals. This may be a conservative value due to the lack of relevant acute toxicity data for workers exposed to concentrations above 45 ppm [75, 76]. (Note: NIOSH recommends as part of its carcinogen policy that the “most protective” respirators be worn for 2-nitropropane at any detectable concentration.)

3.4 Safety Properties of Higher Mononitroalkanes

The autoignition temperature of 2-nitropropane in air is 701 K (802 °F). The Cleveland flash point of 2-nitropropane in air is 313 K (103 °F). The Tag open-cup flash points of 1-nitropropane and 2-nitropropane in air are 322 and 311 K (120 and 100 °F), respectively.

4 Higher Polynitroalkanes

4.1 Physical Properties of Higher Polynitroalkanes

Attaching more than one nitro group to an alkane will improve the oxygen balance and create a multitude of potentially very energetic compounds. Attaching more than one nitro group to an alkane backbone will create various isomers. The nitro groups influence each other and adjacent hydrogens [77]. The physical properties of several polynitroalkanes have already been listed in previous tables along with those of the mononitroalkanes.

4.1.1 Thermodynamic Properties of Higher Polynitroalkanes

Most theoretical computations of thermodynamic data for energetic materials show only results for molecules in the vapor phase, which is of very limited use to the experimental propellant chemist. Computations giving the numbers for energetic com-

pounds in the condensed phase state are lacking. The heat of combustion of 2,2,3,3-tetranitrobutane, $C_4H_6(NO_2)_4$, is 2452 kJ/mol (586.1 kcal/mol) [26].

As part of an evaluation of hexanitroethane/fuel mixtures as monopropellants, the enthalpies of formation of several other polynitroalkanes were tabulated as shown in Table 8.

Table 8: Enthalpy of formation of polynitroalkanes.

Compound	Gross formula	Molecular mass, g/mol	Mols/kg	Enthalpy of formation			
				kcal/100 g	kcal/kg	kcal/mol	kJ/mol
Hexanitroethane	$C_2N_6O_{12}$	300.05	3.3328	9.53	95.3	28.59	119.6
1-Nitropropane	$C_3H_7NO_2$	89.09	11.2246	-45.32	-453.2	-40.38	-168.9
1-Nitrobutane	$C_4H_9NO_2$	103.12	9.6974	-44.69	-446.9	-46.08	-192.8
1,1-Dinitroethane	$C_2H_4N_2O_4$	120.06	8.3292	-28.87	-288.7	-34.66	-145.0
1,1-Dinitropropane	$C_3H_6N_2O_4$	134.09	7.4577	-29.85	-298.5	-40.03	-167.5
1,1,1-Trinitropropane	$C_3H_5N_3O_6$	179.09	5.5838	-15.66	-156.6	-28.05	-117.3

Data source: [28]

A comparison of results from Modified Intermediate Neglect of Differential Overlap, version 3 (MINDO/3), Modified Neglect of Differential Overlap (MNDO), and Austin Model 1 (AM1) calculations to each other and also to available experimental data for 105 nitro compounds, both aliphatic and aromatic, gives data only for the vapor phase. The properties evaluated include heats of formation, dipole moments, ionization potentials, and molecular geometries. In general, MINDO/3 predicted heats of formation, dipole moments, and ionization potentials more accurately than MNDO and AM1 [78, 79].

Table 9 provides a summary of enthalpies of formation for condensed-phase and vapor-phase polynitro compounds derived from methane and ethane. This is a useful table for comparisons in this group of potential rocket propellants and explosives. As a baseline, the heats of combustion of the condensed-phase species are also listed, because the experimentally measured enthalpies of formation are often derived from these numbers. This table is useful when studying the effects of interaction between neighboring multiple nitro groups in polynitroalkanes.

In nitroalkanes with one or two separated nitro groups, the enthalpy of formation can be predicted fairly accurately using one of the conventional rules of additivity of bond energies [81]. With increasing number of nitro groups on a methane or ethane skeleton, the efficient energy of interaction (EEI) among nitro groups increases and results in a measurable difference between measured and theoretically predicted enthalpies of formation for the gas-phase molecules. The actual enthalpy of formation is lower than the enthalpy predicted without the knowledge of interaction between the nitro groups [80] (Table 10). In nitromethanes, the dissociation energy of the C-NO₂ bonds decreases from 254 to 176 kJ/mol (60.8 to 42.2 kcal/mol) while go-

Table 9: Heats of combustion and enthalpies of formation of nitro compounds.

Property	Heat of combustion, $-\Delta H_c^\circ$		Enthalpy of formation, condensed phase, ΔH_f°		Enthalpy of formation, vapor phase, $\Delta H_f^\circ(\text{G})$	
	kJ/mol	kcal/mol	kJ/mol	kcal/mol	kJ/mol	kcal/mol
Units						
Compound						
$\text{CH}_3\text{NO}_2(\text{L})$	709	169.5	-119.2	-28.5	-80.8	-19.3
$\text{CH}_2(\text{NO}_2)_2(\text{L})$	574	137.3	-105.4	-25.2	-59.8	-14.3
$\text{CH}(\text{NO}_2)_3(\text{S})$	492	117.6	-44.8	-10.7	+24.3	+5.8
$\text{C}(\text{NO}_2)_4(\text{L})$	432	103.2	+38.5	+9.2	+82.4	+19.7
For comparison:						
$\text{CH}_4(\text{G})$	—	—	—	—	-74.9	-17.9
Compound						
$\text{C}_2\text{H}_5\text{NO}_2(\text{L})$	1358	324.5	-143.9	-34.4	-102.5	-24.5
$(\text{NO}_2)\text{CH}_2\text{CH}_2(\text{NO}_2)(\text{S})$	1180	282	-178.7	-42.7	-97.1	-23.2
$\text{CH}_3\text{CH}(\text{NO}_2)_2(\text{L})$	1209	289	-149.4	-35.7	-88.3	-21.1
$\text{CH}_3\text{C}(\text{NO}_2)_3(\text{S})$	1103	263.6	-113.0	-27	-41.0	-9.8
$\text{C}_2(\text{NO}_2)_6(\text{S})$	867	207.1	+79.5	+19	+141.4	+33.8
For comparison:						
$\text{C}_2\text{H}_6(\text{G})$	—	—	—	—	-84.0	-20.08

Data source: [80]

Table 10: Efficient energy of interaction among nitro groups in polynitroalkanes.

Nitro derivatives of methane					
Efficient energy of interaction, kcal/mol					
Compound	Nitromethane	Dinitromethane	Trinitromethane	Tetranitromethane	
$\Delta H_f^\circ(\text{g})$ exp.	-17.8	-9.2	+5.8	+19.7	
$\Delta H_f^\circ(\text{g})$ calc.	-17.8	-17.7	-17.6	-17.5	
EEl	0	8.5	23.4	37.2	
Nitro derivatives of ethane					
Compound	Nitroethane	1,2-Dinitro-ethane	1,1-Dinitro-ethane	1,1,1-Trinitro-ethane	Hexanitro-ethane
$\Delta H_f^\circ(\text{g})$ exp.	-24.5	-23.2	-21.1	-9.8	-33.8
$\Delta H_f^\circ(\text{g})$ calc.	-24.5	-27.8	-28.8	-33.1	-46.0
EEl	0	5.6	7.7	23.3	79.8

Data source: [80]

ing from nitromethane to tetranitromethane. Similar interactions are also observed in polynitrobenzenes. See also [82].

In order to compare computational results for 28 aliphatic nitro compounds in the gaseous state with experimental results of 19 compounds, correlation models were established by multivariable linear regression methods considering the number of nitro

groups and use of quadratic relations involving the number of carbon, hydrogen, nitrogen, and oxygen atoms [83]. Both the AM1 and the Parametric Method 3 (PM3) have good agreement with the experimental results. Based on these correlations, heats of formation of some aliphatic nitro compounds can be predicted with only $\pm 5\%$ deviations. Table 11 is a comparison of measured and calculated results. Results from only one of the calculating methods (PM3, Eq. 14) is shown here.

Table 11: Heats of formation of aliphatic nitro derivatives in the vapor phase.

Compound	Experimental		Calculated (PM3, equation 14)	
	kJ/mol	kcal/mol	kJ/mol	kcal/mol
Nitromethane	-51.0	-12.2	-60.0	-14.351
Dinitromethane	-59.8	-14.3	-52.8	-12.609
Trinitromethane	-13.4	-3.2	-11.7	-2.787
Tetranitromethane	77.4	18.5	76.3	18.226
Nitroethane	-98.3	-23.5	-98.3	-23.487
1,1-Dinitroethane	-100.8	-24.1	-92.9	-22.194
1,2-Dinitroethane	-95.8	-22.9	-99.7	-23.82
1,1,1-Trinitroethane	-51.9	-12.4	-51.9	-12.408
Hexanitroethane	149.8	35.8	149.7	35.773
1-Nitropropane	-124.3	-29.7	-127.4	-30.438
2-Nitropropane	-141.8	-33.9	-130.1	-31.101
1,1-Dinitropropane	-108.4	-25.9	-120.4	-28.783
1,3-Dinitropropane	-132.2	-31.6	-133.9	-32
2,2-Dinitropropane	-113.0	-27	-114.8	-27.434
1,1,1-Trinitropropane	-77.0	-18.4	-74.1	-17.707
1-Nitrobutane	-143.9	-34.4	-152.2	-36.379
2-Nitrobutane	-163.6	-39.1	-153.2	-36.605
1,1-Dinitrobutane	-142.7	-34.1	-143.5	-34.295
1,4-Dinitrobutane	-162.8	-38.9	-163.3	-39.037

Data source: [83]

Similar molecular orbital calculations were applied to energetic dinitro compounds based on inter-molecular binding energies, molecular geometries, molecular electrostatic potentials, and conformational energies of model compounds [84]. Non-bonded parameters were derived by fitting experimental densities and heats of vaporizations of model compounds. Torsional parameters were quantified to accurately reproduce the relative conformational energy minima and barriers in 2,2-dinitropropane, bis(methoxymethyl) ether, 2,2-dinitro-3-methoxypropane, and bis(2,2-dinitropropyl)formal, and calculations accurately reproduced thermodynamic and transport properties of 1,1-dinitroethane, 2,2-dinitropropane, and a eutectic mixture of bis(2,2-dinitropropyl)formal and bis(2,2-dinitropropyl)acetal.

Density functional theory (DFT)-based calculations were performed on a series of nitroalkanes and alkyl nitrites representing primary, secondary, and tertiary nitro compounds and their radicals resulting from loss of their skeletal hydrogen atoms [85]. Geometries, vibration frequencies, and thermochemical properties (S°_T and $C^\circ_{p(T)}$) in the temperature range from 10 to 5000 K were calculated by DFT methods and enthalpy of formation values via other methods. Potential energy barriers for the internal rotations were computed, and the lower barrier contributions were incorporated into entropy and heat capacity data. The standard enthalpies of formation of nitroalkane and alkyl nitrite vapors at 298 K were evaluated using iso-seismic reaction schemes with several work reactions for each species. Recommended standard enthalpy of formation values derived from the most stable conformers of respective nitroalkane and alkyl nitrite isomers include -127.9 and -119.0 kJ/mol (-30.57 and -28.44 kcal/mol) for 1-nitropropane and *n*-propyl nitrite, -141.8 and -135.2 kJ/mol (-33.89 and -32.32 kcal/mol) for 2-nitropropane and isopropyl nitrite, -179.0 and -173.0 kJ/mol (-42.78 and -41.36 kcal/mol) for 2-methyl-2-nitropropane and *tert*-butyl nitrite, respectively. For comparison, entropy and heat capacity values were also reported for the vapors of the lower homologues: nitromethane, nitroethane, and corresponding nitrites. See also [86].

4.2 Chemical Properties of Higher Polynitroalkanes

Higher polynitroalkanes are of interest as energetic compounds in propellants or explosives because potentially, so many nitro groups can be attached until the oxygen balance becomes positive. An example is hexanitroethane with an oxygen balance of $+42.7\%$. In addition, the acidity of the few remaining hydrogen atoms becomes so high that these compounds are quasi-acids and can form salts with a wide variety of bases [87]. The salts are also potential propellant additives, like the acid from which they are derived, or they serve as intermediates in the synthesis of other nitro compounds.

The following summary of polynitroalkanes is subdivided by the structure of the carbon skeleton to which the nitro groups are attached. The simplest polynitroalkanes are those with a straight carbon-carbon chain, starting with those based on a chain with only two carbon atoms, the ethane skeleton.

4.3 Sensitivity of Higher Polynitroalkanes

The thermal stability of $C_{n>2}$ polynitroalkanes is generally lower than that of nitromethane. One exception is 1,1-diamino-2,2-dinitroethene, which is a thermally stable explosive. The sensitivity of polynitroalkanes and nitramines to mechanical impact can be correlated to their molecular structure [88]. Similar relationships were established for polynitroaromatic explosives.

5 Straight-Chain Polynitroalkanes and Polynitroalkenes

Adding nitro groups to straight-chain $C_{n>1}$ nitroalkanes will make them more useful as oxidizers and monopropellants, but will in most instances render them less thermally stable and more chemically reactive. Most of the work has been done with polynitroethanes and less work with the higher $C_{n>2}$ polynitroalkanes.

5.1 Polynitroethanes

5.1.1 Dinitroethanes

The oxygen balance for combustion of dinitroethanes to CO_2 is -26.7% . There are two isomers of dinitroethane, the symmetrical 1,2-dinitroethane and the unsymmetrical 1,1-dinitroethane:

$O_2NCH_2CH_2NO_2$	$(O_2N)_2CHCH_3$
1,2-dinitroethane	1,1-dinitroethane
CAS RN [7570-26-5]	CAS RN [600-40-8]

5.1.1.1 1,2-Dinitroethane

1,2-Dinitroethane, $O_2NCH_2CH_2NO_2$, viz-dinitroethane, Chemical Abstracts Service Registry Number (CAS RN) [7570-26-5], molecular weight: 120.06416 g/mol, can be prepared in 70–80% yield by passing ethylene into dinitrogen tetroxide, N_2O_4 , at 263 K (-10°C). The use of a mixture of ethylene with oxygen in the volume ratio of about 4:1 gives good results. Ethylene reacts much more slowly than the higher olefins [89]. 1,2-Dinitroethane forms colorless crystals when crystallized from MeOH or benzene, melting point (m.p.) 312–313 K ($39\text{--}40^\circ\text{C}$), boiling point (b.p.) 408 K (135°C) at 5 mm pressure, density 1.460 g/cm³. It slowly decomposes on storage, turning acidic. It is insoluble in water. The explosive power measured by Trauzl lead block test was 146% of that of picric acid [90]. 1,2-Dinitroethane, its potassium salt, and dinitropropanol are intermediates in the synthesis of energetic plasticizers such as bis(2,2-dinitropropyl) acetal (BDNPA) and bis(2,2-dinitropropyl) formal (BDNPF). Therefore, more economical methods were sought for the production of 1,2-dinitroethane, including electrolytic nitrating methods.

Older sources [91] gave the heat of combustion of 1,2-dinitroethane as -1183 ± 1.2 kJ/mol (282.7 kcal/mol) and the heat of formation derived therefrom was -176 ± 1.2 kJ/mol (42.1 kcal/mol; previously reported number corrected for pressure). Other sources gave the heat of formation of 1,2-dinitroethane as -179 ± 0.8 kJ/mol (-42.8 kcal/mol) [4]. Table 12 gives the physical state of 1,2-dinitroethane at 298 K as a liquid, when actually the pure compound melts only at a higher temperature, 312–313 K. Impure specimens may be liquids at room temperature.

Table 12: Thermodynamic properties of dinitroethanes.

Compound	Physical state	Standard enthalpy of formation ΔH_f^{298}		Enthalpy of evaporation ΔH_{evap} at 298 K		Vapor state enthalpy of formation $\Delta H_f^{298}(\text{G})$	
		kJ/mol	kcal/mol	kJ/mol	kcal/mol	kJ/mol	kcal/mol
1,1-Dinitroethane	Liquid	-149.4 ± 0.4	-35.7 ± 0.1	61.1 ± 0.4	14.6 ± 0.1	-88.3 ± 0.8	-21.1 ± 0.2
1,2-Dinitroethane	Liquid	-178.2 ± 0.4	-42.6 ± 0.1	81.6 ± 0.8	19.5 ± 0.2	-96.7 ± 1.3	-23.1 ± 0.3

Data source: [8]

The molecular structure and theoretical dipole moments for different forms of 1,2-dinitroethane were calculated and compared to measured data. The known experimental value of the dipole moment of this compound ($\mu = 1.12$ D at 305 K = 32 °C) corresponds to a high proportion (~70%) of the *trans* form [92]. Measurements of 1,2-dinitroethane solutions in benzene at 293 K gave a dipole moment of 4.4 ± 0.1 D. The theoretical dipole moment of 1,2-dinitroethane was calculated as a function of the rotation angle separating the two nitro groups. If the two molecule halves were freely rotating, one would expect a dipole moment of 4.13 D, which is close to the measured value in solution.

The slow decomposition of 1,2-dinitroethane can be retarded by addition of aryl-sulfonic acids as stabilizers [93].

The gas-phase enthalpies of formation of 1,1-dinitroethane and 1,2-dinitroethane and the corresponding radicals were calculated using composite methods and DFT theory with various basis sets [94, 95]. The enthalpies of the C—N and C—C bonds dissociation and activation enthalpies for HONO elimination were calculated and compared with available experimental data. It was found that some calculations do provide a reasonable way to tackle the problem of the decomposition channels of 1,1- and 1,2-dinitroethane, including four main mechanisms for gas-phase decomposition of 1,1- and 1,2-dinitroethane: dissociation through direct breaking of the C—N bond, producing two radicals, $\text{C}_2\text{H}_4(\text{NO}_2)_2$, and NO_2 ; elimination of HONO; nitro–nitrite rearrangement; and finally, a mechanism of hydrogen transfer and isomerization to the *aci* form were studied. HONO elimination seemed to be the most favorable mechanism for the decomposition of 1,2-dinitroethane. However, the difference in energies of the HONO elimination and C—N homolytic bond cleavage in 1,1-dinitroethane does not favor any of these channels, especially at low temperature. The *gauche* conformation of 1,2-dinitroethane was predicted to be the lowest-energy minimum.

Examination of the infra-red (IR) and Raman spectra suggested that 1,2-dinitroethane exists in the polar *gauche* conformation in the solid state and as a mixture of the *gauche* and *trans* rotamers in solution [96]. Analysis of the dipole moment and relative permittivity data showed that at 298 K (25 °C) in solution, the compound existed in a ratio of approximately 92% *gauche* to 8% *trans*. The crystal and molecular structure of solid 1,2-dinitroethane was determined by single-crystal X-ray diffraction (XRD). The molecule crystallizes in the tetragonal space group $I4_1/a$, with $a = 13.305(1)$ Å, $c = 11.121(3)$ Å, $V = 1968.8(6)$ Å³, and $Z = 16$. The molecule adopts a *gauche* conformation with a N—C—C—N torsion angle of 73.5(2)°.

5.1.1.2 1,1-Dinitroethane

1,1-Dinitroethane, $(\text{O}_2\text{N})_2\text{CHCH}_3$, $\text{C}_2\text{H}_4\text{N}_2\text{O}_4$, *gem*-dinitroethane, CAS RN [600-40-8], molecular mass = 120.06416 g/mol, is a colorless oil with faint alcoholic odor with

a b.p. of 458–459 K (185–186 °C) at 760 mm Hg and of 346–347.6 K (73–74.5 °C) at 13 mm Hg, and a density of 1.4340 g/cm³ at 293 K (20°) and 1.3503 g/cm³ at 296.6 K (23.5 °C). The oxygen balance is –26.7%. The enthalpy of formation of 1,1-dinitroethane is –289 cal/g = –34.7 kcal/mol = –145 kJ/mol [97]. It forms salts with potassium [98] or sodium or ammonia which are explosive. The ammonium salt NH₃C₂H₃(NO₂)₂ is a yellow salt, m.p. 363–366 K (90–93 °C).

1,1-Dinitroethane, its potassium salt, and dinitropropanol are intermediates in the synthesis of energetic plasticizers such as 2,2-dinitropropyl acetal (BDNPA) and bis(2,2-dinitropropyl) formal (BDNPF). Therefore, more economical methods were sought for the production of 1,1-dinitroethane, including electrolytic nitrating methods [99]. Three methods of converting nitroethane to dinitroethane have been investigated: nitration, oxidative nitration, and oxidation of the readily formed ethylnitrolic acid. Attempts to substitute nitrite for chloride in 1,1-dichloroethane were unsuccessful. Other possible routes to dinitroethane are electrolytic nitration and nitrite displacement on chloronitroethane [100, 101]. The first step in electrolytic methods for the preparation of simple *gem*-dinitroparaffins is the electrolytic oxidation of a silver anode to silver ions [102]. In the preparation of 1,1-dinitroethane, the silver ions react in the anode compartment of the electrolysis cell with nitrite and ethylnitronate ions to form the potassium salt of dinitroethane in solution and silver metal on the surface of the electrode. 1,1-Dinitropropane and 2,2-dinitropropane have been prepared by analogous reactions.

The gas-phase enthalpies of formation of 1,1- and 1,2-dinitroethane and corresponding radical products of decomposition were calculated using density functional theory/orbital bond energy methods [103]. The enthalpies of the C–N and C–C bonds dissociation and activation enthalpies for HONO elimination were compared with available experimental data. It was found that calculations did provide a reasonable way to describe the decomposition channels of 1,1- and 1,2-dinitroethane. Four main mechanisms for gas-phase decomposition of 1,1- and 1,2-dinitroethane were identified. HONO elimination seemed to be the most favorable mechanism for the decomposition of 1,2-dinitroethane. However, the difference in energies of HONO elimination and C–N homolytic bond cleavage in 1,1-dinitroethane did not favor any of these channels, especially at the working temperature. The *gauche* conformation of 1,2-dinitroethane seemed to be the lowest-energy minimum.

5.1.2 Trinitroethanes

The oxygen balance of trinitroethanes for combustion to CO₂ is +8.45%.

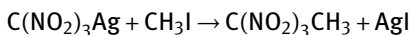
1,1,1-Trinitroethane, (O₂N)₃CCH₃, C₂H₃N₃O₆, molecular mass: 165.0617, CAS RN [595-86-8], forms small white, very volatile cubic crystals with a m.p. of 329–330 K =

56–57 °C and a molten state-specific gravity of 1.4223 g/cm³ at 350.8 K = 77.7 °C. Distillation (with precautions!) is possible with a b.p. of 341 K = 68 °C at 2.26 kPa = 17 mm Hg reduced pressure [104].

1,1,1-Trinitroethane explodes at higher temperatures. 1,1,1-Trinitroethane is very soluble in water and soluble in ethanol, diethyl ether, and in most organic solvents.

The heat of combustion of solid 1,1,1-trinitroethane is -1103 ± 0.8 kJ/mol and the heat of formation is $-113. \pm 0.8$ kJ/mol [4]. The heat of fusion is 11.72 kJ/mol at 329.2 K [105]. The heat of sublimation is 72.0 ± 8.8 kJ/mol. The enthalpy of formation of solid 1,1,1-trinitroethane is -166 cal/g = -274 kcal/mol = -114.6 kJ/mol and the density is 1.528 g/cm³ = 0.0552 lb/in³ [97]. It detonates when hit by a hammer blow.

1,1,1-Trinitroethane can be prepared by the action of a cooled ethereal solution of silver nitroform on an excess of methyl iodide:



After allowing the mixture to stand for a short time, it is filtered to remove AgI and the filtrate is evaporated in a vacuum [106]. In another method of preparation, the more economical potassium salt of nitroform was dissolved in acetone and treated with methyl iodide [107]. Reaction of nitroethane with sodium methylate and then with tetranitromethane gives a mixture of 1,1,1-trinitroethane and 1,1-dinitroethane [108].

5.1.3 Tetranitroethanes

Tetranitroethane, C₂H₂(NO₂)₄, molecular mass 210.07, oxygen balance for combustion to CO₂ +22.8%, may exist in the form of two isomers. 1,1,2,2-Tetranitroethane, *sym*-1,1,2,2-tetranitroethane, (O₂N)₂CHCH(NO₂)₂, is not known in the free state, but its potassium, silver, and lead salts are known. The dipotassium salt is an explosive of the initiating class and is extremely sensitive to friction, impact, and heat, especially if not properly purified. This is a good reason not to use it as a rocket propellant. The salt was prepared at Picatinny Arsenal in 1930 and then again in 1947. However, the compound was considered too dangerous for use as a military explosive and work on it discontinued after what was supposed to be some of the salt exploded in a beaker resulting in the death of a chemist, Dr. P. F. Macy.

The crystal structure of dipotassium tetranitroethide, K(NO₂)₂CC(NO₂)₂K, has been determined by single crystal XRD [109]. The compound crystallizes in the centrosymmetric space group C2/c with cell constants of $a = 13.03$ Å, $b = 7.56$ Å, $c = 13.53$ Å, and $\beta = 140.87^\circ$. Each unit cell contains four molecules, with the anions centered on twofold rotation axes. The C—C bond distance is 1.43 Å.

5.1.4 Hexanitroethane

An extreme example in the series of polynitroethanes is hexanitroethane ($\text{NO}_2)_3\text{CC}(\text{NO}_2)_3$, $\text{C}_2\text{N}_6\text{O}_{12}$, CAS RN [918-37-6], molecular mass 300.0544 g/mol. It belongs to the group of nitrocarbons because it does not contain any hydrogen. It contains 63.98% oxygen. With an oxygen balance of +42.7%, it is a net oxidizer similar to tetranitromethane (TNM), because both compounds contain more oxygen than is necessary for complete combustion of carbon atoms to CO_2 .

Hexanitroethane is one of the few compounds that contain only a carbon skeleton and attached nitro groups. These compounds are called “nitrocarbons.” Other compounds with similar structures are TNM, hexanitrobenzene, octanitrocubane, or decanitrobiphenyl. There is even a book devoted exclusively to these types of chemicals, which make good oxidizers for rocket propellants [110].

5.1.4.1 Physical Properties of Hexanitroethane

Hexanitroethane is a compound of interest as a rocket propellant oxidizer due to its high oxygen content. It forms colorless crystals when crystallized from ether, is non-hygroscopic, slightly volatile at room temperature, explodes on rapid heating above 633 K (360 °C), and by the action of a detonator. It is soluble in diethyl ether, benzene, or chloroform, but only poorly soluble in ethanol and insoluble in water.

Hexanitroethane is a solid at room temperature, melts at 420 K (147 °C = 297 °F), and explodes when heated to near 448 K (175 °C). It readily sublimates and the vapors are very toxic. Good summaries of the physical and chemical properties of hexanitroethane have been published [111–113]. The physical properties of hexanitroethane are summarized in Table 13. Other properties were included in earlier tables showing the properties of nitroalkanes as a group.

The vapor pressure of hexanitroethane is listed in Table 14.

Table 13: Physical properties of hexanitroethane.

Property	SI units	Other units	Reference
Molecular mass	300.0544 g/mol	3.3327 mol/kg	
Melting point	420 K	147 °C	297 °F [2]
Melting point	423 K	150 °C	302 °F [111]
Density, pycn.	1.85 kg/dm ³	1.85 g/cm ³	[2]
Density, XRD	2.25 kg/dm ³	2.25 g/cm ³	[111]
Density	1.998 kg/cm ³	1.998 g/cm ³	
Vapor pressure	67 Pa at 298 K	0.5 mm Hg at 25 °C	[111]

Table 14: Vapor pressure of hexanitroethane.

Temperature		Vapor pressure		
K	°C	Pa	mbar	mm Hg
293	20	50.5	0.5	0.38
303	30	80.8	0.8	0.61
313	40	111	1.1	0.84
323	50	151	1.5	1.1
333	60	222	2.2	1.7
343	70	505	5	3.8
353	80	1515	15	11.4
358	85	2828	28	21.3

Data source: [2]

The vapor pressure of hexanitroethane can be calculated from the equation

$$\log P = 5.0244 - 1590/T$$

where P is the pressure in mm Hg and T is the temperature in kelvin [111].

Optical Properties of Hexanitroethane

The IR and Raman spectra of hexanitroethane in solution (Figure 1) confirmed the D_{3d} symmetry and staggered configuration of this molecule [114]. The D_{3d} symmetry was chosen as the more probable symmetry instead of the D_{3h} symmetry. The latter has an eclipsed structure, with the C—NO₂ plane perpendicular to the C—C axis. The vibrational fundamentals and a number of combination bands could be assigned and compared to similar assignments in two nitroethanes and four nitromethanes.

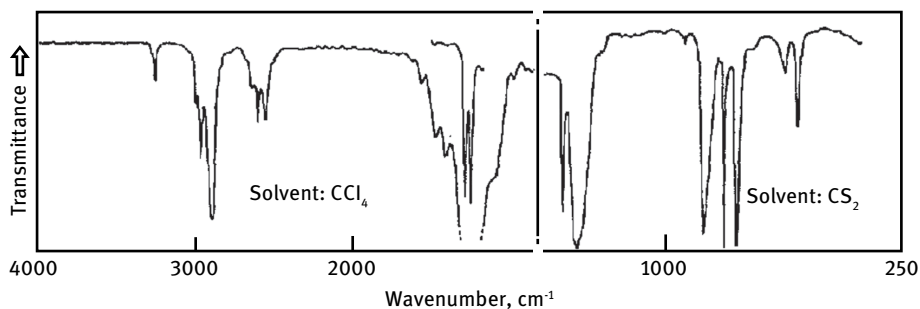


Figure 1: Infrared spectrum of hexanitroethane. (Republished and modified from [114], with permission of © 1974 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

Molecular Structure of Hexanitroethane

The crystal structure of hexanitroethane has been determined in the low-temperature ordered phase at 145 K and found to be space group $P2_1/c$ with $a = 10.152(2) \text{ \AA}$, $b = 9.311(2) \text{ \AA}$, $c = 10.251(2) \text{ \AA}$, $\beta = 97.54(1)^\circ$, $V = 960.6(3) \text{ \AA}^3$, $Z = 4$, with two non-equivalent molecules in the unit cell [115]. The far-IR, IR, and Raman spectra of hexanitroethane in both low-temperature ordered and high-temperature disordered crystal phases were recorded, and the internal modes of vibration were interpreted with the help of normal coordinate analysis and a conformational analysis with the MNDO method. This helped to explain the phase transition mechanism.

Three theoretical types of nitroform derivatives based on the hexanitroethane structure were designed by molecular modeling and their stability and explosive performance was predicted by computations [116]. It was hoped that such calculations would lead to the future development of more thermally stable nitro compounds.

Thermodynamic Properties of Hexanitroethane

The thermodynamic properties of hexanitroethane are summarized in Table 15.

Table 15: Thermodynamic properties of hexanitroethane

Property	SI units		Other units		References
Enthalpy of formation ΔH_f^{298}	+79.5 kJ/mol	+264.9 kJ/kg	+19.0 kcal/mol	+63.3 cal/g	[2]
Enthalpy of formation ΔH_f^{298}	+117 $\pm 8 \text{ kJ/mol}$	+390 $\pm 27 \text{ kJ/kg}$	+28 kcal/mol	+93 cal/g	[111]
Enthalpy of formation ΔH_f^{298}	+108 $\pm 4.2 \text{ kJ/mol}$	+360 $\pm 14 \text{ kJ/kg}$	+25.8 $\pm 1.0 \text{ kcal/mol}$	+86 $\pm 3.3 \text{ cal/g}$	[117]
Enthalpy of formation ΔH_f^{298}	+119 kJ/mol	+397 kJ/kg	+28.5 kcal/mol	+95 cal/g	[97]
Heat of sublimation	71 $\pm 2 \text{ kJ/mol}$	237 kJ/kg	16.97 kcal/mol	56 cal/g	[117]

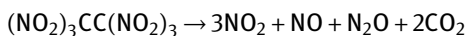
Molecular mass 300.0544 g/mol, 3.333 mol/kg

The heat capacity of the crystalline phase I of hexanitroethane is $327 \text{ J mol}^{-1} \text{ K}^{-1}$ at 291 K [118]. Phase I exists from 190 to 350 K. See also [82].

5.1.4.2 Thermal Decomposition of Hexanitroethane

The rates of decomposition of hexanitroethane were determined in a number of solvents and as the pure solid in the temperature range of 333 to 373 K (60 to 100 °C) [119]. The products of reaction from the complete thermal decomposition of the solid can be

represented by the equation



The decomposition of hexanitroethane for the pure solid and in CCl_4 proceeds by a first-order reaction. The specific first-order rate constants are for solid hexanitroethane

$$k = 10^{18.6} \exp(-38900/RT) \text{ s}^{-1}$$

and for dissolved hexanitroethane in CCl_4

$$k = 10^{18.5} \exp(-37800/RT) \text{ s}^{-1}$$

The gas-phase decomposition of hexanitroethane has been studied over a temperature range of 373 to 433 K (100° to 160 °C) using a manometric method [120]. The reactions were found to be homogeneous and first order. The rates were independent of vapor pressures and of nitric oxide and nitrogen dioxide additions. The results were interpreted in terms of a radical non-chain mechanism, with C—N bond scission being the first step. The flash pyrolysis of hexanitroethane under vacuum forms tetranitroethylene, a very active Diels–Alder additions reagent [121].

5.1.4.3 Explosive Properties of Hexanitroethane

The friction sensitivity of hexanitroethane shows a reaction at a pistil load of 240 N. In the Trauzl lead block test, bulging of the cavity resulted in a volume increase of $245 \text{ cm}^3/10 \text{ g}$. Other sources describe the explosive power by Trauzl test as 115% of that of TNT. The detonation velocity of confined hexanitroethane is $4950 \text{ m/s} = 16240 \text{ ft/s}$ at $\rho = 0.91 \text{ g/cm}^3$. Mixtures of hexanitroethane and boron powder have been evaluated as chlorine-free igniters and explosives [122].

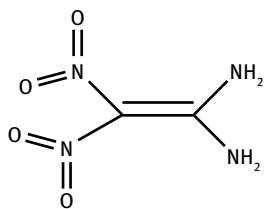
5.2 Polynitroethenes

While most of the work in the past has been on polynitroalkanes, the stabilizing effect of electron conjugation between electrons in the nitro group and electrons in the $\text{C}=\text{C}$ double bond has brought about a flurry of synthesis work with unsaturated nitro compounds [123].

5.2.1 1,1-Diamino-2,2-Dinitroethene

The predominant representative in the group of C_2 polynitroethenes is 1,1-diamino-2,2-dinitroethylene, also known as 1,1-diamino-2,2-dinitroethene, $(\text{H}_2\text{N})_2\text{C}=\text{C}(\text{NO}_2)_2$, $\text{C}_2\text{H}_4\text{N}_4\text{O}_4$, DADNE, DADE, FOX-7, CAS RN [145250-81-3]. It is a less-sensitive explosive,

which could find application as a substitute for RDX (less sensitive but with preservation of performance) in explosive as well as rocket propellant applications. It is a surprisingly simple molecule (compared to complex structures like hexanitrohexaazaisowurtzitane, CL-20), with a molecular mass of 148.07756 g/mol and an oxygen balance of -21.6%. It is not sure if FOX-7 itself will find application as a solid rocket propellant ingredient, but some of its derivatives are useful as energetic ingredients and listed here nevertheless.



1,1-Diamino-2,2-dinitroethylene, FOX-7, DADNE

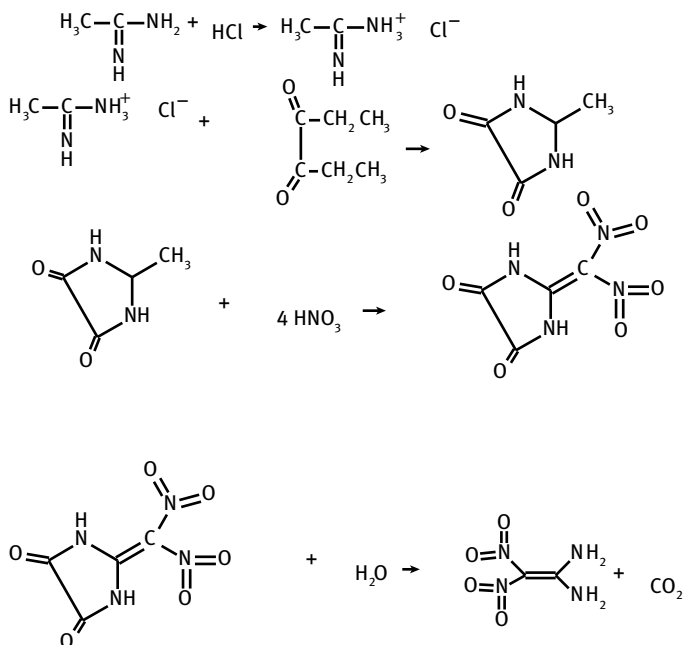
Looking at the history of explosives development, it is surprising that FOX-7 was discovered only a few years ago and that people “stumbled” upon it while they were looking for other compounds.

1,1-Diamino-2,2-dinitroethene (DADNE, FOX-7), an insensitive energetic material, was first synthesized in 1998. It has since attracted the interest of the energetic materials research community for its high potential in diverse applications. FOX-7 was developed in Sweden by the Swedish Defense Research Agency (FOI) and its production was licensed to what is now EURENCO [124]. The first two letters of FOX are derived from the name of the agency (**FOI**) and the X stands for **eX**plosive. FOX-7 has roughly the same performance as RDX but is less sensitive. FOX-7 is a relatively new addition to the arsenal of rocket propellant ingredients and most of the information is scattered over recent publications. This area was still being actively investigated while the manuscript for this book was compiled. There is an on-going flood of publications on this material and new references pour in every month. An excellent summary of the properties of FOX-7, including 61 literature references, was published in 2007 [125]. See also [126–129].

New derivatives of FOX-7 and its hydrazine analogue 1-amino-1-hydrazino-2,2-dinitroethene as well as their potassium salts have been made [130]. Besides the usual spectroscopic characterization, the structures of all compounds were investigated by single-crystal XRD. The compounds demonstrated good thermal stabilities, very high densities, and favorable sensitivity values. The heats of formation were calculated, and together with the room-temperature densities, the detonation parameters were estimated.

5.2.1.1 Preparation of FOX-7

FOX-7 was first synthesized in 1998 [131]. The historically used method started with the condensation of acetamidinium chloride and diethyl oxalate:



FOX-7 can also be prepared by nitration of 4,6-dihydroxy-2-methylpyrimidine, which is commercially available [132]. The intermediate product is 2-dinitromethylene-5,5-dinitrodihydropyrimidine-4,6(1H,5H)-dione, which is hydrolyzed to form 1,1-diamino-2,2-dinitroethene in 90% yield along with dinitromethane as a by-product.

Low-temperature nitration of 2-methylimidazole gave intermediates which were aminated to form 1,1-diamino-2,2-dinitroethylene [133]. The synthesis route in the literature was scaled up and reaction conditions were optimized. The overall yield was 14.9% of the theoretical yield. The structure of FOX-7 was then characterized by IR spectroscopy, mass spectroscopy (MS), nuclear magnetic resonance (NMR), and elemental analysis.

FOX-7 was synthesized by amination of intermediates which were prepared by nitration of 2-methylimidazole [134]. 2-Methyl-4(5)-nitroimidazole and parabanic acid were separated from the filtrate of the intermediates. 2-Methyl-4(5)-nitroimidazole and parabanic acid were also synthesized by nitration of 2-methylimidazole under different conditions, with yields of 67.3 and 63.3%, respectively. An important step was rearrangement of the nitro group. FOX-7 was formed mainly by the following steps: 2-methylimidazole $\rightarrow$ 2-methyl-4,5-dihydro-imidazol-5-one $\rightarrow$

2-(dinitromethylene)-5,5-dinitro-4-imidazolidinone $\rightarrow$ 2-(dinitromethylene)-4(5)-imidazolidinedione $\rightarrow$ FOX-7.

Nitration of 2-methylimidazole gave intermediates which were aminated to form 1,1-diamino-2,2-dinitroethylene [135]. The synthesis route described in the literature was scaled up properly and reactive conditions were optimized. The yield of FOX-7 was 18.8%. The structure of FOX-7 was characterized by IR, MS, NMR, and elemental analysis.

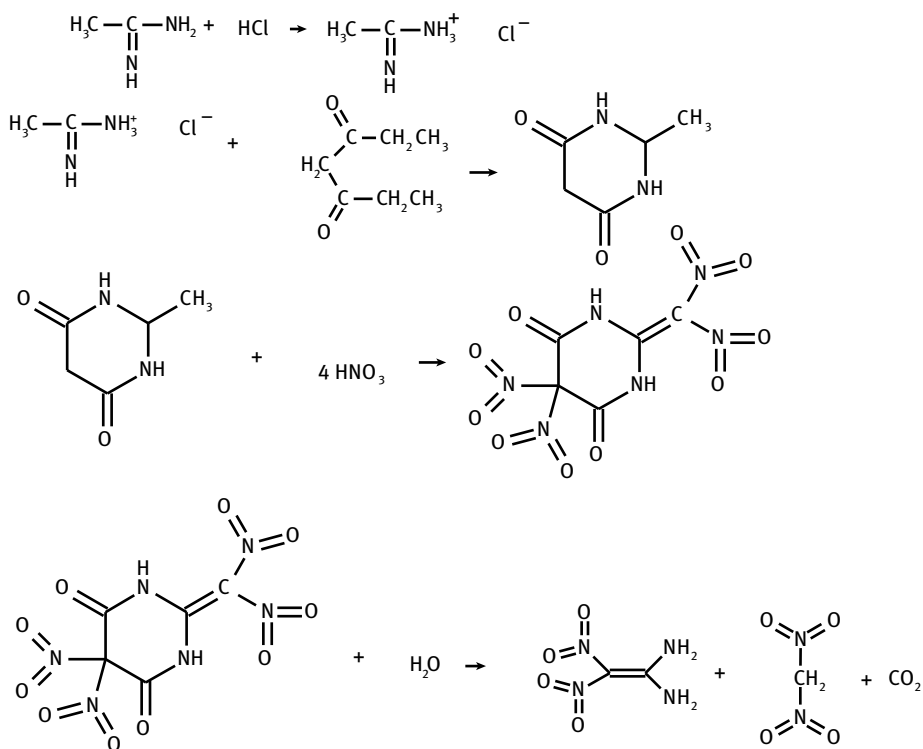
Nitration of 2-methylimidazole at ambient temperature gave 2-(dinitromethylene)-5,5-dinitro-4-imidazolidinone, which reacted with water to give FOX-7 [136]. The key step was ring cleavage of 2-(dinitromethylene)-5,5-dinitro-4-imidazolidinone by addition of water to the reaction mixture or vice versa. By this method, the conversion of 2-methylimidazole to FOX-7 could be achieved in a continuous process. The overall yield was 35.8%.

Nitration of some 2-substituted-1,4,5,6-tetrahydro-pyrimidine-4,6-diones gave several new 2-substituted-1,4,5,6-tetrahydro-5,5-*gem*-dinitropyrimidine-4,6-diones in high yields (>80%) [137]. The *gem*-dinitro products formed were easily attacked by nucleophiles with the formation of *gem*-dinitroacetyl derivatives, which in turn could be further hydrolyzed to the salts of dinitromethane. When the substituent at position 2 was an alkyl group, nitration occurred both at position 5 and at the α -carbon atom of the side chain. If the alkyl group was methyl, the product would be 2-(dinitromethylene)-5,5-dinitropyrimidine-4,6-dione, which was hydrolyzed to form 1,1-diamino-2,2-dinitroethylene (FOX-7) and dinitromethane. Three different synthetic routes leading to FOX-7 were compared and the reaction mechanisms were discussed.

An improved synthetic route for FOX-7 was investigated by nitration of 2-methyl-4,6-pyrimidindione in nitric acid/sulfuric acid and hydrolysis of the intermediate 2-dinitromethylene-5,5-dinitro-dihydro-pyrimidine-4,6-dione with a total yield of over 83% [138]. The structure of FOX-7 made by this method was then characterized by IR, MS, NMR, and elemental analysis.

1,1-Diamino-2,2-dinitroethene (FOX-7) was synthesized with 2-methylpyrimidine-4,6-dione as feedstock by nitration and hydrolysis steps in turn. The yield was 85% [139, 140].

By way of a commercially used method, FOX-7 has been synthesized by treatment of acetamidinium chloride with diethylmalonate to obtain 2-methyl-pyrimidine-4,6-dione, which on nitration gives 2-dinitromethylene-5,5-dinitrodihydropyrimidine-4,6-dione, followed by hydrolysis to give FOX-7 [141]. It is currently used in pilot-scale production in batches up to 600 kg. The main disadvantage of this procedure is the handling of the intermediate 2-dinitromethylene-5,5-dinitrodihydropyrimidine-4,6-dione, which is sensitive to mechanical stimuli and chemically unstable. The by-product dinitromethane is formed at a rate of 0.7 kg for each kilogram of FOX-7, and there is not much of a market for it or its potassium salt.



The theoretically computed explosive and ballistic parameters were close to those of RDX. The synthesized FOX-7 has been used as a precursor for the synthesis of potassium and guanidinium salts and thermal analysis of these salts indicated their exothermic capabilities, making them suitable for incorporation in propellants.

After comparing three possible routes for synthesis, the improved 2-methyl-4,6-pyrimidine-dione method using 2-methyl-4,6-dihydroxy-pyrimidine as raw material was recommended as a good method to produce FOX-7 [142, 143].

An improved process for the preparation of 1,1-diamino-2,2-dinitroethene suitable for scale-up was developed which involved the synthesis of 2-methoxy-2-methylimidazolidine-4,5-dione and its conversion into 2-hydroxy-2-methylimidazolidine-4,5-dione, which is a new intermediate in the synthesis of 1,1-diamino-2,2-dinitroethene [144]. Its nitration produced 2-(dinitromethylidene)-imidazolidine-4,5-dione, whose hydrolysis into 1,1-diamino-2,2-dinitroethene was further improved. The starting reactant acetamidinium chloride was switched to acetamidinium acetate. It is possible to carry this out as a one-pot synthesis without isolation of acetamidinium acetate. The new procedure yields no hazardous by-products or intermediates such as dinitromethane or 2-(dinitromethylidene)-5,5-dinitrodihydropyrimidine-4,6(1H,5H)-dione or methyl nitrate. Thus, the process safety was enhanced in

comparison to the commercial production process starting from 2-methylpyrimidine-4,6-dione.

Nitration reactions are exothermic and improper heat management can result in runaway reactions and explosions. Thermochemistry data such as heat flow curve vs. time, heat transfer coefficient, and heat capacity in the nitration reaction of 2-methylpyrimidine-4,6-dione for the synthesis of 1,1-diamino-2,2-dinitroethylene (FOX-7) were measured in a reaction calorimeter [145]. Results showed that the average heat release rate of nitration reaction during feeding of reactants was about 80 W and in the finishing period about 40 W (depending on the size of the reactor). The total exothermic heat of nitration reaction was 375 kJ/mol, and the adiabatic temperature rise can go as high as 483 K. The thermal stability of the intermediate 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione was analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Results showed that its thermal decomposition process can be divided into two stages: the initial decomposition started at 303 K (30 °C), the peak temperature of the first-stage decomposition was 340 K (67 °C), and the enthalpy of the decomposition reaction was 201 J/g; the peak temperature of the second stage was 360 K (87 °C) and the enthalpy of the decomposition reaction was 1047 J/g. This indicated that the thermal stability of the 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione intermediate is very poor.

The optimum conditions for the synthesis of FOX-7 were determined, this time not experimentally in a test tube, but theoretically by computer, simulating the established route from 2-methylimidazole via oxidation followed by nitration and aminolysis [146]. Possible variations that were distinct from those reported in the literature were simulated, including the use of a solvated oxidative reaction system, the replacement of nitrating agent HNO_3 by N_2O_5 , and the adoption of cupric oxide or ferrous oxide catalysts for aminolysis. The calculations suggested that water is a good medium for the oxidation reaction, N_2O_5 is a better agent for nitration, and iron(II) oxide would be a suitable catalyst for aminolysis in hydrated systems. See also [147, 148].

5.2.1.2 Recrystallization of FOX-7

FOX-7 as obtained from most synthesis methods is not usable in many propellant formulations since the particle size is much too small or the particle size range and shape are too irregular. Therefore, FOX-7 may have to be recrystallized in a mixture of *N*-methylpyrrolidin-2-one and water or dimethyl sulfoxide and water or dilute hydrochloric acid (HCl) [149, 150] or ethanol [151]. The crystal shape depends on the type of solvent used. Cubic-shaped particles with a rather broad size distribution (approximately 30–800 μm) can be obtained (Figure 2).

In order to understand the influence of FOX-7 crystal shape and size on its thermal properties, FOX-7 crystals were obtained from the solvent systems dimethylformamide (DMF)/ H_2O and *N*-methyl-2-pyrrolidone (NMP)/ H_2O by cooling crystallization and also by anti-solvent crystallization [153, 154]. Scanning electron microscope (SEM) examination showed that the obtained crystals had two shapes, namely extended tetra-

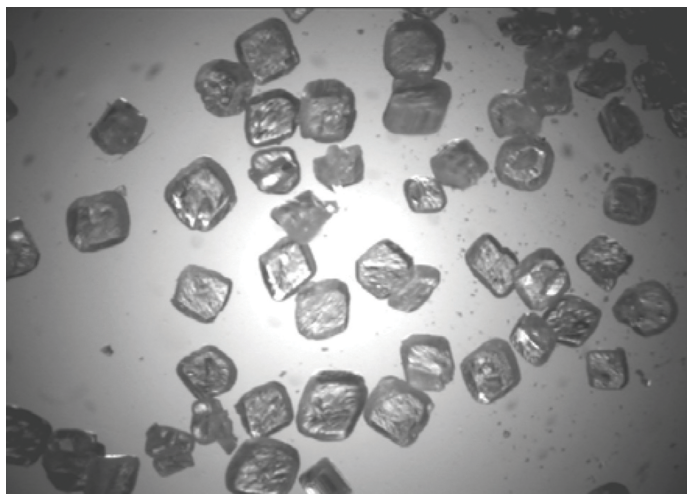


Figure 2: Crystal shapes of recrystallized FOX-7. (From [152].)

hedral or hexahedral prism and rhombohedral prismatic crystals. The crystal shape can be controlled by ultrasonic treatment. The shape of crystals obtained by ultrasonic treatment was more uniform, but the crystals' surface was comparatively rough. DSC results showed that the thermal properties of FOX-7 obtained by different means and different solvent systems were different. This indicated that FOX-7 crystals with different shapes, sizes, and thermal properties can be obtained by crystallization in different manners and solvent systems.

In order to obtain a fine-grain product, FOX-7 was dissolved in NMP while boiling. The solution was poured into water at ambient temperature and the suspension was vigorously stirred. After filtering, the product was slowly dried in an air atmosphere. A fine-grain product of quite regular shapes was obtained by this method [155, 156]. Spherical particles of FOX-7 can be prepared using a microemulsion technique [157].

5.2.1.3 Physical Properties of FOX-7

FOX-7 forms yellow crystals that can crystallize into two polymorphic forms as either α phase or β phase. The molecular mass is 148.08 g/mol. The oxygen balance is -21.61% and it is thus under-oxidized, similar to RDX. A thorough investigation of as-received samples from two different suppliers and recrystallized samples was done by van der Heijden et al. [158, 159]. The materials were characterized by XRD, SEM, pycnometry, differential thermal analysis (DTA)/TGA, DSC, high-performance liquid chromatography (HPLC)/MS, vacuum stability, impact sensitivity, and electrostatic discharge (ESD) sensitivity. See also [160, 161].

Melting Point of FOX-7

The melting point of FOX-7 is 543 K (270 °C) with beginning decomposition.

Phase Changes of FOX-7

FOX-7 crystallizes in at least three different polymorphic forms: α -FOX-7, β -FOX-7, and γ -FOX-7. The α modification converts reversibly to the β form at 389 K. At 435 K the β polymorph undergoes a transition to the γ polymorph and this conversion is irreversible. FOX-7 has several other phases which form on heating the normal α -polymorph and can be identified by DSC. The first phase transition ($\alpha \leftrightarrow \beta$) occurs at 386 K (113 °C), has an endothermic peak of 18 J/g, and is completely reversible. The β polymorph has an orthorhombic crystal structure. The second phase transition ($\beta \rightarrow \gamma$) occurs at 446 K = 173 °C and is only partially reversible. Above 473 K (200 °C) the explosive begins to decompose. The phase-change behavior of FOX-7 crystals depends on the solvent from which they were crystallized.

Phase changes of FOX-7 at pressures up to 10 GPa through isothermal compression at 373 and 473 K (100 and 200 °C) have been studied using synchrotron mid- and far-IR spectroscopy [162]. During isothermal compression at 373 K (100 °C), changes were observed in vibrational spectra with an increase in pressure that were indicative of significant distortion to a monoclinic α phase or a possible structural transformation to a high pressure α' phase at 2.2 GPa and α'' phase at 6.1 GPa. There was no evidence of sample decomposition over the total P - T range investigated, up to ~10 GPa and 473 K (200 °C). The observed changes were partially reversible, with only slight evidence of the high pressure distortion remaining upon complete decompression.

Density of FOX-7

The pycnometric density of FOX-7 at 298 K is 1.885 g/cm³. This density is higher than that of RDX (RDX: 1.82 g/cm³), making FOX-7 a potential candidate for replacement of RDX and the higher density partially compensates for its lower explosive output. The X-ray density is 1.907 g/cm³. The $\alpha \rightarrow \beta$ transition is accompanied by a density decrease of 1.9%. This might cause debonding of FOX-7 crystals embedded in a binder matrix. Density: α polymorph 1.89 g/cm³; β polymorph 1.80 g/cm³.

The density of as-received FOX-7 from two different suppliers was 1.86 and 1.877–1.879 g/cm³, respectively [158, 159]. Other sources reported the crystal density as 1.88 g/cm³ [141].

Optical Properties of FOX-7

The FOX-7 ultraviolet spectrum (in water) exhibits three maxima at 210, 278, and 346 nm. The UV spectrum of FOX-7 vapor indicated a strong band at 216 nm (for a normal carbon–carbon double bond one would expect 165 nm) for a $\pi \rightarrow \pi^*$ transition which corresponds to an ethylene carbon–carbon double bond. The higher value (216 nm as opposed to 165 nm) indicated that the presence of extensive π - π conjugation in the molecule and a stronger band at 279 nm for $n \rightarrow \pi^*$ transition are

due to the presence of nitro groups. The IR spectrum of FOX-7 revealed the presence of primary amino groups at 3408, 3330, and 1636 cm^{-1} and nitro groups at 1520 and 1472 cm^{-1} .

The IR spectrum of solid FOX-7 in KBr pellets showed absorption bands at 3417 (NH_2), 3315 (NH_2), 3200 (NH_2), 1638 (NH_2), 1524 (NO_2), 1471, 1400, 1356 (NO_2), 1234, 1176, 1143, 1027, 752, 652, 521, and 462 cm^{-1} [125].

Raman spectroscopy was used for a temperature-dependent study of the phase transitions of FOX-7, where the N—H band at 3332 cm^{-1} (marked with an asterisk) showed an increase in intensity just before the phase transition, followed by a decrease in intensity (Figure 3).

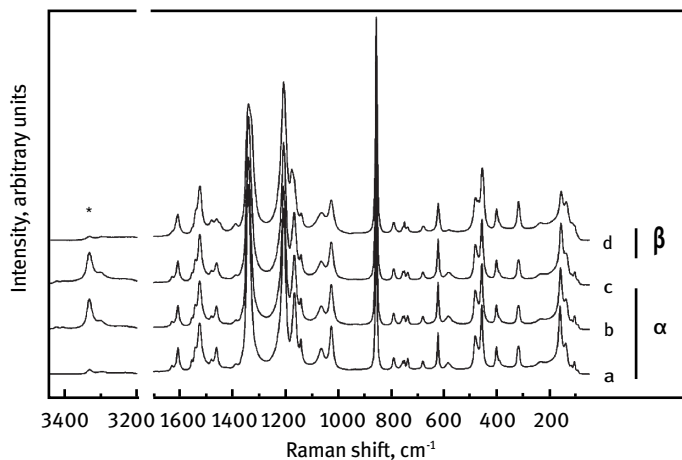


Figure 3: Raman spectra of FOX-7 representing progressive heating at (a) 50, (b) 75, (c) 100, and (d) 105 °C (Reprinted and modified from [163], with permission from © 2007 American Chemical Society.). The band at 3332 cm^{-1} marked with an asterisk is due to N—H. bonds

This change indicated a reorganization of the H-bonding in crystalline FOX-7, leading to stabilization of a different form of FOX-7. Figure 3 presents the Raman spectra of pure FOX-7 subjected to progressive heating, which clearly shows a transition from the α phase to the β phase.

Raman spectroscopy was used to examine the vibrational and polymorphic behavior of 1,1-diamino-2,2-dinitroethene and to elucidate its structural and chemical stability under high pressure [164–166]. Measurements were performed on single crystals compressed in a diamond anvil cell, and data were obtained over the entire frequency range of FOX-7 Raman activity. Several new features were observed with an increase of pressure: (i) new vibrational peaks and discontinuity in the shifts of the peaks at 2 and 4.5 GPa; (ii) apparent coupling or mixing of several modes; and (iii) changes in the NH_2 stretching spectral shape and modes shift. A large pressure

hysteresis regarding the changes at 4.5 GPa implied a reconstructive transformation. FOX-7 has remarkable chemical stability under high pressure.

Solubility of FOX-7

FOX-7 is insoluble in cold water and slightly soluble in acetonitrile and cyclohexanone. FOX-7 is only slightly soluble in common organic solvents and water, but readily dissolves in polar aprotic solvents such as dimethyl sulfoxide, *N,N*-dimethyl formamide, or 1-methyl-2-pyrrolidinone. The solubility of FOX-7 in common solvents is summarized in Table 16.

Table 16: Solubility data for DADNE-FOX-7.

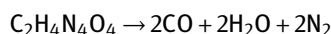
Solvent	Solubility, g/100 mL at 293 K = 20 °C
Acetone, acetic acid, <i>n</i> -butanol	<0.1
Ethyl acetate, nitromethane, water	<0.1
Acetonitrile	<0.5
Cyclohexanone	<0.5
Dimethylformamide	21
<i>N</i> -Methylpyrrolidone	32
Dimethyl sulfoxide	Approximately 45

Data source: [126]

Thermodynamic Properties of FOX-7

Throughout this chapter the properties of FOX-7 have been repeatedly compared to those of RDX, which it may potentially replace. The enthalpy of formation of FOX-7 is negative, while that of RDX is positive. There are varying results for the enthalpy of formation of FOX-7, ranging from −53 to −133.9 kJ/mol or −134 kJ/mol, depending on which source you trust. This requires additional work to eliminate unreliable data. An enthalpy of formation of −130 kJ/mol appears to be a reliable number. In comparison, the enthalpy of formation of RDX is +92.6 kJ/mol (other authors list +67 kJ/mol).

The calculated heat of explosion according to the equation



is −574 kJ/mol = −3.88 MJ/kg = −7.29 MJ/L, which is half of that of RDX on a per-mol basis. For RDX the heat of explosion is −1123 kJ/mol = −5.06 MJ/kg = −9.21 MJ/L. On a volume basis, FOX-7 output is only 21% less than of that of RDX.

The standard molar heat capacity of FOX-7 was determined with two continuous heat capacity at constant pressure C_p modes of operation of a microcalorimeter to be 176.56 and 176.02 J mol^{−1} K^{−1} at 298.15 K, respectively [167]. The relative deviation between these two results was 0.31%. The heat capacity of FOX-7 was also calculated by a DFT method, and the relative deviation between theoretical calculation and experi-

mental determination ranged from 13.27 to 15.46% within the range of 283–353 K. Using the above determination results of heat capacity, thermodynamic functions of FOX-7 relative to the standard temperature 298.15 K were calculated through thermodynamic relationships, and predicted adiabatic time-to-explosion was also calculated.

The heats of combustion of FOX-7 and five of its closed-loop derivatives were determined and the standard molar enthalpies of formation were calculated [168]. The heats of combustion for the six compounds decreased in the order 2-(dinitromethylene)-1,3-diazacycloheptane > 4-methyl-2-(dinitromethylene)-1,3-diazacyclopentane > 2-(dinitromethylene)-1,3-diazacyclohexane > 2-(dinitromethylene)-1,3-diazacyclopentane > 4,5-dihydroxyl-2-(dinitromethylene)imidazolidine > FOX-7. The heat of combustion increased with an increase in the number of C atoms in the molecule. The standard molar heat capacities of the six compounds were 176.59, 205.41, 207.76, 218.89, 217.76, and 215.40 J mol⁻¹ K⁻¹, respectively. The specific heat capacities changed with the number of C atoms in an opposite direction from the heat of combustion. The introduction of hydroxyl groups can markedly decrease the heat of combustion and specific heat capacity.

Gas-phase enthalpies of formation for 3-nitro-1,2,4-triazol-5-one (NTO), FOX-7, LLM-105, TNT, RDX, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), HMX and PETN were calculated using quantum composite methods [169]. Results from some calculations were close to one another, with a larger difference found between other methods. The mean absolute deviations between average experimental values and calculations were 12 to 3 kcal/mol.

Molecular Structure of FOX-7

The molecular structure of FOX-7 possesses bond lengths and angles that are typical for a so-called push–pull alkene, which is an alkene with groups of greatly differing electron affinity at either end. The C=C bond length is 1.456 Å, intermediately between that of a C–C single bond (1.54 Å) and that of a normal C=C bond (1.34 Å). The C–NH₂ and C–NO₂ bonds are shorter than in alkylamines or nitroalkanes.

It has been suggested that the low drop-weight and low friction sensitivity of FOX-7 (compared to that of RDX) is due to the crystal structure. FOX-7 forms yellow/orange crystals which crystallize in the monoclinic form (α phase). The crystals have a graphite-like structure with parallel planes, similar to that of TATB, which allows for internal flexibility. The layers are held together by strong hydrogen bonds [170]. The distance between layers is 3 Å.

Eight amino and/or nitro derivatives of ethene have been investigated computationally by a density functional theory method [171]. The molecular geometries and relative stabilities reflect the varying roles of push–pull electron delocalization and intramolecular hydrogen bonding in compounds like 1,1-diamino-2,2-dinitroethylene. The same two factors affect, to varying extents, the computed C–NO₂ and C–NH₂ bond dissociation energies and the heats of formation, vaporization, and sublimation of the diaminodinitroethylenes.

The effects of pressure on the structural and vibrational properties of the layered molecular crystal of FOX-7 were explored by first principles calculations [172]. Using density functional theory (DFT) methods, significant changes in the calculated structural properties with different corrections for treating van der Waals interactions were observed. In particular, the calculated ground-state lattice parameters, volume, and bulk modulus were found to agree well with experiments. The calculated vibrational frequencies demonstrate the dependence of the intra- and inter-molecular interactions on FOX-7 under pressure.

Crystal Structure of FOX-7

It has been attempted to calculate the equation of state and predict structural changes in FOX-7 from experimental studies and *ab initio* quantum calculations [173].

Molecular computer simulation can be used to calculate energies of molecular systems. There are basically two methods: quantum mechanical calculations and force fields methods. Quantum mechanical calculations give accurate results and can also be used to calculate chemical reactions, but consume a lot of computer time, especially for systems containing several molecules. Force fields methods can describe molecular systems by means of simple mechanical models. Energy terms for bonds, bond angles, torsions, van der Waals-interactions, and electrostatic interactions are available. In comparison to quantum mechanical calculations, the simulation computing time is quite short. A force field method was used to predict the shape of FOX-7 crystals, which depends on the growth rates of the crystal faces during the crystallization process and on the interaction energies of the faces and the solvent molecules [174, 175].

The structure of FOX-7 has been identified by elemental analysis, IR, MS, and NMR [176]. The single crystal of FOX-7 was cultivated from acetonitrile. Its crystal structure was determined by XRD with a single crystal. The results showed that the crystal belongs to a monoclinic system, space group $P2_1/n$, with crystal parameters of $a = 0.6930(14)$ nm, $b = 0.6630(13)$ nm, $c = 1.1360(2)$ nm, $\beta = 90.43(3)^\circ$, $V = 0.5219(18)$ nm³, $Z = 4$, and $D_c = 1.885$ g/cm³.

XRD is the preferred tool for investigation of the crystal structure of energetic materials. XRD has revealed a monoclinic structure of FOX-7 with $a = 6.941$ Å, $b = 6.569$ Å, $c = 11.315$ Å, $\beta = 90.55^\circ$, $V = 515.9$ Å³, $D_x = 1.907$ g/cm³, and $Z = 4$. Whereas positions and intensities of diffraction peaks yield information on the crystal structure, peak profiles (e.g., width at half-height) are related to the real structure determined by crystallite sizes, shapes, and micro-strains. The size/strain broadening of FOX-7 XRD peaks was measured and interpreted based on crystal geometry [177]. The investigations correlated the size/strain broadening with particle processing history and mechanical sensitivities. Compressibility can be different in different axes of the crystal. Shock loading may result in rapid compression in one axis but not in the other, leading to hotspots and accidental ignition of energetic materials. Anisotropic diffraction-peak broadening was found for some of the energetic

materials. Micro-strains are left behind after grinding the materials or as the result of imperfect (hastened) crystal growth. The size/strain broadening of FOX-7 XRD peaks was measured and interpreted based on crystal geometry, contaminants and internal crystal defects, also in comparison to similar measurements on RDX and ammonium dinitramide (ADN). The molecular layer structure is reported to be a model for low-sensitivity materials, such as FOX-7 or TATB. In this model the principal mechanism for release of mechanical load is layer slippage (as in graphite), which retains the internal layer structure undisturbed.

The supersaturation-dependent growth habit of FOX-7 crystals was accurately predicted by step energy calculation and simulations [178]. The rod-like shape of FOX-7 originates from the slowest growth rate of the {111} face because of a large energy barrier of nucleation and a low sticking fraction relative to other faces at low supersaturation. The anisotropic growth habit of crystal faces diminished as the supersaturation increased.

5.2.1.4 Chemical Properties of FOX-7

Due to the strong polarization of the C=C double bond, FOX-7 can undergo a wide variety of reactions, such as transamination and hydrolysis reactions.

Reactions of FOX-7

FOX-7 is quite reactive and can undergo a multitude of reactions like cycloadditions, nitration, halogenation, and acylation [179]. FOX-7 can give unexpected products as a result of its specific reactivity [180]. The structures of the new compounds were identified by XRD. The nucleophilic *gem*-dinitrocarbon of FOX-7 seemed to be directly involved in these transformations.

In reactions with amines, FOX-7 behaves as an electrophile via 1,4 conjugate addition. Although reactions with simple alkyl amines often yield unresolved mixtures of mono- and bis- substituted addition products, reactions with diamines yield cyclic amines in good yield and purity. Conversely, FOX-7 behaves as a nucleophile in amine alkylation and acylation reactions, albeit a poor one. FOX-7 is roughly 25 orders of magnitude less basic than simple alkyl amines ($pK_a = 10.6$). FOX-7 is such a poor nucleophile that *N*-alkylation and *N*-acylation require refluxing conditions.

Amphoteric Behavior of FOX-7

FOX-7 is an acid ($pK_a = 10.6$) and after loss of a proton the anion assumes the structure of an imine $(H_2N)HN=C-C^-(NO_2)_2$. Salts are formed with guanidine or potassium hydroxide. Hydrolysis leads to the potassium salt of dinitromethane.

On the basis of liquid and solid-state ^{13}C and ^{15}N NMR data, XRD analysis, and *ab initio* calculations, it was suggested that 1,1-diamino-2,2-dinitroethylenes are always zwitterionic and that the C=C bond is not a true double bond [181].

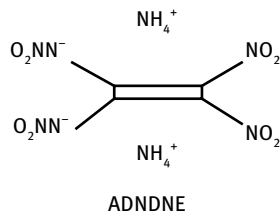
1,1-diamino-2,2-dinitroethene and its hydrazine derivative, 1-amino-1-hydrazino-2,2-dinitroethene (HFOX), form cations with strong acids such as triflic, perchloric,

and hydrochloric acid [182]. The following salts were prepared and characterized: 1-amino-2,2-dinitroethaniminium triflate, 1-amino-2,2-dinitroethaniminium perchlorate, 1-amino-1-hydrazino-2,2-dinitroethaniminium triflate, and 1-amino-1-hydrazino-2,2-dinitroethaniminium chloride. These compounds had thermal stabilities ranging between 347 and 420 K (74 and 147 °C) and crystal densities between 1.53 and 1.94 g/cm³. The isolation of these FOX-7 and HFOX cations extended the chemistry of FOX-7 and HFOX and demonstrated the amphoteric properties of FOX-7 and HFOX. All the salts were found to have energetic properties that exceeded those of TNT, and some were comparable to FOX-7 and RDX.

Salts of FOX-7

The reaction of 1,1-diamino-2,2-dinitroethene with KOH at room temperature forms the potassium salt of 1,1-diamino-2,2-dinitroethene, which on heating to 353 K (80 °C) decomposed to form the potassium salt of dinitromethane. Adding both KOH and guanidinium chloride to 1,1-diamino-2,2-dinitroethene formed the guanidinium salt of 1,1-diamino-2,2-dinitroethene in the form of yellow crystals, which was not more stable than the potassium salt and showed a more complex decomposition pattern in DSC with three peaks. It was more friction and impact sensitive than FOX-7 itself. Cesium, rubidium, cadmium, zinc, and copper complex salts containing FOX-7 have been reported.

It was attempted to increase the acidity and energy content of FOX-7 by converting the two amino groups into two nitramino groups and then stabilizing the compound as the diammonium salt, which would be called diammonium di(nitramido) dinitroethylene (ADNDNE).



The remaining hydrogens on the two amino groups would be more acidic than those in FOX-7 without nitramino groups. However, in spite of trying seven different synthesis routes, the ADNDNE salt was not obtained [183]. The salt was predicted to have a density of 1.77 g/cm³ and an enthalpy of formation of +16.8 kJ/mol (+4.02 kcal/mol). It seems highly premature to start worrying about possible environmental impacts of a chemical that is so unstable that it cannot even be obtained in milligram quantities in the laboratory. The computational methods used for predicting toxicity and environmental impact look very nice, but are, in reality, useless.

Halogenated FOX-7

Halogenated 1,1-diamino-2,2-dinitroethene compounds display hypergolic properties with common hydrazine-based fuels and primary aliphatic amines (ignition delay times of 2–53 ms) [184]. These compounds were characterized by single-crystal XRD, elemental analysis, IR spectra, and DSC.

5.2.1.5 Thermal Stability of 1,1-Diamino-2,2-dinitroethene (FOX-7)

Thermal Stability of 1,1-Diamino-2,2-Dinitroethene (FOX-7) – Experimental Studies

If FOX-7 is heated to above 473 K (200 °C) it begins to decompose without melting. DSC exotherms show up in the area around 513 K (240 °C) and decomposition is complete by the time the sample reaches 573 K (300 °C). Occluded solvents may change the location, the number, and the shape of DSC peaks. The DSC thermogram of FOX-7 showed two decomposition steps with peak maxima at 513 K (240 °C; $\Delta = -473$ J/g) and 552 K (279 °C; $\Delta = -542$ J/g).

Raw FOX-7 does not give thermograms with good reproducibility. They usually have a weak endotherm, with the peak moving from 368 to 383 K (95 to 110 °C), depending on the history of the product, and three exotherms: two weak ones at 473 and 518 K (200 and 245 °C), and a very strong one with the peak position at around 543 K (270 °C). However, recrystallized or reprecipitated products, independent of the type of solvent used, are characterized by two nicely reproducible endotherms – a pronounced one at 391 K (118 °C) and a weak one at ~438 K (~165 °C) – and two exotherms – a broad one with a peak at 518 K (245 °C) and a sharp one with a peak at 548–553 K (275–280 °C). The averaged kinetic parameters characterizing the decomposition process of FOX-7 are

$$E_a = 338.8 \text{ kJ mol}^{-1} \quad A = 1.266 \times 10^{38} \text{ s}^{-1} \quad n = 0.7$$

The DSC thermogram of FOX-7 showed a complex structure with two exothermic peaks, one at 511 K (238 °C) and another at 554 K (281 °C) [152]. From tests at varying heating rates, the activation energy for FOX-7 was measured to be 234 kJ/mol (56 kcal/mol), which, when compared to RDX (167 kJ/mol = 40 kcal/mol) and HMX (146 kJ/mol = 35 kcal/mol), shows that FOX-7 is more thermally stable than RDX or HMX. The TGA curve showed at least two, possibly four steps of weight loss. This indicated that a two-step decomposition dominates the initial decomposition of FOX-7, where the initial intermediate has a low thermal stability. The number of steps in the TGA curve can possibly explain the two peaks in the DSC thermogram. The analysis of thermal decomposition products was initially done on a conventional magnetic sector mass spectrometer and later extended to a time-of-flight (TOF) mass spectrometer with laser pyrolysis. A significant observation was that with a low electron impact ionization of 70 eV, FOX-7 exhibited a very strong molecular peak at a mass-to-charge ratio m/e equal to 148. This indicated that the molecule is very stable in the vapor phase compared to RDX and HMX. Earlier work had shown that NTO and TNT can have small molecular peaks at 70 eV.

The thermal decomposition of FOX-7 under isothermal conditions at constant volume showed a saturating character of gas evolution curves at a very low extent of decomposition [185]. The rate of gas evolution was characterized by an extremely high activation energy value, 385 kJ/mol (92 kcal/mol). Experiments conducted in an open vessel resulted in a significantly lower activation energy, i.e., 198 kJ/mol (47.4 kcal/mol). The reaction products hinder rather than accelerate further decomposition of FOX-7.

FOX-7 is usually transported suspended in water to prevent accidental explosions. In order to check any influence of the presence of water on the thermal stability properties of FOX-7, both wet and dry samples were tested by DSC [186]. By applying different heating rates, an analysis of the decomposition kinetics could be performed, which gives additional information on the activation energy of the decomposition process and the predicted shelf life of the material when stored at above normal temperature.

As a consequence of the extremely high values of the activation energy, FOX-7 is a very stable high explosive even at elevated temperatures. Kinetics of the two-step decomposition of FOX-7 were modelled using dynamic and isothermal DTA/TGA measurements [187]. The reaction product remaining after the first decomposition step (corresponding to about 38% mass loss) was investigated by NMR, XRD, IR, and HPLC. Surprisingly, all methods identified the intermediate solid reaction product as the initial compound FOX-7. The compound decomposing in the first step was assumed to be a less stable, amorphous fraction of FOX-7.

The whole process of thermal decomposition of FOX-7 was investigated by thermolysis with *in situ* cell rapid-scan IR [188, 189]. The activation energies for rupture of C—N, —NO₂, and C—NH bonds were obtained by a thermo-IR isothermal kinetic method: 181.7, 235.8, and 170.7 kJ/mol. The thermal decomposition process of FOX-7 is a two-step process. In the first step, hydrogen bond dissociation and isomerization of the —NO₂ group occur and some NO is released. The second step concludes the dissociation of the main bonds of FOX-7 and, at the same time, HCN and NH₃ are released.

The constant-volume combustion energy, ΔU_{comb} , the thermal behavior, and kinetics and mechanism of the exothermic decomposition reaction of FOX-7 were investigated by a rotating bomb calorimeter, thermal gravimetric analysis-differential thermal gravimetry (TGA-DTG), DSC, rapid-scan FTIR spectroscopy and T-jump/FTIR [190]. The value of ΔH_{comb} was determined as -8518.09 ± 4.59 J/g. Its standard energy of combustion, ΔU_{comb} , and standard enthalpy of formation, $\Delta H_f^{298.15}$, were calculated to be -1254 ± 0.68 and -103.98 ± 0.73 kJ/mol, respectively. The kinetic parameters (the apparent activation energy E_a and pre-exponential factor A) of the first exothermic decomposition reaction in a temperature-programmed mode obtained by Kissinger's method and Ozawa's method were $E_a = 344.35$ kJ/mol, $A_k = 10^{34.50} \text{ s}^{-1}$, and $E_o = 335.32$ kJ/mol. The critical temperature of thermal explosion of DADE was 480 K (207 °C).

The thermal decomposition mechanism of FOX-7 was studied by DSC and TG-DTG techniques [191]. The thermal decomposition of FOX-7 consisted of one endothermic

and two exothermic decomposition processes continuously. The TGA curve consisted of two-stage mass-loss processes. The endothermic peak was attributed to the crystal transformation and the exothermic peaks were due to the decomposition reaction of FOX-7 and its decomposition products.

The thermal decomposition behavior of FOX-7 was measured by DSC and TGA and by *in situ* thermolysis or fast thermolysis with rapid-scan Fourier transform IR spectroscopy and mass spectroscopy [192]. The results showed that there was a phase transition (β -phase to γ -phase) at 392 K (119 °C), and that the gas products of FOX-7 decomposition consisted of CO₂, CO, NO₂, NO, N₂O, HCN, and HNCO, of which CO₂, NO, N₂O, and HCN presented themselves in both the first and second stages of FOX-7 decomposition, whereas CO, NO₂, and HNCO were only evolved by the second-stage process.

In DSC, the endotherms and exotherms of as-received, dried FOX-7 were measured at heating rates of 2, 5, and 10 °C/min [158, 159]. For a heating rate of 2 °C/min there were three endotherms starting at 99.1, 112.8, and 171.0 °C, and two exotherms starting at 202.3 and 240.8 °C. The endotherms are associated with phase changes. On some samples, repeated DSC heating and cooling cycles were recorded to see if the decomposition products change the melting and decomposition behavior and whether all peaks appeared repeatedly in each cycle. The compatibility of FOX-7 with other energetic materials, binders, and curing agents was determined by vacuum stability measurements. Both glycidyl azide polymer (GAP) and hydroxyl terminated polybutadiene (HTPB) are compatible with FOX-7, and FOX-7 can be used as a replacement for RDX in nitramine propellants or plastic bonded explosive (PBX) formulations.

In addition to thermal stability studies of FOX-7 by itself, additional experiments were done with salts derived from FOX-7. It was hoped that some of the salts would have better properties than the parent acid itself. The guanidinium salt of 1,1-diamino-2,2-dinitroethene was prepared by mixing FOX-7 and guanidinium chloride solution in potassium hydroxide solution. Its thermal decomposition was studied under the non-isothermal conditions with DSC and TG/DTG methods [193] and its structure was determined by XRD [194]. The crystals belong to an orthorhombic system with space group Pbca and have a density of $\rho = 1.622 \text{ g/cm}^3$.

The thermal decomposition process of FOX-7 was investigated by using *in situ* FTIR, thermolysis GC/MS and DSC-TG [195]. The thermal decomposition mechanism of FOX-7 was studied through determining the gaseous products and structural changes of the condensed phase during heating. The results showed that the thermal decomposition of FOX-7 proceeds in two stages. In the first stage, the phase transition of FOX-7 is followed by an inter-molecular condensation reaction and NO is released from FOX-7 through nitro–nitrite rearrangement. Subsequently, FOX-7 is further decomposed into small molecule fragments.

Sensitivities of FOX-7 and HTPB propellants with FOX-7 were studied by means of DSC-TGA and various sensitivity test methods [196]. Results showed that the apparent activation energy of thermal decomposition of FOX-7 was 245.2 kJ/mol and the major exothermic DSC peak temperature occurred at 495 K (222 °C). Friction sensitiv-

ity was less than 68%, while impact sensitivity was over 25 J. Mechanical sensitivities and electrostatic discharge sensitivity of HTPB propellants with FOX-7 were more benign when compared to similar RDX formulations. When the content of FOX-7 in an AP/FOX-7/HTPB propellant is 15%, the violent exothermic decomposition of ammonium perchlorate (AP) is weakened and the major exothermic DSC peak occurs at about 533 K (260 °C), which is 40° lower than that of all-RDX/HTPB formulations.

The thermal decomposition process of FOX-7 was investigated by DSC, TGA, and T-jump rapid-scan FTIR coupling techniques [197]. Results showed that isomerization of the $-\text{NO}_2$ group occurs and NO is released, whereafter the decomposition of the main framework of FOX-7 liberates HNCO, HCN, NH_3 , CO_2 , CO, etc. The activation energy E_a was 247 kJ/mol, the decadic logarithm of the pre-exponential factor was 23.81. The reaction order of the early-stage pyrolysis mechanism of FOX-7 was 1.5.

Quantum mechanical computational methods were used to calculate the energy of the decomposition species of FOX-7 [198]. Based on the energy levels obtained by such methods, the rate constants of C– NO_2 cleavage and nitro-to-nitrite rearrangement were calculated in the temperature range of 250–3300 K. It was found that C– NO_2 cleavage would be the dominant initial thermal decomposition step at high temperature, which is consistent with the conclusion based on *ab initio* molecular dynamics simulations. The effects of NO_2 gas on FOX-7 decomposition were predicted. Results showed that the decomposition energy barrier became lower when NO_2 reacted with FOX-7.

The decomposition of FOX-7 was further investigated both theoretically and experimentally [199]. The NO molecule was observed as an initial decomposition product subsequent to electronic excitation. The observed NO product is rotationally cold (<35 K) and vibrationally hot (2800 K). The initial decomposition mechanism was computed by a theoretical method. Potential energy surface calculations illustrated that conical intersections play an essential role in the decomposition mechanism. When FOX-7 decomposes while it exists in the ground electronic state, the vibrational energy of the NO product from FOX-7 is high. The observed rotational energy distribution for NO is consistent with the final transition state structure on the S_0 state.

The ReaxFF molecular dynamics method was used in an investigation of the thermal decomposition mechanisms of FOX-7 and the results were compared to those obtained experimentally using a combination of TGA with online photoionization time-of-flight mass spectrometry (TG-PI-TOF-MS) and online single-photon ionization time-of-flight mass spectrometry (SPI-TOF-MS) [200, 201]. The results of the molecular dynamics simulations showed that the primary decomposition step of FOX-7 is C– NO_2 cleavage; after this, C=O formation occurs via a three-membered ring transition state, followed by NO elimination. The remaining structure loses NH_2 and H, resulting in formation of the $\text{NHC}=\text{C}=\text{O}$ structure, which finally breaks down into HNC and CO. NH_2 reacts with an H atom to produce NH_3 . During the decomposition of FOX-7, the major products are N_2 , NH_3 , CO_2 , and H_2N_2 , and the minor products are H_2O , HN_2 , and H_2 .

Thermal Stability of FOX-7 – Theoretical/Computational Studies

Computational chemistry electron density calculations have attempted to predict the decomposition path for FOX-7 [202]. The thermal decomposition behavior of FOX-7 at high temperature has been simulated using constant-temperature molecular dynamics and density functional theory methods [203]. It was found that most of the energy is released within the first 15 ps of the reaction. The main products are N_2 and H_2O molecules, and their populations generally increase with time. Some charged groups (like NO_2^+ and OH^-), which are observed in the initial stage of decomposition, may promote further reaction.

Ab initio molecular dynamics simulations were conducted to study the thermal decomposition mechanisms of solid FOX-7 [204]. It was found that the initial decomposition of FOX-7 has three main reaction routes and that C– NO_2 bond fission, as reported previously, is indeed the most common route. However, the inter- and intramolecular hydrogen transfers were also found to be valid, which was contradictory to previous energy minimization calculation results. The simulations agreed well with known experimental data in terms of activation energy and reaction side products. The main products are H_2O , CO_2 , and N_2 .

5.2.1.6 Chemical Analysis of FOX-7

Accurate methods for analysis of FOX-7 are required for quality control and to identify contaminants which may be carried over from the production process starting with 2-methylpyrimidine-4,6(1H,5H)-dione.

Three different synthetic routes to FOX-7 were developed and potential by-products were identified by HPLC. The route starting from 2-methyl-pyrimidine-4,6-dione is the method currently used for production of FOX-7 on a pilot plant scale in Sweden. Based on this route, an HPLC-UV-MS method was developed for the analysis of FOX-7, its precursors, and all major by-products [205].

FOX-7 can be analyzed by thin-layer chromatography [206] or by HPLC [207]. For HPLC, two different mobile phases with different pH values, i.e., acetonitrile–water and methanol–water with ammonia and trifluoroacetic acid, were used.

5.2.1.7 Burning Rates of FOX-7

Strand burning rates of FOX-7 were investigated over the 0.2–35 MPa pressure range, where FOX-7 burned slightly slower than RDX [185]. The temperature distribution in the combustion waves of FOX-7 has been measured at pressures from 0.2 to 1.1 MPa.

5.2.1.8 Detonation Velocities of FOX-7

The measured detonation velocity for FOX-7 pressed pellets with 25-mm diameter and a density of 1.780 g/cm^3 was $8325 \pm 80 \text{ m/s}$ [208]. For comparison, a theoretical detonation velocity was estimated by using the thermochemical code CHEETAH [209] with two sets of the Becker-Kistiakowsky-Wilson equation of state (BKW) parameters. Calculated detonation velocity was 8453 and 8499 m/s for BKW-CHEETAH and

BKW-Sandia data sets, respectively. The average heat of detonation from three tests in a calorimetric bomb of volume 5.6 dm^3 filled with argon at a pressure of 2 MPa was $4860 \pm 60 \text{ J/g}$. The isentrope and the constant-gamma isentrope for the detonation products of FOX-7 were also found. See also [210]. Another source gave the detonation velocity of FOX-7 as 8869 m/s.

5.2.1.9 Safety Properties of FOX-7

Drop-Weight (Impact) Sensitivity of FOX-7

The drop-weight (impact) sensitivity of FOX-7 is 20–40 Nm [2]. The drop-weight (impact) sensitivity of as-received and dried FOX-7 was 7.5–15 Nm, and that of re-precipitated FOX-7 was 20 Nm. The particle size has an important influence on FOX-7 sensitivity. Changing to a smaller particle size caused impact and friction sensitivity to increase [211]. After replacing RDX in composition B partially with FOX-7, the mechanical sensitivity of the formulation hardly changed, and the effect of decreasing the sensitivity was very obvious. The results showed that selecting the right particle size and applying a surface coating is an important step to decrease the mechanical sensitivity of FOX-7. FOX-7 that is considered as a replacement for RDX in PBX needs to have good bonding to the fluoropolymer binder [212]. The inter-facial energy and wetting of FOX-7 particles with fluoropolymers are similar to those of TATB. In both cases this will affect the impact sensitivity of the PBX.

The impact sensitivity of coarse DADNE was determined using a drop-weight testing apparatus with a 5-kg hammer [213]. The highest drop height was determined at which no reaction was observed (h_0). Ten trials were conducted at consecutive heights which were changed in steps of 1 cm. The value of 23 cm was found as h_0 , which corresponds with the impact energy of 11.3 J. For comparison, a value of 6 cm (2.9 J) was determined for crystalline RDX under the same conditions.

Slightly different impact energies of 15.5 and 12.4 J were determined for FOX-7 crystals with sizes of 250–355 μm and those with sizes less than 70 μm . A 2-kg drop-weight apparatus was used in these tests and the drop heights were 79 and 63 cm, respectively [152].

The impact sensitivity can also be expressed as the drop height at which 50% initiations occurred (h_{50}). To determine h_{50} for FOX-7, the Bruceton procedure (an up-and-down method) was applied. The total number of tests performed was 30. The medium height was at $h_{50} = 35.2 \text{ cm}$. This height corresponds to an impact energy of 17.3 J. For comparison, the value of 9.6 J was determined for crystalline HMX in the same apparatus.

Friction Sensitivity of FOX-7

The friction sensitivity of FOX-7 is $>550 \text{ N}$ [2]. The friction sensitivity of as-received and dried FOX-7 was 320–324 N, and that of re-precipitated FOX-7 was $>360 \text{ N}$ [158, 159]. The friction sensitivity of FOX-7 was measured on a Julius–Peters machine. No friction

sensitivity was observed up to loading of 353 N for different types of FOX-7 crystals (coarse and fine particles of FOX-7) [214].

Card Gap Sensitivity of FOX-7

The shock sensitivity of FOX-7 was determined by using a gap test. The sensitivity of fine-grain FOX-7 is lower than that of TNT, but the coarse-grain FOX-7 is much more sensitive than TNT [215].

ESD Sensitivity of FOX-7

The ESD sensitivity of as-received and dried FOX-7 was 4.5 J, identical to that of RDX [158, 159].

Cook-Off Behavior of FOX-7

Small-scale safety tests showed that PBX compositions with FOX-7 were not sensitive to friction and the thermal stability was excellent, at 65 °C. Larger-scale detonation tests and small-scale slow cook-off tests showed that the FOX-7-based PBX did not detonate at a diameter of 25 mm and upon slow (3.3 °C/h) heating in a cook-off test, it ignited at 220 °C and burned without damage to the container or the surroundings. See also [210].

5.2.1.10 Environmental Impact of FOX-7

FOX-7 is not biodegradable. The toxicity to aquatic organisms as measured by effective control to 50% growth inhibition (EC₅₀) is 530 mg/mL.

FOX-7 was among four other explosives and oxidizers, including ADN, evaluated as replacements for AP and examined for environmental fate chemistry and potentially persistent pollution [216]. This was investigated in detail to make sure that spilled energetic materials would not cause the same long-term problems in the ground water and aquifers as AP. The oral toxicity of FOX-7 in rats is LD₅₀ = 200–2000 mg/L.

5.3 Substituted Derivatives of 1,1-Diamino-2,2-dinitroethene

The reactivity of FOX-7 was studied in the hope of finding energetic compounds that have higher energy but at least the same thermal stability as FOX-7. Various reactions like cycloadditions, nitration, halogenation, and acylation were performed in order to evaluate the reactivity of the C=C double bond and the amino moieties [179, 217]. Several products were isolated and two of them were characterized by XRD. Two reactive sites on the 1,1-diamino-2,2-dinitroethene molecule were identified. Reaction of FOX-7 with acetic acid gives an acetyl-substituted NH group. Primary amines reacted with FOX-7 to afford *N*-substituted and *N,N'*-disubstituted-1,1-diamino-2,2-dini-

troethenes via transamination reactions. Treatment of FOX-7 with hydrazine led only to the monosubstituted product 1-amino-1-hydrazino-2,2-dinitroethene.

Other derivatives of 1,1-diamino-2,2-dinitroethene exhibit good thermal stability, high density, positive heat of formation, acceptable oxygen balances, and excellent detonation properties, which often are superior to those of RDX [218].

5.3.1 1-Amino-1-hydrazino-2,2-dinitroethene

1-Amino-1-hydrazino-2,2-dinitroethene (AHDNE) was synthesized from hydrazine hydrate and FOX-7 in water [219]. Single crystals suitable for XRD measurement were obtained by slow evaporation of the solvent methanol at room temperature. The crystals belong to an orthorhombic system with space group *Pnma* and cell parameters of $a = 0.6283(4)$ nm, $b = 0.7713(5)$ nm, $c = 1.2280(8)$ nm, $\alpha = \beta = \gamma = 90^\circ$, $V = 0.5950(7)$ nm³, and $\rho_c = 1.821$ g/cm³.

1-Amino-1-hydrazino-2,2-dinitroethene and its salts were characterized by IR, NMR, elemental analysis, DSC, density, and impact sensitivity measurements [220]. 1-Amino-1-hydrazino-2,2-dinitroethene decomposed at 397.6 K (124.5 °C) and the salts decomposed over the range 411.7–454.7 K (138.6–181.6 °C), thus showing higher thermostability than the parent compound. The calculated detonation pressures for these salts ranged from 27.2 to 37.8 GPa, and detonation velocities were predicted to be between 8424 and 9482 m/s; these properties make them competitive energetic materials.

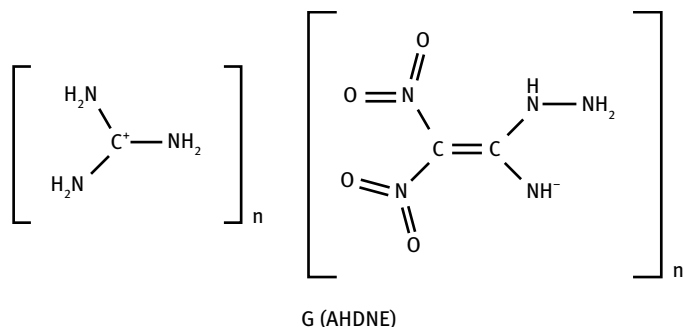
The thermal behavior and non-isothermal kinetics of the exothermic decomposition of 1-amino-1-hydrazino-2,2-dinitroethylene (AHDNE) were studied by DSC and TG/DTG [221]. The reaction rate equation was

$$\frac{d\alpha}{dT} = 10^{19.29} (1 - \alpha) \exp(-1.88 \times 10^4 / T) / \beta$$

The critical temperature of thermal explosion was calculated as 371 K (98 °C). The specific heat capacity of AHDNE was determined, and the standard molar specific heat capacity was 212 J mol⁻¹ K⁻¹ at 298 K. AHDNE was relatively unstable and had a much lower thermal stability than 1,1-diamino-2,2-dinitroethylene.

The potassium salt of AHDNE was synthesized by reacting AHDNE and potassium hydroxide in methanol aqueous solution [222]. The thermal behavior of K(AHDNE) as studied using DSC and TG/DTG is a three-step process. The decomposition enthalpy, apparent activation energy, and pre-exponential factor of the first decomposition process were -2662 J/g, 185 kJ/mol, and 10^{19.63} s⁻¹, respectively. K(AHDNE) had better thermal stability than AHDNE. Similar observations were made with the cesium salt [223].

A high-nitrogen energetic salt, the guanidinium salt of 1-amino-1-hydrazino-2,2-dinitroethylene guanidine, G(AHDNE), was synthesized by reacting 1-amino-1-hydrazino-2,2-dinitroethylene (AHDNE) and guanidinium chloride in sodium hydroxide aqueous solution [224].



The thermal stability of G(AHDNE) was determined by DSC and TG-DTG, showing an intense exothermic decomposition. The enthalpy, apparent activation energy, and pre-exponential constant of the decomposition process were -1060 J/g , 148.7 kJ/mol , and $10^{15.9} \text{ s}^{-1}$, respectively. The critical temperature of thermal explosion of G(AHDNE) was $425 \text{ K} = 152^\circ\text{C}$. The adiabatic time-to-explosion of G(AHDNE) was calculated to be between 60 and 72 s. The detonation velocity and detonation pressure were also estimated. G(AHDNE) is suitable as a nitrogen-rich propellant ingredient.

5.3.2 1-Amino-1-methylamino-2,2-dinitroethene

Replacing one of the amino groups in DADNE with a methylamino group may improve the thermal stability of the molecule. These compounds can be prepared by transamination reactions, replacing one of the amino groups with an alkylamino group.

1-Amino-1-methylamino-2,2-dinitroethylene (AMFOX-7), was synthesized from 1,1-diamino-2,2-dinitroethylene reacting with methylamine in *N*-methyl pyrrolidone (NMP) at 353 K (80°C), and its structure was determined by single-crystal XRD [225, 226]. The crystal is monoclinic, space group $P2_1/m$ with crystal parameters of $a = 6.361(3) \text{ \AA}$, $b = 7.462(4) \text{ \AA}$, $c = 6.788(3) \text{ \AA}$, $\beta = 107.367(9)^\circ$, $V = 307.5(3) \text{ \AA}^3$, $Z = 2$, and $\rho_c = 1.751 \text{ g} \cdot \text{cm}^{-3}$. The enthalpy, apparent activation energy, and pre-exponential constant of the exothermic decomposition reaction of AMFOX-7 were -303 kJ/mol , 230.7 kJ/mol , and $10^{21.03} \text{ s}^{-1}$, respectively. The critical temperature of thermal explosion is 518.4 K (245.3°C). AMFOX-7 has higher thermal stability than FOX-7.

A similar compound can be obtained by replacing one amino group in DADNE with an ethylamino group instead of a methylamino group. 1-Amino-1-ethylamino-2,2-dinitroethylene (AEFOX-7) was synthesized by the reaction of FOX-7 and ethylamine aqueous solution at 365 K (92°C) [227]. The thermal behavior of AEFOX-7 was studied by DSC and TGA/DTA, and can be divided into a melting process and an exothermic decomposition process. The enthalpy, apparent activation energy, and pre-exponential constant of the exothermic decomposition reaction were -375 kJ/mol , 169.7 kJ/mol , and 10^{19} s^{-1} , respectively. The critical temperature of thermal explosion of AEFOX-7 was 418.3 K (145.2°C). The thermal stability of AEFOX-7 was much lower than that of FOX-7.

5.4 Tetranitroethylene

Tetranitroethylene (tetranitroethene) had not previously been isolated but was suspected as an intermediate in the reaction of hexanitroethane with anthracene [228]. It is one of the known nitrocarbons which do not contain any hydrogen.

Tetranitroethylene was later isolated in 50% yield by flash vacuum pyrolysis of hexanitroethane [121]. Critical for the isolation was a trap temperature such that dinitrogen tetroxide was not condensed. Tetranitroethylene reacted quantitatively with anthracene to give 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene. Tetranitroethylene was at least an order of magnitude more reactive in Diels–Alder additions than tetracyanoethylene. Tetranitroethylene reacted with cyclopentadiene to give 5,5,6,6-tetranitronorbornene. Tetranitroethylene is a suitable intermediate for the synthesis of other nitro compounds that might be useful as propellant ingredients.

6 Nitroalkynes

Nitroacetylene (nitroethyne), or maybe even dinitroethyne, would be very energetic compounds, but they have not yet been prepared in a pure state. Dinitroacetylene and other nitroacetylenes would be attractive precursors to high-energy-density materials, but suffer from high reactivity and thermal instability. Dissolved nitroacetylene can be prepared by the reaction of NO_2PF_6 with trimethylsilylacetylene [229, 230]. It was stable at room temperature in dilute solution for about a week. The ^1H and ^{13}C NMR spectra of nitroacetylene revealed strong ^1H – ^{14}N and ^{13}C – ^{14}N spin couplings. Nitroacetylene reacted rapidly with nucleophiles. It gave a 1,4-Diels–Alder adduct with cyclopentadiene. It has been attempted to stabilize nitroethynes as ligands in metalorganic complexes with cobalt carbonyl or by attaching a trimethylsilyl group.

The reaction of nitroacetylene with furan or vinyl ethers gave nitrovinylisoxazoles. Mechanisms were proposed that would account for these unexpected products. The mechanisms were modeled computationally in vinyl methyl ether, calculating ΔH and the activation barriers [231]. Using other computational procedures, the molecular geometry of nitroacetylene, the gas- and liquid-phase heats of formation, and the molecular surface electrostatic potential of nitroacetylene were calculated.

The C– NO_2 bond dissociation energy in nitroethyne has been calculated and indicated that this molecule is expected to be very unstable [232]. Another potential but as yet unknown energetic compound is 1-azido-2-nitroethyne. Only calculations of the molecular structure and heat of formation of 1-azido-2-nitroethyne have been reported.

Forty-five years after their first preparation, nitroalkynes retain interest for their unique chemical behavior and their potential as energetic materials or building blocks for cycloadditions to heterocyclic compounds [233, 234].

1,1,1,6,6,6-Hexanitrohexyne-3 can be made by a metathetical reaction between silver nitroform and 1,4-dibromo-butyne-2 or 1,4-dichlorobutyne-2 in an inert volatile solvent [235]. It is a white crystalline solid which melts at 402.5–402.8 K (129.4–129.7 °C). It is detonated by a hammer blow. Ignition temperature is 478 K (205 °C).

7 Straight-Chain C₃ Polynitropropanes

7.1 Dinitropropanes

Geminal dinitro compounds can be prepared by catalyzed oxidative nitration of nitronate salts [236]. This method avoids the use of silver salts and instead uses a mixture of peroxydisulfate and potassium hexacyanoferrate(III). 2,2-Dinitropropanol is an intermediate in the synthesis of energetic plasticizers.

2,2-Dinitropropane forms face-centered, cubic crystals at room temperature, with $a_0 = 8.78 \pm 0.05 \text{ \AA}$ and four molecules per unit cell [237].

The pyrolysis of 2,2-dinitropropane vapor was investigated at 448 to 483 K (175 to 210 °C) [238]. Mass spectrometric analyses of the early products of the reaction indicated that the initial products were acetone, NO, and NO₂ in equimolar amounts. As acetone and NO₂ accumulated, the NO₂ was reduced to NO by reaction with acetone to yield H₂O, CO, and CO₂.

The heats of combustion of 1,1-dinitropropane, H₃CCH₂CH(NO₂)₂; 2,2-dinitropropane, (H₃C)₂CH(NO₂)₂; and 1,3-dinitropropane, O₂N(CH₂)₃NO₂, are 1867, 1850, and 1814 kJ/mol (446.3, 442.2, and 433.6 kcal/mol), respectively [26].

The thermal explosion times of some isomeric dinitropropanes at a constant pressure of 10 kbar were measured in the temperature range 403–583 K (130–310 °C) [239]. For a constant thermal explosion time of 20 s, the dinitropropanes that did not have a hydrogen atom on the same carbon as the dinitro group required a higher temperature than those that did have such a hydrogen. Specifically, the temperatures corresponding to a 20-s explosion time at 10 kbar pressure were 2,2-dinitropropane 542 K (269 °C), 1-fluoro-1,1-dinitropropane 515 K (242 °C), 1,1-dinitropropane 445 K (172 °C), and 1,2-dinitropropane 435 K (162 °C). The physical properties of 1,1- and 2,2-dinitropropane are summarized in Table 17. See also [240, 241].

The thermal decomposition of 1,1-dinitropropane and 2,2 dinitropropane was compared to better understand the effect of the location of nitro groups on the stability of nitro compound molecules. The thermal decomposition of neat, liquid 1,1-dinitropropane (1,1-DNP) at 1 and 1000 atm and 408–428 K (135–155 °C) gave over 90% propionic acid with small amounts of acetic acid, with conversions ranging from 29% in 1.5 h at 408 K (135 °C) and 1000 atm to 10% in 21 h at 428 K (155 °C) and 1 atm [243]. At 1000 atm and 155 °C, decompositions were unpredictable, sometimes proceeding smoothly for up to 125 min and at other times exploding after only 25 min. 2,2-Dinitropropane (2,2-DNP), in contrast, decomposed slowly at 438 K (165 °C) to

Table 17: Physical and thermodynamic properties of 1,1- and 2,2-dinitropropane at 60 °C.

Property	Compound	
Abbreviation	1,1-DNP	2,2-DNP
CAS RN	[601-76-3]	[595-49-3]
Molecular mass, g/mol	134.1	134.1
Density, g/cm ³	1.201 ± 0.01	1.221 ± 0.01
Coefficient of thermal expansion, K ⁻¹	(~1.0 ± 0.1) × 10 ⁻³	(~0.98 ± 0.1) × 10 ⁻³
Velocity of sound, mm/μs	1.33 ± 0.05	1.24 ± 0.05
Enthalpy of formation, cal/g	-283 ± 20	-300 ± 20
Detonation velocity, mm/μs	6.414 ± 0.018 at 25 °C	6.318 at 60 °C
Unconfined failure diameter, mm	>15 at 25 °C	>38 at 60 °C

Data source: [242]

give only acetone, NO₂, and NO. Pressure retarded the reaction slightly. At 463 K (190 °C), 2,2-DNP had a half-life of 15 h. The unimolecular decomposition of four dinitropropanes has been studied in the gas phase using a low-pressure pyrolysis technique. 1,2-Dinitropropane was found to undergo cyclic elimination of HONO, giving 1- and 2-nitropropene. Three *gem*-dinitroalkanes, 1,1-DNP and 2,2-DNP and 1-fluoro-1,1-dinitropropane, underwent C–N scission rather than HONO elimination, with essentially the same rate constant. Major decomposition products in these cases were propionaldehyde and acetone in the case of the 1,1- and 2,2-dinitropropanes, and propionyl fluoride in the case of 1-fluoro-1,1-dinitropropane. The detonation failure diameters of four liquid nitroalkanes (nitromethane, 1,1-dinitroethane, 1,1-DNP, and 2,2-DNP) were measured for the cases of heavy confinement in thick-walled lead cylinders and weak-shell confinement (Table 17).

The thermal decomposition of 2,2-DNP was investigated in a shock tube over the temperature range 970–1200 K, under high dilution in argon at total pressures of 456–557 kPa (4.5–5.5 atm) [36]. The decay of 2,2-DNP and the production of NO₂ were followed spectrophotometrically at 280 and 405 nm, respectively. The derived unimolecular rate constant for dissociation was

$$k_{\infty} = 10^{13.1} \exp(-23000/T) \text{ s}^{-1}.$$

The products of pyrolysis of 2,2-DNP were identified and quantified using FTIR, GC, and GC/MS. The principal products were CO, NO, (CH₃)₂CO, CH₃C≡H, CH₂C=CH₂, CH₃CN, CO₂, CH₃OH, CH₄, H₂O, and CH₂O. The first step in the decomposition appears to be C–NO₂ bond fission. However, the temporal profiles of NO₂ during the decomposition were distinctively different from those recorded during the decomposition of CH₃NO₂ or 2-nitropropane. The following intermediates play critical roles in the decomposition: H, OH, NO₂, HCO, and HNO.

8 C_{n>3} Polynitroalkanes

8.1 Straight-Chain C_{n>3} Polynitroalkanes

The physical properties of trinitroalkanes with terminal trinitromethyl groups are listed in Table 18. Although these compounds have a better oxygen balance than the mononitroalkanes, they have not found any applications as propellants.

Compared with the well-established 2,2,2-trinitroethyl group in the chemistry of energetic materials, the 3,3,3-trinitropropyl group is less investigated regarding its chemical and energetic properties. Syntheses of several compounds containing the 3,3,3-trinitropropyl group were performed and their properties compared with compounds containing the 2,2,2-trinitroethyl group [244]. All materials were thoroughly characterized by XRD, DSC, and their sensitivities towards impact, friction, and electrostatic discharge. The energies of formation were calculated and several detonation parameters such as the velocity of detonation and the propulsion performance were estimated with the program package EXPLO5.

Reactions of nitric acid, dinitrogen tetroxide, or dinitrogen pentoxide with alkenes result in mixtures of dinitro and nitro/nitrate compounds. Oxidation of oximes or isocyanates leads to conversion of the oxime or isocyanate ligand to a nitro group. The chemistry of polynitroalkanes becomes more and more complex the more carbon atoms are in the skeleton backbone and the more nitro groups are attached. Some of these polynitroalkanes serve as intermediates in the synthesis of other, more useful nitro compounds.

There are many energetic compounds that contain nitro —NO₂ as well as nitrate —ONO₂ groups. We could discuss these compounds either here in the chapter “Nitroaliphatic Compounds” or later in the chapter “Nitrate Esters.” A compromise was achieved by deciding that those which contain more nitro groups than nitrate (nitroxy) groups or equal numbers of both will be discussed here and those that contain more nitrate (nitroxy) groups than nitro groups will be discussed later.

Geminal dinitro compounds can be obtained by the reaction

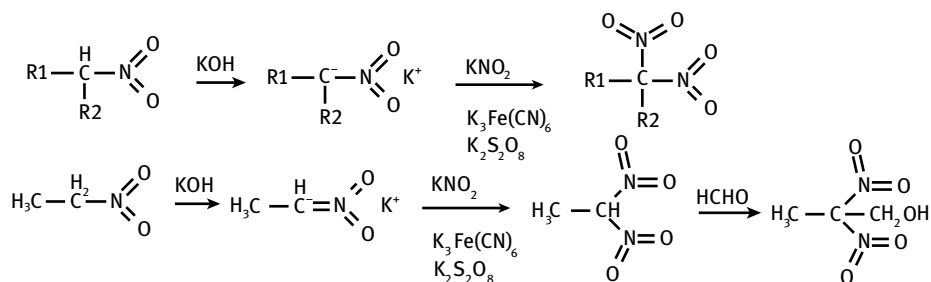


Table 18: Physical properties of trinitroalkanes.

Compound name	Formula	Boiling point		Melting point		Density g/cm ³	Refractive index <i>n_D</i>
		K	°C	K	°C		
1,1,1-Trinitropropane	(NO ₂) ₃ CCH ₂ CH ₃	296 at 0.26 kPa	23 at 2 mm Hg	215.4	-57.7	1.3938 at 22 °C	1.4432 at 22 °C
1,1,1-Trinitro- <i>n</i> -butane	(NO ₂) ₃ CCH ₂ CH ₂ CH ₃	—	—	250	-23	1.3253 at 23 °C	1.4424 at 23 °C
1,1,1-Trinitroisobutane	(NO ₂) ₃ CCH ₂ C(CH ₃) ₂	306 at 46 Pa	33 at 0.35 mm Hg	282.6	9.5	1.3452 at 23 °C	1.4436 at 23 °C
1,1,1-Trinitro- <i>n</i> -pentane	(NO ₂) ₃ CCH ₂ CH ₂ CH ₂ CH ₃	323 at 93 Pa	50 at 0.7 mm Hg	—	—	1.2740 at 25.5 °C	1.4438 at 25.5 °C
1,1,1-Trinitroisopentane	(NO ₂) ₃ CCH ₂ C(CH ₃) ₂	293 at 1.33 kPa	20 at 10 mm Hg	—	—	1.2743 at 25.5 °C	1.4443 at 25.5 °C
1,1,1-Trinitro- <i>tert</i> -pentane	(NO ₂) ₃ CC(CH ₃) ₃	—	—	412– 414	139– 141	—	—

Data source: [108]

The reaction of nitroethane, potassium hydroxide, formaldehyde, potassium nitrite, and potassium persulfate in the presence of potassium ferricyanide as a catalyst gave a reaction mixture from which 2,2-dinitropropanol could be extracted with ether [245]. A continuous process has been developed for the production of 2,2-dinitropropane by nitration of 2-nitropropane [246]. 2,2-Dinitropropane is used as an additive in diesel fuels.

The time lag prior to explosion of six trinitromethyl explosives: 2,2,2-trinitroethyl-*N*-nitromethyl amine (TNMA), bis(2,2,2-trinitroethyl-*N*-nitro) ethylene diamine (BTNEDA), 2,2,2-trinitroethyl-4,4,4-trinitrobutyrate (TNETB), bis(2,2,2-trinitroethyl) formal (BNTF), 1,1,1,3-tetranitropropane (TETNP), and bis(2,2,2-trinitroethyl)-nitramine (BTNNA) at different temperatures was measured by an explosion temperature test apparatus and the apparent activation energy and pre-exponential constant of the explosive decomposition rate equation and the value of T corresponding to time lag $t = 5$ s were calculated [247]. The thermal stability of the six trinitromethyl explosives decreased in the order TNETB > BNTF > BTNEDA > TETNP > TNMA > BTNNA.

The theoretical chemical mechanisms involved in the decomposition of trinitroethyl compounds were studied for both aliphatic and aromatic derivatives using density functional theory calculations [248]. At first, in the case of 1,1,1-trinitrobutane, two primary channels were highlighted among the five investigated ones: the breaking of the C—N bond and HONO elimination. Then, the influence of various structural parameters was studied for these two reactions by varying the length of the carbon chain or adding substituents or double bonds along the carbon chain.

Trinitroalkyl compounds with positive oxygen balance were evaluated as non-toxic, environmentally friendly replacements for AP in composite solid propellants [249].

A unique trinitroalkyl compound is (2,2,2-trinitroethyl) carbonate, $C_5H_4N_6O_{15}$, which contains 61.83% oxygen [250]. Intra- as well as inter-molecular C—H $\cdots$ O and dipolar nitro-group interactions account for its exceptionally high density of 1.975 g/cm³. For a given volume, this compound contains available oxygen in amounts even superior to that of liquid oxygen.

8.2 Branched-Chain Polynitroalkanes

While most nitro compounds that have been considered as energetic plasticizers were derived from straight-chain alkanes, there are a few polynitroalkanes based on branched-chain alkanes, such as 2,3-dimethyl-2,3-dinitrobutane (DMDNB) where rotation along the C—C axis is hindered and rotational isomers may be observed by IR spectroscopy [251]. This appears to be a thermally more stable nitroalkane [252]. In the DTA, it had a phase change at 383.4 K (110.3 °C), and the start of an exotherm

at 478.5 K (205.4 °C) and a sharp exotherm at 521 K (248 °C) when tested in closed test cells. DMDNB is used as a more volatile tracer for PBX to make them more detectable at security check points.

8.3 Cycloaliphatic Polynitroalkanes

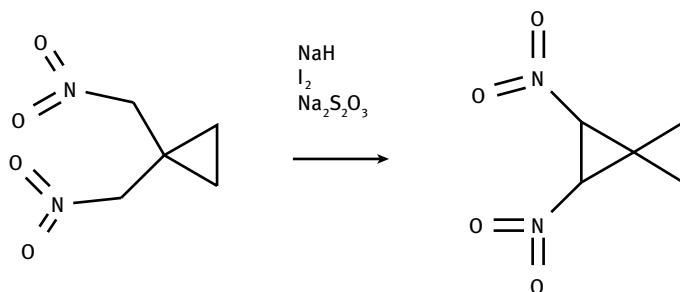
Laser-induced chemistry possesses the potential to drive some nitration reactions in an efficient and selective manner, such as in the laser-induced reaction of nitrogen dioxide with each of three cycloalkanes [253]. A carbon dioxide infrared laser was used to drive the reaction between nitrogen dioxide and cyclopropane, cyclobutene, or cyclopentane under a variety of reaction conditions. The major products resulted from either ring cleavage or product dissociation, nitration, or oxidation. The product mixtures were found to be highly sensitive to the specific reaction conditions.

Nitrocyclobutane would be more energetic than nitro-*n*-butane or nitroisobutane because the strained ring adds to the energy content. Aminocyclobutanes can be oxidized to the corresponding nitrocyclobutanes. 1,3-dinitrocyclobutane, 1,1,3-trinitrocyclobutane, and 1,1,3,3-tetranitrocyclobutane have been synthesized, but only in trace quantities.

8.3.1 Nitrocyclopropanes

The heat of formation of the parent hydrocarbon, cyclopropane, is approximately +276 kJ/mol with a corresponding bond strain energy of 230 kJ/mol. The enthalpy of combustion of cyclopropane is 2091.3 kJ/mol, or about 49.8 kJ/g⁻¹. Consequently, polynitro derivatives of cyclopropane and spirocyclopropane should be very energetic materials [254]. The idea of adding oxidizing groups like nitro groups to the cyclopropane backbone is not new. Nitrocyclopropane, C₃H₅NO₂, was prepared by mixing cyclopropane vapors with N₂O₄ at 693–728 K (420–455 °C) or with HNO₃ vapors at 663–683 K (390–410 °C) for several seconds in a spiral Pyrex tube, then immersing the tube in an ice water bath and collecting and purifying the resulting liquid [255]. Nitrocyclopropane was isolated in 4–15% yield; the boiling point was 338–340 K (65–67 °C) and the density was 1.136 g/cm³. It was noted that nitrocyclopropane was relatively unreactive towards oxidation, bromination, or the presence of alkalis. Nitrocyclopropane does not form salts in strong alkaline media as *n*-nitropropane would. It can be reduced to cyclopropyl amine.

trans-1,2-Dinitrocyclopropane was synthesized by oxidative cyclization of the corresponding open-chain 1,3-dinitronate dianions with iodine in dimethyl sulfoxide [256]. *trans*-1,2-Dinitrospiropentane was prepared using a similar strategy with 43% yield by treating the dianion of 1,1-bis(nitromethyl)-cyclopropane [257]:



Nitrocyclopropanes can be prepared from nitrodiazomethanes [258, 259].

Density functional theory calculations of cyclopropane molecules with three or more nitro groups suggested that all molecules can exist as minimum-energy stationary states [260]. Some nitrocyclopropanes have a specific enthalpy of decomposition in excess of 8 kJ/g. Table 19 lists the calculated enthalpies of formation and the resulting enthalpies of combustion and decomposition of several nitrocyclopropanes. The enthalpies of formation are all positive and become more so as the nitro content of the molecule increases. This is consistent with an increased steric interference, as bulky nitro groups start amassing on the second side of the cyclopropane backbone.

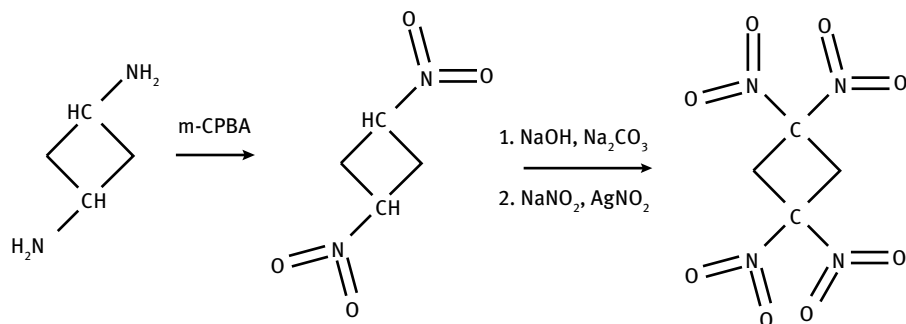
Table 19: Enthalpies of reaction and formation of nitrocyclopropanes.

	ΔH_f	ΔH_{comb}	ΔH_{decomp}	
	kJ/mol	kJ/mol	kJ/g	kJ/mol
Trinitrocyclopropane	73.8	1683.1	9.51	-1258.6
Tetranitrocyclopropane	114.9	—	—	-1611.3
Pentanitrocyclopropane	244.1	—	—	-1567.6
Hexanitrocyclopropane	338.2	—	—	-1518.7

Data source: [260]

8.3.2 Nitrocyclobutanes

Aminocyclobutanes can be oxidized to the corresponding nitrocyclobutanes when using *m*-chloroperoxybenzoic acid (*m*-CPBA) as the oxidant. Using this strategy, 1,3-dinitrocyclobutane was prepared from 1,3-diaminocyclobutane in 38% yield. Oxidative nitration of the disodium salt of 1,3-dinitrocyclobutane with a mixture of silver nitrate and sodium nitrite generated a mixture of 1,1,3,3-tetranitrocyclobutane $\text{C}_4\text{H}_4\text{N}_4\text{O}_8$ and 1,1,3-trinitrocyclobutane, from which the former was isolated in 38% yield after fractional recrystallization [261, 262]:



1,1,3,3-Tetranitrocyclobutane had a crystal density of 1.83 g/cm³, and although the compound rapidly degraded in alkaline solution, it was thermally stable up to its melting point of 438 K (165 °C).

XRD of 1,1,3,3-tetranitrocyclobutane single crystals gave the following crystal structure parameters: triclinic crystals, space group $P\bar{1}$, $a = 6.301(1) \text{ \AA}$, $b = 7.858(1) \text{ \AA}$, $c = 8.736(1) \text{ \AA}$, $\alpha = 85.88^\circ$, $Z = 2$ (two half molecules per asymmetric unit), and $\rho_{\text{XRD}} = 1.831 \text{ g/cm}^3$ [263]. The cyclobutane rings are exactly planar (each one sits on a separate crystallographic inversion center) with the *gem*-dinitro substituents disposed symmetrically above and below the ring plane.

The 1,3,3-trinitro derivative of azacyclobutane, TNAZ, is a new explosive and energetic additive to propellants that has been thoroughly investigated. The properties of TNAZ are discussed in *Encyclopedia of Liquid Fuels*, chapter "Heterocyclic Amines", based on the structure of the ring molecule to which the nitro groups have been attached.

8.3.3 Nitrocyclohexanes

The thermal decomposition of 1,1-dinitro-cyclohexane and 1,1,4,4-tetranitrocyclohexane was compared to that of 1,4-dinitropiperazine and other nitramines and difluoroamino compounds [264]. Geminal bis(difluoroamino) compounds appeared to be somewhat more stable than the corresponding *gem*-dinitro compounds, though they released more heat during decomposition. The decomposition of *gem*-bis(difluoroamino) and *gem*-dinitro compounds exhibited similarities. Both experienced loss of one geminal NX₂ group followed by the rearrangement of the remaining —NX₂. Where X was oxygen, loss of the initial nitro by homolysis was favored; rearrangement of the remaining nitro followed by homolysis of NO resulted in a CO bond. The density of nitrocyclohexane is 1.061 g/cm³.

9 Bridged and Fused-Ring Structure Cycloaliphatic Polynitroalkanes

There is a group of bridged hydrocarbons which have found application as high-density fuels for air-breathing cruise missiles and similar applications. It would be of interest to combine these energetic hydrocarbon skeletons with one or more nitro groups to soup up the energy content of the material to beyond that of a fuel and maybe reaching that of a monopropellant or explosive. The all-hydrocarbon skeleton analog to RDX or HMX would still be a very energetic molecule, even without the nitramine linkages.

Bicyclo[1.1.1]pentane is a highly strained hydrocarbon system due to close proximity of non-bonded bridge head carbons, and attaching nitro groups would make it even more energetic. Densities, detonation velocities, and detonation pressures for a series of polynitrobicyclo[1.1.1]pentanes, as well as their thermal stabilities were investigated by computational chemistry [265]. Calculations of the bond length and bond dissociation energies of the C—NO₂ bond indicated that this may be the possible trigger bond in the pyrolysis mechanism. 1,2,3-Trinitrobicyclo[1.1.1]pentane, 1,2,3,4-tetranitrobicyclo[1.1.1]pentane, and 1,2,3,4,5-pentanitrobicyclo[1.1.1]pentane have promising predicted energetic characteristics with better stability and insensitivity.

A highly strained ring molecule is [1.1.1]propellane, where not only two but three cyclopropyl rings share a common side of three triangles. In [2.2.2]propellane, three cyclobutane rings share one side of the squares. Nitro groups can be attached to the free >C—H bridges in these molecules [266].

10 Caged Cycloaliphatic Polynitroalkanes

Energetic compounds based on strained or caged alicyclic skeletons with one or more nitro groups attached have received substantial interest because of their high density and high detonation velocities. The synthesis of these compounds poses a challenge for the synthetic chemist. An excellent summary of synthetic efforts to prepare nitrocubanes and similar compounds is presented in [267]. Initial evaluation of the shock sensitivity of such compounds showed that they are relatively insensitive to shock but have a higher density than some of their open-chain aliphatic analogs.

Similar cubanoid structures called azacubanes in which one or more CH groups in the corner of the cube have been replaced by nitrogen have been considered. The gas-phase enthalpies of formation of azacubanes with many nitro groups have been obtained via isodesmic reactions in which the azacubane cage skeleton is not destroyed [268]. After full nitration of 1,4-diazacubane or 1,3,5,7-tetraazacubane, the weakest C—N bond in the 1,3,5,7-tetraazacubane cage skeleton strengthens slightly, but in the 1,4-diazacubane cage skeleton, it weakens. For highly nitrated azacubanes, the introduction of an —NH₂ group results in destabilization of the neighboring

C—N bond in the cage skeleton. The shock stability of 2,4,6,8-tetranitro-1,3,5,7-tetraazacubane (TNTAzC) is superior to that of 2,3,5,6,7,8-hexanitro-1,4-diazacubane (HNDaZC). The detonation velocity and pressure of TNTAzC are predicted to reach 11.10 km/s and 101.7 GPa, respectively.

Another caged cycloaliphatic alkane is tetrahedrane, where the four sides of a tetrahedron are formed by cyclopropane rings. The parent hydrocarbon is not known, but derivatives tetra(*tert*-butyl)tetrahedrane and tetra(trimethylsilyl)tetrahedrane are known. It was hoped that attachment of nitro groups to form tetranitrotetrahedrane (another nitrocarbon) would stabilize the molecule, but the opposite rather appears to be the case. This compound exists so far only in the imagination of computational chemists. The predicted properties of nitrotetrahedranes were compared to the properties of nitrocubanes.

Computational studies on a series of nitro derivatives of tetrahedrane were carried out by optimizing the molecular geometries and calculating the vibrational frequencies [269]. The electronic structures were analyzed using natural bond orbital theory and atoms in molecules theory. The results showed that the skeleton, a tetra-carbon cage, is heavily stressed. C—C bonds of tetrahedrane are weaker than normal C—C bonds. The introduction of a nitro group reduces the stability of the tetra-carbon cage and the C—N bond is still weak. The more nitro groups are introduced, the weaker the C—N bonds are. For $C_4(NO_2)_4$, the C—N bond is more readily broken than the C—C bond. Heats of formation of nitro derivatives were calculated by assuming isodesmic reactions. Values of heats of formation were all positive and increased with an increase in the number of nitro groups.

Compounds containing carbon-based cages have a highly strained molecular structure and have become a subject of interest because they possess high heats of formation and are highly energetic. *Ab initio* density functional theory molecular modelling calculations have been performed to analyze 28 carbon-cage structures with the aim of identifying the best candidates for synthesis and for use in propellant compositions [270]. Calculated heats of formation and densities of the compounds were then used to compute their specific impulses and density-specific impulses in various configurations (solid and liquid). Detonation properties of the compounds have also been calculated and a correlation of the properties of the cage compounds with their molecular structures was attempted.

10.1 Nitrocubanes

The cubane skeleton has a high enthalpy of formation (+620 kJ/mol = +148 kcal/mol) because it has a lot of internal molecular strain. Nitro derivatives of cubane would give a better performance as propellants or explosives than nitroadamantanes because in adamantane, 6-membered rings are similar to unstressed cyclohexane.

In theory, it should be possible to replace all eight hydrogens on cubane with nitro groups and arrive at a very energetic molecule $C_8(NO_2)_8$ that does not contain any hydrogen. The molecular mass of octanitrocubane is 464.1 g/mol and the oxygen balance is $\pm 0.0\%$. A propellant that does not contain hydrogen would not form any water as the product of combustion and thus have no condensables in the exhaust, making it a low-signature or no-signature propellant which may have tactical advantages for certain military applications. It was predicted that octanitrocubane would enhance the energy output of propellants and explosives by 14% compared to HMX.

There has been a substantial experimental effort to synthesize nitrocubanes. These compounds have so far only been obtained in gram quantities and it is unlikely that they will ever be used as rocket propellants. They are primarily intended as explosives. They are more of academic interest but may show pathways for synthesis of more energetic rocket propellants, possibly by direct synthesis from readily available raw materials such as acetylene or ethene and dinitrogen tetroxide. Systematic studies on the effect of increasing the number of nitro groups attached to a caged molecule have given us a better understanding of the internal workings of energetic materials, and this knowledge can be applied to other propellants, not only explosives. This is the reason for the nitrocubanes being listed in this book, particularly work conducted within the last decade. The interest in nitrocubanes has stimulated work on other cubane derivatives, mostly cubylcarbonic acids and aminocubanes that are used as intermediates in the preparation of nitrocubanes. It is very misleading to learn that the dimethyl ester of cubane-1,4-dicarboxylic acid is now (as of 2013) produced on the **pilot scale** [271], but when reading the details of the paper it becomes apparent that they are only making several grams at a time.

The plain cubane hydrocarbon (without any nitro groups) has been considered as a fuel for solid fuel air-breathing ramjets and as a building block for binders for solid propellants (See *Encyclopedia of Liquid Fuels*, chapter “Cycloaliphatic Hydrocarbons”) but of course the limited quantities available have prevented any such use. Cubane is a kinetically stable compound (decomposition temperature above 473 K = 200 °C), and a thermodynamic store of energy ($\Delta H_f = +620$ kJ/mol) which corresponds to a total strain energy of 694.5 kJ/mol. Attaching energetic group to the cubane skeleton opens the door to high- (higher-)energy density materials. For oxidizers, groups to be attached are nitro, nitrato, nitramino, or difluoroamino groups. The melting point of tetranitrocubane is above 543 K (270 °C). The density of tetranitromethane is 1.814 g/cm³.

The numbering of substituents on cubane may be a little confusing at first glance. The numbering of substituent sites is illustrated in Figure 4. It seems the numbering goes clockwise on the front face in positions 1 through 4, then moves from 4 to the back face, starting with 5, and continues clockwise all the way to position no. 8.

Highly nitrated cubanes are predicted to be very dense materials with great potential for explosives and propellants. Unfortunately, strained hydrocarbon nitro

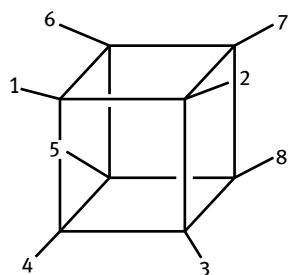


Figure 4: Numbering of substituent sites in cubane.

derivatives cannot generally be prepared directly, e.g., by nitration of the parent hydrocarbons, because the stressed cage structures do not survive the harsh reaction conditions. Very good summaries of polynitropolycyclic cage molecules including polynitrocubanes and polynitroadamantanes are presented in [272] and in [273–275]. Cubane, cubylcubane, and nitrocubanes were included in a summary on energetic materials and their molecular structures [276]. See also [277–279]. The successful synthesis of nitrocubanes has opened new paths for the development of other energetic materials, including ammonium dinitramide [280–284].

10.1.1 Density of Nitrocubanes

The density of nitrocubanes increases with increasing number of nitro groups attached to the cube (Table 20). The correlation between theoretically predicted and experimentally measured density is pretty good until four or five nitro groups are attached, but the predicted density for octanitrocubane is much higher than the best density measured for octanitrocubane to date. It is interesting to follow the increase in density of cubane with increasing substitution of hydrogens by nitro groups and to compare predicted with measured densities [285]. Similar calculations were performed for nitroadamantane. A similar table was found in another source, Table 21.

Table 20: Density of four nitrocubanes.

Compound	Density, measured g/cm ³	Density, calculated g/cm ³
Cubane	1.29	1.37
1,3-Dinitrocubane	1.65	1.74
1,4-Dinitrocubane	1.66	1.74
1,3,5-Trinitrocubane	1.74	1.84
1,3,5,7-Tetranitrocubane	1.814	1.92

Data source: [285]

Table 21: Density of cubane and five nitrocubanes.

Molecule	Density, calculated g/cm ³	Density, measured g/cm ³
Cubane	1.29	1.29
1,4-Dinitrocubane	1.66	1.66
1,3,5-Trinitrocubane	1.77	1.76
1,3,5,7-Tetranitrocubane	1.86	1.81
1,2,3,5,7-Pentanitrocubane	1.93	1.96
Octanitrocubane	2.13	1.98

Data source: [286]

The progressive nitrocubane substitution of hydrogen with nitro groups showed a pattern by which single nitro-substitutions starting from cubane lead ultimately to octanitrocubane. Of the 22 member species, densities have been experimentally measured for only 8, and these were used to estimate the densities of the other 14 members [287].

10.1.2 Thermodynamic Properties of Nitrocubanes

Ab initio molecular orbital (SCF) calculations were performed on cubane, tetraazacubane, and their nitro derivatives [288]. The group equivalent method was used to calculate strain energies. Such calculated values showed that the substitution of carbons by nitrogen atoms in the cubane cage increases the strain energy. Increasing nitro substitution beyond four has a similar effect and this is more pronounced in the tetraazacubane system.

The heats of formation for 21 polynitrocubane compounds were calculated using several semiempirical molecular orbital methods and for eight of 21 polynitrocubanes containing one to four nitro groups using a density functional theory method by means of designed isodesmic reactions [289, 290]. All 21 polynitrocubane compounds have high heats of formation, implying that they can be very powerful energetic materials. By comparing the results, a relationship between the heats of formation and molecular structures for polynitrocubanes could be established.

The theoretically predicted strain energy of cubane is 708 kJ/mol = 169.13 kcal/mol, which was in good agreement with an experimental value. The variation of strain energy with respect to the number of substituents was calculated for polynitrocubane and polydifluoroaminocubane and it increased slightly as up to four substituent groups were added to the cage skeleton [291]. On the contrary, the strain energy dramatically increased when the number of substituent groups increased from five up to eight. For polynitratocubane, the strain energy decreased slightly at the beginning then increased as the number of groups increased. For polyazidocubane, there were very small group effects on the strain energy. Among four types of substituent groups, the nitro group had the greatest

effect on the strain energy of the caged cubane skeleton. The calculated strain energy of octanitrocubane is 1076 kJ/mol = 257.20 kcal/mol, while that of octaazidocubane is 697 kJ/mol = 166.48 kcal/mol. The substituent groups withdraw electrons from the cubane, reducing the repulsion between C—C bonds. This relieves the strain of the skeleton for isomers with fewer substituents. Group repulsions increased sharply as more and more nitro, nitrato, and difluoroamino groups were attached to cubane, resulting in large strains of the skeleton.

The enthalpy of formation, crystal density, detonation velocity, and pressure for polynitrocubanes have been calculated using various theoretical methods [292]. It has been observed that for polynitrocubanes the introduction of $-\text{NH}_2$ groups onto the skeleton resulted in destabilization of the neighboring C—C bonds on the skeleton. The C—C and C— NO_2 bonds of octanitrocubane were stronger than those of partly nitrated cubanes, implying that the shock stability of octanitrocubane should be superior to that of partly nitro-substituted cubanes. For polynitrocubanes the calculated crystal density was within 0.07 g/cm³ of the experimental crystal density, being more accurate than by the group additivity method. The detonation velocity, the detonation pressure, and the energy output all increased from tetranitrocubane to octanitrocubane. The detonation velocity and detonation pressure of octanitrocubane were predicted to reach 9.58 km/s and 60 GPa, respectively. The energy output of octanitrocubane is about 80% larger than that of HMX.

Calculations of enthalpies of formation of polynitrocubanes using density functional theory indicated that ΔH_f first decreased (number of nitro substituents $m = 0-2$) and then increased ($m = 4-8$) with each additional nitro group introduced into the cubane skeleton [293]. The enthalpy of formation of octanitrocubane in the vapor state was predicted to be +808 kJ/mol. The Gibbs free energy of formation increased by about 40–60 kJ/mol with each nitro group added to the cubane when the substituent number was fewer than four, then increased by about 100–110 kJ/mol with each additional group attached to the cubic skeleton. Both the detonation velocity and the pressure for polynitrocubanes increased as the number of substituents was increased. Other sources gave the enthalpy of formation of solid octanitrocubane as +98.9 kJ/mol.

Thermochemical calculations were conducted on the parent unsubstituted tetrahedrane and cubane hydrocarbons, and a list of 20 mono- and poly-functionalized derivatives with azo, **nitro**, and peroxy explosophoric substituents [294]. The high, mass-normalized gas-phase enthalpies of formation for both the tetrahedrane and cubane derivatives exceeded those of well-established primary and secondary (RDX and HMX) explosives by up to an order of magnitude.

10.1.3 Molecular Structure of Nitrocubanes

The structures of 1,4-dinitro-, 1,3,5-trinitro-, 1,3,5,7-tetranitro-, 1,2,3,5,7-pentanitro-, 1,2,3,4,5,7-hexanitro-, 1,2,3,4,5,6,8-heptanitro-, and octanitro-cubane had been reported prior to 2003 [295]; however, the structure of the simplest member of this series, nitrocubane (mononitrocubane), was reported later [296]. Nitrocubane

crystallized in orthorhombic crystals, space group *Pnma*, with cell dimensions $a = 17.507(5) \text{ \AA}$, $b = 6.584(2) \text{ \AA}$, and $c = 5.832(2) \text{ \AA}$, with four molecules in the unit cell and an X-ray density of 1.453 g/cm^3 .

Charge distributions in nitro derivatives of cubane, $\text{C}_8\text{H}_{8-n}(\text{NO}_2)_n$ ($n = 1-8$) have been derived employing *ab initio* Hartree–Fock and hybrid density functional theory methods [297]. The electron-rich regions around the oxygen atoms of the nitro group get smaller with increasing number of nitro groups in the series. Within different isomers of nitrocubane, the lowest energy isomers engender large electron-rich regions relative to the other isomers, which has been supported by the shallow electron density minima near oxygen atoms of nitro groups. The electrostatic potential at the center of the cube (cage critical point) on the other hand increased from mono- to octa-nitrocubane. The successive replacement of cubyl hydrogens by NO_2 groups pushes the added electrons along a cube with an increase of curvature of the C–C bonds. The electron density at the bond critical point and the curvature of the C–C bonds in a cubanoid increased from mono- to octa-nitrocubane. Heats of formation increased with increased destabilization in the nitrocubane isomers.

The impact sensitivity of some alkyl nitrates and cubane derivatives can be correlated with their heat of explosion and chemical structure [298]. These correlations revealed ways to reduce the explosion hazard in the handling of these compounds.

10.1.4 Thermal Stability of Nitrocubanes

It has been suggested that the higher decomposition temperatures of some nitrocubanes, which are higher than those of the parent hydrocarbon, may be due to the fact that nitro groups withdraw electrons from the skeleton and thus stabilize the system. The onset of exotherm temperatures of several nitrocubanes are listed in Table 22.

Quantum mechanical calculations were used to determine the structural and energetic characteristics of polynitrocubanes $\text{C}_8\text{H}_{8-n}(\text{NO}_2)_n$, where $n = 1-8$ [299]. Comparing minimum heights of the energy barriers to the decay of metastable clusters, it was shown that nitro groups destabilize the cubic carbon skeleton. For octanitrocubane the temperature dependence of the characteristic decay time at temperatures 500–1000 K and activation energy and frequency factor of the Arrhenius equation were calculated.

Table 22: Thermal stability of nitrocubanes

Compound	DSC onset temperature	
	K	°C
1,4-Dinitrocubane	530	257
1,3,5-Trinitrocubane	540	267
1,3,5,7-Tetranitrocubane	550	277

Data source: [286]

High-order electronic structure calculations with empirical bond additivity corrections have been applied to thermal decomposition reactions of nitrocubanes and validated by comparisons of different levels of theory and by comparison with experiments [300]. These methods provide a cost-effective means of obtaining thermal rate data and show promise of being applicable to reactions involving large polyatomic molecules important in nitrocubane decomposition.

10.1.5 Predicted Explosive Performance of Nitrocubanes

Thermodynamic studies of several polynitropolycyclic systems including nitrocubanes were used to calculate the explosive performance of such compounds [301]. The detonation velocity, the detonation pressure, and the energy output all increased from tetranitrocubane to octanitrocubane. The detonation velocity and pressure of octanitrocubane were predicted to reach 9.58 km/s and 60 GPa, respectively. The energy output of octanitrocubane is about 80% larger than that of HMX.

Other calculations predicted a theoretical detonation velocity of octanitrocubane of 9900 m/s, while the same method predicted for hexanitrobenzene, HMX, and CL-20 the detonation velocities of 9500, 9100, and 9200 m/s, respectively [302].

10.2 Mononitrocubane

Mononitrocubane was synthesized via a 14-step synthesis starting with cyclopentanone [303]. The heat of decomposition and the onset temperature of thermal decomposition were determined.

10.3 Dinitrocubane

1,4-Dinitrocubane can be prepared by first converting cubane-1,4-dicarboxylic acid to 1,4-aminocubane and then oxidizing that with *m*-chloroperbenzoic acid [304]. The yield in the last stage was 40%. This material did not decompose below its melting point of 533 K = 260 °C, which is higher than the start of decomposition (473 K = 200 °C) of the unsubstituted cubane hydrocarbon itself. Introduction of two nitro groups seemed to stabilize the molecule.

1,4-Dinitrocubane crystals undergo phase changes at high pressures. The pressure–temperature reaction phase diagram for 1,4-dinitrocubane was determined using optical polarizing microscopy and FTIR spectroscopy in conjunction with a high-pressure diamond anvil cell and the ruby fluorescence method of pressure measurement [305]. The phase transformation is of an order–disorder type.

10.4 Trinitrocubane

Systematic substitution of hydrogens on the cubane nucleus with nitro groups, illustrated with the examples of 1,3,5-trinitrocubane and 1,3,5,7-tetranitrocubane, has given us a better understanding of the effects of progressive substitution on thermal stability and enthalpy of formation of such molecules [306].

10.5 Tetranitrocubane

A precursor in the preparation of tetranitrocubane is cubane-1,2,4,7-tetracarboxylic acid [307]. 1,3,5,7-Tetranitrocubane is an extraordinary material. It is a crystalline solid with a very high density (1.814 g/cm³). Although a very energetic compound, it is kinetically quite stable, not melting until 543 K (270 °C), and then only with decomposition, not detonation.

The hydrogen atoms in the beta position to the nitro groups are very acidic. The measured pK_a is 21, at least 20 powers of ten more acidic than cubane itself. Much of this enhanced acidity must be the result of the tremendous inductive electron-withdrawing power of the nitro groups stabilizing the anion. Salts of tetranitrocubane are readily formed and can be used in the synthesis of higher nitrated cubanes. The sodium salt of tetranitrocubane has been used to convert tetranitrocubane to pentanitrocubane. Pentanitrocubane is about a thousand times more acidic than tetranitrocubane, and its sodium salt was converted in turn by interfacial nitration to hexanitrocubane, an even more acidic material.

Nitro groups on alternate corners of cubane enhance the acidity of cubyl hydrogen ($pK_a \sim 21$) and provide sufficient activation for ready anion formation. The sodium salt of 1,3,5,7-tetranitrocubane reacted easily with electrophiles and allowed the synthesis of more highly substituted cubanes [308, 309]. Dinitrogen tetroxide reacted with the anion of tetranitrocubane to give 1,2,3,5,7-pentanitrocubane, the first cubane to contain vicinal nitro groups. The reaction probably involved oxidation of the anion to the corresponding radical. Similarly, the anion of pentanitrocubane was used to prepare 1,2,3,4,5,7-hexanitrocubane, the most highly nitrated cubane known as of 1997. The crystal structures of both penta- and hexanitrocubane were examined by single-crystal XRD.

The push–pull electron effect of nitro and amino groups at opposite ends of a molecule leads to a significant stabilization of the dinitrodiaminoethene molecule (see Section “Physical Properties of FOX-7”). It was hoped that a similar effect would lead to stabilization of aminonitrocubanes and aminonitroazacubanes. *Ab initio* self-consistent-field molecular orbital computational studies of the structures and bond orders (as measures of relative bond strengths) of nitro and aminonitro derivatives of cubane and some azacubanes showed that the NO₂ group had a conformation-dependent effect on relative bond strengths [310, 311]. When the plane of the nitro

group was perpendicular to that of an endocyclic bond, that bond was weakened. An aza nitrogen adjacent to C—NO₂, however, eliminated the bond-weakening effect due to a “perpendicular” nitro group, except when a C—NH₂ was also adjacent to the C—NO₂. The NH₂ group had a direction-specific bond-weakening effect on one endocyclic bond. The influences of NO₂ and NH₂ were essentially independent; when these substituents were on adjacent carbons the effects were reinforcing. Thus, the combination of a “perpendicular” NO₂ and an NH₂ on adjacent carbons in cubane and azacubanes produced a marked bond weakening.

1,3,5,7-Tetranitrocubane is a crystalline solid with high density (1.814 g/cm³) and is kinetically quite stable, not melting until 543 K (270 °C). The full non-rigid group behavior of NO₂ groups in tetranitrocubane and octanitrocubane was modeled with computational methods [312, 313].

If four carbons in the cubane cube are replaced by nitrogens, and four hydrogens are replaced by nitro groups, one obtains a new class of energetic compound, tetranitrotetraazacubanes [314]. Density functional theory and molecular mechanics computations predicted a density of 2,4,6,8-tetranitro-1,3,5,7-tetraazacubane (TNTAC) of about 2.12 g/cm³, a detonation velocity of 10.42 km/s, and detonation pressure of 52.82 GPa, all of which are higher than those of octanitrocubane.

10.6 Pentanitrocubane

Pentanitrocubane is the first example of a nitrocubane with nitro groups on adjacent carbons. Nitro groups on alternate corners of cubane enhance the acidity of cubyl hydrogen and provide sufficient activation for ready anion formation. The sodium salt of 1,3,5,7-tetranitrocubane can react easily with electrophiles and can lead to yet more highly substituted cubanes, like carbomethoxy- and (trimethylsilyl)-tetranitrocubane. Anions from these species are also easily formed and are useful for further substitution on the cubane skeleton. Dinitrogen tetroxide reacted with the anion of tetranitrocubane to give 1,2,3,5,7-pentanitrocubane, the first cubane to contain vicinal nitro groups [315]. Similarly, the anion of pentanitrocubane was used to prepare 1,2,3,4,5,7-hexanitrocubane, the most highly nitrated cubane made to that date.

10.7 Hexanitrocubane

In the hexanitrocubane structure, C₈H₂N₆O₁₂, the H atoms participate in short hydrogen-bonding contacts to the nitro O atoms in adjoining molecules, thus linking molecules into a two-dimensional sheet in the *bc* plane [316]. In addition, the O···O contacts in hexanitrocubane are shorter than van der Waals contact distances. The shortest of these, with a length of 2.766(3) Å, involve the O atoms of one of the attached nitro groups. These contacts involve molecules in an extended two-dimensional sheet parallel to the *ab* plane.

10.8 Heptanitrocubane

Heptanitrocubane was an intermediate in the synthesis of the long-sought octanitrocubane [317]. In the first synthesis of heptanitrocubane, four of the eight nitro groups were introduced by functional group modification and three more by low-temperature N_2O_4 nitration of sequentially formed polynitrocubyl anions.

Heptanitrocubane is easier to make than octanitrocubane. Heptanitrocubane has a very high density (2.028 g/cm^3). Surprisingly, the predicted density of heptanitrocubane is higher than that of octanitrocubane. It has a calculated heat of formation only about 6% less than octanitrocubane.

Heptanitrocubane forms colorless crystals when its solution in fuming nitric acid is diluted with sulfuric acid. Single-crystal X-ray analysis confirmed the assigned structure and provided an accurate density at 294 K (21 °C) of 2.028 g/cm^3 , impressively high for a CHNO compound. Although octanitrocubane received more interest due to its symmetry and predicted explosive performance, heptanitrocubane is easier to make than octanitrocubane. It may prove to be a more powerful explosive and/or monopropellant as it is denser, has a calculated heat of formation only about 6% less than octanitrocubane, and will produce some lighter molecular mass gaseous products as it is not perfectly oxygen balanced.

10.9 Octanitrocubane

Octanitrocubane, $\text{C}_8(\text{NO}_2)_8$, ONC, CAS RN [99393-63-2], is one of a unique group of strongly oxidizing chemicals called “nitrocarbons” that consist only of a carbon skeleton and nitro groups. Other compounds in this group with similar structures are TNM, hexanitroethane, hexanitrobenzene, or decanitrobiphenyl. There is even a book devoted specifically to these types of chemicals [110]. Octanitrocubane has a perfect oxygen balance of 0% for combustion of all carbon to carbon dioxide. It is unlikely that octanitrocubane will ever be used as a rocket propellant. It is mentioned here only as an example of energetic material synthesis driven to the extreme.

10.9.1 Preparation of Octanitrocubane

In the first synthesis of octanitrocubane, four of the eight nitro groups were introduced by functional group modification, three more by low-temperature N_2O_4 nitration of sequentially formed polynitrocubyl anions, and the eighth and last by nitrosation of the heptanitrocubyl anion followed by ozonation [273, 317, 318]. Addition of excess NOCl to a solution of the lithium salt of heptanitrocubane in dichloromethane at 195 K (−78 °C) followed by ozonation at 195 K (−78 °C) gave the long-sought octanitrocubane in 45–55% yield. Octanitrocubane was the sixth known nitrocarbon discovered and the first new one to be made in the 18 years preceding 2000.

At this time, octanitrocubane is still very difficult to prepare and available only in gram quantities for further characterization. Other methods of synthesis are sought. One particularly enticing approach recognizes the fact that four molecules of dinitroacetylene are a stoichiometric (atom-by-atom) equivalent of one molecule of octanitrocubane. Perhaps octanitrocubane can be made directly by tetramerization of dinitroacetylene. Unfortunately, dinitroacetylene is not yet a known compound and it is most likely very unstable.

10.9.2 Physical Properties of Octanitrocubane

Based on XRD, the calculated theoretical density of octanitrocubane is 2.10 g/cm^3 for the most stable polymorph of octanitrocubane. Other sources report a density of 1.979 g/cm^3 [319].

Octanitrocubane is a stable, white solid, somewhat soluble in hexane and readily soluble in polar organics, but often crystallized with water of hydration, even from non-aqueous solvents. The density was measured at 1.979 g/cm^3 which, though high, was at the lower end of the original range of theoretical predictions. Taking into account the available data on polynitrocubane crystal structure, calculations predicted a density of 2.135 or 2.123 g/cm^3 for the most stable polymorph of octanitrocubane. Many nitro compounds have multiple polymorphs of remarkably different density. Octanitrocubane sublimes unchanged at atmospheric pressure at 473 K (200 °C).

In examining the IR spectra of octanitrocubane, a new type of vibration (quartic concerted torsional mode, abbreviated as QCTM) has been predicted for octanitrocubane which has been attributed to the rotation of the NO_2 group.

10.9.2.1 Thermodynamic Properties of Octanitrocubane

As of 2002, the most recently published calculated value for the heat of formation of solid octanitrocubane was 594 kJ/mol . It was predicted that the combustion of octanitrocubane to carbon dioxide and nitrogen would release 3475 kJ/mol .

One calculated value for the heat of formation of solid octanitrocubane, $(\text{CNO}_2)_8$, is 594 kJ/mol , corresponding to 74 kJ/mol per (CNO_2) increment. For comparison, the highest calculated ΔH_f of solid hexanitrobenzene, $(\text{CNO}_2)_6$, one of the most energetic explosives known, is about 200 kJ/mol , corresponding to 33 kJ/mol per (CNO_2) moiety, less than half that of octanitrocubane. The energy content of hexanitrobenzene is lowered by the stabilizing resonance energy of the aromatic ring. The energy content of octanitrocubane is increased by the strain energy of its unique carbon skeleton [318].

The molecular geometries, IR vibrational spectra, and thermodynamic properties of octanitrocubane were calculated using a density functional theory method [320]. The heat of formation of octanitrocubane in the gas phase is 726.47 kJ/mol . The sublimation enthalpy, density, and heat of formation for octanitrocubane crystals were calculated as 220.63 kJ/mol , 2.189 g/cm^3 , and 505.84 kJ/mol , respectively. The predicted detonation velocity and detonation pressure of octanitrocubane were

10.26 mm/ μ s and 520.86 kbar, respectively. Calculations showed that the pyrolysis initiation reaction of octanitrocubane is to initially form a diradical by the single C—C bond breaking in the cube. The second C—C bond breaking results in formation of a nitrocyclooctatetraene. The calculated activation energy for the pyrolysis initiation reaction of octanitrocubane was 155.30 kJ/mol.

10.9.2.2 Molecular Structure of Octanitrocubane

The molecular structure of octanitrocubane is that of a box with eight —NO₂ handles on it (Figure 5).

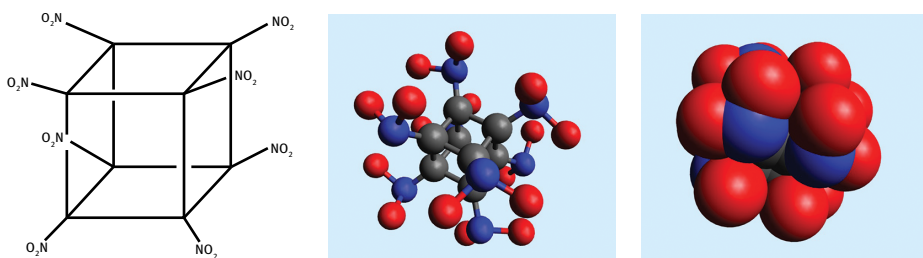


Figure 5: Molecular structure of octanitrocubane.

Ab initio molecular orbital and density functional theory calculations on isodesmic disproportionation reactions of nitrated cubanes indicated that the repulsion between nitro groups on adjacent carbons in octanitrocubane is surprisingly small and that the energy required for successive substitutions of nitro groups on the cubane frame diminishes progressively with increasing substitution [321]. As a consequence of the inductive effects of the nitro groups on one another, the negative charge on the oxygens also decreases with increasing substitution, reducing the magnitudes of the Coulomb repulsion between nearest-neighbor nitro groups. The O...O interactions remained very small throughout 180° rotations about the C—NO₂ bonds, a process that was computed to be nearly barrierless.

Homodesmotic reactions and isodesmotic reactions were designed for the computation of strain energies for a series of cubane derivatives [291]. The strain energy value of cubane itself is 708 kJ/mol = 169.13 kcal/mol for a homodesmotic reaction, which is in good agreement with the experimental value. The strain energy values of polynitrocubane and polydifluoroaminocubane increased slightly as up to four substituent groups were added to the cage skeleton. On the contrary, the strain energies dramatically increased when the number of substituent groups, *m*, increased from five up to eight. For polynitratocubane, the strain energies decreased slightly at the beginning, then increased as the number of nitro groups increased. For polyazidocubane, there were very small group effects on the strain energies. Among four types of substituent groups considered in this study, the nitro group had greatest effect on the

strain energy of the caged cubane skeleton. The calculated strain energy value of octanitrocubane was $1076 \text{ kJ/mol} = 257.2 \text{ kcal/mol}$, while that of octaazidocubane was $696.6 \text{ kJ/mol} = 166.5 \text{ kcal/mol}$.

Cubanes with *N,N*-dinitroamino instead of nitro pendants have not yet been synthesized, but their molecular structure and energy potential has already been calculated. The heats of formation, the detonation velocity, and the detonation pressure of poly-*N,N*-dinitroaminocubanes were calculated by density function theory (DFT) methods [322]. The results showed that all cubane derivatives have positive heats of formation, which increase with increasing number of dinitroamino groups attached to the cube. The detonation performances of polydinitroaminocubanes were estimated by the Kamlet–Jacobs equation, and the results indicated that most cubane derivatives have good detonation performance, better than RDX or HMX.

10.9.3 Experimental Study of Octanitrocubane Thermal Decomposition

Because octanitrocubane is difficult to obtain, there are only few reports on experimental determination of thermal stability and thermodynamic properties. As of 2005, the onset of thermal decomposition of tetranitrocubane was reported as 550 K (277°C), but the onset of thermal decomposition of octanitrocubane was still unknown. In the literature, there are ten times more theoretical than experimental studies on the thermal stability and bond strength of octanitrocubane.

10.9.4 Computations of Octanitrocubane Thermal Decomposition

The explosive properties of octanitrocubane had been predicted by quantum mechanical computational chemistry methods many years before even the precursors in its synthesis had been made. The question is whether the thermal decomposition of octanitrocubane starts with a nitro–nitrite isomerization or with C–C bond rupture yielding a biradical intermediate.

A semi-empirical molecular orbital theory was used to calculate some possible decomposition pathways of nitrocubanes and nitroazacubanes [323]. The calculations indicated that the most likely reaction in cubane, dinitrocubane, tetranitrocubane, hexanitrocubane, and octanitrocubane thermolysis involves an initial opening of a cube C–C bond, followed by an opening of the C–C bond of the seven-bonded intermediate to form a nitrocyclooctatetraene. The reaction is exothermic. Similar reaction pathways were predicted for nitroazacubanes.

The initial pyrolysis process of condensed-phase octanitrocubane at high temperature was investigated using ReaxFF reactive molecular dynamics simulation [324]. The computation showed that it is the C–C bond of the octanitrocubane cage skeleton structure that breaks first, then the octanitrocubane cage skeleton structure is gradually destroyed, and small molecules such as NO_2 and O_2 occur only afterwards. The simulation identified three different damage pathways of the cage skeleton. The main products of octanitrocubane thermal decomposition at high temperature were pre-

dicted to be NO_2 , O_2 , CO_2 , N_2 , NO_3 , NO , CNO , and CO , of which N_2 and CO_2 are the ultimate products. The composition of decomposition products depends on temperature.

Bond dissociation energies and activation barriers for primary decomposition reactions for a series of caged polynitroamino and polynitro compounds, such as octanitrocubane, CL-20, and hexanitro derivatives of adamantane, were predicted using domain-localized pair natural orbital modifications of coupled-cluster techniques [325]. For all species studied, $\text{C}-\text{NO}_2$ or $\text{N}-\text{NO}_2$ radical decomposition channels dominated over molecular scission. The gas-phase enthalpy of formation of octanitrocubane was predicted to be $+704 \pm 6 \text{ kJ/mol}$ ($+168.2 \pm 1.5 \text{ kcal/mol}$).

10.9.5 Explosive Performance of Octanitrocubane

We are mostly interested in octanitrocubane as a propellant ingredient and not as an explosive, so calculations of its detonation parameters are of less interest, but we list them here nevertheless, such as [326]. One theoretical estimation of the detonation velocity for octanitrocubane gave 9900 m/s. This is higher than experimental values for hexanitrobenzene of 9500 m/s or HMX of 9100 m/s or CL-20 with 9200 m/s.

10.9.6 Predicted Propellant Performance of Octanitrocubane

The theoretical performance of a propellant containing octanitrocubane was calculated for sea-level operation under standard conditions ($p_c/p_e = 70:1$) [327]. Replacing ammonium perchlorate with octanitrocubane in an HTPB-bonded propellant increased the specific impulse by 125 N s kg^{-1} . A nitrocellulose/glycerol trinitrate/ONC smokeless composite modified double-base propellant had a specific impulse of 2545 N s kg^{-1} , and a GAP/ONC/RDX smokeless propellant had a specific impulse of over 2600 N s kg^{-1} .

10.9.7 Nitrosocubanes

Nitrosocubanes would have a lower oxygen content than nitrocubanes and may be more difficult to synthesize. Octanitrosocubane should have thermodynamic properties similar to octanitrocubane. Optimized structures, vibrational frequencies, enthalpies of formation, and specific enthalpies of combustion for a series of nitrosocubanes ranging from mononitrosocubane to octanitrosocubane have been predicted by computational chemistry [328].

10.10 Nitroadamantanes

The direct nitration of adamantane with concentrated nitric acid in glacial acetic acid at elevated temperature and pressure produced a mix of 1-nitro-, 1,3-dinitro-, and 1,3,5-

trinitroadamantanes, the last in very low yield [329]. 1-Nitroadamantane and 1,3-dinitroadamantane can be prepared by direct nitration of adamantane with acetic acid and nitric acid in a pressure reactor [330]. 1-Nitroadamantane melts at 431.6–432.1 K (158.5–159 °C) in a sealed capillary. 1,3-Dinitroadamantane melts at 487–488 K (214–215 °C).

The photochemical reaction of N_2O_5 with adamantane yielded only mononitroadamantane.

The oxidation of 1-aminoadamantane with permanganate has been used for the synthesis of 1-nitroadamantane [331, 332]. Another compound prepared during that time was azoadamantane.

It was hoped that 1,3,5,7-tetranitroadamantane, $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_8$, Figure 6, would rival HMX, CL-20, or some of the other caged high-energy compounds in explosive performance and thermal stability. However, despite such optimism, only a few other polynitroadamantanes have been reported since 1980. It appears that there is no significant advantage of adding more nitro groups to the caged structure.

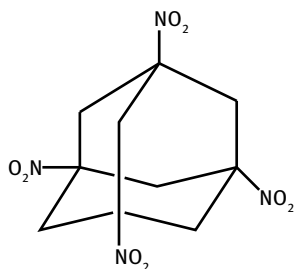


Figure 6: Molecular structure of 1,3,5,7-tetranitroadamantane.

1,3,5,7-Tetranitroadamantane, with its high melting point of ca. 623 K (350 °C, with incipient decomposition), can be of value as a heat-resistant explosive but not necessarily an ingredient for rocket propellants. 1,3,5,7-tetranitroadamantane can be prepared by oxidation of 1,3,5,7-tetraaminoadamantane with permanganate [333, 334], where 1,3,5,7-tetraaminoadamantane was obtained by hydrolysis of 1,3,5,7-tetraacetamidoadamantane as an intermediate. The heat of combustion was 16.5 kJ/g (3.952 kcal/g) compared to 15.7 kJ/g (3.750 kcal/g) for TNT.

A modification of this synthesis route led to some improvements, in particular the yield of 1,3,5,7-tetraacetamidoadamantane could be improved from 51 to 95% [335]. The total yield of 1,3,5,7-tetranitroadamantane from adamantane was raised to 18% compared to 8% reported in the literature.

Nitroadamantanes bearing *gem*-dinitro groups on bridge carbons were synthesized from oximinoadamantanes by reaction with nitric acid, or, alternatively, by reaction with aqueous hypobromite, reduction of the intermediate *gem*-bromonitroadamantanes, and oxidative nitration [336]. The presence of two *gem*-dinitro groups in 2,2,6,6-tetranitroadamantane greatly enhanced the density,

which was now 1.75 g/cm^3 , compared to a related open, uncaged structure, 2,2,6,6-tetranitrobicyclo[3.3.1]nonane, with a density of only 1.45 g/cm^3 .

2,2-Dinitroadamantane and 2,2,6,6-tetranitroadamantane had been synthesized by oxidation of the corresponding oximes which were made from the oxo carbonyl ke-toadamantane. Similar attempts to make 2,2,4,4-tetranitroadamantane failed, apparently due to proximity effects. A different procedure replaced one carbonyl at a time and was more successful [337].

In view of the difficulties associated with the oxidation of vicinal amino groups, an alternate route of synthesis by way of an oxime was chosen for 1,2,2-trinitroadamantane [338].

The heats of formation of a series of polynitroadamantanes were calculated systematically using a density functional theory method without breaking the adamantane skeleton (i.e., choosing adamantane as a reference compound) [339]. The relative stability of these compounds was illustrated according to the results calculated by heat of formation, the energy gaps between the frontier orbitals, and the bond order of C–NO₂.

2,2,4,4-Tetranitroadamantane was synthesized using adamantan-2-one as raw material [340]. First, the synthesis conditions of an important intermediate 4,4-(ethylenedioxy)adamantan-2-one were optimized. The *gem*-nitration of 4,4-(ethylenedioxy)adamantan-2-one oxime was then performed using N₂O₅. The optimum reaction conditions of the reaction were: methylene chloride as solvent, the molar ratio of 4,4-(ethylenedioxy)adamantan-2-one oxime to N₂O₅ was 1:3, reaction temperature 318 K (45 °C), and reaction time 30 min with yields of 52.3%. The overall yield of 2,2,4,4-tetranitroadamantane was 14.2%, which was 1.9-times better than that reported in the literature.

1,3,5,7-Tetranitroadamantane crystallized in a tetragonal crystal shape, space group $P4_21c$, with cell parameters of $a = b = 7.874(2) \text{ \AA}$, $c = 10.552(2) \text{ \AA}$, $V = 654.2(2) \text{ \AA}^3$, $Z = 2$, and $\rho_{\text{XRD}} = 1.605 \text{ g/cm}^3$ [341]. The nitro groups were rotated approximately 15° from a symmetrical eclipsed position. The crystal symmetry was identical to that of the low-temperature form of unsubstituted adamantane. The melting point was 634–636 K, which is very high!

A review of adamantane, polynitroadamantanes, and polynitroazaadamantanes was given in [342]. The CAS RN of hexanitroadamantane is [143850-71-9].

A study of molecular mass/density and oxygen content/sensitivity relationships of polynitroadamantanes and their aliphatic counterparts showed that densities, sensitivities, and detonation properties of polynitroadamantanes obtained/calculated were similar to those of standard high explosives [343]. Some of them might be better than TNT and similar to PETN or RDX. Their non-caged aliphatic counterparts with a similar number of nitro groups and gross formulas may be exceptionally sensitive, which excludes them from possible use as high explosives or propellants.

Crystals of 1-amino-3,5,7-trinitroadamantane, C₁₀H₁₄N₄O₆, crystallize in monoclinic crystals, space group $P2_1/n$, with cell parameters of $a = 14.089 \text{ \AA}$, $b = 13.806 \text{ \AA}$,

$c = 14.414 \text{ \AA}$, $\beta = 118.86^\circ$, $V = 2455 \text{ \AA}^3$, and $Z = 8$, and the X-ray density is $\rho_{\text{XRD}} = 1.55 \text{ g/cm}^3$ [344].

The heats of combustion and enthalpies of vaporization for oxygen-containing, nitro-, and nitrate-derivatives of adamantane were measured by precision calorimetry methods [345]. On the basis of these data, the enthalpies of formation in the standard state and in the gaseous phase were calculated. Table 23 gives a summary of the heats of combustion, heats of formation, and heats of sublimation of adamantane, nitroadamantanes, and adamantyl nitrates.

Table 23: Thermodynamic properties of adamantane, nitroadamantanes, and adamantyl nitrates.

Compound	Heat of combustion kJ/mol	Heat of formation, solid kJ/mol	Heat of sublimation kJ/mol	Heat of formation, gas kJ/mol
Adamantane	6028.3 ± 1.2	193.3 ± 1.2	58.2 ± 1.2	135.1 ± 1.7
Adamantanone	5615.1 ± 1.2	319.7 ± 1.2	76.1 ± 1.5	243.6 ± 1.9
1-Adamantanol	5832.5 ± 2.0	389.1 ± 2.0	82.0 ± 1.5	307.1 ± 2.5
1-Nitroadamantane	5822.0 ± 2.2	256.9 ± 2.0	81.2 ± 2.0	175.7 ± 2.8
1,3-Dinitroadamantane	5622.0 ± 1.2	313.4 ± 1.2	103.8 ± 1.5	209.6 ± 1.9
2,2-Dinitroadamantane	5685.2 ± 2.2	250.6 ± 2.2	89.1 ± 1.5	161.5 ± 2.7
1-Adamantyl nitrate	5773.9 ± 2.0	305.0 ± 2.0	79.9 ± 1.5	225.1 ± 2.5
1,3-Adamantanediyl dinitrate	5522.0 ± 2.0	413.8 ± 2.0	105.9 ± 1.7	307.9 ± 2.6

Data source: [345]

Predicted IR spectra of polynitroadamantanes were obtained by vibrational analysis based on fully optimized molecular geometries and electronic structures and compared to experimental results [346, 347]. Thermodynamic properties were then calculated based on these IR frequencies and the principles of statistic thermodynamics. The dependence of thermodynamic functions on temperature and the number of nitro groups was examined. It was found that the nitro groups obeyed a good group additivity rule. As an example of this method, a fully optimized molecular geometry and electronic structure of 1,3,5,7-tetranitroadamantane supplemented by predicted IR spectra was used to calculate thermodynamic properties by statistic thermodynamics [348]. A potential pyrolysis mechanism was identified via a semi-empirical MO method, providing the transition state and activation energy, and concluding that rupture of the C—NO₂ bond is the first step. Additionally, the predicted detonation velocity and detonation pressure were evaluated by means of the Kamlet–Jacobs equation based on the calculated theoretical density and heat of formation. The synthesis of decanitroadamantane remains an elusive target. Similar calculations were performed for polynitrohexaazaadamantanes [349].

While adamantane can be nitrated directly with nitric acid/acetic acid at high temperature/pressure and with photolyzed N₂O₅, it was predicted by theory that nitration

with NO₂ will encounter a barrier obstacle. Density functional theory and semi-empirical molecular orbital methods were employed to study the reaction mechanism of the nitration of adamantane with NO₂ [350]. The calculated results showed that the H atom in adamantane cannot be directly substituted with NO₂.

The molecular crystal packings of three polynitroadamantanes with 8–10 –NO₂ groups were assigned among the seven most probable space groups using a molecular mechanics computational method [351]. Thereafter, *ab initio* periodic calculations and density of states calculations showed that the C–N bond was the most likely trigger bond of polynitroadamantane thermal decomposition.

Sixteen different polynitroadamantanes were designed by computer and their properties were studied by predicting IR spectra, thermodynamic properties, thermal stability, and detonation performance [352]. It was noted that the frequencies of symmetric stretching vibrations of the nitro group in polynitroadamantanes showed a bathochromic shift with an increasing number of nitro groups. However, the frequencies of asymmetric stretching vibrations had a contrary trend. The heat of formation, detonation velocity, and pressure of 16 polynitroadamantanes were estimated by the Kamlet–Jacobs formula. The predicted thermal stabilities of polynitroadamantanes were studied by the bond dissociation energy and an energy level difference calculation. The number of nitro groups was in direct proportion to improved detonation properties, but was in inverse proportion to the stability of polynitroadamantanes. Among the polynitroadamantanes having the same number of nitro groups, those in which the nitro group linked with a methylene group had better properties than those in which the nitro group linked with a methyldiyne group.

2,2-Dinitroadamantane and 2,2,4,4,8,8-hexanitroadamantane were analyzed by HPLC using acetonitrile/water (80/20 volume ratio) as a mobile phase, which allowed exceptionally good separation on these two analytes when the flow rate was 1.0 mL/min [353]. Results showed that the detection limit, linear range, linear correlation coefficient, and precision of 2,2-dinitroadamantane are 0.003 mg/mL, 0.005–1.000 mg/mL, 0.9987, and 1.382%, respectively. Correspondingly, the same parameters for 2,2,4,4,8,8-hexanitroadamantane were 0.001 mg/mL, 0.005–1.000 mg/mL, 0.9984, and 1.300%, respectively.

10.11 Nitrofullerenes

Is it possible to make nitro-buckminsterfullerene C₆₀ with 1 to 60 nitro groups? Apparently some nitrofullerenes have been reported, but it is unlikely that there will ever be sufficient material available to use it as a rocket propellant [354–357]. The all-hydrocarbon caged skeleton analog to CL-20, decorated with nitro groups, would still be a very energetic molecule, even without the nitramine linkages.

Prolonged treatment of C_{60} in benzene with very high concentrations of N_2O_4 formed a new polynitro [62]fullerene whose composition was determined as $C_{60}(NO_2)_{14}$ by TGA [358]. The compound was unstable and deflagrated above 443 K (170 °C) when heated under nitrogen or in air with the release of a considerable amount of heat as observed by DTA and DSC. The decomposition steps of $C_{60}(NO_2)_{14}$ were followed by TGA coupled with FTIR. At the deflagration point, $C_{60}(NO_2)_{14}$ released a mixture of nitrogen oxides: NO_2 and NO with minor amounts of N_2O . The deflagration left a residue of oxidized carbon which upon heating released CO_2 and CO and at 973 K (700 °C) was converted to a carbonaceous matter free from residual oxygenated groups, showing also the presence of small amounts of C_{60} fullerene.

11 Nitroalkanols

Up until this section of the chapter on “Nitroaliphatic Compounds” we have summarized information on aliphatic nitro compounds that did not contain any other substituents on the carbon skeleton other than nitro groups. In the following there are several sections where the aliphatic compound contains other substituents such as hydroxy, oxo, amino, nitramino, azido, azo, and other substituent groups attached to the alkyl skeleton. The question was whether these compounds should be discussed here under nitro compounds or in the chapters “Alcohols,” “Aliphatic Amines,” and “Nitramines”. At the moment, we have done both, which results in some duplication and overlap of different sections.

11.1 2-Nitroethanol

The lowest member in the family of nitroalkanols, nitromethanol, O_2NCH_2OH , is not stable. 2-Nitroethanol, $O_2NCH_2CH_2OH$, is somewhat more stable but still hazardous. 2-Nitroethanol freezes at 193 K (−80 °C) and boils at 467 K (194 °C) at sea level pressure or at 375–378 K (102–105 °C) at 14 mm Hg. The density of 2-nitroethanol is 1.270 g/cm³. The heat of combustion of 2-nitroethanol at constant volume is 1154 kJ/mol = 275.8 kcal/mol [359, 360]. The CAS RN of 2-nitroethanol is [625-48-9]. 2-Nitroethanol can be prepared by condensation of nitromethane and formaldehyde [361].

The synthesis of 2-nitroethanol was used as an example for continuous flow synthesis in a microreactor [362]. Flow synthesis has the advantage that only a small amount of reactants are at the high temperature and the reaction mixture is quickly chilled after it leaves the reaction zone.

2-Nitroethanol has been patented as a monopropellant, as a separate co-injected monopropellant or an intimate mixture with hydrazine [363].

Certain nitroalkanols where the nitro group is attached to a secondary or tertiary carbon atom are used as disinfectants and bactericides because they act as formalde-

hyde donors. Some nitroalkanols such as glycerol dinitrate are the result of incomplete nitration of polyols. Other nitroalkanols are useful intermediates in the synthesis of other energetic compounds.

11.2 2,2,2-Trinitroethanol

The most useful compound in this group is 2,2,2-trinitroethanol, $C_2H_3N_3O_7$, $(O_2N)_3CCH_2OH$, $M = 181.07$ g/mol, because it is an intermediate in the synthesis of a large number of energetic compounds with 2,2,2-trinitroethyl groups which have very desirable properties. One example are the esters of 2,2,2-trinitroethanol with acrylic acid or methyl acrylic acid, which can be polymerized to form energetic binders. Trinitroethanol can be reacted with different moieties through the Mannich reaction, such as ammonia, aliphatic amines, hydrazine, and even urea as the amine component in order to synthesize the corresponding trinitroethyl derivatives. Examples include 3-(*N*-2,2,2-trinitroethyl)amino-1,2,4-triazole, 4-(*N*-2,2,2-trinitroethyl)amino-1,2,4-triazole, 4-(*N*-Nitro-*N*-(2,2,2-trinitroethyl))amino-1,2,4-triazole, and bis(2,2,2-trinitroethyl) amine [364]. Physical, explosive performance, and sensitivity properties of ten 2,2,2-trinitroethyl derivatives, mostly those with triazole rings, were compared to those of TNT, RDX, and HMX.

2,2,2-Trinitroethanol can easily be synthesized by reaction of nitroform with paraformaldehyde [365]. The method was later improved. For preparation of 2,2,2-trinitroethanol with carbon tetrachloride as a solvent, the mixture of trinitromethane and paraformaldehyde, a turbid solution/suspension, was heated with stirring for 3 h at 333–338 K (60–65 °C) and then at reflux for 30 min [366, 367]. Concentrating the solution and cooling in the refrigerator gave trinitroethanol in the form of long needles with m.p. 345 K = 72 °C. The overall yield was 80%. This melting point is lower than the melting point reported by other sources and must be due to an impure product. Trinitroethyl alcohol is an unstable, crystalline compound. Its thermal initiation temperature is about 393 K (120 °C). It can be distilled (with precautions) and boils at 376 K = 103 °C at 14 mm Hg. 2,2,2-Trinitroethanol is a relatively strong acid, $K_a = 4.3 \times 10^{-3}$. The high acidity can be explained by the strong electron drawing force exerted by the three nitro groups. See also [368]. Trinitroethanol at 200 K forms orthorhombic crystals, space group $P2_1/c$ (no.14) with $a = 6.1218(4)$ Å, $b = 18.8120(12)$ Å, $c = 11.7391(8)$ Å, $\alpha = 90^\circ$, $\beta = 104.997(4)^\circ$, $\gamma = 90^\circ$, $V = 1305.87(15)$ Å³, $Z = 8$, and $\rho = 1.842$ g/cm³.

Similar results were obtained in a more recent investigation which showed that 2,2,2-trinitroethanol crystallized in monoclinic crystals with space group $P2_1/c$, with cell parameters of $a = 6.1242(4)$ Å, $b = 18.8223(7)$ Å, $c = 11.7446(4)$ Å, $\beta = 104.962(3)^\circ$, $V = 1308.14(11)$ Å³, $Z = 8$, $\rho = 1.839$ g/cm³ [369]. The structure displayed intra-molecular O—H···O hydrogen bonds as well as inter-molecular O—H···O and C—H···O hydrogen

bonding; the O—H...O hydrogen bonds, forming rings and dipolar nitro–nitro interactions, account for the high density of 1.839 g/cm³.

Physicochemical properties of β -nitro alcohols and some of their derivatives are listed in Table 24.

Table 24: Physicochemical properties of β -nitro alcohols and their derivatives.

Compound	Boiling point (at P, Pa)	Boiling point (at P, mm Hg)	Melting point		Refractive index n_D^{20}	Density ρ_4^{20} g/cm ³
	K	°C	K	°C		
2-Nitroethanol	336 (66)	63 (0.5)	—	—	1.443	1.296
2,2,2-Trinitroethanol	355 (266)	82 (2)	345	72	—	—
2-Nitropropanol	372 (1329)	99 (10)	—	—	1.4379	1.1841
2-Nitropropanediol-1,3	430–431 (1329)	157–158 (10)	331–332	58–59	—	—
2,2-Dinitropropanediol	—	—	415	142	—	—
Acetate of 2-nitroethanol	391–392	118–119	—	—	—	1.2132
Acetate of 2,2,2- trinitroethanol	391 (531)	118 (4)	—	—	1.4479	1.474
Nitrate of 2-nitropropanol-1	344 (266)	71 (2)	—	—	1.447	1.348

Data source: [370]

Other polynitroalkanols and polynitroalkanediols of interest as plasticizers or intermediates for the synthesis of energetic plasticizers include 2,2-dinitro-1,3-propanediol [371], 3,3-dinitropentane-1,5-diol, and 4,4-dinitroheptane-1,7-diol [372].

Other energetic derivatives of trinitroethanol include tris(2,2,2-trinitroethyl)borate, B[OCH₂C(NO₂)₃]₃ with a density of 1.524 g/cm³; tetrakis(2,2,2-trinitroethyl)orthocarbonate, C[O—CH₂—C(NO₂)₃]₄ with a density of 1.84 g/cm³ and a decomposition temperature of 436 K (163 °C), TNEOC; 2,2,2-trinitroethyl carbamate, (O₂N)₃CCH₂O—CO—NH₂, TNC with a density of 1.839 g/cm³; bis(2,2,2-trinitroethyl) oxalate, (O₂N)₃CCH₂O—CO—CO—O—CH₂—C(NO₂)₃, BTNEO, with a density of 1.884 g/cm³; and 2,2,2-trinitroethyl nitrocarbamate, (O₂N)₃CCH₂O—CO—NH—NO₂, TNC-NO₂ [373–375].

Infrared absorption spectra of β -nitroalcohols in solution showed predominantly monomeric hydroxyl —OH absorption and single nitro —NO₂ stretching bands, indicative of non-bonded species, but some bonding due to inter-molecular hydrogen bonds probably occurs in the solid state [376].

2,2-Dinitro-1-methoxypropane was used as a model compound whose structure resembled that of more complex nitro plasticizer components [377]. A decomposition

mechanism was proposed for 2,2-dinitro-1-methoxypropane based on existing decomposition mechanisms for similar nitro compounds. The proposed decomposition mechanism began with HONO elimination and leads to intermediates that can produce CO, CO₂, NO, and N₂O gases. A high-temperature mechanism involved NO₂ scission.

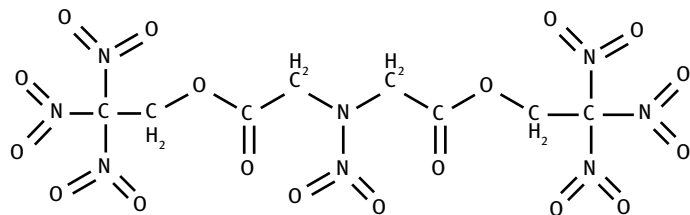
2,2,2-Trinitroethanol, 2,2-dinitropropanol, and 2,2-dinitropropanediol-1,3 underwent enantiotropic transitions at 312.4, 282.2, and 341.1 K (39.3, 9.1, and 68.0 °C), respectively. All of the high-temperature forms were cubic and possessed properties of the plastic crystalline state. DSC was used to measure the heats of fusion and the heats of transition. The heats of transition were 2,2,2-trinitroethanol: 18.0 kJ/mol = 4.3 kcal/mol; 2,2-dinitropropanol: 15.1 kJ/mol = 3.6 kcal/mol; and 2,2-dinitropropanediol-1,3: 21.3 kJ/mol = 5.1 kcal/mol [378]. The difference between the heat of transition of each nitroalkanol and its corresponding nitroalkane has been interpreted as a measure of hydrogen bonding energy in the low-temperature form of the nitroalkanol.

In addition to 2,2,2-trinitroethanol with three terminal nitro groups, its homologue 3,3,3-trinitropropanol has also been considered as a building block for energetic materials. Compared with the well-established 2,2,2-trinitroethyl group in the chemistry of energetic materials, the 3,3,3-trinitropropyl group is less investigated regarding its chemical and energetic properties. Investigations on the syntheses of several compounds containing the 3,3,3-trinitropropyl group were performed and their properties compared with the 2,2,2-trinitroethyl group [379]. All materials were characterized by DSC, single-crystal XRD, and the sensitivities towards impact, friction, and electrostatic discharge were tested using a drop hammer, a friction tester, and an ESD tester.

Other nitroalkanols once evaluated as propellant ingredients are 1,1,1-trinitro-3-hydroxybutanol, C₄H₇N₃O₈, (O₂N)₃CCHOHCH₂CH₂OH, *M* = 225.11 g/mol, with an enthalpy of formation of -373 cal/g = -83.97 kcal/mol and 1,1,1-trinitro-2-hydroxybutanol, C₄H₇N₃O₈, (O₂N)₃CCH₂CHOHCH₂OH, with an enthalpy of formation of -373 cal/g = -83.97 kcal/mol [97]. These would most likely be esterized with acrylic acid to serve as energetic binders. The heat of combustion at constant volume of tris(hydroxymethyl)nitromethane is 2125 kJ/mol = 507.8 kcal/mol [359].

The mono-trinitroethyl esters of nitramino glycine have a tendency to form dimers [380]. Some of these compounds have a positive oxygen balance and are potentially suitable as rocket propellants.

The di-ester of trinitroethanol with nitraminodiacetic acid, 2-[carboxymethyl (nitro)amino]acetic acid, 2,2'-(nitroimino)diacetic acid, C₄H₆N₂O₆, is a high-energy compound suitable as a rocket propellant ingredient [381]. It has an X-ray density of 1.84 g/cm³ at 155 K (-118 °C) and a decomposition point of 453 K (180 °C).



Nitraminodiacetic acid bis(2,2,2-trinitroethyl) ester

11.3 Fluorodinitro Alcohols

The molecular mass of 2-fluoro-2,2-dinitroethanol, $\text{F}(\text{NO}_2)_2\text{CCH}_2\text{OH}$, $\text{C}_2\text{H}_3\text{O}_5\text{N}_2\text{F}_1$, is 154.05 g/mol. The enthalpy of formation is $-741 \text{ cal/g} = -114 \text{ kcal/mol} = -478 \text{ kJ/mol}$ [97]. Fluorodinitroalkanols can be prepared by three different methods: **(1)** fluorination of 1,1-dinitrocarbanion salts with perchloryl fluoride, **(2)** aqueous fluorination of 1,1-dinitrocarbanion salts, **(3)** reactions of fluorotrinitromethane with various nucleophiles. The reaction of 30% H_2O_2 , formaldehyde, methanol, and fluorotrinitromethane gives 2-fluoro-2,2-dinitroethanol [382].

Another method for preparation of 2-fluoro-2,2-dinitroethanol is the reaction of potassium hydroxide in water and methanol to which 2,2-dinitropropanediol-1,3 in methanol was added dropwise, the temperature being kept below $285 \text{ K} = 12^\circ\text{C}$ [383]. The precipitated potassium 2,2-dinitroethanol was separated from solvent and washed twice with methanol and once with ether. To the residue after evaporating the ether, dimethylformamide was then added, the mixture cooled to $288 \text{ K} = 15^\circ\text{C}$, and perchloryl fluoride bubbled in at this temperature. The mixture was acidified with sulfuric acid and the dimethylformamide removed under vacuum. The product was extracted with ether, the ether removed, and the residue distilled in vacuum where it boiled at $328\text{--}330 \text{ K} = 55\text{--}57^\circ\text{C}$ at 1.7 mm Hg. The yield of 2-fluoro-2,2-dinitroethanol thus obtained was 25% of the theoretical yield. The product was colorless, had a slightly nitrous odor, and froze at $282\text{--}283 \text{ K} = 9\text{--}10^\circ\text{C}$. The utility of this compound was demonstrated by preparing several esters with orthocarbonic acid and nitrocarbonic acids.

The direct aqueous fluorination of potassium dinitroethanolate gave fluoro-dinitroethanol, which was further characterized as the formal [384]. Fluorination of nitroform under these conditions gave fluorotrinitromethane. The reaction of sulfur tetrafluoride with 2,2-dinitropropanol, 2,2-dinitro-1,3-propanediol, and trinitroethanol gave 1-fluoro-2,2-dinitropropane, 1,3-difluoro-2,2-dinitropropane, and 2,2,2-trinitrofluoroethane, respectively. The reaction of tetrafluorohydrazine with the sodium salts of 1,1-dinitroethane and 1,1-dinitrobutane gave the dinitrodifluoroalkanes. The product of the former was very sensitive to impact.

Similar to 2,2,2-trinitroethanol, 2-fluoro-2,2-dinitroethanol can be used for the synthesis of a wide range of energetic compounds [385–387]. 2-Fluoro-2,2-dinitroethanol is a useful intermediate for the synthesis of fluorodinitroethyl amines and esters [388]. See also [389].

12 Fluorodinitroalkyl Amines

Fluorodinitroalkyl amines will be discussed in detail in *Encyclopedia of Liquid Fuels* chapter “Aliphatic Amines.” They can be prepared from fluorodinitroethanol or fluordinitromethane. The enthalpy of formation of bis(2-fluoro-2,2-dinitroethyl)amine (BFDNA) is -531 kJ/mol ($-126.952 \text{ kcal/mol}$) [390].

13 Higher Mono- and Polynitroethers

It was the objective of several decades' worth of synthetic efforts to synthesize oxygen-rich compounds containing several nitro and/or nitroxy groups as replacements for glycerin trinitrate as a plasticizer in double-base propellants. Such replacements had to be thermally more stable, less volatile than glycerin trinitrate, and have a better oxygen balance. The oxygen balance of polynitro alkane compounds can be improved by introducing oxygen links (ether groups) into the molecule and/or replacing some of the hydrogen by fluoro groups.

Two ether linkages can be introduced into a molecule by reacting polynitroalkans with formaldehyde or acetaldehyde, forming formals and acetals.

13.1 Polynitroalkyl Ethers

2-Nitroethyl ethyl ether, $\text{O}_2\text{NCH}_2\text{CH}_2\text{OC}_2\text{H}_5$, is a colorless liquid having a sharp odor and a boiling point of 451 K (178°C) at sea level pressure or $345 \text{ K} = 72^\circ\text{C}$ at 12 mm Hg reduced pressure. The density is 1.079 g/cm^3 at $298 \text{ K} = 25^\circ\text{C}$ and the refractive index is $n_D^{25} = 1.4160$. 2-Nitroethyl ethyl ether can be prepared by reaction of 1,2-dinitroethane or 2-nitroethyl nitrate with ethanol in refluxing ethanol where the top of the condenser is kept warm enough that all low-boiling ethyl nitrite is removed soon after it has formed [391].

2,2-Dinitroethyl ethyl ether, $(\text{O}_2\text{N})_2\text{HCH}_2\text{C}-\text{O}-\text{C}_2\text{H}_5$, is a colorless oil with a boiling point of 373 K (100°) at 11 mm Hg reduced pressure, which can be prepared by reacting trinitroethane with potassium ethoxide.

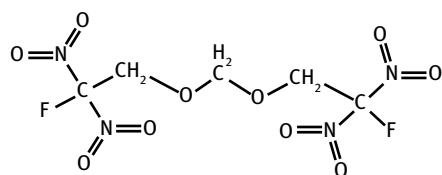
Attempts to synthesize trinitromethyl methyl ether or trimethylsilyl trinitromethyl ether or trinitromethyl *tert*-butyl ether were not successful [392].

Bis(2,2,2-trinitroethyl)formal, also known as $[(\text{NO}_2)_3\text{CCH}_2\text{O}]_2\text{CH}_2$, TEFO, can be used as plasticizer [393]. The onset of thermal decomposition of trinitromethyl or trinitroethyl ethers depends on the molecule they are attached to. A study of rapidly heated thermal decomposition of $[(\text{NO}_2)_3\text{CCH}_2\text{O}]_x\text{CH}_4-x$, $x = 2-4$ (TEFO, TNEOF, TNEOC, respectively) by rapid-scan FTIR spectroscopy with temperature profiling as a function of pressure showed that they melted 40 °C or more below the decomposition point when rapidly heated (70–200 °C/s) [394]. The first detected thermolysis step was homolysis of a few C–NO₂ bonds per molecule liberating NO₂(G). The temperature at which this occurred at 15 psi Ar was TEFO (145 °C) TNEOF (180 °C) TNEOC (200 °C).

Nitromethyl nitroxymethyl ether, nitromethoxy methanol nitrate, O₂NO–CH₂–O–CH₂–NO₂, is a colorless oily liquid with a density of 1.50 g/cm³, a boiling point of 321 K at 2 kPa (48 °C at 15 mm Hg), and which is an energetic explosive. Its shock sensitivity and thermal stability are worse than that of ethylene glycol dinitrate (EGDN) and it is also more volatile. The lead block indentation of nitromethyl nitroxymethyl ether is 420 cm³ which is 93% of that of GTN. The synthesis of nitromethyl nitroxymethyl ether starts with formaldehyde and hydrogen chloride to prepare bis-chloromethyl ether which is then nitrated with mixed acid.

13.2 Bis(2-fluoro-2,2-Dinitroethyl) Formal (FEFO)

There may be some overlap in the information provided in this book on difluoroamino compounds and nitro compounds. If one requires a complete evaluation of those mixed substituent energetic compounds, one will need to read both sections. The group of energetic polynitroethers includes bis(2-fluoro-2,2-dinitroethyl) formal (FEFO) and 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2,2-bis(difluoroamino) propane (SYEP).



FEFO

Both FEFO and SYEP are energetic plasticizers that are used in formulating solid propellants and plastic-bonded explosives. The most thoroughly investigated fluoro-dinitroalkyl formal is bis(2-fluoro-2,2-dinitroethyl)formal, also known as bis(2-fluoro-2,2-dinitroethoxy)methane, 1,1'-[methylenebis(oxy)]bis(2-fluoro-2,2-dinitroethane), $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{F}$, $\text{C}_5\text{H}_6\text{N}_4\text{O}_{10}\text{F}_2$, FEFO, CAS RN [17003-79-1].

FEFO has a high energy content but is quite volatile and toxic and has a relatively high melting point. FEFO has an oxygen balance of +14.88% assuming combustion to CO and -9.99% assuming combustion to CO₂. Its drop-weight impact sensitivity is $H_{50} = 26$ to 28 cm (2 kg weight) compared to 15 cm for glycerin trinitrate. FEFO is hydrolytically unstable.

Both bis(2-fluoro-2,2-dinitroethyl) formal (FEFO) and bis(2,2-dinitropropyl) formal (BDNPF) are used as energetic plasticizers in explosive and propellant compositions.

13.2.1 Preparation of FEFO

An efficient three-step process to prepare FEFO was developed and scaled up to production plant equipment in 100–1000 gallon reactors [395]. Starting with the elemental fluorination of nitroform, high yields and purities of the process intermediates and final product were realized.

The purity of FEFO can be verified by gas chromatography [396]. Gas chromatographic analysis can detect small concentrations of FEFO [397]. Purity requirements and methods of analysis of FEFO are covered by Military Specification MIL-SPEC RM-253202.

13.2.2 Physical Properties of FEFO

FEFO is a liquid explosive with a density of 1.60 g/cm³. The heat of formation of FEFO is -690 kJ/mol = -165 kcal/mol. The properties of FEFO are listed in Table 25.

Table 25: Properties of FEFO.

Property	SI units	Other units	Source
Molecular mass	320.12 g/mol	3.124 mol/kg	
Density at 293 K	1.59 g/cm ³	—	Rocketdyne data sheet
Density at 293 K	1.607 g/cm ³	—	[398]
Melting point	287 K	14 °C	Rocketdyne data sheet
Melting point	284.5–286.1 K	11.3–12.9 °C	[398]
Boiling point	393–397 K at 40 Pa	120–124 °C at 0.3 mm Hg	[398]
Vapor pressure	28.5 mPa at 298 K	0.000214 mm Hg at 25 °C	[398]
Compressibility	4.03 mm ² /N	4.04 × 10 ⁻¹¹ cm ² /dyn	[399]
Velocity of sound	1.25 km/s	—	[399]
Heat of formation ΔH_f^{298}	-745 kJ/mol	-178 kcal/mol	[398]
Heat of formation ΔH_f^{298}	-746 kJ/mol	-557 cal/g = -178 kcal/mol	[97]
Heat capacity	1.05 J g ⁻¹ K ⁻¹ at 200 K	0.25 cal g ⁻¹ °C ⁻¹ at -73 °C	[398]

13.2.3 Reactions of FEFO

Compatibility between FEFO and a number of organic and metallic materials has been evaluated at 295 and 347 K (22 and 74 °C) for up to 8 months [400, 401]. The 300 series stainless steels, Al 6061-T6, and Monel 400 showed evidence of surface attack (oxidation or pitting). Polished gold coupons became discolored. Platinum, iridium, titanium, tantalum, and Ta-10% W showed little evidence of reaction. Kalrez, fluorinated ethylene propylene (FEP), and perfluoroalkoxy alkane polymer (PFA) were compatible. Among the organic materials, the perfluorinated materials showed only slight interaction with the FEFO while polyethylene, polyester, and Aclar[®] were attacked by the liquid. These interactions manifested themselves in changes in color, net weight gain, and mechanical properties. The changes were aggravated by higher temperatures.

13.2.3.1 Thermal Decomposition of FEFO

The thermal decomposition of three energetic plasticizers containing the formal group, FEFO, TEFO, and DITEFO have been studied by rapid-scan IR spectroscopy [402]. The five *gem*-trinitro compounds studied to that date all displayed a transition from decomposition to deflagration according to the gas products evolved during the first second of rapid thermolysis. FEFO was the first compound without a *gem*-trinitro group to exhibit this transition in the same experiment. Under directly comparable conditions, fluoro dinitro compounds were confirmed to be more thermally stable than the analogous *gem*-trinitro compounds.

In the DSC at a heating rate of 10 °C/min., the first onset of exotherm was at 482 K (209 °C) and it peaked at 518 K (245 °C). The theoretical considerations which led to the initial synthesis of compounds containing the $\text{FC}(\text{NO}_2)_2$ group indicated that the enhanced sensitivity and thermal stability properties of 1-fluoro-1,1-dinitro compounds relative to corresponding 1,1,1-trinitro compounds are primarily due to reduced steric hindrance, which allows free rotation of the nitro groups about the C—NO₂ bonds, such free rotation acting in effect as an internal energy sink [403]. When steric hindrance to free rotation is reintroduced, as when the $\text{FC}(\text{NO}_2)_2$ group is α or β to another *gem*-dinitro function or β to an aromatic ring, the sensitivity and thermal stability properties become relatively poor.

The simultaneous TGA-modulated beam mass spectrometry (STMBMS) technique has been applied to measure the vapor pressures and evaluate the thermal decomposition chemistry of two energetic plasticizers, bis(2-fluoro-2,2-dinitroethyl)formal (FEFO) and bis(2-fluoro-2,2-dinitroethyl)difluoroformal (DFF) [404]. The resulting heat of vaporization (ΔH_{vap}) and vapor pressure at 298 K (25 °C) were 84.9 ± 0.8 kJ/mol (20.3 ± 0.2 kcal/mol) and 0.05 Pa (0.4 ± 0.1 $\mu\text{m Hg}$) for FEFO, and 72.4 ± 0.8 kJ/mol (17.3 ± 0.2 kcal/mol) and 0.068 Pa (5.1 ± 1.1 m Hg) for DFF. The thermal decomposition of FEFO indicated that there are six major pyrolysis pathways where FEFO initially decomposed at 423 K (150 °C) by rearrangement of the nitro group to the nitrite group,

followed by loss of NO. Some NO₂ was also formed at 443 K (170 °C). Between 473 and 573 K (200–300 °C), further pyrolysis occurred. In one pathway, the FEFO backbone remained intact and a high-molecular-weight product was formed. The other three pathways involved scission of the FEFO backbone, one yielding CO₂ (possibly N₂O), one yielding CH₂O and CO, and one yielding C₃H₂NOF.

13.2.4 Toxicity of FEFO

Experience gained by 13 known users of FEFO was documented in interview transcripts with several appendices [405]. The first of these, Appendix A, was a survey on worker experiences with FEFO. Appendix B was a toxicology screening study of FEFO. Appendix C was a material safety datasheet on FEFO. Appendices D and E were formerly classified documents. Appendix F was a file on medical treatment associated with FEFO exposure. FEFO was shown to be quite biologically active by all observers. It was also stated that by correct use of strict industrial hygiene controls it can be used in large amounts with relative safety.

13.2.5 Explosive Sensitivity of FEFO

A series of detonation experiments was carried out on FEFO to determine the non-reactive equation of state and initiation sensitivity to one-dimensional shock loading [406]. The material was found to be extremely insensitive, requiring a shock pressure of approximately 13.0 GPa to initiate it. Pressure records indicated that the build-up to detonation may occur within the FEFO and not at the impactor–sample interface as is often assumed. In addition, it was found that the compression vs. detonation induction time behavior between FEFO and three nitroalkanes were approximately the same, although the shock pressure thresholds were quite different.

The shock initiation of FEFO was studied using a two-stage gas gun with magnetic gauges to measure the compression wave profiles during a shock-to-detonation transition [407]. Unreacted Hugoniot data, time-to-detonation (overtake) measurements, and reactive wave profiles were obtained from each experiment. FEFO was found to initiate by the homogeneous initiation model, similar to other liquid explosives (nitromethane, isopropyl nitrate). FEFO is very insensitive, with about the same shock sensitivity as the TATB-based explosive PBX9502 and cast TNT.

It was hoped that replacement of some of the hydrogen in polynitroalkanes would reduce the sensitivity of the compounds. Therefore, the impact sensitivities of several compounds with and without hydrogen substitution by fluorine were compared. The desensitization of explosive compounds has been studied by the synthesis and testing of analogs of selected molecular structures in which part of the hydrogen was replaced by fluorine. The objectives were to demonstrate whether or not “chemical desensitization” could be achieved with fluorine in specific positions and groupings, to infer from the results how the fluorine affected the initiation process and to permit the de-

sign and synthesis of high-energy and relatively insensitive compounds [408]. Methods of synthesis and physical properties of several dozen nitro-fluoro compounds were described in this report. Desensitization of the ether, bis(fluorodinitroethoxy)ethane, was obtained by substituting the four hydrogens with fluorine; and results from impact and shock initiation tests showed that the fluorine analog was definitely less sensitive and was as energetic as the hydrogen compound. In the card gap test, the positive initiation of FEFO to high velocity detonation (HVD) occurred at 80–85 cards, and even with a very thick spacer of 1500 cards the material would still explode in LVD mode (100 cards corresponds to approximately 1 inch). The impact sensitivity of FEFO in a Technoproducts Dropweight Tester was 6 kg-cm. For comparison, the impact sensitivity of ethyl nitrate was 1–2 kg-cm. In the Bureau of Mines test apparatus with a no. 12 tool, the impact sensitivity (50% point) of FEFO was 28 cm with a 5-kg weight.

In a U-tube adiabatic compression sensitivity test apparatus with variable, preselected push pressure and constant bubble size, the push pressure required to explode FEFO was higher than that of GTN, EGDN, or DEGDN, but below that of *N,N*-bis(β -nitroxyethyl)nitramine (DINA) or 2-nitroxyethyl *n*-butyl nitramine (BuNENA) [409].

13.2.6 Explosive Performance of FEFO

The heat of detonation and the products of detonation of FEFO were compared to those of HMX and TNT [410, 411]. The heats of detonation determined in a calorimeter ranged from 4581 to 6192 J/g (1095 to 1480 cal/g).

The detonation velocity of FEFO is 7861 m/s [399]. The critical diameter for propagation of detonation is in the order of millimeters.

13.2.7 FEFO Mixtures

Bis-(2-fluoro-2,2-dinitroethoxy)-(1-fluoro-1,1-dinitro-2-propoxy)methane, also known as M-FDNEOF, $(\text{O}_2\text{N})_2\text{CFCH}(\text{CH}_3)\text{OCH}[\text{OCH}_2\text{CF}(\text{NO}_2)_2]_2$, is a plasticizer that can be used in combination with FEFO [412]. M-FDNEOF is a low melting solid (m.p. 320–322 K = 47–49 °C) with a calculated liquid density at 298 K = 25 °C of 1.60 g/cm³. Its heat of formation was estimated to be –1314 kJ/mol = –314 kcal/mol. M-FDNEOF is almost equal to FEFO in energy content (calculated detonation pressure, 243 kbar vs. 248 kbar for FEFO). Therefore, the addition of M-FDNEOF to FEFO does not significantly change the energy content of the system. M-FDNEOF is miscible with FEFO in all proportions, and forms a binary eutectic with FEFO in the approximate weight ratio of FEFO:M-FDNEOF = 70:30, m.p. 278 K = +5 °C. Thus, the addition of M-FDNEOF, particularly in this amount, to FEFO results in a significant decrease of the plasticizer melting point. This will impart improved low-temperature properties to propellants or plastic-bonded explosives using the plasticizer mixture in place of FEFO alone.

13.3 Other 2-Fluoro-2,2-Dinitroethyl Ethers and Formals

2,2-Dinitropropyl-2-fluoro-2,2-dinitroethyl formal can be prepared by the following steps: (1) reacting one mol of formaldehyde with two mols of 2,2-dinitropropanol in the presence of an excess of aluminum chloride to produce chloromethyl 2,2-dinitropropyl ether; (2) isolating the product chloromethyl 2,2-dinitropropyl ether; (3) reacting one mol of 2-fluoro-2,2-dinitroethanol with chloromethyl 2,2-dinitropropyl ether in the presence of titanium tetrachloride to produce 2,2-dinitropropyl 2-fluoro-2,2-dinitroethyl formal; and (4) isolating the product 2,2-dinitropropyl 2-fluoro-2,2-dinitroethyl formal [413].

Another compound taking advantage of the fluorodinitromethyl energetic pendant is bis(2-fluoro-2,2-dinitroethoxy)acetonitrile, $\text{N}\equiv\text{C}-\text{CH}[\text{OCH}_2\text{CF}(\text{NO}_2)_2]_2$, CYANO-FEFO [414]. The use of bis(2-fluoro-2,2-dinitroethoxy)acetonitrile as a co-plasticizer for bis(2-fluoro-2,2-dinitroethyl)formal (FEFO) provides several advantages over the use of FEFO by itself. CYANO-FEFO is useful as a co-plasticizer with bis(2-fluoro-2,2-dinitroethyl)formal in energetic plasticizer mixtures for plastic-bonded explosives. CYANO-FEFO is a low melting solid (m.p. 314–315 K = 41–42 °C) with a liquid density at 296 K = 23 °C of 1.62 g/cm³. Its heat of formation was estimated to be -732 kJ/mol = -175 kcal/mol, and the calculated detonation pressure was 244 kbar.

Bis(2-fluoro-2,2-dinitroethyl) ether can be prepared by reacting a stable intermediate bis(2,2-dinitro-3-hydroxypropyl) ether with a fluorinating agent in the presence of a base [415]. In order to prepare bis(2-fluoro-2,2-dinitroethyl) ether, the intermediate bis(2,2-dinitro-3-hydroxypropyl) ether in a solvent in the presence of a base is contacted with the fluorinating agent (elemental fluorine diluted with nitrogen in a ratio of between 0.5:1.5 to 1.5:0.5 or gaseous perchloryl fluoride) at 0–5 °C until slightly acidic and the original yellow color begins to disappear.

Polynitroethyl ethers can be prepared by nitration of the corresponding oximes. Nitroethers prepared in this way which are of potential interest as propellant ingredients are 2-fluoro-2,2-dinitroethyl-2,2-dinitroethyl ether, bis(2-fluoro-2,2-dinitroethyl) ether, (2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropyl formal, and 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropane [416]. It is not clear whether any of these have advantages over the established energetic plasticizers like BDNPA/F.

13.4 Other Trinitroethyl Ethers and Formals

2,2,2-Trinitroethyl 2-nitroxyethyl ether, $(\text{O}_2\text{N})_3\text{CCH}_2\text{OCH}_2\text{CH}_2\text{ONO}_2$, TNEN, can be prepared by the following reaction sequence: **(1)** reacting one mol of potassium nitroform with one mol of chloromethyl 2-bromoethyl ether to produce the intermediate 2,2,2-trinitroethyl 2-bromoethyl ether; **(2)** reacting the 2,2,2-trinitroethyl 2-bromoethyl ether with silver nitrate to form 2,2,2-trinitroethyl 2-nitroxyethyl ether [417]. The energy

content of TNEN is between that of glycerin trinitrate (GTN) and butanetriol trinitrate (BTTN). The melting point of TNEN is lower than that of nitroglycerin (284 K = 11 °C vs. 287 K = 14 °C) and TNEN is less volatile and thus less toxic than nitroglycerin. The TNEN density is 1.55 g/cm³. 2,2,2-Trinitroethyl 2-nitroxyethyl ether is useful as an energetic plasticizer.

14 Nitroalkyl Esters

2,2,2-Trinitroethanol is an intermediate in the synthesis of a large number of energetic compounds with 2,2,2-trinitroethyl groups which have very desirable properties. One example is the esters of 2,2,2-trinitroethanol with acrylic acid or methyl acrylic acid which can be polymerized to form energetic binders.

Another ester, 2,2-dinitro-1,3-propanediol-diformate, $\text{HOOCCH}_2\text{—C(NO}_2)_2\text{—CH}_2\text{COOH}$, is a low-sensitivity, energetic plasticizer that is useful in explosive and propellant compositions. 2,2-Dinitro-1,3-propanediol diformate can be synthesized by the esterification of 2,2-dinitro-1,3-propanediol [418]. 2,2-Dinitro-1,3-propanediol-diformate can be made by reacting 2,2-dinitro-1,3-propanediol with acetic formic anhydride in the presence of pyridine and a solvent. The properties of 2,2-dinitro-1,3-propanediol-diformate are listed in Table 26.

Table 26: Properties of 2,2-dinitro-1,3-propanediol-diformate

Property	SI units	Other units
ΔH_f (heat of formation)	−609 kJ/mol (measured)	−145.5 kcal/mol (measured)
Density	1.474 kg/dm ³	1.474 g/cm ³
Boiling point	about 363 K @ 6.6 Pa	about 90 °C @ 0.05 mmHg
Vacuum thermal stability (100 °C/48 h)	1.602 cm ³	—
Freezing point	Below 210 K	Below −60 °C
ABL impact sensitivity	0.11 m	11 cm
ABL friction sensitivity	3.52 kN @ 2.43 m/s	800 lbf @ 8 ft/s
ESD sensitivity, unconfined	More than 8J	—
ESD sensitivity, confined	8J	—
SBAT onset	395 K	122 °C (252 °F)
Card gap sensitivity	NO GO @ 0 cards	—
DSC onset temperature	562 K	289 °C

Data source: [418]

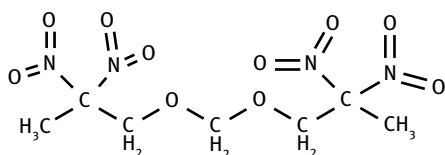
Dinitropropyl acrylate, $\text{C}_6\text{H}_8\text{N}_2\text{O}_6$, molecular mass = 204.14 g/mol, can be polymerized into an energetic binder. Its enthalpy of formation is −514 cal/g = −104.9 kcal/mol = 439 kJ/mol and its density is 1.304 g/cm³ = 0.0471 lb/in³ [97].

15 Nitroalkyl Formals and Acetals

Formals and acetals are dialkyl ethers with substituents on the alkyl groups and two oxygens linked to a central carbon atom.

15.1 Bis(2,2-dinitropropyl)formal

Bis(2,2-dinitropropyl)formal, also known as $C_7H_{12}N_4O_{10}$, bis(2,2-dinitropropoxy)-methane, $[H_3C-C(NO_2)_2-CH_2-O-]_2CH_2$, BDNPF, CAS RN [5917-61-3], $M = 312.21$ is sometimes used as a plasticizer by itself, but most often it is used in a mixture with bis(2,2-dinitropropyl)acetal (BDNPA) [419].



Bis(2,2-dinitropropyl)formal, BDNPF

BDNPF can be synthesized by the condensation reaction between 2,2-dinitropropanol and paraformaldehyde in methylene chloride.

The use of methylene chloride, an environmentally troublesome solvent, can be avoided by reacting 2,2-dinitropropanol at low temperature with a stoichiometric excess of formaldehyde in the presence of a protic acid catalyst, such as H_2SO_4 , HCl , H_3PO_4 , or HBr [420]. Although 2,2-dinitropropanol is not very soluble in water, solid 2,2-dinitropropanol is mixed with an excess of a formaldehyde source to form a reaction slurry. Addition of a small amount of hexane helps solubilize the solid reactants and BDNPF product and does not participate in the reaction. The formaldehyde source could be either s-trioxane or paraformaldehyde. To inhibit by-product formation, the reaction temperature is maintained from about 243 to 303 K (–30 to 30 °C). After completion of the reaction, the mixture is neutralized with caustic soda and the product is extracted with methyl *tert*-butyl ether. The yield is 60–70% based on the starting quantity of 2,2-dinitropropanol.

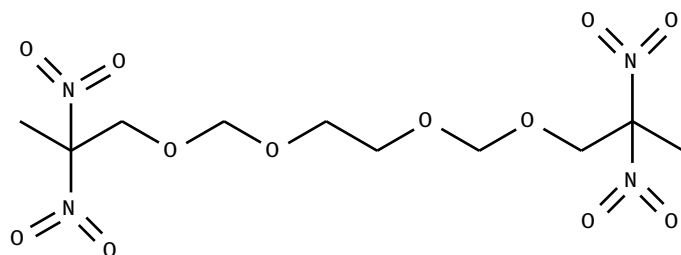
Bis(2,2-dinitropropyl)formal crystallizes as monoclinic crystals, space group $C2/c$, with the axis parameters $a = 23.330(3) \text{ \AA}$, $b = 6.207(3) \text{ \AA}$, $c = 10.009(6) \text{ \AA}$, $\beta = 109.60(3)^\circ$, $V = 1365.6(11) \text{ \AA}^3$, $Z = 4$ [421]. In the crystal structure, molecules are linked into chains running parallel to the b axis by inter-molecular $C-H \cdots O$ hydrogen bond interactions, which explains the high melting point of this compound.

Oral LD50 toxicity for rats of bis(2,2-dinitropropyl) formal, bis(2,2-dinitropropyl) acetal, and a 1 : 1 mixture of the two was 1920, 2918, and 1994 mg/kg, respectively [422]. An analysis of data suggested that acute toxicity of the two ingredients is additive.

These substances caused methemoglobinemia in a dose–effect relationship, and led to degenerative lesions in hepatocytes and epithelial cells of the renal proximal tubule but did not show any obvious irritating effect on the skin and eyes of rabbits. Consistent with the *Salmonella*/microsome assay, any of the three failed to increase chromosome aberrations and SCE frequency in mammalian cells.

15.2 Other Nitroalkyl Formals

Bis(2,2-dinitropropyl ethylene) formal (BDNPEF), a new *gem*-dinitro energetic plasticizer,

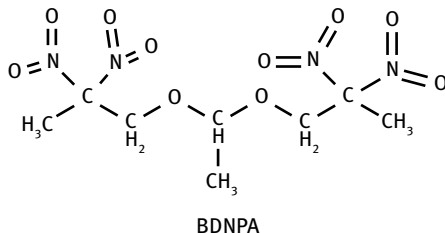


can be synthesized by aldol condensation of formaldehyde (trioxane) with 2,2-dinitropropanol and ethylene glycol with boron trifluoride etherate as the catalyst [423]. The yield was 23%. One of the by-products of this process was bis(2,2-dinitropropyl) formal (BDNPF) with 18% yield, which can be separated and also used as an energetic plasticizer. Compared to commercial nitro plasticizers, BDNPEF showed improved plasticization efficiency with a decrease in glass transition temperature (T_g) and viscosity of uncured glycidyl azide polymer (GAP) blends, as well as a substantial ability to plasticize GAP-based polyurethanes. The T_g of BDNPEF and BDNPF was 206.61 K = -66.54°C and 203.67 K = -69.48°C , respectively. BDNPEF was predicted to have a density of 1.499 g/cm^3 , heat of formation of $979\text{ kJ/mol} = 234\text{ kcal/mol}$, and impact sensitivity of 230 cm.

Based on calculations of fully optimized molecular geometric structures via a molecular orbital method, IR spectrum, heat of formation, and detonation performances of BDNPEF were predicted [424]. The bond dissociation energies and bond orders for the weakest bonds were analyzed to investigate the thermal stability. The results showed that the four N–NO₂ bond dissociation energies are nearly equal to each other with values of near 164 kJ/mol, which showed that this should be a stable compound. The detonation velocity and pressure were evaluated using Kamlet–Jacobs equations based on the theoretical density and condensed heat of formation. The crystal structure obtained by molecular mechanics belongs to a $P2_1$ space group, with lattice parameters $Z = 2$, $a = 13.8017\text{ \AA}$, $b = 13.4072\text{ \AA}$, $c = 5.5635\text{ \AA}$.

15.3 Bis(2,2-dinitropropyl)acetal

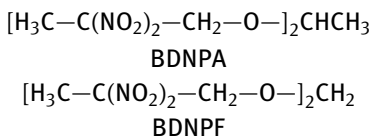
Bis(2,2-dinitropropyl)acetal, also known as $[\text{H}_3\text{C}-\text{C}(\text{NO}_2)_2-\text{CH}_2-\text{O}-]_2\text{CHCH}_3$, BDNPA, CAS RN [5108-69-0],



can be prepared by reaction of 2,2-dinitropropanol at low temperature with an acetaldehyde source in the presence of an acid catalyst, such as a Lewis acid catalyst or protic acid catalyst [425]. To inhibit by-product formation, the reaction temperature is maintained below 273 K. Upon completion of the reaction, the reaction solution is quenched with water and washed with an aqueous hydroxide solution. The hydroxide concentration should be sufficient to neutralize any acid formed during the quenching step and to solubilize unreacted 2,2-dinitropropanol as well as other aqueous soluble by-products in the reaction solution. The BDNPA product can be extracted with methyl *tert*-butyl ether. The solvent is evaporated to yield BDNPA. The BDNPA yield can be 50% of theoretical based on the starting quantity of 2,2-dinitropropanol. The density of BDNPA is 1.47 g/cm³.

15.4 Bis(2,2-dinitropropyl)acetal/Bis(2,2-dinitropropyl)formal Mixtures

The acronym for this widely used mixture is BDNPA/F.



Bis (2,2-dinitropropyl) formal (BDNPF) is an energetic plasticizer used in insensitive high-performance explosives and propellants. However, it has an inherent disadvantage in that it is a solid at room temperature such that it cannot be used by itself. Thus, to make it usable as a plasticizer, a eutectic mixture of BDNPF with its homologue is used, which is a liquid called BDNPA/F. The purity requirements and methods of analysis of BDNPA/F are described in Military Specification MIL-SPEC WS-1141.

The plasticizer containing a eutectic mixture of BDNPA/F has been commercially available and widely used in explosives and propellants. But it is well known that the thermal/chemical stability of an acetal group in BDNPA is lower than that of the formal group in BDNPF. A plasticizer which is an approximately 1:1 molar binary eutectic mixture of bis(2,2-dinitropropyl) formal and 2,2-dinitrobutyl 2,2-dinitropropyl formal avoids some of these shortcomings [426]. This is a two-component mixed formal, BDNPF and 2,2-dinitropropyl 2,2-dinitrobutyl formal (DNPBF), in which DNPBF was used as an inhibitor of crystallization in BDNPF. The two-component mixed formal is obtained by reacting a mixture of 2,2-dinitropropanol and 2,2-dinitrobutanol with formaldehyde, but it is also known that about 10% of bis(2,2-dinitropropyl) diformal is always lost as an unwanted by-product.

BDNPA/F mixture is an excellent plasticizer for polyurethanes, polyethylene glycols (PEG), and cellulose acetate butyrates (CAB). It has a low melting point (about 285 K = 12°C) and a low vapor pressure. A significant shortcoming of this mixture is the limited chemical and thermal stability of BDNPA. Thus, when heated separately at 423 K = 150°C in a vacuum for 48 h, BDNPF remains essentially unchanged whereas BDNPA decomposes to the extent of at least 30% with formation of new solid and liquid products which, in turn, undergo further decomposition. BDNPA is also more sensitive to acid hydrolysis than BDNPF. These undesirable properties of BDNPA are also exhibited by its eutectic mixture with BDNPF and adversely affect the utility of this mixed plasticizer.

Homologues to BDNPA/F containing butyl groups in place of propyl groups have similar properties and are also effective in lowering the melting point of BDNPF or BDNPA [427].

15.4.1 Production of BDNPA/F

Geminal dinitro energetic plasticizers are not easy to synthesize. In order to produce the mixture of BDNPA/F, the 2,2-dinitropropanol can be reacted with a mixture of formaldehyde and acetaldehyde, or the two compounds are produced separately, purified, and mixed later.

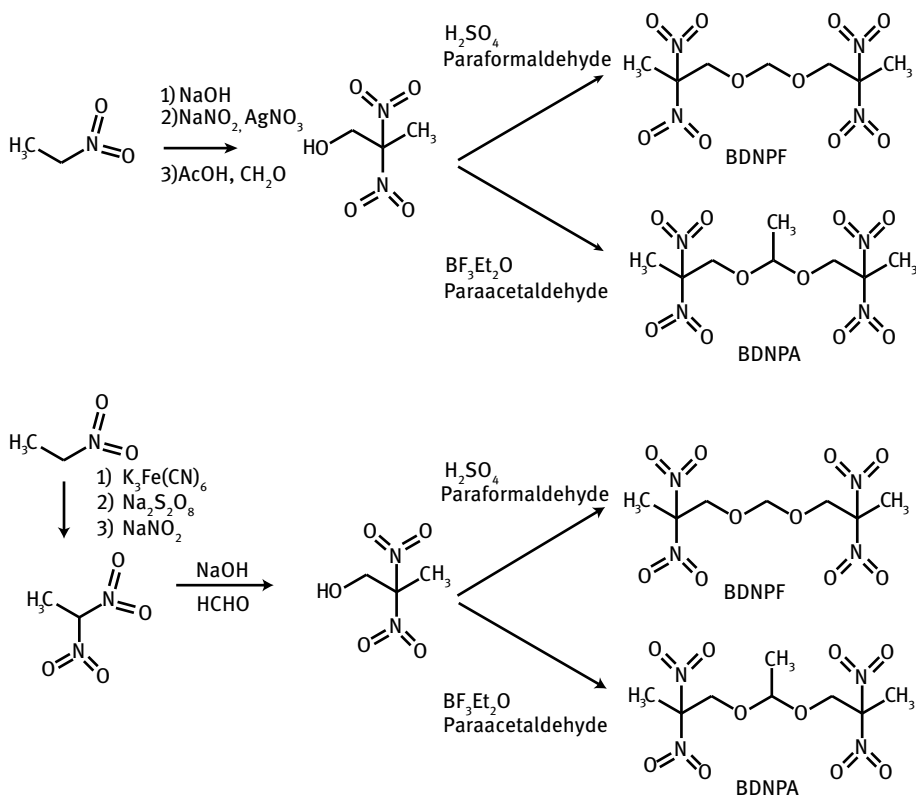
The oxidative nitration route and the chlorination-nitration route synthetic methods for production of bis(2,2-dinitropropyl)acetal/bis(2,2-dinitropropyl)formal (BDNPA/BDNPF, BDNPA/F) plasticizers were developed in the USA. The chlorination-nitration route is suitable for large-scale production.

Specifically, it has been found that boron trifluoride is an excellent catalyst in the production of bis(2,2-dinitropropyl) acetal, and that concentrated sulfuric acid (90–99% by weight) gives superior yields of formaldehyde, bis(2,2-dinitropropyl) formal [428].

A process for production of bis(2,2-dinitropropyl)formal (BDNPF) avoiding use of solvents reacts 2,2-dinitropropanol with a formaldehyde source in the presence of

a protic acid catalyst, such as H_2SO_4 , HCl , H_3PO_4 , or HBr at low temperatures between -30 and $+30^\circ\text{C}$ [429].

A similar process is used for production of bis(2,2-dinitropropyl)acetal (BDNPA) [425]. By replacing chlorinated solvents with MTBE (methyl-*tert*-butyl ether), the process has been made environmentally more friendly. The nitration can be carried out with inexpensive peroxy sulfate salts as the oxidant with a catalytic amount of potassium ferricyanide. The synthesis of BDNPA/F can be automated and run continuously to give a high output of product. The Thiokol Corporation has developed an environmentally friendly process which avoids the use of chlorinated solvents [430].



BDNPA/F was originally prepared by Kaplan and Schechter by oxidative nitration of nitroethane using silver nitrate as a catalyst. Due to process waste problems, and a loss of approximately 1% of silver, the process was considered economically and environmentally unattractive. Therefore, the Kaplan and Schechter route was eventually abandoned in the 1990s. The process was later modified by using selective chlorination of nitroethane to 1-chloronitroethane which improved the efficiency; however, the process was still considered environmentally unfriendly. The more recent manu-

facturing process for BDNPA/F used dinitropropanol (DNPOH) as a key intermediate [431]. DNPOH was prepared by selective chlorination of nitroethane to 1-chloro-1-nitroethane, followed by a ter Meer reaction of the later with nitrite ion in basic media to give the nitrate salt of 1,1-dinitroethane. This salt can then be easily converted to DNPOH. Through process improvement by minimizing the amount of buffering agent, the product per reactor volume was increased by a factor of eight. Similar improvements in the process for BDNPA were also achieved using acetaldehyde and an ion exchange resin.

BDNPA/F was commercially produced for many years using the ter Meer process. This chemistry was economical, efficient, and highly reproducible. Unfortunately, it utilized several environmentally unfavorable materials. Under US Army funding, the Thiokol Corporation developed and demonstrated a process which was environmentally more friendly [432]. The process was based on laboratory work done at Fluorochem on oxidative nitrations using aqueous, non-chlorine chemistry. Modifications to the original chemistry involved replacement of the chlorinated solvent with environmentally benign solvents in formation of the dinitropropanol (DNPOH) intermediate. The conversions of DNPOH to the acetal (A) and formal (F) were accomplished in non-solvent processes for the ether formation followed by a simple aqueous/methyl-*tert*-butyl ether-extractive work-up. In these reactions, no chlorinated solvents were used at any stage of the process. Yields and purity were demonstrated to be similar to those obtained by earlier processes. This process has been demonstrated in a pilot plant operated by the Thiokol Corporation and shown to produce material that meets all specification requirements as well as or better than the previous process but without multi-step purification. The process was scaled up to be used in larger pilot-scale production.

The thermal and chemical stabilities of BDNPA were worse than those of BDNPF, and several improved alternate compositions were proposed [433]. The energy content of DNBPF/BDNBF composite plasticizers is equal to that of the BDNPA/F mixture, but its chemical stability is better; therefore, it has some advantages and was predicted to eventually replace BDNPA/F. See also [434].

An energetic plasticizer which is a mixture of bis(2,2,2-trinitroethyl)formal, bis(2,2-dinitropropyl)formal, and 2,2-dinitropropyl 2,2,2-trinitroethyl formal was described in [435]. This patent described binary and ternary mixtures of BDNPF, bis(2,2,2-trinitroethyl)formal (TEFO), and 2,2-dinitropropyl-2,2,2-trinitroethylformal (TNEPF) as plasticizers for energetic propellant compositions. The general advantages of the binary and ternary mixtures of TNEPF, TEFO, and BDNPF are low volatility and good thermal stability (better than GTN or BTTN), coupled with a relatively high energy content [higher than BDNPA/F, diethylene glycol dinitrate (DEGDN), or trimethylolethane trinitrate (TMETN)]. These mixtures can be advantageously used in place of BDNPA/F, TMETN, or BTTN for many propellant applications. They are particularly suitable for plasticizing polymers like cellulose acetate butyrate (CAB), NC, polyethylene glycol (PEG), or polycaprolactone (PCP).

15.4.2 Physical Properties of BDNPA/F

BDNPA/F has good density ($\rho = 1.383\text{--}1.397\text{ g/cm}^3$) and viscosity and low toxicity properties and is compatible with many components of propellants and explosives [436]. Due to its good thermal stability, BDNPA/F can replace NG in formulations and reduce their impact sensitivity [437]. Due to the energy content and the excellent oxygen balance and heat of reaction values, BDNPA/F can replace inert plasticizers in formulations and improve the burning rate and specific impulse. It is widely used in double-base (DB) and CMDB propellants and explosive formulations such as PBX and Picatinny Arsenal Explosive (PAX). It is one of the most versatile energetic plasticizers for preparing insensitive energetic materials.

The heat of vaporization (ΔH_{vap}) and vapor pressure at 298 K (25°C) are $93.01 \pm 0.38\text{ kJ/mol}$ and $1.4532 \pm 0.40 / -0.27\text{ mPa}$ for BDNPA, and $84.77 \pm 0.88\text{ kJ/mol}$ and $2.20 \pm 1.87 / -1.07\text{ mPa}$ for BDNPF [438].

Molecular orbital calculations applied to a eutectic mixture of bis(2,2-dinitropropyl)formal and bis(2,2-dinitropropyl)acetal allowed predictions of thermodynamic and fluid properties [439].

15.4.3 Thermal Stability and Decomposition of BDNPA/F

Simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) and Fourier-transform ion cyclotron resonance (FTICR) instruments have been used to measure the mass spectra, measure vapor pressures, and evaluate the thermal decomposition mechanism of bis(2,2-dinitropropyl)acetal (BDNPA) and bis(2,2-dinitropropyl)formal (BDNPF) [438]. The FTICR mass spectra provided the identity of the ion fragments formed in the mass spectra of BDNPA, BDNPF, and their decomposition products, and provided a basis for predicting possible structures of the ion fragments. STMBMS data supported a nitro–nitrite ($\text{NO}_2 \rightarrow \text{ONO}$) rearrangement mechanism for both compounds. Upon rearrangement, both NO and NO_2 are cleaved from the structure, thus producing a ketone radical. The nitro–nitrite rearrangement begins to occur at appreciable rates between 433 and 435 K (160 and 180°C). Additional decomposition products included amines, imines, and amides, as well as CO_2 and H_2O at higher temperatures. The major difference between the decomposition of the two compounds is the slower reaction rate of BDNPF. It was postulated that the less sterically hindered carbon atom at the formal group of BDNPF subjects it to interactions with an intermediate, thus forming a complex and delaying its release.

In investigating complex reaction processes that control the behavior of heterogeneous energetic materials in munitions throughout their life cycle, the decomposition of BDNPA/F was studied by developing mathematical models of complex reaction processes [440].

The ease of hydrolysis of BDNPA/F limits its useful life in a moist environment, but also makes the disposal during demilitarization a little easier. The kinetics and mecha-

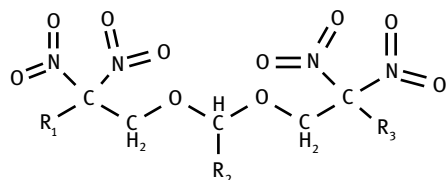
nism for the basic hydrolysis of BDNPA and BDNPF have been investigated [441]. Both BDNPA and BDNPF were found to react with slightly more than four mols of base to yield nitrite, 1,1-dinitroethane, acetate, and formiate anions. Second-order rate constants were obtained for both BDNPA and BDNPF for the expression

$$-d[\text{BDNPA}]/dt = k_1[\text{BDNPA}] = k_2[\text{B}^{(-)}][\text{BDNPA}]$$

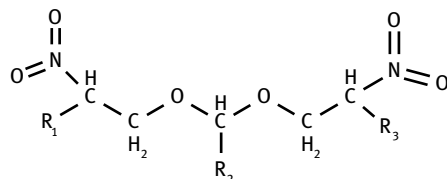
where k_1 is the first order rate constant with excess base, $\text{B}^{(-)}$. BDNPA and BDNPF were found to react faster in dioxane/water than in water. The rates of disappearance of both BDNPA and BDNPF were very nearly equal to one half of the combined rates for the formation of nitrite and 1,1-dinitroethane anions. On the basis of relative k_2 values, BDNPA and BDNPF were found to react 40-times faster with aqueous base than triethylene glycol dinitrate (TEGDN), but 1000-times slower than RDX.

15.5 Other Nitroalkyl Formals and Acetals

Bis(dinitroalkyl)acetals and formals having the formula I



(R_1 , R_3 = independently straight or branched chain alkyl; R_2 = H, Me, Et, *n*-Pr, or isopropyl), particularly bis(2,2-dinitropropyl)acetal (BDNPA) and bis(2,2-dinitropropyl)formal (BDNPF), can be produced by oxidative nitration of compounds having the formula II



preferably via a sodium or other alkali metal, or alkaline earth metal, salt of II [442]. For example, condensation of 2-nitro-1-propanol with formaldehyde gave bis(2-nitropropyl)formal (BNPF), which produced bis(2,2-dinitropropyl)formal (BDNPF) by oxidative nitration with sodium nitrite.

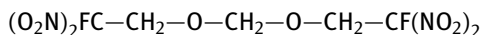
The heat of formation of bis(2,2,2-trinitroethyl)formal, CAS RN [6263-74-7], was determined by combustion calorimetry, using a Pt-lined rotating-bomb calorimeter and was found to be $-403.3 \pm 2.68 \text{ kJ/mol} = -96.40 \pm 0.64 \text{ kcal/mol}$ [443].

An energetic plasticizer consists of bis(2,2-dinitropropyl)formal and a freezing point depressant that keeps BDNPF from crystallizing out, such as bis(2,2-dinitropropyl)diformal (BDNPDF) [444]. In cases where BDNPDF is used to prevent BDNPF from crystallizing out, BDNPF was not crystallized even though it was stored at 253 K (−20 °C) for more than 6 months, while its thermal and chemical properties were similar to those of conventional plasticizers. Also, by using BDNPDF, which had previously been considered as a unfavorable side product, as an inhibitor of crystallization, is no additional process required to remove BDNPDF.

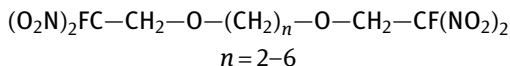
A eutectic mixture consisting of bis(2,2-dinitropropyl)formal, 2,2-dinitropropyl-2,2-dinitrobutylformal, and bis(2,2-dinitrobutyl)formal also avoids the unwanted crystallization of BDNPF [427].

15.5.1 Fluoronitroalkyl Formals and Acetals

An energetic plasticizer, bis-2-fluoro-2,2-dinitroethoxymethylene,



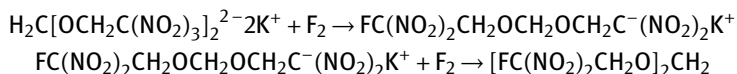
which for brevity was given the acronym FEME, was prepared by condensation of fluorodinitroethanol with the appropriate alkyl ditriflates [445]. These plasticizers had been developed specifically for use with the dinitropropylvinyl ether polymer (DNPVEP). These plasticizers may also be used as replacements for FEFO or glycerin trinitrate which have availability and/or sensitivity problems. Preliminary evaluation of FEME indicated a high degree of both thermal and hydrolytic stability. DNPVEP plasticized with FEME showed excellent physical properties. Similar, less volatile plasticizers were developed that had more than one methylene group in the middle:



A variety of polynitroaliphatic acetals and ethers could be prepared under mild reaction conditions [446]. Purification was simple and no costly high-pressure or high-temperature laboratory techniques were necessary to produce a variety of polynitroaliphatic compounds not available via previously described synthetic methods. These energetic polynitroaliphatic acetals and ethers prepared from 2-fluoro-2,2-dinitroethanol could provide precursor compounds for eventual application as energetic binders or plasticizers in solid propellant and/or explosive formulations. Several activated alkenes and one alkyne were reacted with polynitroaliphatic alcohols directly to produce acetal and ether compounds. Difunctional polynitroalcohols reacted similarly with divinyl ether to produce low-molecular-weight acetal prepolymer compounds which were either vinyl or hydroxyl terminated. In one case, fluorodinitromethane was added to an alkene; however, the resultant product turned out to be unstable at room temperature and gradually decomposed.

The direct, one-step addition of 2-fluoro-2,2-dinitroethanol (FDNEOH) to certain unsaturated hydrocarbons formed 2-fluoro-2,2-dinitroethoxy acetal and ether compounds in high yield [447]. These non-aqueous mercury salt-catalyzed Markovnikov additions with FDNEOH were achieved under mild, neutral reaction conditions.

The fluorination of aqueous solutions of the salts of two formals, bis(2,2-dinitroethyl) formal (I) and bis(2,2,4,4-tetranitrobutyl) formal (II), with elemental fluorine resulted in the formation of fluorodinitroalkyl formals, bis(2-fluoro-2,2-dinitroethyl) formal, and bis(4-fluoro-2,2,4,4-tetranitrobutyl) [448]. Example (I) is shown:



The two selected salts represent in some way limiting compounds in a series of polynitro alcohol formals in that they exhibit a broad range of conditions for the aqueous fluorination of this class of compounds. The reaction for the fluorination of nitro compounds with elemental fluorine in water represents a system of two competing reactions: the reaction of fluorine with water, and the reaction of fluorine with the dissolved substance.

16 Fluoronitroalkanes

Many of the nitroalkanes discussed up to this point contained hydrogen on the alkyl group, making the compounds potential monopropellants but also increasing their sensitivity toward accidental explosions. Because some of the oxygen on the nitro groups is consumed to combust the hydrogen in the alkyl groups, these nitroalkane compounds are usually poor oxidizers. The oxygen balance of nitroalkanes can be improved by replacing some or all of the hydrogen in the alkyl group with fluorine. A wide variety of fluoronitroalkanes, fluoronitroethers, fluoronitroesters, and fluoronitroamines have been synthesized and evaluated as energetic plasticizers. Most of these have been patented but have never seen any practical applications. The energy content was often increased by adding difluoroamino or nitrate or azido groups to the molecule. Only a few randomly selected examples of these compounds are referenced in this book; a comprehensive summary would have exceeded the scope. Several fluoronitroalkanes have been evaluated as rocket propellants.

16.1 Fluorotrinitromethane

The simplest fluoronitroalkane is fluorotrinitromethane, fluoronitroform, $\text{FC}(\text{NO}_2)_3$, CAS RN [1840-42-2]. It can be prepared by fluorination of nitroform. Over-fluorination

can be avoided by continuously monitoring the concentration of remaining fluoroform by its UV absorption in a side stream that is returned to the reactor [449].

Fluorotrinitromethane can be synthesized by reacting tetranitromethane with an adduct of an alkali metal fluoride and a fluorinated or chlorofluorinated acetone in an aprotic dipolar solvent [450]. Chlorine or bromine may have to be added during the reaction so as to eliminate side reactions [451]. Physical properties of fluorotrinitromethane were summarized in [452].

Fluorotrinitromethane has been evaluated as a freezing point depressant for N_2O_4 . Physical properties were reported as follows [453]: its freezing point is $244.1\text{ K} = -29^\circ\text{C}$; the boiling point is $357.3\text{ K} = 84.2^\circ\text{C}$ at 760.1 mm Hg ; the standard enthalpy of formation of trinitrofluoromethane is $-217.5 \pm 2.0\text{ kJ/mol}$ ($-51.99 \pm 0.48\text{ kcal/mol}$). The density of fluorotrinitromethane for the range $293\text{--}338\text{ K}$ ($20\text{--}65^\circ\text{C}$) can be calculated from

$$\rho = 1.8459 - 0.002415t$$

where ρ is the density in g/cm^3 and t is the temperature in $^\circ\text{C}$. The vapor pressure for the range $273\text{--}357\text{ K}$ ($0\text{--}84^\circ\text{C}$) can be calculated from

$$\log P = 6.8187 - 1785.71/T$$

where P is the vapor pressure in mm Hg and T is the temperature in kelvin. The calculated heat of vaporization (Clausius–Clapeyron) is $\Delta H_{\text{vap}} = 34.2\text{ kJ/mol} = 8.171\text{ kcal/mol}$. The refractive index n_D^{25} is 1.3944.

The density reported by Zimmer et al. in 1966 was later corrected and shown to be 1.7954 g/cm^3 at 293 K (20°C) [454].

16.2 C₂ Fluoronitroalkanes

1-Fluoro-1,1-dinitroethane can be prepared by bubbling perchloryl fluoride into a suspension of potassium 1,1-dinitroethane in methanol/water at $313\text{ K} = 40^\circ\text{C}$, about 7 hours being required for complete replacement of the insoluble yellow crystals by white potassium chlorate [383]. After filtering off KClO_3 , dilution with water and extraction with ether, the ether phase was washed several times with water to remove most of the methanol, dried over calcium chloride, and the ether evaporated off *in vacuo*. Fractionation of the residue through a jacketed column packed with glass helices yielded 54% pure fluorodinitroethane, b.p. $313.6\text{--}314.6\text{ K}$ @ $2.6\text{ kPa} = 40.5\text{--}41.5^\circ\text{C}$ @ 20 mm Hg , n_D^{24} 1.3960.

16.3 Higher Fluoronitroalkanes

Fluoropolynitro organic formals like bis(2-fluoro-2,2-dinitroethyl)formal (FEFO, 2,2-dinitropropyl 2-fluoro-2,2-dinitroethyl formal) were evaluated as energetic plasticizers in propellant and explosive compositions and compared to BDNPF [413]. FEFO has a higher energy content but is volatile and toxic and has a relatively higher melting point. Furthermore, FEFO is unstable because it has a formal linkage which is hydrolytically unstable. BDNPF is comparatively low in energy and has a higher melting point, requiring the use of a melting point depressant at the expense of energy content. Mixtures of FEFO and BDNPF can be used to obtain a lower melting point and intermediate levels of energy and volatility.

In the series, $\text{CF}(\text{NO}_2)_2\text{—CH}_2\text{—O}(\text{—CH}_2\text{—O—})_n\text{—CH}_2\text{—CF}(\text{NO}_2)_2$, two oxymethylene homologues of FEFO ($n=1$) with $n=2$ and $n=3$ were prepared from 2-fluoro-2,2-dinitroethanol and formaldehyde in sulfuric acid [455]. Not unexpectedly, they were less thermally stable than FEFO. Vacuum thermal stability tests of the lowest member of this series, bis(2-fluoro-2,2-dinitroethyl) ether, $n=0$, made from bis(2-nitroethyl) ether by oxidative nitration and aqueous fluorination of the product, indicated that it possessed greater thermal stability than FEFO.

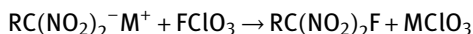
A homologue of FEFO, bis(2-fluoro-2,2-dinitroethoxy)-(1-fluoro-1,1-dinitro-2-propoxy) methane (M-FDNEOF) has been found to be useful as an energetic co-plasticizer for bis(2-fluoro-2,2-dinitroethyl) formal (FEFO) in PBX formulations [456]. M-FDNEOF is a low melting solid (m.p. 320–322 K = 47–49 °C) with a calculated liquid density at 298 K = 25 °C of 1.60 g/cm³. Its heat of formation was estimated to be –1314 kJ/mol = –314 kcal/mol. M-FDNEOF is almost equal to FEFO in energy content.

A general reaction of the transformation of the fluorodinitromethyl group into the fluoronitromethyl group by de-nitration upon treatment with Na₂SO₃ or KI in aqueous formaldehyde was found and a preparative method for synthesizing fluoronitroalcohols was developed on the basis of this reaction [457]. In this reaction, the compound loses one of its two nitro groups and a –CH₂OH group is added in its place. The fluorine remains attached.

The aim of the following work was to examine the possibility of applying an equation that correlates the frequency of the C–F valence vibration in IR spectra with the electronegativity of substituents in monofluoronitroalkanes of varied structure, and at the same time to study the influence of inter-molecular hydrogen bonding and the structure of the molecules on the vibration frequency of the C–F bond [458]. Compounds studied included fluoronitroform, fluorodinitromethane, 1-fluoro-1,1-dinitroethane, 1-fluoro-1-nitroethane, 1-fluoro-1,1-dinitropropane, 1-fluoro-2,2,2-trinitroethane, and 1-fluoro-3,3,3-trinitropropane. Fluorine takes part in the formation of inter-molecular hydrogen bonds in the fluoronitroalkanes because the frequency shifted with increasing dilution in a solvent.

A method was developed for the preparation of 1-fluoro-1-nitroalkanes and the principal physicochemical properties of eight members of a homologous series were described [459]. Two attempts have already been reported in the literature on the α -fluorination of primary mono-nitroalkanes with perchloryl fluoride and elemental fluorine. The first attempt proved to be completely unsuccessful, and a fluorine-containing nitroalkane could not be obtained.

Different classes of α -fluoropolynitrohydrocarbons, and specifically aliphatic (saturated and unsaturated) and aralkyl derivatives, were obtained by the action of perchloryl fluoride in various solvents on the alkali and ammonium salts of polynitrohydrocarbons [460]. Previously it had been shown that perchloryl fluoride (FCIO_3) was capable of fluorinating the salts of trinitromethane and *gem*-dinitroalkanes with the formation of the corresponding α -fluoropolynitroalkanes. The salts of different classes of polynitrohydrocarbons, and specifically the salts of polynitroalkanes, polynitroalkenes, and aralkyl polynitro compounds, and also the salts of halopolynitroalkanes were prepared in this way. The general equation for the reaction is



where $\text{R} = \text{NO}_2, \text{Cl}, \text{Br}, \text{H}, \text{alkyl}, \text{alkenyl}, \text{etc.}$, and M is the cation of an alkali metal. Table 27 gives a summary of properties of fluorodinitroalkanes prepared by this method.

Table 27: Properties of fluorodinitroalkanes.

Compound	Boiling point or boiling range (pressure)		Freezing point		Refractive index	Density
	K (kPa)	°C (mm Hg)	K	°C	n_D^{20}	g/cm^3
$\text{FC}(\text{NO}_2)_3$	356.6 (98.9)	83.5 (744)	228*	-45*	1.3950	1.5966
$\text{FCH}(\text{NO}_2)_2$	313 (3.2)	40 (24)	—	—	1.4060	1.6035
$\text{FC}(\text{NO}_2)_2\text{CH}_3$	403.6 (99.8)	130.5 (751)	235	-38	1.3992	1.4308
$\text{FC}(\text{NO}_2)_2\text{CH}_2\text{CH}_3$	323.1–323.6 (2.6)	50–50.5 (20)	—	—	1.4030	1.3339
$\text{FC}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{CH}_3$	329.1–329.6 (1.9)	56–56.5 (14)	—	—	1.4090	1.2603

Data source: [460]

* This melting point does not agree with data from [453]

The enthalpy of formation of bis(dinitro) fluoropropane, $\text{C}_3\text{H}_5\text{N}_2\text{O}_4\text{F}_1$, with a molecular mass of 152.08 g/mol is $-530 \text{ cal/g} = -80.6 \text{ kcal/mol} = -337 \text{ kJ/mol}$ [97].

The reaction of 2-fluoro-2,2-dinitroethanol with dichlorine heptoxide gives 2-fluoro-2,2-dinitroethyl perchlorate, a very potent oxidizer [461]. Perchloryl fluoride reacted with 2-fluoro-2,2-dinitroethanol in methanol to give 2-fluoro-2,2-dinitroethyl methyl ether.

Thermal explosion times as a function of temperature have been measured for six dinitroalkanes and fluorodinitroalkanes at 1, 10, and 50 kbar [462]. For a constant thermal explosion time of 30 s, the thermal explosion temperatures were: 1,1-dinitroethane (at 1 kbar) 456 K = 183 °C and (at 10 kbar) 435 K = 162 °C; 1,1,1-fluorodinitroethane (at 1 kbar) 531 K = 258 °C and (at 10 kbar) 528 K = 255 °C; 1,1-dinitropropane (10 kbar) 435 K = 162 °C; 1,1,1-fluorodinitropropane (10 kbar) 530 K = 257 °C; 1,2-dinitropropane (1 kbar) 498 K = 225 °C, (10 kbar) 445 K = 172 °C, and (50 kbar) 416 K = 143 °C; and 2,2-dinitropropane (10 kbar) 530 K = 257 °C and (50 kbar) 571 K = 298 °C. The results for the dinitroalkanes showed that the presence of an α -hydrogen atom decreased the explosion temperature at constant pressure and increased the sensitivity to pressure. See also [463].

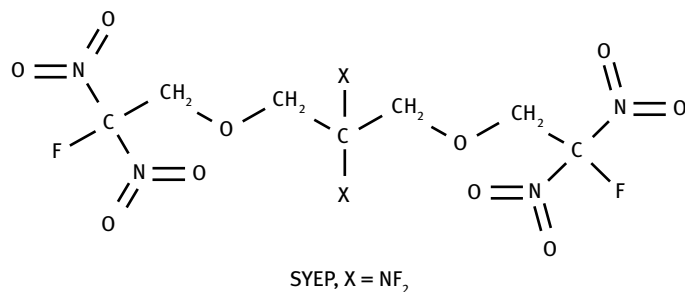
16.3.1 Compounds with Terminal Fluorodinitromethyl Groups

From steric and energetic theoretical considerations [464, 465] it was predicted that compounds containing the $(\text{O}_2\text{N})_2\text{FC}-$ grouping would constitute a class in which reduced sensitivity to impact and improved thermal stability could be achieved without excessive sacrifice of explosive power. A family of fluorodinitro high explosives and plasticizers was synthesized for which the prediction of reduced sensitivity and improved thermal stability with relatively little loss in explosive power appears to have been borne out [466]. Of particular interest were fluorodinitroethyl fluorodinitrobutyrate, bis-fluorodinitroethyl carbonate, and fluorodinitroethyl orthocarbonate. Alkyl nitrate esters with terminal fluorodinitromethyl groups have exceptional thermal stability and good energy content.

16.3.2 1,3-Bis(2'-Fluoro-2',2'-Dinitroethoxy)-2,2-Bis(Difluoroamino)Propane

There may be some overlap in the information provided in this book on difluoroamino compounds and nitro compounds. If one requires a complete evaluation of those mixed substituent energetic compounds, one will need to read both sections.

Another high-energy liquid which makes a good plasticizer is 1,3-bis(2'-fluoro-2',2'-dinitroethoxy)-2,2-bis(difluoroamino)propane, also known as $[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2]_2\text{C}(\text{NF}_2)_2$, SYEP, CAS RN [7790-98-9].



Another energetic plasticizer and intermediate is 2,2-bis(difluoroamino)-5-fluoro-5,5-dinitro-1-pentanol, $(\text{O}_2\text{N})_2\text{FC}-\text{CH}_2-\text{CH}_2-\text{C}(\text{NF}_2)_2-\text{CH}_2-\text{OH}$, which can be synthesized by reacting 2,2-bis(difluoroamino)-5-fluoro-5,5-dinitro-1-pentyl trifluoroacetate with methanol [469]. It melts at 287 K (14 °C) and boils at 352–353 K (79–80 °C).

17 Nitroazidoalkanes (Azidonitroalkanes)

Compounds that contain both nitro groups and azido groups attached to a carbon skeleton are very energetic and can be used as energetic plasticizers. In trying to decide if these compounds should be listed here under “Nitroaliphatic Compounds” or in the organic “Azides and Azido Compounds”, it was decided that these compounds should be listed here under “Nitroaliphatic Compounds”, and not under “Azides and Azido Compounds.” This was done although the International Union of Pure and Applied Chemistry (IUPAC) conventions require us to form the name of nitro-azido-alkanes and nitro-azido-ethers by listing the number of nitro groups first and the number of azido groups last (not in alphabetical order). This is because in the IUPAC Decreasing Order of Precedence for the Major Functional Groups, *nitro* takes precedence over *azido* as a substituent on an alkyl group.

Similar compounds are formed by adding an azido group to the alkyl group in alkyl nitrates. These azidoalkyl nitrate compounds are discussed in chapter “Nitrate Esters” of *Encyclopedia of Oxidizers*.

An electrochemical method for the synthesis of geminal azidonitro compounds involved electro-oxidative coupling of azide anions with salts of nitro compounds and produced geminal azidonitroalkanes, azidonitrocycloalkanes, and diazidodinitrocycloalkanes in 45–92% yields [470]. Geminal azidonitroalkanes, azidonitrocycloalkanes, and diazidodinitrocycloalkanes are of considerable interest as compounds with a high energy capacity and promising synthons for construction of various polynitrogenous structures. However, only a few compounds of these types have been obtained and characterized to date: 1-azido-1-nitroethane, 1-azido-1-nitrobutane, 1-azido-1-nitrocyclohexane, 2-azido-2-nitropropane, 1,4-diazido-1,4-dinitrocyclohexane, and 2,5-diazido-2,5-dinitronorbornane. The best results were attained in oxidative coupling of azide anions with salts of nitro compounds with $\text{K}_3\text{Fe}(\text{CN})_6$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the oxidants. A significant drawback of the methods is that a multiple molar excess of the oxidant and azide ions should be used which leads to the generation of a large amount of toxic waste. In contrast, the electro-oxidative coupling of azide with the anions of nitro compounds is a clean process.

α -Nitro-azides can be prepared by two routes involving intermediate radical anions and undergo substitution by an $\text{S}_{\text{RN}}1$ mechanism with azides, sulfonates, thiolates, and nitronates [471].

Oxidative azidation reactions of C-nitro-substituted saturated heterocyclic compounds, in particular the nitro derivatives of oxetane, azetidine, 1,3-dioxane, tetrahydro-1,3-oxazine, and hexahydropyrimidine, resulted in the formation of geminal nitro azides [472]. A recent book on liquid explosives contains a chapter on azido liquid explosives [473]. Azido fluorodinitro amines will be discussed in more detail in the section on substituted alkyl amines in *Encyclopedia of Liquid Fuels*, chapter "Aliphatic Amines" [474, 475].

Azidonitroalkane plasticizers have attracted attention due to their excellent performance as rocket propellant ingredients. In a search for new and promising azidonitroalkanes for plasticizers, a systematic theoretical investigation was performed using density functional theory and molecular dynamics methods [476]. In the first part, a series of azidonitroalkanes were designed and studied using the DFT method, showing high chemical and thermal stabilities. In the second part, an azidonitroalkane was taken as an example to explore the plasticizing effect of azidonitroalkanes on GAP.

17.1 C₂ Nitroazidoalkanes

1,1-Dinitro-1-azidoethane (1-azido-1,1-dinitroethane) can be prepared by reaction of 1,1,1-trinitroethane with lithium azide in a dipolar aprotic solvent (dimethylformamide or dimethylsulfoxide) [477]. This method gives a better yield than electrolysis of a slightly alkaline solution of a primary geminal dinitroalkane and sodium azide on a smooth platinum electrode [478].

1-Azido-1,1-dinitroethane may be too sensitive to be used as a monopropellant by itself, so it was proposed to desensitize it by addition of 10 to 30% methanol, 2-azidoethanol, 1,3-diazidopropanol, or 1,4-diazido-1,1-dinitrobutane and use those mixtures as monopropellants [479].

17.2 C₃ Nitroazidoalkanes

2-Azido-2-nitropropane and 1-azido-1-nitrocyclohexane can be prepared by reactions involving intermediate radical anions (S_RN_1 and oxidative addition) [480]. S_RN_1 reactions between α -nitroazides and azide, benzenesulfinate, and p-chlorobenzenethiolate proceeded with loss of nitrite. The S_RN_1 reaction between 1-azido-1-nitrocyclohexane and the anion of 2-nitropropane proceeded with loss of azide.

Another azidonitro compound which is of interest as an energetic plasticizer is 2,2-dinitro-1,3-diazidopropane [481].

17.3 C₄ Nitroazidoalkanes

The reaction of salts of 1-*aci*-nitroethane and 1-*aci*-nitrobutane with sodium azide and ammonium peroxodisulfate in a methylene chloride/water two-phase system resulted in 1-azido-1-nitroethane and 1-azido-1-nitrobutane, respectively [482].

4,4-Dinitro-1-butanol can be prepared by reacting trinitromethane with acrolein, reducing the resulting trinitroaldehyde to provide the corresponding alcohol, and reducing the alcohol [483]. 4-Azido-4,4-dinitro-1-butyl acetate can be prepared by reacting 4,4-dinitro-1-butanol with acetyl chloride to yield the corresponding acetate and reacting the acetate with an alkali metal azide in an electrolysis cell.

17.4 C₅ Nitroazidoalkanes

Another example of an azidonitroalkane is 1,2-diazido-3-fluoro-dinitroethoxypropane, C₅H₇FN₈O₅, (O₂N)₂CF—CH₂—O—CH₂—CH(N₃)—CH₂N₃, DAFP, which is a yellow liquid with a density of 1.44 g/cm³ and a refractive index of $n_D^{25} = 1.4832$. The enthalpy of formation is +368 kJ/mol (+88 kcal/mol). It froze to a glass at 243 K (−30 °C) and in the DSC had an onset of exotherm at 458 K (185 °C) [484].

17.5 C₆ Nitroazidoalkanes

Aliphatic ethers containing both fluorodinitro and azido moieties are 2-fluoro-2,2-dinitroethyl 2-azidoethyl ether, (NO₂)₂FC—CH₂—O—CH₂—CH₂—N₃ [485]. 1,3-Diazido-2-propyl 2'-fluoro-2',2'-dinitroethyl formal, (NO₂)₂FC—CH₂—O—CH₂—O—CH(CH₂—N₃)₂ is a light-yellow liquid, $n_D^{25} = 1.4798$. Azidomethyl 2-fluoro-2,2-dinitroethyl ether is a light-yellow liquid, $n_D^{27} = 1.4478$, $d^{25} = 1.4707$ g/cm³.

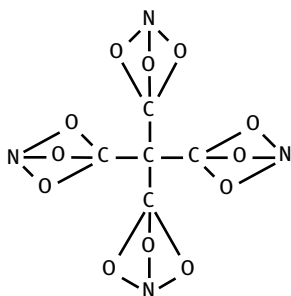
17.6 C₇ – C₁₀ Nitroazidoalkanes

Tri(azido-acetoxymethyl)nitromethane, (N₃CH₂CO—O—CH₂)₃CNO₂, was synthesized with a total yield of 83% using tris(hydroxymethyl)nitromethane as raw material, via a two-step reaction of esterification and azidation [486]. Its molecular structure was confirmed by IR, NMR, and elemental analysis. The density was 1.45 g/cm³, decomposition temperature was 509 K (236 °C), glass transition temperature was 247 K (−26 °C), drop-weight impact sensitivity was $H_{50} = 44.7$ cm (2 kg).

18 Other Polynitroalkyl Derivatives

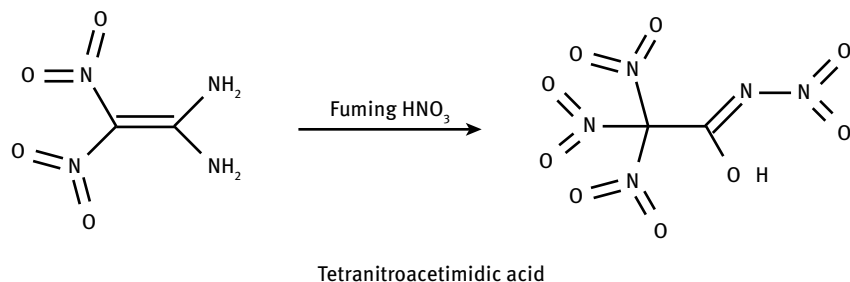
The structures and properties of the isomers of the first three members of the series $C_n(CNO_3)_{2n+2}$ ($n=0,1,2$) compound featuring NO_3 groups bound to a carbon through their three oxygen atoms were examined by computational chemistry [487]. The first member of the series, $(CNO_3)_2$, has six possible isomers, di(nitrato-O)acetylene, *cis*- and *trans*-di(nitrato-O,O-)ethylene, di(nitrato-O,O,O)ethane or bis(nitratoxycarbon), di(nitroso)oxalate, and the mixed isomer nitroso(nitrato-O,O,O)acetate. The most stable of these isomers is di(nitroso)oxalate, followed by nitroso(nitrato-O,O,O)acetate, and bis(nitratoxycarbon). Of the two higher members of the series investigated, $C_n(CNO_3)_{2n+2}$ ($n=1,2$), each has two isomers: the nitritocarbonyl-substituted systems analogous to di(nitroso)oxalate and the nitratoxycarbon-substituted systems (neglecting mixed isomers containing both nitritocarbonyl and nitratoxycarbon moieties). The nitritocarbonyl derivatives were found to be significantly more thermodynamically stable than the nitratoxycarbon derivatives.

The vibrational stability of the theoretical molecule tetrakis(nitratoxycarbon)-methane, designated CLL-1,

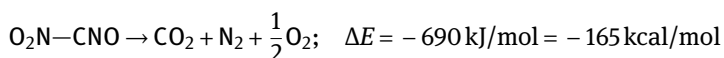


was predicted by *ab initio* electronic structure calculations [488]. The gas-phase enthalpy of formation, predicted to be +1029.3 kJ/mol, and the estimated density of 1.87 g/cm³ were used to predict the explosive performance properties using the equilibrium thermochemical code CHEETAH. The predicted detonation velocity (8.61 km/s) and pressure (33.1 GPa) were similar to those of RDX, but with a significantly higher detonation temperature (6740 K). The synthetic chemists still have to follow the act of the theoretical chemists to make this molecule a reality. If they succeed, it would be an organic oxidizer with good oxygen content and high performance potential.

Tetranitroacetimidic acid, TNAA, $C_2H_1N_5O_9$, has been synthesized by way of cationic FOX-7 and fully characterized [489, 490]. It contains 60.2 mass-% oxygen. The properties of TNAA were found to be encouraging, with a calculated specific impulse exceeding that of AP, indicating its potential as a replacement for AP. TNAA can be synthesized easily in a one-step process by nitration of FOX-7 at room temperature in high yield (93%):



Molecules with the gross formula $C_1N_2O_3$ should be good oxidizers but have not been found yet. They exist only on paper or the computer screen. Structures and energies of $C_1N_2O_3$ isomers have been investigated theoretically by *ab initio* calculations in search of new high-energy molecules [491]. The most energetically favorable isomer, five-membered cyclic nitrous carbonate, had only a 67 kJ/mol (16 kcal/mol) dissociation barrier toward decomposition into CO_2 and N_2O . Nitroisocyanate, O_2N-NCO , was 121 kJ/mol (29 kcal/mol) higher in energy than nitrous carbonate and has a 46 kJ/mol (11 kcal/mol) barrier in the exothermic decomposition into CO_2 and N_2O , which involves formation of an intermediate four-membered cyclic form. Nitrofulminate has a higher C–N bond dissociation energy and is expected to be a more stable molecule than nitrosofulminate



Nitrofulminate was suggested as a potential energetic oxidizer. Another CN_2O_3 isomer, dinitrosocarbonyl, $OC(NO)_2$, has a low stability toward decomposition into CO and NO radicals.

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Nitroaromatic Compounds

Coverage of nitro compounds had to be spread out over four chapters because a single chapter on the topic would have been very large and would have made it more difficult for readers to find information on a specific compound. In addition, arranging 30 chapters among 5 subvolumes in such a way that each subvolume was about the same size represented a formidable challenge. A book with smaller chapters made our task easier.

The other chapters in the group of nitro compounds are entitled “Nitro Compounds,” “Nitroaliphatic Compounds,” and “Nitromethanes.”

1 Nitroaromatic Compounds (Nitroarenes)

Nitroaromatic compounds, aromatic C-nitro compounds, also called nitroarenes, are nitro compounds where the nitro group(s) is (are) attached to an aromatic ring, typically a benzene ring. Because the benzene ring is more stable than some aliphatic chains with similar chemical compositions, nitroaromatic compounds are thermally more stable and in several instances more energetic than nitroaliphatic compounds. In spite of this, few nitroaromatic compounds are used in rocket propellants, and they may be used, if at all, as energetic additives in solid propellants. The main applications of nitroaromatic compounds are in explosives, not in rocket propellants.

The current chapter on nitroarenes is by far not as detailed as the earlier chapter on nitroalkanes. This is partially because there are sufficient other sources of information on this class of chemicals. A few of those are listed here as examples. The summary paper by Sikder and Sikder [1] contains numerous examples of nitroaromatic thermally stable explosives, such as hexanitrostilbene (HNS), 1,3,7,9-tetranitro-6H-benzotriazole[2,1-a]benzotriazole-5-onium inner salt (Z-TACOT), dipicramide (DIPAM), 2,2',2'',4,4',4'',6,6',6''-nonanitro-1,1':3',1''-terphenyl (NONA), 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX), styphnic acid, picryl-substituted heterocyclic compounds, and others.

An excellent summary of the chemistry of nitroaromatic compounds with 305 references is Chapter 4 in the book by Agrawal and Hodgson 2007 [2]. It lists a wide array of methods for preparing nitroaromatic compounds, which are the mainstay of industrial and military explosives production, including 2,4,6-trinitrotoluene (TNT), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), HNS, picric acid, and many others.

1.1 Preparation of Nitroaromatic Compounds

The methods of preparation and a comparison of physical properties presented in the following sections apply to all nitroaromatic compounds as a group. Methods for specific nitroaromatic compounds will be discussed further down, one at a time.

Nucleophilic aromatic substitution is the main route to aromatic nitro compounds. The nitrating agent is mixed acid of nitric acid and sulfuric acid.

1.2 Physical Properties of Nitroaromatic Compounds

1.2.1 Melting Points of Nitroaromatic Compounds

Crystalline compounds melt when the thermal energy exceeds the intermolecular crystal bond strength. This process can be modeled by computer programs based on group additivity methods and gives fairly accurate predictions for nitroaromatic compounds [3–6]. Melting points depend on the number of hydrogen and nitrogen atoms as well as the contribution of some specific functional groups and the existence of ortho or para isomers in disubstituted benzene derivatives. Predicted melting points had an average deviation of 5%.

1.2.2 Densities of Nitroaromatic Compounds

Because nitroaromatic compounds are usually well crystallized and the densities have been measured accurately, these chemicals have often been used as model compounds to test the accuracy of predictive methods for the densities of energetic compounds. Different methods, such as group additivity methods and quantum mechanical approaches, can be used to estimate the density of many energetic organic compounds, in particular nitroaromatics. Since the reliable prediction of the density of energetic compounds is important for estimating their explosive performance, different approaches have been developed to predict the densities of energetic compounds. An improved method for the prediction of the density of energetic compounds using their molecular structure considered the fact that the presence of specific polar groups and molecular moieties may enhance or reduce the density of molecular packing [4, 7–9].

1.2.3 Thermodynamic Properties of Nitroaromatic Compounds

Similar density functional theory and *ab initio* methods are available to predict the thermodynamic properties of nitroaromatic compounds from their molecular structure.

1.2.3.1 Enthalpy of Formation of Nitroaromatic Compounds

The heats of formation of various aromatic nitro compounds were calculated with semi-empirical molecular orbital theory and molecular mechanics methods [10]. The enthalpies of formation ΔH_f° of energetic materials were predicted with sufficient accuracy to use ΔH_f° for energy hazard predictions. In the case of aromatic polynitro compounds, both methods may be able to calculate accurate ΔH_f° .

The heats of formation of nitrobenzenes and nitrotoluenes were calculated by quantum mechanical methods [11]. The accuracy of correlation for heats of formation between the theoretical calculations and experimental results was evaluated by a weighted least-squares multi-variable method. Based on these correlations, the heat of formation of some aromatic nitro compounds can be predicted accurately compared to the weighted least-squares multi-variable fitting to theoretical gas-phase and experimental crystal heats of formation for nitrobenzenes and nitrotoluenes. From these numbers, the heat of sublimation can be predicted theoretically. See also [12].

The ideal gas (**not** condensed phase!) thermodynamic properties of 29 nitro and nitrate compounds, high explosives such as TNT, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), and pentaerythritol tetranitrate (PETN), were predicted from spectroscopic data and compared to calorimetric results reported in the literature [13, 14]. The fundamental vibrations, the bond lengths, and the moments of inertia of all molecules were calculated using semi-empirical methods. The resulting thermodynamic properties were represented in polynomial form, ready for use in rocket propulsion I_{sp} calculations. The format used was the old NASA Chemical Equilibrium Compositions (CEC) polynomial format and consisting of two sets of polynomial coefficients for each species. The first set of seven coefficients represented the properties above 1000 K, and the second from 200 to 1000 K. Both polynomials gave the same values at 1000 K for the properties. The results are summarized in Table 1.

Table 1: Ideal gas thermodynamic properties of nitro compounds.

Gaseous (vapor) compound name	Formula	ΔH_f^{298} kJ/mol	S^{298} JK ⁻¹ mol ⁻¹	C_p^{300} JK ⁻¹ mol ⁻¹
RDX hexogen	C ₃ H ₆ N ₆ O ₆	+192.00	482.44	231.26
HMX octogen	C ₄ H ₈ (N—NO ₂) ₄	+187.86	568.83	276.66
Nitrobenzene	C ₆ H ₅ NO ₂	+68.53	348.80	121.06
<i>n</i> -Nitrohexane	C ₆ H ₁₃ NO ₂	-185.35		
1,3,5-Trinitrobenzene	C ₆ H ₃ (NO ₂) ₃	+62.34	485.34	206.45
2,4,6-Trinitrotoluene	C ₇ H ₆ (NO ₂) ₃	+24.10	501.32	215.23

Data source: [14]

One model assumed that the heat of formation of a nitroaromatic compound of composition $C_aH_bN_cO_d$ could be expressed as a correlation that depends on elemental composition and various structural and special functional group contributions. Condensed-phase heats of formation predicted using this method had a root mean square (RMS) deviation of 5.9 kcal/mol for 19 well-known organic nitroaromatic compounds [15–18].

Gas-phase enthalpies of formation of nitroarenes TNT and TATB were calculated using the G2, G3, G4, and correlation consistent composite approach (ccCA-PS3) quantum composite methods [19]. G3 and G4 calculations are typically close to one another, with a larger difference found between these methods and ccCA-PS3. Although there is significant uncertainty in experimental values, the mean absolute deviation between the average experimental value and calculations were 12, 6, 7, and 3 kcal/mol for G2, G3, G4, and ccCA-PS3, respectively.

1.2.3.2 Heat of Combustion of Nitroaromatic Compounds

Methods similar to those for the prediction of enthalpy of formation can also be used to predict the heat of combustion of nitroarenes and other nitro compounds [20].

1.2.3.3 Enthalpy of Fusion of Nitroaromatic Compounds

The heats of fusion of nitroaromatic carbocyclic energetic compounds can be predicted using some structural parameters, elemental composition, and the contribution of some specific polar functional groups [21, 22]. Predicted heats of fusion for 41 nitroaromatic carbocyclic compounds were compared with experimental data. Calculated heats of fusion had an RMS deviation of 3 kJ/mol for these energetic compounds. A similar method can be used to predict the enthalpy of sublimation of nitroaromatic compounds [23].

1.3 Chemical Properties of Polynitroarenes

1.3.1 Thermal Stability and Thermolysis of Polynitroarenes

The activation energies of 20 polynitroarenes determined by differential scanning calorimetry (DSC) were compared to the kinetic data of a gas evolution manometric method and detonation properties [24]. There was no clear correlation between these properties.

The values of activation energies E_p from differential thermal analysis (DTA) measurements for the low-temperature intervals at the beginning of thermal decomposition T_d of nitroaromatic compounds corresponded to the non-autocatalyzed start of thermolysis [25]. This was documented by the existence of relationships between the values of E_p/T_d ratios and the characteristics of molecular structure, namely, the moments of inertia of alkyl groups in *N*-alkyl-2,4,6-trinitroanilines. There also exist

relationships between the values of E_p/T_d ratios and the values of Arrhenius parameters resulting from a gas evolution manometric method applied to the thermolysis of polynitroarenes.

Seventy-three polynitro compounds were subjected to thermal decomposition measurements using a manometric method or DSC [26]. From the kinetic data of the initial stage of the decomposition, corresponding values were calculated of the natural logarithm of equilibrium constants of the activated complex ($\ln K$). A relationship was found between the values $\ln K$ and $\ln D$, where D was the detonation velocity at maximum theoretical density of the compounds. Taking into account the relationships between thermochemical kinetic characteristics from DTA and detonation characteristics of polynitroaromatic compounds, it was concluded that the initial steps of thermolysis and initial detonation reactions of organic polynitro compounds are identical.

The activation energy or the Arrhenius parameter E_a of thermolysis in the condensed state for different polynitroarenes can be expressed as a function of optimized elemental composition as well as the contribution by specific molecular structural parameters [27]. The method can predict E_a of thermolysis and has an RMS and average deviations of 13.79 and 11.94 kJ/mol, respectively, for 20 typical polynitroarenes with different molecular structures.

1.4 Safety Properties of Polynitroarenes

Although polynitroarenes are used mainly as explosives and not as rocket propellants, it is interesting to follow relationships between molecular structure and sensitivity to accidental explosions. Similar relationships may apply to other energetic materials that are used as rocket propellants. The sensitivity of polynitroarenes and nitramines to mechanical impact and electrostatic discharge can be correlated to their molecular structure.

1.4.1 Impact Sensitivities of Polynitroarenes

The impact sensitivities of organic high explosives are primarily functions of the rates of the thermal decomposition processes taking place in the narrow temperature spikes generated under the impact hammer. For classes of explosives with similar decomposition mechanisms, there appear to be statistically significant linear relationships (sensitivity/composition trends) between logarithmic 50% impact heights and oxygen balance. It was shown that polynitroaromatic explosives containing a C—H linkage in the α -position to the aromatic ring are more sensitive as a class than explosives lacking such a linkage [28]. The products of thermal decomposition of TNT indicated a preferred site of inter- and intramolecular oxidative attack to be at the α C—H linkage.

The impact reactivity of 22 polynitroarenes was expressed as the drop energy, E_{drop} , required for 50% initiation probability. Relationships have been found between the E_{drop} values and heats of fusion, on the one hand, and ^{13}C NMR chemical shifts of carbon atoms in reaction centers, on the other [3].

In a similar study, published data of impact sensitivity of 33 polynitro compounds were expressed as the drop energy required for 50% initiation probability, and a logarithmic relationship was found between the E_{drop} values and heats of fusion of these compounds [29]. An analogous application of heats of sublimation has not given convincing results.

Simple correlations for the prediction of the impact sensitivity of $\text{C}_a\text{H}_b\text{N}_c\text{O}_d$ explosives using molecular weight and structure information were applied to test different polynitroaromatics, benzofuroxans, and nitramines, and the results were compared with experimental data and some models of complex quantum mechanics computation [30, 31]. The predicted impact sensitivities of 46 explosives had a RMS of deviation from experiment of 24 cm, which showed good agreement with respect to measured values compared to five different quantum mechanical models. The method can also be applied to polynitroheteroarenes [32]. Besides for polynitroarenes, similar relationships were established for nitropyridines, nitroimidazoles, nitropyrazoles, nitrofurazanes, nitrotriazoles, nitropyrimidines, benzofuroxans, nitramines, and nitroaliphatics containing other functional groups and alkyl nitrate energetic compounds [33].

1.4.2 Impact and Friction Sensitivities of Polynitroarenes

The impact and friction sensitivities of polynitroarenes are listed in Table 2. For additional data on impact sensitivity of polynitroaromatics see [34, 35].

Table 2: Impact and friction sensitivities of polynitroarenes.

Compound name	Impact sensitivity	Friction sensitivity, pistil load	
	N m	N	kg _f
Picric acid	7.4	no reaction at 353	no reaction at 36
Dinitrotoluene	no reaction at up to 50	no reaction at up to 353	no reaction at up to 36
Dinitrobenzene	39	no reaction at up to 353	no reaction at up to 36
1,3,5-Trinitrobenzene	7.4	no reaction at up to 353	no reaction at up to 36
Styphnic acid	7.4	no reaction at up to 353	no reaction at up to 36
2,4,6-Trinitrotoluene	15	no reaction at up to 353	no reaction at up to 36

Data source: Meyer, Koehler, and Homburg, 6th Ed. (2007); in the following abbreviated as MKH [36]

1.4.3 Electrostatic Discharge Sensitivities of Polynitroarenes

A simple correlation was introduced for predicting the electric spark sensitivity of nitroaromatic compounds. This approach was based on the number of carbons and hydrogens as well as the ratio of hydrogens to oxygens and the presence of certain groups, i.e., alkyl or alkoxy groups, attached to an aromatic ring [37]. The model was optimized using a set of 17 polynitroaromatic explosives as model set and then applied to 14 explosives from a variety of chemical families in order to assess the predictive capability of this method. Predicted results were reasonably close to the measured values for both model and test sets.

1.4.4 Explosive Performance of Polynitroarenes

A method proposed for quickly estimating heats of detonation of aromatic energetic compounds does not use any experimental or computed data of energetic materials. The methodology assumes that the heat of detonation of an energetic CHNO compound can be obtained from the number of nitrogens, ratios of oxygen to carbon and hydrogen to oxygen, and the contribution of some specific functional groups [38]. Predicted heats of detonation of pure energetic compounds with the product H_2O in the liquid state for 31 aromatic energetic compounds had an RMS of deviation of 0.32 kJ/g from experiment.

1.4.4.1 Detonation Pressure of Polynitroarenes

The Trauzl lead block indentations of typical nitroarenes are summarized in Table 3.

Table 3: Trauzl lead block indentations of polynitroarenes.

Compound	Lead block indentation, $\text{cm}^3/10 \text{ g}$
TATB	175
2,4-Dinitrotoluene	240
<i>m</i> -Dinitrobenzene	242
2,4,6-Trinitrotoluene	300
Picric acid	315
1,3,5-Trinitrobenzene	325
Tetryl	410

Data source: [36]

1.4.4.2 Detonation Velocity of Polynitroarenes

The confined detonation velocities of typical nitroarenes are summarized in Table 4.

Table 4: Detonation velocities of polynitroarenes.

Compound	Detonation velocity, m/s	Loading density, g/cm ³
2,4-Dinitrotoluene	5200	1.5
<i>m</i> -Dinitrobenzene	6100	1.47
2,4,6-Trinitrotoluene	6900	1.60
1,3,5-Trinitrobenzene	7300	1.71
TATB	7350	1.80
Picric acid	7350	1.7
Tetryl	7570	1.71

Data source: [36]

2 Nitrobenzenes

2.1 Nitrobenzene

Nitrobenzene, also known as mononitrobenzene, C₆H₅NO₂, CAS RN [98-95-3] is a light yellow liquid with a distinguishing odor of bitter almonds. Nitrobenzene does not contain sufficient energy to be used as a rocket propellant. It has been used as a fuel or solvent or desensitizer for other nitro compounds and alkyl nitrates and is an intermediate in the synthesis of many other aromatic compounds. The physical properties of nitrobenzene are summarized in Table 5.

Table 5: Physical properties of nitrobenzene.

Property	SI units	Other units	References
Molecular mass	123.1094		
Freezing point	278.9 ± 0.2 K	+5.8 °C	[39]
Boiling point	484 ± 2 K	211 °C	[39]
Density	1.2037 at 293 K		[40]
Vapor pressure	133 Pa at 317 K	1 mm Hg at 44 °C	[40]
Enthalpy of formation, liquid	+12.5 ± 0.54 kJ/mol	+2.99 kcal/mol	[39]
Refractive index, n _D ²⁰		1.5562 at 20 °C	[40]
Heat of combustion	3093 kJ/mol	739.2 kcal/mol	[41]
Heat of combustion	3088 kJ/mol	738 kcal/mol	[39]

2.2 Dinitrobenzenes

There are three stereoisomeric dinitrobenzenes, *o*-, *m*-, and *p*-dinitrobenzene, $C_6H_4(NO_2)_2$, $C_6H_4N_2O_4$. They are more energetic than nitrobenzene but have not been used as rocket propellants. The oxygen balance is -95.2% and the nitrogen content is 16.67% N. The most commonly used dinitrobenzene is the *meta* isomer, *m*-dinitrobenzene, 1,3-dinitrobenzene, CAS RN [99-65-0]. It exists in the form of pale yellow needles at room temperature. Dinitrobenzene is sparingly soluble in water. It is prepared by direct nitration of benzene or nitrobenzene and is an insensitive explosive. For the purposes of official transport regulations, the sensitivity and reactivity of dinitrobenzene are just on the limit between high-explosive and the non-dangerous zone. Dinitrobenzenes are toxic and produce cyanosis. The maximum permissible concentration of *m*-dinitrobenzene in workplace air is 1 mg/m³. The compound is of little interest as an explosive, but mixtures of *m*-dinitrobenzene and nitric acid have been used as explosives. The physical properties of *m*-dinitrobenzene are listed in Table 6.

Table 6: Physical properties of *m*-dinitrobenzene.

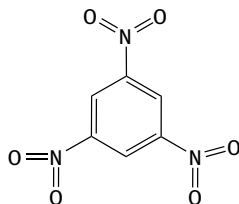
Property	SI units		Other units	References
Molecular mass	168.1070 g/mol	5.9486 mols/kg		
Melting point	362.7 K		89.6 °C = 193.3 °F	[36]
Density	1.575 kg/dm ³		1.575 g/cm ³	[36]
Enthalpy of formation	-27.2 kJ/mol	-161.8 kJ/kg	-38.7 kcal/kg	[36]
Heat of combustion	2907 kJ/mol	17293 kJ/kg	694.7 kcal/mol	[41]

In the Trauzl lead block test, the cavity enlargement was 242 cm³/10 g. The detonation velocity of steel-wall-confined samples was 6100 m/s = 20 000 ft/s at $\rho = 1.47$ g/cm³. When heated, dinitrobenzene samples evaporated at 564 K = 291 °C = 556 °F but there was no deflagration. The drop weight impact sensitivity was 39 Nm and the friction sensitivity test showed no reaction up to the maximum load of 353 N (in the Bundesanstalt für Materialforschung und -prüfung (BAM) apparatus).

2.3 Trinitrobenzenes

There are three trinitrobenzene isomers, depending on the distribution of the three nitro groups on the benzene ring in symmetrical, asymmetrical, or vicinal positions. The most frequently used symmetrical 1,3,5-trinitrobenzene, also known as $C_6H_3(NO_2)_3$,

$C_6H_3N_3O_6$, TNB, CAS RN [99-35-4] contains nitro groups in the 1, 3, and 5 positions of the benzene ring:



1,3,5-TNB can be synthesized by converting phloroglucinol into its trioxime by reaction with aqueous hydroxylamine followed by oxidation of the trioxime product with 90% nitric acid [42].

2.3.1 Physical and Chemical Properties of Trinitrobenzenes

1,3,5-Trinitrobenzene forms greenish-yellow crystals that melt at 396.3 K (123.2°C = 253.7°F) [43]. In spite of the fact that TNB explosive yield and detonation velocity are higher than those of TNT, TNB has not found practical application as an explosive because it is more difficult to prepare than TNT. For the same reason, it will not find applications as a rocket propellant ingredient. In the solid state, TNB exists in two phases. The physical properties of TNBs are listed in Table 7.

Table 7: Physical properties of trinitrobenzenes.

Compound	1,3,5-Trinitrobenzene		1,2,4-Trinitrobenzene		References
	SI units	Other units	SI units	Other units	
CAS RN	99-35-4		610-31-1		
Molecular mass	213.1045 g/mol	4.6925 mol/kg	213.1045 g/mol	4.6925 mol/kg	
Melting point	396.3 K	123.2°C	334 K	61°C	[44]
Melting point	394.2 K	121.1°C			[39]
Density	1.6888 g/cm ³	at 298 K	1.730 g/cm ³	at 298 K	[44]
Enthalpy of formation	-35.5 kJ/mol	-8.49 kcal/mol	+19.96 kJ/mol	+4.77 kcal/mol	[44]
Enthalpy of formation	-37 ± 1 kJ/mol	-8.84 kcal/mol			[39]
Heat of fusion	4.0 ± 0.1 kJ/mol	0.96 kcal/mol			[39]
Heat of combustion	2777 kJ/mol	663.7 kcal/mol	2819 kJ/mol	673.7 kcal/mol	[41]

2.3.2 Amino-trinitrobenzenes

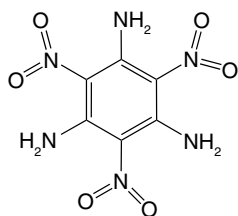
The introduction of amino groups into a benzene ring that already has several nitro groups is one of the simplest approaches to enhancing the thermal stability of explosives. This is evident from a comparison of monoamino-2,4,6-trinitrobenzene (MATB), 1,3-diamino-2,4,6-trinitrobenzene (DATB), and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), where the order of increasing thermal stability is MATB < DATB < TATB [45].

2.3.2.1 1,3,5-Triamino-2,4,6-trinitrobenzene

1,3,5-Triamino-2,4,6-trinitrobenzene, also known as 1,3,5-benzenetriamine 2,4,6-trinitro-; *sym*-triaminotrinitrobenzene, $C_6(NH_2)_3(NO_2)_3$, $C_6H_6N_6O_6$, TATB, CAS RN [3058-38-6], has excellent thermal stability all the way up to the range 533–563 K (260–290 °C). TATB is an explosive with unusual insensitivity and heat resistance, and at the same time respectable performance, which makes it a prime-usage, thermally stable, and safe explosive [46]. 1,3,5-Triamino-2,4,6-trinitrobenzene is an explosive with exceptional thermal stability. There is evidence of strong intermolecular and intramolecular hydrogen bonding in TATB. Its thermal stability is the result of a sandwiched crystal structure in which both hydrogen bonding and π - π -interactions determine the arrangement of molecules in the crystal.

There is also the trinitrated diaminobenzene, diaminotrinitrobenzene, DATB, with a CAS RN of [1630-08-6].

There are no known uses of TATB as a rocket propellant. It resists heat up to 573 K (300 °C = 570 °F) and is relatively insensitive to friction and impact, but the critical diameter is large. TATB can be obtained by nitration of trichlorobenzene and conversion of the trinitrotrichlorobenzene to TATB. The unique structural features of the TATB molecule are as follows: (1) extremely long C—C bonds in the benzene ring, (2) very short C—N (amino) bonds, and (3) six furcated hydrogen bonds:



The net result is that TATB lacks an observable melting point and has a low solubility in all common solvents except concentrated H_2SO_4 .

TATB is not used as a rocket propellant, but its unique properties may lead propellant chemists to more energetic and thermally more stable propellant ingredients. The physical properties of TATB are listed in Table 8. The published data for the enthalpy of formation of TATB vary over a wide range.

Table 8: Physical properties of triaminotrinitrobenzene.

Property	SI units		Other units	References
Molecular mass	258.1484 g/mol	3.8737 mol/kg	3.8737 mol/kg	
Melting point	decomposes before melting			
Density	1.938 g/cm ³			[36]
Enthalpy of formation	-140 ± 5.0 kJ/mol	-542 ± 19 kJ/kg	-33.46 kcal/mol	[47]
Enthalpy of formation	-154 kJ/mol	-596 kJ/kg	-36.91 kcal/mol = -143 cal/g	[48, 49]
Enthalpy of formation	-139.7 kJ/mol	-541.3 kJ/kg	-33.40 kcal/mol	[36]
Heat of combustion	3079 ± 2 kJ/mol	11927 ± 8 kJ/kg	735.9 ± 0.5 kcal/mol	[47]

In the lead block test the enlargement of the cavity was 175 cm³/10 g. The detonation velocity in steel confinement was 7350 m/s at $\rho = 1.80$ g/cm³. The deflagration point was 657 K = 384 °C, which is one of the highest known for any high explosive. The impact sensitivity was 50 Nm, and the friction sensitivity test showed no reaction at the maximum pistil load of 353 N (BAM test apparatus).

Table 9 lists properties of TATB in comparison to those of other common explosives.

2.4 Hexanitrobenzene

Hexanitrobenzene is one of the compounds that contain only a carbon skeleton and nitro groups. These compounds are called nitrocarbons. Other compounds with similar structures are tetranitromethane (TNM), hexanitroethane, octanitrocubane, or decanitrobiphenyl. The density of hexanitrobenzene is 1.988 g/cm³. There is even a book devoted to these types of chemicals [51].

2.5 Decanitrobiphenyl

Decanitrobiphenyl is one of the compounds that contain only a carbon skeleton and nitro groups. The synthesis starts with *p*-chlorobenzoic acid over seven steps [52]. These compounds are called nitrocarbons. Other compounds with similar CNO compositions without any hydrogen are TNM, hexanitroethane, hexanitrobenzene, or octanitrocubane.

Table 9: Properties of TATB in comparison to those of other explosives.

Compound	Compound name	Gross formula	T _{dec} °C	ρ g/cm ³	ΔH _f kJ/mol	OB %	IS J	P _{CJ} GPa	V _{Det} m/s	FS N
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene	C ₆ H ₆ N ₆ O ₆	330	1.93	-154.2	-55.8	50	31.2	8114	>360
NTO	3-Nitro-1,2,4-triazol-5-one	C ₂ H ₂ N ₄ O ₃	275	1.92	-237.8	-24.6	>40	31.1	8558	360
CL-20	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	C ₆ H ₆ N ₁₂ O ₁₂	210	2.04	438.2	-10.9	4	43	9650	94
RDX	1,3,5-Trinitro-1,3,5-triazacyclohexane	C ₃ H ₆ N ₆ O ₆	230	1.82	92.6	-21.6	7	34.9	8748	120

Data source: [50]
Legend: OB = oxygen balance; IS = impact sensitivity; FS = friction sensitivity

3 Nitrotoluenes

Mononitrotoluene is a pale yellow liquid with empirical formula $C_7H_7O_2N$. There are three isomers, of which only the *ortho* and *para*-isomers can yield pure 2,4,6-trinitrotoluene on further nitration. Mononitration of toluene yields mostly the *ortho* compound, as well as 4% of the *meta*- and about 33% of the *para*- compound. Nitrotoluene is of importance as an intermediate or precursor for in the manufacture of dinitrotoluene (DNT) and TNT.

3.1 2,4-Dinitrotoluene

There are four dinitrotoluenes. The most important one is 2,4-dinitrotoluene, also known as 2,4-DNT, DNT, 1-methyl-2,4-dinitrobenzene, benzene 1-methyl-2,4-dinitro-, $C_7H_6N_2O_4$, CAS RN [121-14-2]. The oxygen balance is -114.4% , and the nitrogen content is $15.38\%N$. 2,4-DNT is an intermediate not only in the production of 2,4,6-trinitrotoluene, but also in the production of toluene diisocyanate, an important crosslinking agent for polyurethane polymers, which are used as binders in solid rocket propellants and many other industrial applications. DNT is produced in large quantities, and as a result, poor housekeeping has caused environmental pollution in the proximity of current and former production sites. Environmental cleanup efforts are in progress at many current and former DNT production sites and various cleanup techniques are being evaluated.

DNT has been used as an ingredient in castable explosives for warheads and bombs, although its energy content is less than that of trinitrotoluene. DNT has been proposed or used temporarily in a few rocket propellant and pyrotechnic formulations, mostly patent applications that never matured to actual applications on an industrial scale.

There is so much information on DNT production, applications, and disposal that it would overflow the scope of this book. Sufficient information on DNT is available from other sources. For that reason we abbreviated DNT from the usual data collection format in this book, and the same rationale was applied to 2,4,6-TNT, which is only briefly discussed in the following section.

The isomers 2,3-DNT and 3,5-DNT are rarely formed and have no significance as energetic materials or precursors. At worst, they are encountered as contaminants in 2,4-DNT and 2,4,6-TNT.

3.1.1 Physical Properties of 2,4-Dinitrotoluene

The physical properties of 2,4-dinitrotoluene are summarized in Table 10. See also [53].

Table 10: Physical properties of 2,4-dinitrotoluene.

Property	SI units		Other units	References
Molecular mass	182.1335 g/mol		5.4905 mols/kg	
Melting point	341 K		68 °C	[39]
Density	1.521 g/cm ³			[36]
	1.317 g/cm ³		0.0476 lb/in ³	[49]
Vapor pressure at melting point	0.11 mbar		0.08 mm Hg	[36]
Enthalpy of formation	-66.4 ± 3.0 kJ/mol	-364 ± 16 kJ/kg	-15.87 ± 0.7 kcal/mol	[39]
	-68.2 kJ/mol	-374.7 kJ/kg	-16.31 kcal/mol	[36]
	-54.1 kJ/mol	-297 kJ/kg	-71 cal/g	[49]
Heat of combustion	3552 kJ/mol	19.5 kJ/g	849 kcal/mol	[41]
Heat of fusion	20.12 kJ/mol	0.11 kJ/g	4.81 kcal/mol	[39]
	19.83 kJ/mol	109 kJ/kg	4.74 kcal/mol	[36]
Heat of sublimation at 270–315 K	94.7 ± 2.3 kJ/mol	520 ± 13 kJ/kg	22.63 ± 0.55 kcal/mol	[39]

The vapor pressures of 2,4,6-TNT, 2,4-DNT, and 2,6-DNT have been measured by an electron-capture gas-chromatographic method in a temperature range of 287.15 to 329.65 K for TNT, 277.15 to 344.15 K for 2,4-DNT, and 277.15 to 323.15 K for 2,6-DNT [54]. The temperature dependence of the vapor pressure can be expressed by the following equations:

$$\text{TNT: } \log \left(\frac{p}{\text{Torr}} \right)_{10} = (12.31 \pm 0.34) - (5175 \pm 105) \frac{K}{T}$$

$$\text{2,4-DNT: } \log \left(\frac{p}{\text{Torr}} \right)_{10} = (13.08 \pm 0.19) - (4992 \pm 59) \frac{K}{T}$$

$$\text{2,6-DNT: } \log \left(\frac{p}{\text{Torr}} \right)_{10} = (13.99 \pm 0.18) - (5139 \pm 52) \frac{K}{T}$$

The values for the enthalpy of sublimation are $\Delta H_{\text{sub}}(\text{TNT}) = (23.7 \pm 0.5) \text{ kcal/mol}$, $\Delta H_{\text{sub}}(\text{2,4-DNT}) = (22.9 \pm 0.3) \text{ kcal/mol}$, and $\Delta H_{\text{sub}}(\text{2,6-DNT}) = (23.5 \pm 0.2) \text{ kcal/mol}$. The indicated uncertainties are standard errors.

In the Trauzl lead block, the indentation increase of DNT was 240 cm³/10 g. In the BAM impact sensitivity test at the maximum rating of the machine at 50 Nm there was no reaction. In the BAM friction sensitivity test there was no reaction at the maximum pistil load of 353 N.

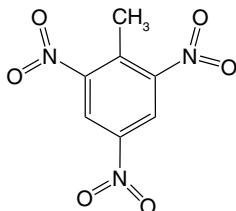
The critical diameter of 2,4-DNT was between 3.8 and 5.04 cm. The ideal detonation velocity as a function of density can be calculated from

$$v_D = 4125 + 2270(\rho - 1.0)$$

where v_D is the detonation velocity in m/s and ρ is the loading density in g/cm³.

3.2 2,4,6-Trinitrotoluene

2,4,6-Trinitrotoluene, also known as *sym*-trinitrotoluene, TNT, C₇H₅N₃O₆, CAS RN [118-96-7] is not used as a rocket propellant because it is an explosive. The oxygen balance is -73.9% and the nitrogen content is 18.50% N. It may be used as an additive in rocket propellants as long as the concentration does not exceed 5 mass-% (to stay on the safe side):



TNT is produced by the nitration of toluene with mixed nitric and sulfuric acid in several steps. The trinitration step needs high concentrated mixed acids with free SO₃. Already around 1902, the Germans and the British had experimented with TNT, first prepared by Wilbrand in 1863. Pure 2,4,6-TNT was prepared in 1880 by Hepp, and its structure was established in 1883 by Claus and Becker. By 1914, TNT had become the standard explosive for all armies during World War I, replacing picric acid in this application. The use of a mixture of TNT and ammonium nitrate (AN), called *amatol*, became widespread to relieve temporary shortages of TNT. TNT is underoxidized (oxygen balance -73.9%) so that the addition of AN as an oxidizer results in near-stoichiometric compositions with higher energy output. The physical properties of TNT are summarized in Table 11. See also [55, 56].

The detonation velocity of confined TNT was 6900 m/s at a packing density of 1.60 g/cm³. In the Trauzl lead block, the indentation increase caused by TNT was 300 cm³/10 g. In the BAM impact sensitivity test the 50% point was at 15 Nm. In the BAM friction sensitivity test there was no reaction at the maximum pistil load of 353 N.

Table 11: Physical properties of 2,4,6-trinitrotoluene.

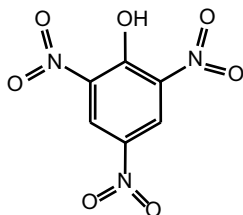
Property	SI units		Other units		References
Molecular mass	227.1311 g/mol		4.4027 mol/kg		
Melting point	355.1 K		83.0 °C		[39]
Density	1.654 g/cm ³				[36]
Vapor pressure at melting point	0.057 mbar		0.04 mm Hg		[36]
Enthalpy of formation	-63.2 ±	-278 ±	-15.10 ±	-66.4 ±	[47]
	5.0 kJ/mol	22 kJ/kg	1.2 kcal/mol	5.2 cal/g	
	-67.07 kJ/mol	-295.3 kJ/kg	-16.03 kcal/mol	-70.58 cal/g	[36]
	-75.07 kJ/mol	-330.5 kJ/kg	-17.94 kcal/mol	-79 cal/g	[49]
Heat of combustion	3410 ±	15013 kJ/kg	815 ±	3588 kcal/kg	[39]
	20 kJ/mol		4.8 kcal/mol		
	3418 kJ/mol	15048 kJ/kg	816.9 kcal/mol	3597 kcal/kg	[41]
Heat of fusion	23.43 kJ/mol	103.1 kJ/kg	5.60 kcal/mol	24.6 kcal/kg	[39]

4 Nitrophenols

The heats of combustion of *o*-, *m*-, and *p*-nitrophenol, C₆H₄OH(NO₂), are 2883, 2863, and 2871 kJ/mol (689.1, 684.4, and 686.2 kcal/mol), respectively. The heat of combustion of 2,4-dinitrophenol, C₆H₃OH(NO₂)₂, is 2711 kJ/mol (648 kcal/mol) [41]. Nitrophenols have been used as blocking agents for polymers in liners for solid propellant rocket motors.

4.1 2,4,6-Trinitrophenol (Picric Acid)

2,4,6-Trinitrophenol, picric acid, also known as C₆H₂OH(NO₂)₃, C₆H₃N₃O₇, CAS RN [88-89-1] is a very sensitive explosive that has been the cause of numerous accidents in munitions factories and munitions storage magazines. It is not suitable as a rocket propellant:



4.1.1 History of Picric Acid Usage

In 1885, Turpin found picric acid to be a suitable explosive as a replacement for black powder. In 1888, black powder was replaced by picric acid in British munitions under the name Lyddite. In Russia, Panpushko prepared picric acid in 1894 and soon realized its potential as an explosive. Eventually, picric acid and its salts were accepted in many industrialized countries as the basic explosive for some military uses and were used for several decades until eventually being replaced by TNT. Picric acid has been used as a dye for fabrics and as an analytical reagent for identification of amino compounds, typically for naturally occurring alkaloids.

Various picrates of heavy metals are used as primary, stab-sensitive explosives in percussion caps due to their high impact sensitivity and detonating power. The ammonium salt of picric acid has been used as an explosive for the filling of artillery shells, similar to the parent acid itself.

4.1.2 Properties of Picric Acid

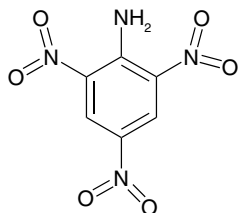
Picric acid forms yellow crystals that are soluble in water. With a molecular mass of $229.1 \text{ g/mol} = 4.365 \text{ mol/kg}$, the enthalpy of formation is $-944.3 \text{ kJ/kg} = -216.3 \text{ kJ/mol} = -51.7 \text{ kcal/mol} = -225.7 \text{ kcal/kg}$. The heat of combustion of 2,4,6-trinitrophenol is $2599 \text{ kJ/mol} = 621.1 \text{ kcal/mol}$ [41].

4.2 Styphnic Acid

2,4,6-Trinitro-1,3-benzenediol, also known as styphnic acid, trinitroresorcinol, $\text{C}_6\text{H}(\text{OH})_2(\text{NO}_2)_3$, $\text{C}_6\text{H}_3\text{N}_3\text{O}_8$, CAS RN [82-71-3] forms yellow crystals. The compound can be used as a yellow dye for fabrics similar to picric acid. Styphnic acid can be prepared by the nitration of resorcinol with a mixture of nitric and sulfuric acids. Several styphnates are used as additives for solid propellant formulations. Lead styphnate is stab-sensitive and can be used in percussion initiators and in blasting caps. Styphnates are sometimes called trinitroresorcinates or tricinates.

5 Picramide

2,4,6-Trinitroaniline, also known as picramide, $\text{C}_6\text{H}_4\text{N}_4\text{O}_6$, CAS RN [489-98-5] can be prepared by reacting trinitrochlorobenzene with ammonia or by nitration of 4-nitroaniline:



It is a very sensitive explosive with a detonation velocity of 7300 m/s at $\rho = 1.72 \text{ g/cm}^3$ and is not used as a rocket propellant. Picramide has a molecular mass of 228.12 g/mol = 4.384 mol/kg, density of 1.792 g/cm^3 , and a melting point of 461 K = 188 °C = 370 °F. The heat of formation is $-368.1 \text{ kJ/kg} = -84.0 \text{ kJ/mol} = -20.1 \text{ kcal/mol} = -88.0 \text{ kcal/kg}$.

If one combines two picramide entities as in a biphenyl compound, one obtains 3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl, dipicramide, DIPAM, CAS RN [17215-44-0], which is a powerful explosive.

6 Tetryl

2,4,6-Trinitro-phenylmethylnitramine, also known as tetryl, tetranitromethylanilin, *N*-picryl-*N*-methylnitramine; benzenamine, *N*-methyl-*N*,2,4,6-tetranitro-; $\text{C}_7\text{H}_5\text{N}_5\text{O}_8$, CAS RN [479-45-8], with a molecular mass of 287.14 g/mol = 3.483 mol/kg, is a primary explosive and often used in blasting caps and primers. The detonation velocity is 7570 m/s at $\rho = 1.71 \text{ g/cm}^3$. The lead block indentation is $410 \text{ cm}^3/10 \text{ g}$. It is not used in rocket propellants. Tetryl has a density of 1.73 g/cm^3 , a melting point of 402.6 K = 129.5 °C = 265 °F, a heat of formation of $+69.7 \text{ kJ/kg} = +20.0 \text{ kJ/mol} = +4.78 \text{ kcal/mol} = +16.7 \text{ kcal/kg}$, and a heat of fusion of $19.1 \text{ kcal/kg} = 5.48 \text{ kcal/mol} = 1.31 \text{ kcal/mol} = 80 \text{ kJ/kg}$. Other sources gave a heat of fusion at 400.5 K of $\Delta H_{\text{fus}} = 6.18 \pm 0.07 \text{ kcal/mol}$ and a heat of decomposition at 445 K of $-94 \pm 2 \text{ kcal/mol}$.

7 Nitronaphthalenes

Nitronaphthalenes, ranging from mononitronaphthalene to tetranitronaphthalene, and nitronaphthols, ranging from mononitronaphthol to tetranitronaphthol, are described in detail in Fedoroff's *Encyclopedia of Explosives and Related Items*, Vol. 8, p. N7-N20. Nitronaphthalenes have been evaluated as additives to other, more commonly used explosives like TNT to lower the melting point for castable explosives. There are no advantages to the use of nitronaphthalenes as rocket propellants.

The heats of combustion of nitronaphthalene, 1,5-dinitronaphthalene $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$, and trinitronaphthalene $\text{C}_{10}\text{H}_5(\text{NO}_2)_3$ are 4981, 4831, and 4641 kJ/mol (1190.5, 1154.6, and 1109.3 kcal/mol), respectively [12, 41].

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Nitro Compounds

The chapters in *Encyclopedia of Oxidizers*, deal with nitro compounds and nitric acid esters, also called nitrate esters. The topic of nitro compounds had to be distributed over four subchapters, because a single chapter would have been very large, which would have made it more difficult for readers to find information on a specific compound; in addition, it would have been difficult to arrange 30 chapters among 5 subvolumes in such a way that each subvolume is about the same size. That spatial arrangement was made easier by dealing with smaller chapters.

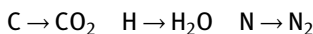
This chapter, “Nitro Compounds,” serves as an introduction to the individual chapters, titled “Nitromethanes,” “Nitroaliphatic Compounds,” and “Nitroaromatic Compounds,” and to some extent it also relates to the chapter on nitrate esters. Very few of these compounds contain excess oxygen and are properly listed in this volume under oxidizers. Even fewer compounds are exactly balanced for combustion to carbon dioxide, nitrogen, and water, leaving behind neither unused oxygen nor unburned hydrogen or carbon. The majority of nitro compounds discussed here are oxygen deficient and would require additional oxygen to achieve complete combustion to carbon dioxide, nitrogen, and water. In practice, however, it is not necessary to achieve complete combustion to carbon dioxide because combustion to carbon **monoxide** may be sufficient to obtain a good rocket monopropellant. Nevertheless, oxygen balances are commonly calculated for complete combustion to carbon dioxide instead of partial combustion to carbon monoxide. Very few organic compounds are true oxidizers with excess oxygen beyond that consumed by burning structural carbon to CO or CO₂ and burning all attached hydrogen (if any) to water. Several organic true oxidizers are included in this chapter, but most of the others are underoxidized and would be better characterized as potential monopropellants or partially oxidized fuels than as oxidizers. We do not wish to separate this group of chemicals based on their oxygen balance, but we discuss their physical and chemical properties together here in the same oxidizer chapter. Many of these compounds undergo autodecomposition when heated, and many are sensitive to stimuli that will trigger explosions. Investigations of decomposition in an academic setting are discussed here, while actual applications as monopropellants in rockets, gas generators, or torpedoes will be discussed in *Encyclopedia of Monopropellants*.

1 General Properties of Nitro Compounds as a Family Group

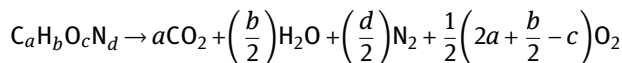
1.1 Oxygen Balance of Oxygen-rich Organic Compounds

An important parameter in judging organic oxidizers and monopropellants is their **oxygen balance**.

Oxygen balance is defined as the number of oxygen equivalents per unit of propellant when a sample burns or detonates and all atoms in the molecule finally convert into the following molecules as combustion products:



Therefore, when the empirical formula of a propellant is represented by $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$, the reaction for the combustion or explosion is expressed as follows:



Organic oxygen-rich compounds having the general formula $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$ are of interest as oxidizers for rocket propellants. Very few energetic materials happen to be stoichiometrically balanced, theoretically giving only carbon dioxide, nitrogen, and water as exhaust products. Most are underoxidized with an oxygen balance (*OB*) of < 100 , and a few (most of those discussed here) have an excess of oxygen ($OB > 100$), which qualifies them as organic oxidizers.

The definition of oxygen balance (*OB*, in %) is given by the following equation:

$$OB = \left(c - 2a - \frac{b}{2}\right) \frac{1600}{M}$$

where M is the molecular mass of the compound, a is the number of carbon atoms, b is the number of hydrogen atoms, and c is the number of oxygen atoms. The presence of nitrogen has no effect on the oxygen balance since it is assumed to be non-reactive and it all converts to dinitrogen N_2 . In calculating the molecular mass, one should use the natural isotope composition of hydrogen (including a natural distribution of deuterium) instead of the atomic mass of pure H, but the difference is only minor.

For $\text{C}_a\text{H}_b\text{O}_c\text{N}_d\text{X}_x$ compounds that contain halogens X (chlorine, fluorine) in addition to CHNO, the *OB* formula becomes

$$OB = \left(c + \frac{x}{2} - 2a - \frac{b}{2}\right) \frac{1600}{M}$$

Since solid propellants consist of binder, oxidizer, and some additives, x , y , z , and u in $\text{C}_x\text{H}_y\text{O}_z\text{N}_u$ are calculated from the molecular formula of each ingredient and the composition percentage. For example, $\text{C}_x\text{H}_y\text{O}_z\text{N}_u$ of the propellant composed of a mass ratio of oxidizer : binder of 80 : 20 is calculated using the molecular formula of the oxidizer ($\text{C}_a\text{H}_b\text{O}_c\text{N}_d$) and the binder ($\text{C}_e\text{H}_f\text{O}_g\text{N}_h$) as follows:

$$x = 0.8a + 0.2e$$

$$y = 0.8b + 0.2f$$

$$z = 0.8c + 0.2g$$

$$u = 0.8d + 0.2h$$

Halogens are oxidizers with an equivalence half that of oxygen. Use of a computer to calculate the possible number of organic chemical compounds containing only C, H, N, and O reveals that the number of theoretically possible compounds decreases from compounds with a small *OB* (fuels) to compounds with a large *OB* (oxidizers) [1]. For an initial survey, the search was restricted to compounds containing no more than a total of 12 atoms.

Sometimes the *OB* is also expressed as a fraction with the symbol λ instead of as a percent number.

1.2 Nomenclature of Nitro Compounds and Nitrate Esters

The commonly used names nitroglycerin and nitrocellulose are incorrect because these are not nitro compounds but the nitric acid esters of glycerol, correctly called glycerol trinitrate, and cellulose, correctly called cellulose nitrate, but hardly anybody recognizes them by those legal names. Compounds that contain an NO group connected to the organic moiety via the O atom instead of the N atom are not nitro compounds. They are the esters of nitrous acid HONO, sometimes called nitrites, and they are isomers of nitro compounds, but quite different in chemical properties and rarely used as rocket propellants. In nitrous acid esters (alkyl nitrites) and nitric acid esters (alkyl nitrates), the NO₂ or NO₃ group is connected to the organic skeleton by an oxygen —C—O—N— bridge. Alkyl nitrites are less stable and less energetic than alkyl nitrates and have not achieved any practical importance as propellant ingredients. Nitroalkanes and alkyl nitrates are very energetic compounds, sometimes so energetic and so sensitive (too energetic and too sensitive) that the borderline between liquid explosive and liquid propellant becomes blurred.

Nitro compounds are only those that contain the —NO₂ group connected to an organic rest via the N atom, and not via an —O— bridge. A different and special category are the nitramines, where the nitro group is connected to the organic skeleton, not directly but via a nitrogen atom that may or may not carry a hydrogen atom. These compounds have good thermal stability and form many of the high explosives currently in use. In combination with proper phlegmatizers and binders, they also form the key ingredients of a group of solid rocket and gun propellants called nitramine propellants. Nitramines as chemicals and propellant ingredients are discussed in *Encyclopedia of Liquid Fuels*, in the chapter “Nitramines.”

The three chapters “Nitromethanes”, “Nitroaliphatic Compounds” and “Nitroaromatic Compounds” contain information on the physical and chemical properties of nitro compounds, including information on their safety properties, which need to be known and respected, literally for the sake of survival. The mechanisms and kinetics of thermal and controlled catalytic decomposition and combustion will be discussed there, while applications as monopropellants are covered in *Encyclopedia of Monopropellants*. Safety properties such as detonability and shock sensitivity will be dis-

cussed in sections immediately following descriptions of the physical and chemical properties of these compounds. This will include a few sections on the detonability and shock sensitivity of mixtures containing liquid nitro compounds. Future parts of this *Encyclopedia of Rocket Propellants* will also contain extensive chapters on solid nitro compounds and nitrate esters such as those used in solid propellants and energetic additives, in particular the volume on double-base solid propellants, which are mostly derived from nitrated cellulose and glycerol. Other nitrate esters are used as energetic plasticizers for double-base propellants.

Nitro compounds and nitrate esters are produced by a variety of nitration reactions. Nitration is a fundamental chemical process by which less reactive hydrocarbons or alkanols are converted to energetic compounds. Nitration is an important chemical reaction not only for the production of rocket propellants and explosives but also for the chemical process industry in general, by which many intermediates are produced that are eventually converted to dyes, pharmaceuticals, polymers, or pesticides. Several books are available that summarize the kinetics and industrial applications of nitration reactions and that deal with nitration in general, not necessarily for the synthesis of propellants or explosives [2, 3].

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- [3] Albright, L. F., R. V. C. Carr, and R. J. Schmitt (Eds.), *Nitration; Recent laboratory and industrial developments*, *Am. Chem. Soc., ACS Symp. Series Vol. 623*, 281+xii pp. (1996); ISBN 9780841233935; <https://doi.org/10.1021/bk-1996-0623>

Nitrogen Dioxide

Coverage of nitrogen oxides had to be spread out over seven chapters because a single chapter on the topic would have been very large and would have made it more difficult for readers to find information on a specific compound. In addition, arranging 30 chapters among 5 subvolumes in such a way that each subvolume was about the same size represented a formidable challenge. A book with smaller chapters made our task easier.

The other six chapters in this series are titled “Nitrogen Oxides,” “Nitrous Oxide,” “Nitric Oxide,” “Dinitrogen Trioxide,” “Dinitrogen Tetroxide,” and “Dinitrogen Pentoxide.”

Nitrogen dioxide, NO_2 , CAS RN [10102-44-0], exists mostly as a gas as a product of dissociation of dinitrogen tetroxide or a product of oxidation of nitric oxide. Nitrogen dioxide is a free radical, which explains its high reactivity with a large number of compounds. It has an unpaired electron. When condensed, it dimerizes to form N_2O_4 and loses its red color.

Nitrogen commonly forms several different oxides with oxygen, depending on the state of oxidation of the central atom, nitrogen. The state of oxidation of nitrogen can be +1, +2, +3, +4, +5, or +6. The correct names of the six oxides are nitrous oxide, N_2O , nitric oxide, NO , dinitrogen trioxide, N_2O_3 , nitrogen dioxide, NO_2 , dinitrogen pentoxide N_2O_5 , and nitrogen trioxide NO_3 . The current chapter is on nitrogen dioxide, NO_2 , which is used mostly in its dimeric form, dinitrogen tetroxide, N_2O_4 , which can be stored as a liquid at room temperature. The state of oxidation of nitrogen in dinitrogen tetroxide is the same as that in nitrogen dioxide. Nitrogen forms at least six covalently bound oxides, N_2O , NO , N_2O_3 , NO_2 , N_2O_5 , and NO_3 , which are all thermodynamically unstable with regard to their tendency to decompose to dinitrogen and dioxygen. Nitrogen dioxide dimerizes by way of $\pi^*-\pi^*$ -interactions. Although all nitrogen oxides (in the gas phase) have positive enthalpies of formation, they still are not intrinsically unstable.

As far as rocket propellants are concerned, the first two oxides in this family of nitrogen oxides, nitric oxide and nitrous oxide, have not found the same widespread application as dinitrogen tetroxide and its mixtures with dinitrogen trioxide or nitric acid.

Many of the physical properties of pure NO_2 are difficult to determine because the gas may contain an equilibrium amount of N_2O_4 or even NO (at higher temperatures). At higher temperatures, NO_2 dissociates reversibly into nitric oxide, NO , and dioxygen, O_2 .

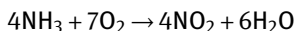
1 Natural Occurrence of Nitrogen Dioxide

Other than as a noxious atmospheric pollutant in Earth's atmosphere, nitrogen dioxide has been identified on other planets and in comets. In search of extraterrestrial resources that could be used as rocket propellants or sources of breathing oxygen, coming upon an extraterrestrial polar ice cap that consists mostly of frozen nitrogen dioxide and dinitrogen tetroxide would be a real bonanza.

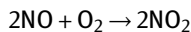
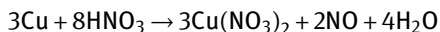
Nitrogen dioxide has been identified in the atmosphere of Mars, which has an overall oxidizing environment, indicated by the fact that most iron on the surface of Mars is in its trivalent state, and that gives Mars its distinct rust brown color that is visible even to the unaided eye from Earth. The current Martian atmosphere contains only 0.2 mbar of nitrogen. The lower atmosphere of Mars contains 1.7 ppb of NO. Nitrogen dioxide is a highly photolabile gas and will be photodissociated by visible and UV radiation on Mars and anywhere else in the universe. The photochemical equilibria of nitrogen oxides on Mars have been computed from the observational upper limits on the NO and O₂ abundances [1, 2].

2 Production of Nitrogen Dioxide

Nitrogen dioxide is a major industrial product as an intermediate in the production of nitric acid, most of which goes into fertilizer production in the form of ammonium nitrate. Only very little nitrogen dioxide is side-tracked from the process stream and condensed in the form of dinitrogen tetroxide to be used as a rocket propellant. The main method for the production of nitric acid is the catalytic combustion of ammonia over a platinum gauze (Ostwald process)



For small quantities of NO₂ to be prepared in the laboratory, copper shavings can be reacted with concentrated (not fuming) nitric acid while passing an excess of air over the reacting mixture to convert all NO to NO₂:

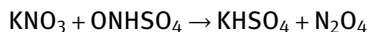


The reaction of nitric oxide with oxygen has been investigated experimentally for many years and is of great technical importance. It has two unusual properties: **(1)** it is kinetically a third-order reaction and **(2)** the velocity constant, *k*, decreases with increasing temperature [3]. Computational chemistry has supported the experimental measurements [4]. The best estimate of the activation energy was 6.47 kJ/mol.

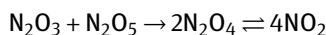
An easy method of preparing NO_2 in small quantities is the decomposition of carefully dried lead(II) nitrate at 723 K (450 °C):



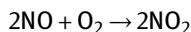
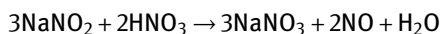
A clean laboratory method for preparing small samples of NO_2 is the reaction between potassium nitrate and nitrosyl bisulfate:



The reaction of dinitrogen trioxide (N_2O_3) with dinitrogen pentoxide (N_2O_5) gives dinitrogen tetroxide. The only problem is that N_2O_5 is not stable and has to be prepared immediately beforehand. A mixture of nitric acid and phosphorus pentoxide behaves as dinitrogen pentoxide. When these constituents are mixed, nitrogen dioxide is evolved:



Acidifying sodium nitrite with nitric acid will liberate nitrous acid, which promptly decomposes to nitric oxide that with additional air will form nitrogen dioxide:



Preparing NO_2 from the elements, as in air, by passing the gas through an electric discharge is the process that takes place on a global scale in nature in lightning discharges. The industrial version of this process, the Birkeland process, was practiced until 100 years ago in countries with ample hydroelectric power prior to the invention of the Haber-Bosch process for ammonia production and the Ostwald process for ammonia oxidation.

Oxides of nitrogen available from commercial sources are often not pure enough for spectroscopic studies. It is difficult to obtain pure oxides of nitrogen free from water and other oxides of nitrogen. There are convenient methods for preparing oxides of nitrogen and purifying them in the laboratory in small quantities just enough for spectroscopic studies [5].

It sometimes helps to purify NO before converting it to NO_2 [6]. This report also described methods for the detection and measurement of residual impurities in the final products.

3 Physical Properties of Nitrogen Dioxide

The physical properties of nitrogen dioxide are invariably tied to the physical properties of dinitrogen tetroxide and its dimer with which it exists in equilibrium over a wide temperature range from below its boiling point to above 298 K. Pure nitrogen dioxide exists only at temperatures above 420 K when most of the N_2O_4 is dissociated, but at

the same temperature NO_2 starts decomposing into NO and O_2 . So it is really difficult to obtain pure NO_2 in the gaseous state for physical measurements. The molecular mass of nitrogen dioxide is 46.0055 g/mol.

3.1 Optical Properties of Nitrogen Dioxide

3.1.1 UV/Visible Absorption Spectra of Nitrogen Dioxide

A thorough knowledge of the absorption spectra of nitrogen dioxide allows us to develop analytical methods for detecting NO_2 in the atmosphere of working rooms or propellant storage areas in the parts-per-million (ppm) or even parts-per-billion (ppb) range. The absorption spectra also help us to determine N_2O_4 and NO_2 dissociation equilibria and identify intermediates in the reactions of NO_2 and N_2O_4 with hypergolic fuels, reactions that determine the ignition delay, an important parameter for rocket applications. Rocket propellant storage areas where dinitrogen tetroxide (NTO) is stored must be monitored for potential leakage. Spectral methods provide the best methods for area surveillance and can trigger an alarm when a leak is detected. The air in work rooms where NTO is handled must be monitored continuously to comply with government regulations for maximum allowable exposure of working personnel to NO_2 vapors. A large selection of spectrographic equipment is available to serve this purpose. Accurate absorption cross sections of atmospheric pollutants like NO_2 or O_3 must be known to correctly interpret the flood of remote sensing data that are beamed down from environmental satellites, looking at the atmosphere from above. The spectral overlap of N_2O_4 absorption with NO_2 absorption in the near-UV interferes with the accurate experimental determination of the absorption cross section of NO_2 at wavelengths shorter than 400 nm. To remove and compensate for the contribution of N_2O_4 from studies of NO_2 profiles in the atmosphere, either the form of the temperature dependence of the equilibrium constant for the equilibrium of N_2O_4 and NO_2 , $K_p(T)$, must be known or K_p must be measured at the specific temperature of interest.

Unfortunately, not all absorption cross-section data were reliable, and a critical literature review was conducted to eliminate data whose accuracy was dubious. The available laboratory measurements of UV-vis (240–790 nm) absorption cross sections of O_3 and NO_2 were critically reviewed taking into account the variation of the cross sections with temperature (in the 200–300 K range) and with total pressure (<101 kPa) [7].

It would be best to calibrate satellite-borne instruments in a large atmospheric simulation chamber with known concentrations of NO_2 and O_3 . The dependence of the absorption cross section on temperature and pressure also enters the calibration and data reduction. The NO_2 absorption cross sections in the 240–790 nm region (Figure 1) can be separated into two principal systems: the D-X band system below 250 nm and the broad B-X and A-X band systems between 300 and 790 nm, with a maximum at around 400 nm. Due to interactions the forbidden C-X transition can also contribute

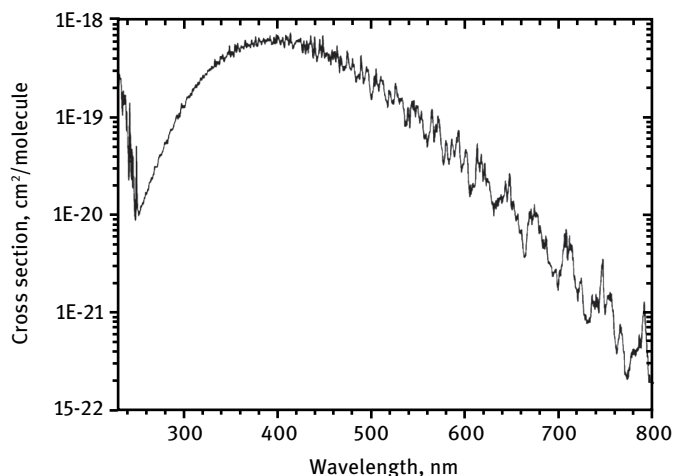


Figure 1: NO₂ UV-visabsorption spectrum at room temperature. (Reprinted and modified from [7], with permission from © 2003 Elsevier; permission conveyed through RightsLink.)

to the visible spectrum of NO₂. The shape of the visible absorption spectrum is close to that of a Gaussian bell-shape function, but there is a lot of spectral fine structure superimposed on it. Due to the complexity of the excited electronic states of NO₂, it is almost impossible to predict its spectrum from molecular quantum theory within experimental accuracy. The average absorption cross section of NO₂ at room temperature collected and averaged from 14 different publications was 4.50×10^{-17} in the range 400–500 nm and 2.77×10^{-17} in the range 400–500 nm with a standard deviation (1σ) of $\pm 2.4\%$.

The electronic absorption spectra of NO₂/N₂O₄ equilibrium mixtures were measured in non-polar and polar solvents [8]. In non-polar solvents, the spectra were very similar to those of NO₂/N₂O₄ equilibrium mixtures in the gas phase. However, in solvents with unshared electron pairs, particularly in ethers, esters, ketones, and tertiary amines, complex multi-band spectra were observed at room temperature. These are assumed to be of the electron donor-electron acceptor type molecular complex (Lewis adducts).

Because of the equilibrium $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$, it is difficult to separate the absorption spectra of NO₂ and N₂O₄ in the vapor phase. Measurements at different pressures showed the increase and decrease of absorption bands. Bands increasing with pressure belong to N₂O₄, and bands decreasing with pressure belong to NO₂. Optical density ($\log I_0/I$) curves were obtained of the equilibrium $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ mixture over the range 2400–5000 Å [9]. From three absorption curves taken at a constant temperature of 298 K (25 °C), three total pressures ($P = 33, 126, \text{ and } 307 \text{ mm Hg}$), and three different absorption cell path lengths, the spectra of the two compounds could be separated mathematically (Figure 2).

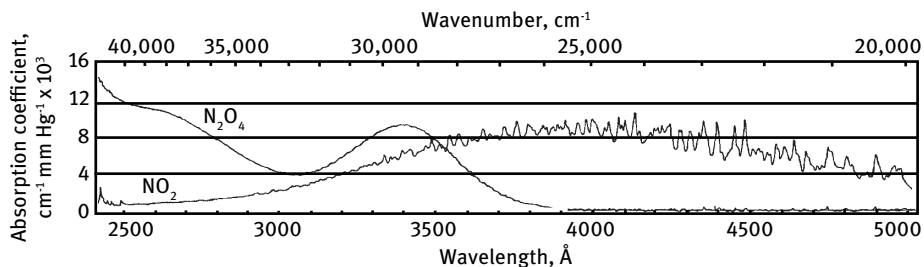


Figure 2: Absorption coefficients and resolved absorption spectra of nitrogen dioxide and dinitrogen tetroxide at 298 K. (Republished and modified from [9], with permission of © 1952 American Institute of Physics; permission conveyed through Copyright Clearance Center Inc.)

No fine structure was recorded in the spectrum of N_2O_4 . This is probably due not to its absence but rather to extreme fineness, which may prove almost impossible to resolve. The sharp, well-defined structures in the NO_2 spectrum do not appear in the N_2O_4 spectrum, probably because of the large number of closely spaced energy levels introduced into the molecule by the formation of the weak N—N bond. The low energy of the N—N bond stretching as well as its possible low-energy torsional vibration probably gives rise to a fine structure, resulting in further broadening.

One might consider NO_2 a free radical because it carries a free electron that is also responsible for its deep red color because it absorbs light in the visible region of the spectrum, where its dimer N_2O_4 does not. The electronic energy levels excited by visible light and UV have been studied extensively because a better understanding of these energy levels will help the interpretation of reactivity of NO_2 and dissociation of NO_2 under reacting conditions in a rocket engine and in the upper atmosphere.

The extinction coefficient of NO_2 was measured in the spectral range from 185 to 410 nm as a function of temperature between 235 and 298 K [10]. To correct for the effect of dimer absorption, the extinction coefficient of N_2O_4 has also been measured.

NO_2 concentrations in the air can be measured by fluorescence spectroscopy. The mean lifetime of fluorescence of NO_2 vapor was measured at pressures in a range of 12 to 0.6 μm using a direct method [11]. A linear dependence of lifetime on pressure was found, and extrapolation to zero pressure gave 44 μs for the lifetime in absence of collisions. The fluorescence spectrum in the region 4600–8000 Å was photographed with 4358 and 5461 Å excitation, with somewhat different results, indicating two excited electronic levels, one of which is not connected optically to the normal state and which is responsible for the long-lived fluorescence.

The excitation spectrum for the ν_2 fluorescence mode of NO_2 was measured throughout its visible absorption spectrum [12]. The spectra showed several narrow regions where the ν_2 fluorescence intensity was about two orders of magnitude larger than that found elsewhere.

Nitrogen dioxide has absorption features in the ultraviolet, blue, and green regions of the optical spectrum. Values of total columnar NO_2 range from 0.4×10^{-3} to about 5×10^{-3} cm NO_2 at standard temperature and pressure (STP) and yield optical depths from 0.008 to 0.087 at 390 nm, the wavelength of maximum absorption [13].

The absorption cross section of NO_2 has been measured above the 3979 Å predissociation limit in the region of 3920 and 3950 Å and in the discretely structured areas around 4112 and 4140 Å [14, 15]. The measurements of the absolute-absorption cross section of NO_2 were made from 3910 to 3925 Å, 3948 to 3953 Å, 4107 to 4115 Å, and 4131 to 4145 Å. All measurements were performed at 300 K and at several pressures of N_2 diluent ranging from 20 to 400 mm Hg. Measurements were also performed from 4107 to 4112.5 Å and 4132 to 4143 Å at 251 K. Spectra were taken in a dual-beam arrangement using a tunable, pulsed dye laser with 0.05 bandwidth. This represented an improvement of at least a factor of three over the resolution employed in previous studies. On the basis of the onset of rotational diffuseness, other investigators placed the predissociation limit at 3979 Å. Below 3979 Å, the spectra were continuous with occasional diffuse rotational lines superimposed. The spectra taken above 4100 Å revealed a wealth of structural complexity. Only slight variations in the measured cross sections were observed between 300 and 250 K. An example of a high-resolution spectrum of NO_2 for a very narrow frequency range from 4138.3 to 4143.3 Å is shown in Figure 3. There are several more high-resolution spectra like this one in the report.

The absorption cross sections of NO_2 have also been measured in a wavelength range of 200–700 nm at 298 K with a spectral resolution of 0.04 nm [16]. The data were acquired digitally, allowing post-processing by integration over different wavelength intervals and their use in solar photolysis calculations.

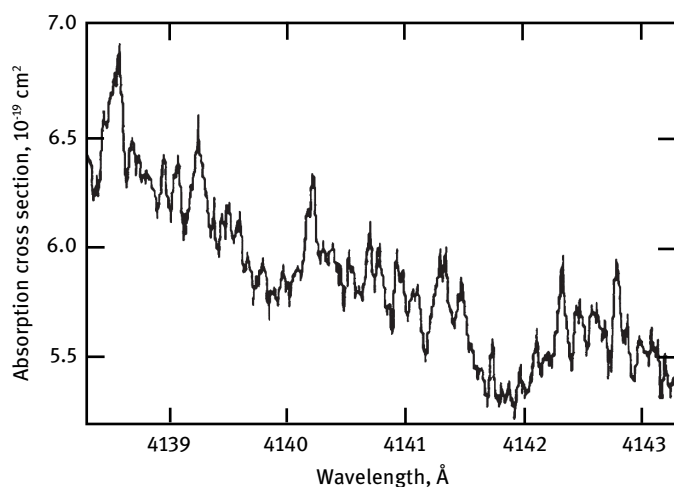


Figure 3: Absolute absorption cross section of NO_2 in air from 4138.3 to 4143.3 Å at 300 K. (Reproduced and modified from [15] Koffend et al. 1987.)

The spectral region from 440 to 460 nm is of special interest for remote sensing applications. The interpretation of absolute NO_2 absorption cross section in the 440- to 460-nm region at different temperatures is complicated by the coexistence of NO_2 and its dimer N_2O_4 . In one experiment, both NO_2 and N_2O_4 absorption features were observed and different approaches were used to obtain the partial pressure of NO_2 , giving a new estimate of the $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ equilibrium constant [17]. Within experimental errors, the overall shape of the spectrum did not show a dependence on temperature, but only a slight increase of a few maxima and a decrease of other maxima and of the minima were observed when the temperature was lowered.

Errors in the cross sections of $\text{NO}_2/\text{N}_2\text{O}_4$ reported by various authors at low to room temperature may be between $\pm 3\%$ and $\pm 8.8\%$. Of these errors, up to $\pm 3.5\%$ was contributed by errors in the equilibrium constant, K_p , in those measurements where the pressure was above 0.1 mbar. For example, IR measurements of the partial pressure of NO_2 ignored the dependence of absorption on total pressure. There are no measurements of NO_2 cross sections below 230 K. Extrapolation of these cross sections to analysis of measurements of NO_2 at the low temperatures of the Arctic and Antarctic stratosphere is inaccurate. For satisfactory analysis of polar spectra, the NO_2 cross sections should be measured at temperatures down to 190 K with a relative accuracy of $\pm 1\%$. This difficult experiment would need a cell of minimum length 32 m whose length can be adjusted [18]. The optimum experiment might therefore simultaneously measure the visible and IR spectra.

Based on measurements of NO_2 absorption cross sections between 300 and 500 nm at ambient temperature with improved experimental conditions – low gas pressures, long absorption paths, suitable absorbance values, and narrow spectral bandwidths of 0.01 nm – it was found that in the photolysis region below 400 nm, absorption cross sections were larger than those previously published, suggesting that the photodissociation coefficient calculated from other data sets may have been underestimated [19]. In the structured region of the spectrum above 400 nm, improvement of the resolution gave more precise values useful for future optical measurements in the Earth's atmosphere.

Two different single-mode diode lasers were used to record high-resolution absorption spectra of NO_2 (dilute in Ar) near 670.2 and 394.5 nm over a range of temperatures (296 to 774 K) and total pressures (2.4×10^{-2} to 1 atm) and to measure variations of the spectral absorption coefficients with temperature and pressure [20, 21].

Previous experiments in the 400- to 500-nm region [19] have been extended to the 200- to 400-nm region to determine the absorption cross sections of NO_2 at 220 K [22]. The NO_2 and N_2O_4 cross sections were obtained simultaneously from a calculation applied to the data resulting from measurements at low pressures. A comparison between the NO_2 cross sections at 220 K and at ambient temperature showed that the low-temperature cross sections are generally lower, except in the region of the absorption peaks. Other investigators have measured the absorption cross sections of NO_2 with high spectral resolution over a wider temperature range [23].

3.1.2 Infrared Absorption Spectra of Nitrogen Dioxide

The NO_2 free radical plays an important role in the chemistry of Earth's atmosphere. In the troposphere, NO_2 is the main source of ozone and has an active role in the urban photochemical pollution. Accurate measurements of NO_2 concentrations in the atmosphere at different altitudes and different times of the day are important and depend on the exact knowledge of the absorption cross sections of NO_2 at all wavelengths. NO_2 and N_2O_4 may also be carried in the atmosphere adsorbed to aerosol particles. Detection of N_2O_4 leaks in propellant storage areas would also be possible by IR beam attenuation at specific wavelengths.

3.1.3 Infrared Absorption Spectra of Gaseous Nitrogen Dioxide

Absorption coefficients of NO_2 were measured at a number of wavelengths in the spectral region 1080–2700 Å with a resolution of 0.2 Å by a photoelectric method [24]. Several bands observed in the region 1080–1200 Å fitted a Rydberg series, and its convergence limit at 11.62 eV was interpreted as the second ionization potential of NO_2 . The first ionization potential was found to be 9.78 eV by the photoionization method. The ionization continuum showed a break at 10.83 eV, which may have been due to a dissociative-ionization process.

The IR spectrum of the ν_1 band of $^{14}\text{N}^{16}\text{O}_2$ has been recorded with a resolution of about 0.025 cm^{-1} in the region extending from 1480 to 1270 cm^{-1} [25]. From about 1350 cm^{-1} , the absorption became progressively weaker, and no absorption could be detected below the band origin located at 1319 cm^{-1} . Because series with low values of K_a could not be measured, constants that depend strongly upon the molecular asymmetry could not be determined.

Using a Fourier transform spectrometer coupled to a multiple reflection cell, high-resolution NO_2 absorption cross sections were obtained at 0.05 cm^{-1} in the near-IR region ($10800\text{--}15100\text{ cm}^{-1}$) and at 0.1 cm^{-1} in the visible region ($13800\text{--}26000\text{ cm}^{-1}$), under various pressure conditions (pure NO_2 and NO_2 /air mixtures) and at three temperatures (220, 240, and 294 K) [26]. The effects of temperature and pressure on the NO_2 cross sections revealed a decrease of the absorption at the maxima of the absorption bands and an increase at the minima with increasing temperature. The absorption cross-section values obtained at 294 K are plotted in Figure 4 (low resolution) and Figure 5 (high resolution) for the whole spectral region, showing the presence of high-resolution structures in the NO_2 spectrum. The temperature effect is illustrated on a small part of the spectrum at an expanded scale, shown in the insert box. See also [5].

Fourier transform infrared (FTIR) spectra of NO and NO_2 were used for the analysis of NO in mixed oxides of nitrogen (MON) [27]. The NO_2 absorption peaks at 2888.8 and 2918.7 cm^{-1} were selected for the calibration curve.

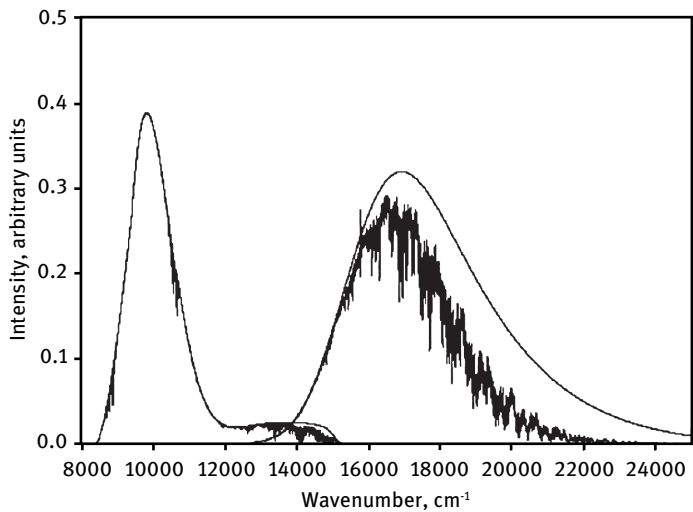


Figure 4: Low-resolution visible and near-IR spectra of nitrogen dioxide gas (Republished and modified from [26], with permission of © 2002 John Wiley & Sons – Books; permission conveyed through Copyright Clearance Center Inc.)

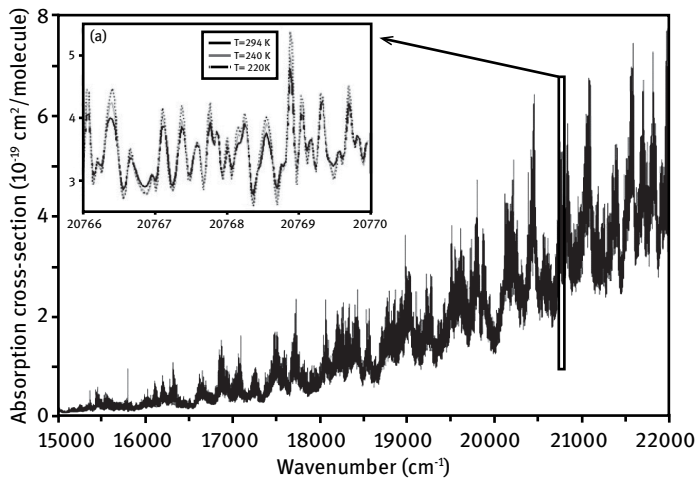


Figure 5: Absorption cross section of nitrogen dioxide gas at 294 K. (Republished and modified from [26], with permission of © 2002 John Wiley & Sons – Books; permission conveyed through Copyright Clearance Center Inc.)

3.1.3.1 Infrared Absorption Spectra of Frozen or Matrix-Isolated Nitrogen Dioxide

Ordinarily, if NO_2 is cooled slowly and without dilution, it will have a chance to dimerize and the condensate would be mostly N_2O_4 . However, if the gas is highly diluted and flash frozen, the dimerization equilibrium does not have a chance to establish itself and the condensate will be mostly NO_2 . In those cases, it is difficult to separate the spectra of NO_2 and N_2O_4 .

The IR spectrum of frozen nitrogen dioxide was studied in carbon dioxide, argon, oxygen, nitrogen, nitrous oxide, and hydrogen matrices, and in the pure state [28]. Isolation of the monomer was favored by the use of high dilution and slow deposition rates and a rigid matrix (CO_2 as opposed to Ar). Sixteen bands were observed, five of these occurred in the ONO bending region around 750 cm^{-1} , three in the NO_2 symmetric stretching region around 1280 cm^{-1} , seven in the NO_2 asymmetric stretching region around 1740 cm^{-1} , and one at 1829 cm^{-1} . The relative intensities of these bands were largely dependent on the conditions of deposition (choice of matrix, dilution ratio, window temperature, and deposition rate). When the sample was warmed from a liquid helium temperature to a liquid nitrogen temperature, new bands appeared in the neighborhood of 1740 cm^{-1} that were assumed to be caused by the dimer. Regardless of the matrix or mode of deposition, when the stable dimer was present, two bands were always observed in the 1740-cm^{-1} region. Some bands were assigned to the asymmetrical isomer ONO-NO_2 . The argument in favor of the existence of a dimer of this structure was supported by absorption bands at 787 cm^{-1} (ONO bend), 1290 cm^{-1} (NO_2 symmetric stretch), 1645 cm^{-1} (NO_2 asymmetric stretch), and 1829 cm^{-1} (N=O stretch).

3.1.4 Raman Spectra of Nitrogen Dioxide

The Raman spectrum of NO_2 excited at 355 nm was found to be dominated by bands containing up to six quanta of the bending vibration and four quanta of the symmetric stretch, with an almost complete absence of bands containing asymmetric stretch quanta [29]. These results were interpreted within a time-dependent view to provide insight into the predissociation dynamics of NO_2 .

3.2 Microwave Spectra of Nitrogen Dioxide

Complete knowledge of the microwave spectra of NO_2 would help in identifying NO_2 in interstellar gas and on planetary bodies. If NO_2 (and N_2O_4) was found on other planets, it would be a welcome *in situ* resource to use as a rocket propellant (although the atmosphere would not be very breathable).

Some 69 microwave absorption lines from three isotopic modifications of NO_2 have been observed and identified [30]. This spectrum has been completely analyzed in terms of moments of inertia, magnetic fine structure, and centrifugal distortion. The results obtained for $^{14}\text{N}^{16}\text{O}_2$ were as follows: rotational constants, odd electron expec-

tation values with respect to N nucleus, and reduced spin-rotation coupling constants. The magnetic coupling constants were discussed in terms of a simplified electronic structure of NO_2 . The agreement between this predicted structure and the experimental parameters was moderately good.

3.3 Magnetic Properties of Nitrogen Dioxide

NO_2 gas is paramagnetic, frozen N_2O_4 is diamagnetic. Paramagnetism gives nitrogen dioxide a volume susceptibility of $\chi = 3 \times 10^{-15}$ cgs units.

3.4 Electron Spin Resonance Spectra of Nitrogen Dioxide

Since NO_2 carries a free electron, it is paramagnetic and can be investigated by electron spin resonance (ESR) spectroscopy. It acts like a free radical. The ESR spectrum of liquid N_2O_4 at room temperature consists of a single, broad, unstructured band with a half-width of approximately 150 G and a g value of about 2.0. This has been attributed to NO_2 formed by the dissociation of N_2O_4 . The unpaired electron on NO_2 is most likely in an orbital of a_1 symmetry partially localized on the nitrogen atom. The ESR signal should be a triplet (due to the electron-nuclear-spin interaction). Failure to resolve this band at temperatures in the region of 273 K was attributed to a rapid rate of dimerization and dissociation, which is sufficient to broaden the lines beyond the point of resolution. The resolved spectrum of NO_2 molecules was obtained by trapping NO_2 radicals in various matrices, usually by irradiation of a matrix containing alkali metal nitrates. The resolved spectrum was shown to consist of an anisotropic triplet.

The ESR spectrum of dinitrogen tetroxide has been examined in the liquid and solid states between 77 and 300 K [31]. The nature of the equilibrium $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ has been studied in the liquid state, and the concentrations of NO_2 have been determined by measuring the strength of the ESR signal. The equilibrium constant decreased from 43.54 ± 1.5 mol/L at 296 K to 0.11 ± 0.01 mol/L at 247 K, giving a heat of reaction of $\Delta H = 15.6 \pm 0.5$ kcal/mol for the dissociation. When the liquid was quenched to 77 K, an anisotropic set of triplets was observed with g values of g_x 2.0063, g_y 1.9960, g_z 2.0029, and g_{avg} 2.0018 and hyperfine-splitting constants (in G) of A_x 507, A_y 50.1, A_z 67.0, and A_{iso} 56.0. When the sample was warmed to 180 K, the triplets decreased in intensity and became isotropic with a splitting of 57 G. On recooling, the original anisotropic triplet was recovered.

3.5 Molecular Properties, Structure, Dipole Moment, Molecular Orbital Calculations of Nitrogen Dioxide

3.5.1 Molecular Properties and Structure of Nitrogen Dioxide

The reactivity of nitrogen dioxide and dinitrogen tetroxide is based on their molecular structure. The structure of nitrogen dioxide is unique in that it contains an odd number of electrons, 17 electrons, leaving an unpaired electron that seeks to pair itself. That can be done by pairing with itself in a labile bond forming dinitrogen tetroxide. Thus it both dimerizes and undergoes association reactions with other free radicals, adds to double bonds in unsaturated molecules, and takes part in hydrogen-abstraction reactions just as the methyl radical does. The molecular structure of nitrogen dioxide has been identified by spectroscopic investigations and by modeling its structure with computational chemistry.

The molecular structure of NO_2 is shown in Figure 6. The nitrogen dioxide molecule is in the shape of a triangle. The $\angle \text{O}-\text{N}-\text{O}$ bond angle between the two oxygen atoms is $134^\circ 4'$. The $\text{N}=\text{O}$ atom distance is $1.188 \pm 0.004 \text{ \AA}$. An exhaustive summary of the connections between the molecular structure of nitrogen dioxide and its reactivity with 441 references to the literature is given in [32] and [3]. The numerous reactions NO_2 can undergo are briefly summarized in Section 4.4.

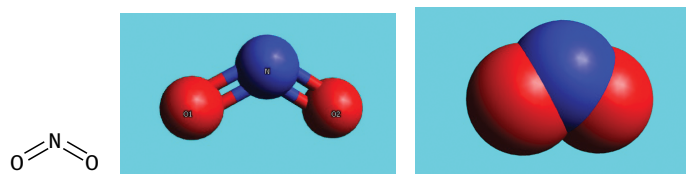


Figure 6: Molecular structure of nitrogen dioxide

3.5.2 Molecular Orbital Calculations of Nitrogen Dioxide

A non-empirical self-consistent field method has been applied to the ground state and to a series of excited states of NO_2 to obtain potential-energy curves by varying the bond angle [33]. The resulting equilibrium bond angle for the ground state compared favorably with the experimental value. It was found that five transitions fall into the range covered by the long-wavelength spectrum, which explains the complexity of the spectrum. From the correlations between the electronic states of the bent molecule and those of the linear system, an attempt was made to obtain indications concerning the potential-energy surfaces of the $\text{NO} + \text{O}$ system as the NO_2 begins to dissociate. An attempt was made to explain the mechanism of the photolysis of NO_2 , and the anomalously long radiative lifetime of its first doublet excited state resulting from fluorescence decay. Oscillator strengths of the allowed and forbidden transitions in NO_2 were obtained [34]. The NO_2 excitation energies, potential energy surfaces, and os-

cillator strengths computed were then compared to experimental spectroscopic data, namely, absorption, fluorescence, chemiluminescence, predissociation, photolysis, and the absence of phosphorescence [35]. It was found that the main components of the visible spectrum are due to the transitions $2B1 \leftarrow 2A1$ and $2B2 \leftarrow 2A1$, with the $2B2$ state being responsible for the observed fluorescence emission, which has an anomalously long lifetime.

The electronic structures and spectra of nitrogen dioxide have been calculated by a semi-empirical method and the self-consistent molecular orbitals and energies of the π -electron system have been calculated [36]. However, for the non-bonding σ -electron system Hückel-type molecular orbitals were used. In nitrogen dioxide the totally symmetric combination of 2p oxygen orbitals and the sp^2 non-bonding nitrogen orbital mix strongly to form slightly bonding and slightly anti-bonding molecular orbitals. For nitrogen dioxide a series of transition energies was obtained, which may explain the experimental results. The complexity of the empirical data, however, precluded definite assignment of the observed band systems.

3.6 Solubility Properties of Nitrogen Dioxide

3.6.1 Solubility Properties of Nitrogen Dioxide in Other Liquids

The solubility of nitrogen dioxide in water is an important property because it is part of the industrial process in the production of nitric acid, it is important for the absorption of NO_2 in stack gases and pressurization gases vented from propellant tanks in water spray scrubbers, and it is the first step in a long chain of toxic reactions if NO_2 is accidentally inhaled by propellant-handling personnel. It is difficult to differentiate between the solubility of NO_2 and N_2O_4 because under most conditions at room temperature an equilibrium between the two exists in the solution as well as in the vapor space above the solution. The degree of dissociation of N_2O_4 in non-reactive solvents depends on the dielectric constants and polar properties of the solvents. The most important solution of NO_2/N_2O_4 equilibrium mixtures are those in concentrated nitric acid, commonly referred to as red fuming nitric acid (RFNA). Nitric acid and dinitrogen tetroxide are not completely miscible over the entire range of compositions. The phase behavior, miscibility limits, vapor pressure, and vapor composition of RFNA are discussed in *Encyclopedia of Oxidizers*, in the chapter "Red Fuming Nitric Acid."

NO_2 reacts immediately with H_2O upon dissolution, which prevents direct measurements on the physical phase equilibria of the chemical system. The reaction does not go to completion, and under certain conditions a two-phase system is formed [37]. Modeling this reacting system is a challenging task due to the complexities arising from the heterogeneous nature of the chemical reaction, the multiple components that are involved in the phase equilibria, ionic dissociation in water, self- and cross-associations among the molecules, and multiple chemical reactions that may occur before physicochemical equilibria is reached [38].

3.7 Thermodynamic Properties of Nitrogen Dioxide

3.7.1 Heat Capacity of Nitrogen Dioxide

The heat capacity of gaseous nitrogen dioxide at 298 K is $36.974 \text{ J mol}^{-1} \text{ K}^{-1}$. The heat capacity of gaseous nitrogen dioxide as a function of temperature can be calculated from the following polynomial equation:

$$C_p^\circ = A + B \times \tau + C \times \tau^2 + D \times \tau^3 + \frac{E}{\tau^2}$$

where C_p is the heat capacity in $\text{J mol}^{-1} \text{ K}^{-1}$, τ is the temperature in kelvin divided by 1000, and A, B, C, D, and E are constants listed in Table 1 for two different temperature ranges. Note that NO_2 is unstable at temperatures above 1000 K and the column for the higher temperature range 1200–6000 K is only of academic value.

Table 1: Thermodynamic property polynomial equation coefficients for gaseous nitrogen dioxide.

Temperature range, K	298–1200	1200–6000
A	16.10857	56.82541
B	75.89525	0.738053
C	−54.38740	−0.144721
D	14.30777	0.009777
E	0.239423	−5.459911
F	26.17464	2.846456
G	240.5386	290.5056
H	33.09502	33.09502

Data source: [39, 40]

3.7.2 Enthalpy of Formation of Nitrogen Dioxide

Table 2 is a summary of standard enthalpy of formation data assembled from various sources.

Table 2: Summary of literature data for standard enthalpy of formation (ΔH_f°) of gaseous nitrogen dioxide.

Enthalpy of formation		Author	Year	References
kJ/mol	kcal/mol			
+33.32	+7.964	Giauque and Kemp	1938	[41]
+33.095	+7.910 ± 0.2	JANAF	1971	[42]
+33.10	+7.911	NIST Chemistry WebBook	1964	[39]

Molecular mass 46.0055 g/mol

The differential enthalpy of formation of gaseous nitrogen dioxide as a function of temperature can be calculated from the following polynomial equation:

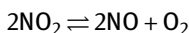
$$\Delta H = H^\circ - H^\circ_{298.15} = A \times \tau + \frac{B \times \tau^2}{2} + \frac{C \times \tau^3}{3} + \frac{D \times \tau^4}{4} - \frac{E}{\tau} + F - H$$

where ΔH is the enthalpy in kJ/mol, τ is the temperature in kelvin divided by 1000, and A, B, C, D, E, F, and H are constants listed in Table 1 for two different temperature ranges.

4 Chemical Properties of Nitrogen Dioxide

4.1 Thermal Decomposition of Nitrogen Dioxide

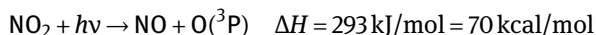
The thermal decomposition of nitrogen dioxide leads to nitric oxide and dioxygen in reversal of the formation of NO_2 from these gases at lower temperatures



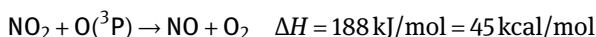
The kinetics of the thermal decomposition of nitrogen dioxide were studied in a Vycor vessel over a temperature range of 630 to 1020 K for nitrogen dioxide concentrations from 10^{-8} to 10^7 molecule/cm³ [43, 44]. The reaction was found to be of second order with respect to nitrogen dioxide and to involve an activation energy of 112.5 kJ/mol (26.9 kcal/mol).

4.2 Photolysis of Nitrogen Dioxide

In the photolysis of NO_2 , using shorter and shorter wavelength light, the absorption of radiation and the formation of excited NO_2 molecules becomes noticeable at 6000 Å. This energy of excitation is not enough to dissociate the molecule, and it is either quenched or re-radiated as fluorescence. At shorter (4000 Å) wavelengths, the absorption becomes diffuse and fluorescence fades as dissociation begins:

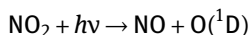


Because of the competition from fluorescence and quenching the quantum yield is small. As the wavelength is further decreased and the energy of quanta increased, dissociation predominates. The intensity of fluorescence is zero by 3650 Å, absorption is continuous, and the quantum yield approaches 2. This leads to the second reaction:



and a total change of two molecules of NO_2 decomposed per quantum absorbed. Sharp absorption bands near 2596 Å support dissociation. The second diffuse region near

2459 Å corresponds to dissociation into nitric oxide and an excited oxygen atom:



Photolysis of NO_2 is of interest not only for atmospheric chemistry, but also for rocket propellant chemistry. If it is possible to isolate and stabilize some of the intermediate excited species, this might lead to more energetic oxidizers for rockets. Photolysis might also be a useful method of destroying NO_2 in waste gases.

Nitrogen dioxide photolysis has been studied by various investigators under different conditions, all at wavelengths between 3100 and 3700 Å [45, 46] and at 3660 and 4047 Å [47]. The proposed mechanisms differ in that one postulated that atomic oxygen attacks NO_2 in two ways, yielding NO and O_2 in one case and excited NO_3^* in the other. The excited NO_3^* can decompose to form atomic oxygen and NO_2 , it can be deactivated, or it can react with NO_2 . The second mechanism postulated a single mode of attack on NO_2 by atomic oxygen, again yielding excited NO_3^* . Of the two mechanisms, the first was rated as being more consistent with the thermal reactions of NO_2 and NO_3 . It is believed that both the linear and triangular forms of NO_3 play important roles in the photolysis of NO_2 .

The quantum yields of oxygen production in the photolysis of nitrogen dioxide have been determined at a series of wavelengths at room temperature and as a function of temperature at 3660, 4047, and 4358 Å [48, 49]. These values were satisfactorily correlated with the extent of dissociation into NO and O atoms by means of $^{18}\text{O}_2$ tracer techniques. A general mechanism was proposed for the photolysis of NO_2 from 3130 to 4047 Å. Temperature effects were correlated in terms of a theoretical calculation based on the population of the rotational energy levels of NO_2 . This led to a spectroscopic-photochemical determination of the dissociation energy of NO_2 that was in good agreement with one calculated from thermodynamic data.

Relative quantum yields for the photolysis of NO_2 to give NO have been measured at 5- or 10-nm intervals in the range of 295 to 445 nm and at several longer wavelengths [50]. The behavior of the quantum yield as a function of photon energy can be separated into three distinct wavelength regions: At all wavelengths shorter than 398 nm the quantum yield is almost constant and independent of NO_2 pressure in the range 0.5–4 mm Hg. The photodissociation probability of NO_2 remains close to unity for photolysis by all wavelengths shorter than the dissociation limit at 398 nm. At wavelengths longer than 430 nm, there is a small quantum yield for NO formation that decreases slowly with increasing wavelength. Quenching studies and variations in light intensity showed that these small yields are caused by the reaction of an electronically excited NO_2 molecule with ground state NO_2 . In the wavelength region between 400 and 430 nm, the quantum yield fell abruptly. Isotopic exchange experiments involving oxygen-18 confirmed that free oxygen atoms are produced in this region, even though the energy of the photolyzing quantum is less than the NO_2 dissociation energy.

The near-UV photodissociation of NO_2 has been investigated at excess energies from 600 up to 1700 cm^{-1} above the $\text{NO}_2 v = 1 + \text{O}^3\text{P}$ dissociation limit [51]. A complete

analysis of the $\text{NO}_x v=1$ fragment, including internal and translational energy as well as the angular properties of its vectorial parameters, was performed using resonance-enhanced multi-photon ionization with time-of-flight mass spectrometry. Two types of final state distributions of the fragments were found; the difference depending upon the excess energy with respect to the $\text{NO}_x v=1 + \text{O}^3\text{P}$ dissociation limit. Above the threshold, statistical rotational behavior with non-vanishing anisotropies was observed.

Velocity-map ion imaging has been applied to the photodissociation of NO_2 via the first absorption band at 308 nm using (2+1) resonance-enhanced multi-photon ionization detection of the atomic $\text{O}(^3\text{P}_j)$ products [52]. The resulting ion images were analyzed to obtain information about the speed distribution of the $\text{O}(^3\text{P}_j)$ products, the translational anisotropy, and the electronic angular momentum alignment.

Photochemical removal of NO_2 in N_2 or air (5–20% O_2) mixtures was studied using 172-nm Xe_2 excimer lamps at atmospheric pressure without using any catalysts [53]. When a high-power lamp (300 mW/cm^2) was used, the conversion of NO_2 (200–1000 ppm) to N_2 and O_2 in N_2 was >93% after 1 min of irradiation, whereas that to N_2O_5 , HNO_3 , N_2 , and O_2 in air (10% O_2) was 100% after 5 s of irradiation in a batch system. In a flow system, about 92% of NO_2 (200 ppm) in N_2 was converted to N_2 and O_2 , whereas NO_2 (200–400 ppm) in air (20% O_2) could be completely converted to N_2O_5 , HNO_3 , N_2 , and O_2 at a flow rate of 1 L/min. It was found that NO could also be decomposed to N_2 and O_2 under 172-nm irradiation, though the removal rate was slower than that of NO_2 by a factor of 3.8.

4.3 Radiolysis of Nitrogen Dioxide

Radiolysis of nitrogen dioxide would occur in the upper strata of the stratosphere where cosmic radiation both ionizes the oxygen and ozone and initiates the reaction of oxygen atoms and nitrogen atoms, but also destroys the nitrogen dioxide thus formed. The radiolysis of liquid N_2O_4 is discussed in *Encyclopedia of Oxidizers*, “Dinitrogen Tetroxide.”

4.4 Reactions of Nitrogen Dioxide

The nitrogen dioxide equilibrium mixture is extremely reactive, entering into chemical reactions with inorganic as well as organic reaction partners. In interpreting a particular reaction, the first problem is to determine whether the free radical NO_2 or its dimer molecular N_2O_4 or the ionic nitrosyl nitrate form of N_2O_4 is the reacting species. Thus in gas-phase reactions at high temperature, NO_2 monomer greatly outweighs the N_2O_4 dimer, while in the liquid state the opposite is true. A good overview over reactions of NO_2 and N_2O_4 and the connections between the molecular

structure of nitrogen dioxide and its reactivity is given in two historic reviews by Gray and Yoffe [3, 32].

In our book, we are mostly interested in the reactions of NO_2 that lead to hypergolic ignition with reactive fuels. These hypergolic ignition reactions will be discussed in a future volume of this series in the *Encyclopedia of Rocket Propellants*.

4.4.1 Reactions of Nitrogen Dioxide with Inorganic Compounds

4.4.1.1 Reactions of Nitrogen Dioxide with Hydrogen

While a combination of nitrogen dioxide with hydrogen could theoretically be used as a rocket propellant, the disparate boiling points of the two liquids would make a practical design very difficult. The reaction of nitrogen dioxide with hydrogen has been examined mostly as part of kinetic and ignition studies. The combination is not hypergolic.

4.4.1.2 Reactions of Nitrogen Dioxide with Water

The most important reaction of NO_2 with any other inorganic chemical is the reaction with water. The reactions of nitrogen dioxide are a complex pattern of its free radical and non-radical modes of reaction.

One of the most important reactions involving nitrogen dioxide is the absorption in water and the reaction with water, leading to the formation of nitric acid in large-scale industrial nitric acid production plants [54, 55]. The NO_2 gas dissolves in water physically before it reacts chemically. Not all dissolved NO_2 will react, and some remains as a physical solution in the resulting nitrous acid/nitric acid/water mixture [56]. This reaction also takes place on a global scale in the atmosphere of our planet Earth. The nitrogen dioxide in the atmosphere will form by lightning or as a result of combustion processes, both natural combustion like forest fires and industrial, residential, and automotive emissions. The absorption in and reaction with water is an important step in scrubbers for the removal of NO_2 from pressurant gases vented from dinitrogen tetroxide tanks at rocket test sites and in reusable spacecraft that have been returned from space.

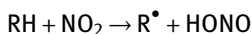
Studies of the gas-phase reaction of water vapor and ppm concentrations of nitrogen dioxide were made at atmospheric pressure and near ambient temperatures [57]. The initial rate of disappearance of nitrogen dioxide was first order with respect to water and second order with respect to nitrogen dioxide. Nitric oxide and nitric acid were the principal products. A third-order rate constant of $(5.50 \pm 0.29) \times 10^4 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ was found at 25°C . These results are applicable to air pollution studies but also for NO_x scrubbers based on the absorption of nitrogen dioxide into aqueous solutions.

The heterogeneous reaction of NO_2 with water has been known for decades to generate HONO, a major source of $\cdot\text{OH}$ that drives the formation of ozone and other air pollutants in urban areas. The reaction is first order in NO_2 and in water vapor, and the formation of a complex between NO_2 and water at the air-water interface has been

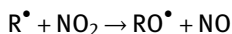
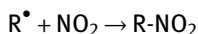
hypothesized as being the key step in the mechanism. Long-optical-path-length FTIR studies of the loss of gaseous NO_2 and the formation of the products HONO, NO, and N_2O were carried out to measure species generated on the surface during the reaction, including HNO_3 , N_2O_4 , and NO_2^+ [58]. A reaction mechanism was proposed that hypothesized that the symmetric form of the NO_2 dimer, N_2O_4 , is taken up on the surface and isomerizes to the asymmetric form, ONONO_2 . The latter autoionizes to $\text{NO}^+ \text{NO}_3^-$, and it is this intermediate that reacts with water to generate HONO and surface-adsorbed HNO_3 . Nitric oxide is then generated by secondary reactions of HONO on the highly acidic surface.

4.4.2 Reactions of Nitrogen Dioxide with Organic Compounds

The abstraction of hydrogen atoms from alkanes is a characteristic reaction of free radicals, which is how nitrogen dioxide reacts with alkanes:



This initial step is succeeded by rapid secondary reactions of the alkyl radical and oxidation. Prominent among these competing reactions are nitration by radical-radical association:



NO_2 reacts readily with unsaturated organic compounds. The primary products of the addition of NO_2 to olefins are α,β -dinitro-compounds and α -nitro- β -nitrites, often in nearly equal proportions. It is the reactivity of NO_2 and N_2O_4 with organic compounds, which severely limits the choice of polymeric materials for gaskets and propellant expulsion bladders and diaphragms in propellant tanks.

For additional information about reactions of NO_2 and N_2O_4 with organic compounds, we refer readers to other publications in the literature [59]. Other reactions are summarized in conference proceedings about nitration methods [60].

4.5 Analysis of Nitrogen Dioxide

Analytical methods for determination of nitrogen dioxide in the air would be of importance for monitoring workplaces at rocket test and launch facilities where personnel work in proximity to oxidizer run tanks, tank trucks, and storage areas. Such analytical methods are also widely used for monitoring atmospheric air pollution in urban areas.

In the case of accidental releases of dinitrogen tetroxide into the atmosphere, the initial release may be in the form of N_2O_4 , but as soon as the liquid evaporates and the vapor cloud is diluted as it diffuses into ambient air, most of it will convert to NO_2 .

Therefore, analysis methods are only calibrated for NO_2 and not for N_2O_4 , which may accompany the NO_2 but only in small concentrations.

This section overlaps with and partially duplicates a similar section on the analysis of nitrogen oxides in the chapter on N_2O_4 . That section deals mostly with the analysis of liquid N_2O_4 but includes some information on the analysis of NO_2 in the gas phase.

4.5.1 Analysis of Nitrogen Dioxide in Air at Rocket Test Facilities

This section on the analysis of NO_2 in air overlaps with a similar or nearly identical section for the analysis of N_2O_4 in the air of work spaces.

A portable monitor for recording NO_2 concentrations in workroom air and stack gases allowed the gas sample to flow concurrently with the reagent, N-1naphthylethylenediamine dihydrochloride, through a beaded column [61]. Diazotization of the reagent produced a colored solution that was measured by a flow-through colorimeter. Concentrations ranging from 0.5 to 15000 ppm could be measured.

The best wavelength for detection of red NO_2 gas in air is 400 nm. For continuous spectrophotometric analysis of NO_2 in air by drawing sample air through a 10-cm UV-vis spectrophotometer cell, a correction needs to be applied for invisible N_2O_4 based on the known dissociation curve, and the accuracy is $\pm 2.5\%$ relative for NO_2 concentrations up to 4 vol.-% [62].

For occasional spot checks of NO_2 concentrations in air at the workplace, the easiest method is with gas detection tubes made from glass tubes that contain an indicator supported on a granular material, which changes color when exposed to NO_2 . Such tubes are available from Dräger, MSA, “Kitagawa,” and others. Gas detection tubes are sensitive to as little as 0.5 ppm NO_2 and can measure up to 100 ppm NO_2 with 10 strokes of a manually operated bellows pump. Dräger NO_2 gas detection tubes are available for two ranges of concentrations (Table 3).

Table 3: Dräger nitrogen dioxide gas detection tubes and CHIP boards.

Type	Tube designation	Concentration range	Dräger part number
Glass tube	Nitrogen Dioxide 0.5/c	0.5–25 ppm	CH 30 001
Glass tube	Nitrogen Dioxide 2/c	2–100 ppm	67 19 101
CHIP 10-capillary board	Nitrogen Dioxide	0.5–25 ppm	64 06 120

Data source: https://www.draeger.com/en-us_us/Products/Sampling-Tubes-and-Systems; accessed 17-Oct-2021

The Dräger CHIP is a self-contained unit that has a pump and a digital readout. Each disposable chip board contains 10 measurement capillaries filled with a substance-

specific reagent system. The reactive preparations necessary for detection are kept in hermetically sealed glass capillaries until needed. When the chip is inserted into the analyzer, all information required for detection is transferred to the analyzer by means of a bar code:

- type of gas,
- measuring range,
- measuring time,
- parameters for the calibration function,
- required flow rate

The analyzer records the measurement effect optoelectronically, thereby eliminating human error in reading a color scale. In the CHIP measuring system, miniaturization has resulted in a reduction in the sample volume necessary for a measurement (compared to the manual bellows pump with 10 strokes). For a typical measurement, only 30 mL of air is needed for a measuring time of approximately 2 min and a flow of 15 mL/min. The power needed for operation of the analyzer is provided by four AA batteries. After inserting the chip, an optical system calculates the number of remaining measurements still available on the chip being used and displays this together with the gas type and the measuring range. Up to 50 measurement results can be stored in the machine with the name of the measured substance, the concentration, date and time of the measurement, and a code letter to help identify the measurement location. Newer equipment is available with analyzers in the Pac[®], X-dock[®], and X-am[®] series.

The popular Dräger tube for NO₂ was tested again for accuracy with NO₂ vapors from a vapor generator that was calibrated with the Saltzman reagent method on air samples drawn through an impinger with NaOH [63]. These tubes change color from white to blue gray based on the reaction of NO₂ with diphenylbenzidine. This indication is affected by free halogens. The end point on the NO₂ tubes was difficult to read, but all results for NO₂ tubes were on the unsafe side (low readings). At 6.3 ppm NO₂ the deviations from the true, analyzed concentration were -13 and -28%. This deviation may have been corrected in the meantime.

A method for determining 2 to 10 ppm of NO₂ in air, a liquid absorption method, is based on a Griess-Ilosvay reaction in which nitrogen dioxide recovery can be improved by the incorporation of sodium arsenite in an alkaline absorption solution [64]. The same author also described a cheap test-paper method unaffected by humidity and air that involved the use of papers treated with p-anisidine and glycerol, with a storage life of 3 months.

As part of an effort to upgrade the sensor technology background information, NASA requested information from a total of 27 manufacturers of portable multi-gas instruments [65]. A set of criteria was established to determine which vendors would be selected for laboratory evaluation. Each of the 27 manufacturers of multi-gas analyzers was sent a copy of the criteria and asked to fill in the appropriate information pertaining to their instrumentation. Based on the results of the sensor criteria work-

sheets, a total of 9 vendors out of 27 surveyed manufacturers were chosen for evaluation. Each vendor included in the final evaluation process was requested to configure each of two analyzers with NO₂, NH₃, O₂, and combustible sensors.

Recording and monitoring instruments need to be calibrated from time to time with NO₂/air mixtures with exactly known NO₂ concentrations. Considering the high reactivity of NO₂, it is not possible to keep NO₂/air calibration mixtures in compressed gas cylinders for longer times. Fresh NO₂/air mixtures with accurate and reproducible NO₂ concentrations can be generated by permeation tubes. NO₂ gas mixtures in the range of 5 to 15 μmol/mol with a standard relative uncertainty of 0.4% can be produced with permeation tubes. Nitric acid contamination present in the gas mixtures was determined using a FTIR spectrometer and a non-dispersive UV analyzer and subtracted from the NO₂ readings [66].

Numerous electrochemical semiconductor sensors that have been calibrated for NO₂ and other atmospheric contaminants are based on tin(IV) oxide.

One of the main applications of conducting polymers in chemiresistor sensors for sensing hazardous hypergolic liquid propellant vapors at explosive, toxic, and threshold limit value concentration levels is for vapors of NO₂ and MON-3 [67]. The same instruments can also detect vapors of hydrazines, such as hydrazine, methylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) and HCl, in the exhaust plumes of solid propellant rockets. To properly use these instruments, one must understand electrical conducting mechanisms during sensing, thickness of sensing layer, factors that influence conductivity, response time, recovery time, detectable range, interference from other pollutants, and minimum detectable limit of the sensors. Advantages and disadvantages of conducting polymer coated fabrics as novel chemiresistor sensors over inorganic substrates need to be evaluated.

Both badge- and tube-type passive samplers can be used to monitor NO_x pollution in areas where expensive electronic equipment is not available. Passive samplers are less reliable, and results may vary with how they are applied under field conditions [68].

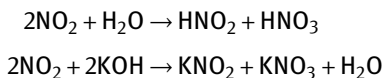
The methods summarized in this chapter are subdivided into those that analyze nitrogen oxides in air directly and those that absorb oxides first into water or another solvent for subsequent analysis by a wet chemical method. The development of NO₂ detectors went on hand in hand with the development of analytical instruments for the detection of other hazardous substances in air [69]. Hundreds of instruments are available commercially for the analysis of NO_x in polluted urban atmospheres, in stack gases of stationary power plants, and in automobile exhaust. Many of those can be used at rocket test sites as well.

4.5.2 Direct Reading Instruments for Analysis of Nitrogen Dioxide in Air at Workplace

At the beginning of the Space Shuttle era, an NO₂ analyzer was developed specifically for use in the fueling of the Shuttle Orbital Maneuvering System (OMS) and Attitude Control System (ACS) tanks with MON [70]. The instrument was developed for NASA by what was then Energetics Science, Inc. The instrument consisted of a sample pump, an electrochemical cell, and control and display electronics. The pump pushed the air sample through an electrochemical cell where the vapors were analyzed, and an output proportional to the NO₂ concentration was produced. The output was displayed on a panel meter and also available at a recorder jack for a permanent record and monitoring with a threshold alarm. The electrochemical cell contained platinum electrodes, and the sensing and counter electrodes were potentiostatically controlled at -200 mV with respect to the reference electrode. The cell was filled with electrolyte, consisting of 13.5 cm³ of a 23% solution of KOH (which would of course change with time due to absorption of atmospheric CO₂). The range was 0.1–10 ppm, and the 90% response time was 20 s.

4.5.3 Analysis of Nitrogen Dioxide in Air with Absorption into Water

Instruments that first absorb NO₂ into water or a mildly caustic solution rely on the initial conversion of NO₂ into nitrate and nitrite in aqueous solution:



As the next step, it is much easier to analyze for nitrite than it would be to analyze for nitrate. Nitrite in aqueous solution is typically analyzed by the Saltzman reagent (also called Lunge's Reagent, Griess-Ilosvay Diazo reagent) which forms an intensely red colored diazo dye with traces of nitrite [71]. Chlorine, sulfur dioxide, nitrosyl chloride, ozone, and reducing agents would interfere in this reaction. These wet methods are more time consuming than modern instrumentations that give direct readings and are now only used as referee methods to verify proper operation of some of the direct-reading instruments in use.

A crude indication of the presence of NO₂ (or other oxidizing gases) in air can also be achieved by moist potassium iodide-starch paper, which turns purple-brown as the result of the oxidation of iodide by NO₂. Chlorine, sulfur dioxide, ozone, and any other oxidizing gas will interfere. See also [72].

A spectrophotometric method determined the NO₂ content by absorption at 400 nm in a cell with a 10-cm optical path and applied a correction factor for undissociated (invisible) N₂O₄. The accuracy was ±3.5% relative for concentrations up to 4 vol.-% NO₂ [73].

The spectrophotometric Saltzman (Griess-Ilosvay) reagent wet method is more accurate, less susceptible to interference, and faster to perform than the phenyldisulfonic acid method, which was once recommended as an ASTM procedure [74, 75]. Both methods depend on the complete conversion of all NO in the sample using oxygen instead of air to achieve complete conversion to NO₂, which is a very slow process. Depending on the initial NO concentration and O₂ partial pressure, the complete conversion can take from several hours up to a day.

A comparison of wet chemical spectrophotometric methods for the analysis of nitrogen dioxide in fumes from explosives showed that results obtained with three different methods agreed with each other, but that some reagents required excessively long contact times for complete absorption of NO₂ (on the order of 12h overnight). Much faster absorption, by shaking a gas sample with liquid for only 3 min, was possible with a dilute NaOH solution, achieving 92% of the completeness of an overnight contact time with the acidic reagent in direct contact with the gas [76].

A method for determining 2 to 10 ppm of NO₂ in air is a liquid absorption method based on a Griess-Ilosvay reaction in which nitrogen dioxide recovery can be improved by the incorporation of sodium arsenite in an alkaline absorption solution [64]. The same author also described a cheap test-paper method that was unaffected by humidity and air and involved the use of papers treated with p-anisidine and glycerol, with a storage life of 3 months.

The sodium arsenite method has a constant-high collection efficiency (82%) for nitrogen dioxide and is insensitive to normal variations in operating parameters [77]. Nitric oxide and carbon dioxide are positive and negative interferents, respectively.

4.5.4 Dosimeters for Cumulative Analysis of Nitrogen Dioxide in Air

Gas detection tubes containing an indicator on a solid sorbent (silica gel) that changes color irreversibly are very popular for a quick but less accurate, semi-quantitative indication of nitrogen oxides in air, requiring active pumping either by hand with a bellows pump counting the number of strokes or using a mechanical pump with calibrated air flow rates. Common brands include Dräger, MSA, and Kitagawa.

Thin-film personal dosimeters patterned after those used for ionizing radiation can be used to monitor the cumulative exposure of rocket test stand personnel to toxic vapors [78, 79]. They are often worn as badges on work clothing, on a lapel button close to the nose.

A simple personal dosimeter for NO₂ can be prepared by dipping discs cut from a silica gel chromatogram sheet into a solution of diphenylamine and oxalic acid in methanol and drying them in air [80]. The strips suffer from exposure to heat and/or light and should be covered by a perforated plate in a lapel-mounted plastic holder. Nitrogen dioxide forms a green color while other oxidizers form a blue color. The impregnated disc is mounted on a color standard for concentration-time products of 50, 100, and 300 ppm-minutes.

A cumulative air sampling method for the collection of air samples containing both NO₂ and NO in the range of 0.5 to 5 ppm NO₂ and 9 to 50 ppm NO is based on trapping the two gases in a solid sorbent sampling tube by collecting NO₂ on a triethanolamine (TEA)-impregnated molecular sieve surface [81]. Nitric oxide is oxidized to NO₂ by a solid oxidizer and the converted NO collected on another section of TEA sorbent. The trapped NO/NO₂ on each TEA section is desorbed and the concentrations are determined spectrophotometrically. At all concentrations tested, the collection efficiency for NO₂ averaged approximately 96%. The collection efficiencies for NO were as follows: at 9 ppm, 97%; at 11 ppm, 106%; at 24 ppm, 84%; and at 50 ppm, 67%.

4.5.5 Continuously Reading Direct Readout Monitors of Nitrogen Dioxide in Air

There is a large number of air monitoring instruments on the market, some of which are specific to nitrogen dioxide, while others can detect more than one propellant contaminant at a time, e.g., hydrazine or MMH. The problem with procuring one of those instruments is that this is a very limited market, and companies enter and leave the market at a high rate. Other companies are bought out or merge and change their names. Instruments may not be supported with spare parts for more than a few years. An evaluation of commercially available portable nitrogen dioxide detectors done in 1990 may be without value 10 years later and would have to be redone every few years [82].

Under contract to USAF Edwards Air Force Base, Mine Safety Appliances Company once developed an instrument suitable for continuous monitoring of toxic levels of NO₂, UDMH, B₅H₉, N₂H₄, F₂, and ClF₃, but this is no longer in use [83].

4.5.5.1 Infrared Absorption NO₂ Monitors

Nitrogen dioxide in air can be detected by its IR absorption spectrum. Instruments based on the IR absorption of NO₂ can measure the toxic gas concentration, record the variation during a full work shift to document compliance with workplace safety regulations, and sound an alarm if the tolerable concentration is exceeded. The threshold where the alarm starts ringing would be set close to the Threshold Limit Value – Time Weighted Average (TLV-TWA) established by the occupational health agencies [84].

4.5.5.2 Wet Chemistry Spectrophotometric NO₂ Monitors

For this continuous analysis method, the gas stream to be analyzed is aspirated into a capillary glass spiral column where it flows concurrent or countercurrent to a stream of absorbent solution, which may or may not already have the color-forming reagent in it [85]. The most commonly used reagent for NO₂ analysis in these instruments is the Griess-Saltzman reagent [86, 87]. The detection limit is about 1×10^{-10} by volume for 1-h measuring periods. The question was which calibration method should be preferred, feeding a known NO₂ concentration in a gas stream from a permeation device into

the instrument or using a standardized sodium nitrite solution to replace the effluent from the absorption loop [88]. Permeation tubes were used to prepare standard atmospheres at realistic levels, 0.02 to 1.8 ppm of NO_2 . It was shown that 1 mol of nitrogen dioxide is equivalent to 0.764 mol of nitrite ion with use of the unmodified Saltzman reagent. Two absorbers provide separate analyses, one for NO_2 alone and one for the sum of NO and NO_2 after oxidizing the sample stream with ozone or chlorine dioxide, followed by a wet Griess-Saltzman reagent online analyzer [89].

4.5.5.3 Fiber-Optic NO_2 Monitors

A fiber-optic chemical dosimeter system was patented that can detect the presence of nitrogen dioxide using colorimetric sensors that react selectively with the NO_2 and then absorb laser light pulses communicating through a fiber-optic network having a diode laser source transmitting interrogation pulses to a multi-station array of distributed sensors covering a wide area propellant storage or rocket launch site, the sensor being reactive cladding or distal end types, both providing optical reflective returns transmitted to an optical reflectometry monitor to determine the concentration and location of gas clouds over the monitored area [90]. For example, phosphomolybdic acid reagent in the reduced (blue) state can be coated at the end of a fiber optic for reacting to the presence of nitrogen dioxide and changing color. The same apparatus can also be used for detecting hydrazine vapors, starting with phosphomolybdic acid reagent in the yellow state, changing color to blue in the presence of hydrazine.

A fiber-optic NO_2 and hydrazine sensor used an acid-base indicator that underwent color changes depending on which gas was present [91, 92]. Bromothymol blue bromocresol green mixture (1/1) in hydrogel (1/1) produced a blue-green indicator for hydrazine and/or NO_2 . The sensor was tested several times over a period of 8 weeks, and the response was consistent when exposed to 52 and 18 ppm hydrazine or 400 and 200 ppm NO_2 .

4.5.5.4 Thin-Film Sensors

Chemiresistors change their electric conductivity in the presence of certain chemicals. A review article covered the main applications of conducting polymers in chemiresistor sensors for sensing hypergolic liquid propellant vapors and toxic exhaust plume acidic vapors of solid rocket motors at threshold limit value concentration levels [67]. This review included NO_2 and MON-3. The discussion of key features of sensors, such as conducting mechanisms during sensing, thickness of sensing layer, factors that influence conductivity, response time, recovery time, detectable range, and minimum detectable limit, is a good introduction to this topic.

4.5.6 Leak Detection Instruments

In addition to active leak detectors that sound an alarm if a leak is detected, passive leak detectors will not only alert the observer, but also locate the leak.

4.5.7 Remote Sensing of Nitrogen Dioxide for Atmospheric Air Pollution Studies

The concentration of NO_2 in Earth's atmosphere has been determined in real time and with a sensitivity of 1 ppm by laser excitation at 4416 and 4880 Å and fluorescence at 0.7 to 0.8 μm [93]. The method was tested on typical smoggy days in the Los Angeles area.

Using a pulsed dye laser and a non-resonant optoacoustic detector, the absorption spectrum of NO_2 has been measured in the spectral region of 480–625 nm at various cell pressures and at various concentrations in air [94]. The results of the measurements as a function of NO_2 concentration in air demonstrated the detection sensitivity of the system. An extrapolated sensitivity of 4 ppb NO_2 /W of laser power was achieved. Similar equipment can be used to remotely monitor N_2O_4 storage areas for potential leaks.

5 Toxicity of Nitrogen Dioxide

Most toxicity studies are related to the inhalation of NO_2 from atmospheric pollution, often in combination with other air pollutants. Other studies are concerned with the formation of NO_2 during the combustion of propellants in guns and detonation of explosives in military ordnance in battlefield situations.

The hazard index, the vapor pressure divided by the toxicity number, of nitrogen dioxide and dinitrogen tetroxide is the highest among all currently used rocket propellants. There have been dozens of industrial and agricultural worker fatalities due to nitrogen dioxide poisoning, although few of them were caused by the use of N_2O_4 as a rocket propellant. Although the previous sections in this book dealt mostly with N_2O_4 , the inhalation toxicity studies are done almost exclusively only with the dissociation product of N_2O_4 , NO_2 vapor, at low concentrations. In most cases the leakage and spill accidents we are concerned with will involve the equilibrium mixture of dinitrogen tetroxide and nitrogen dioxide at the natural boiling point, just above room temperature. The small percentage of N_2O_4 present in the vapor has been neglected by most investigators. The contribution of N_2O_4 to NO_2 toxicity is unknown. In most cases, either of the two nitrogen oxides reacts quickly with water in body fluids to form nitric acid and nitrous acid. There are many summary publications on the toxicity of nitrogen oxides, mostly relating to the occurrence of nitrogen oxides in smog in polluted urban and industrial atmospheres. Relatively few experiments, many of those sponsored by rocket-propellant-using agencies, have used pure nitrogen dioxide for animal exposure tests and the establishment of the safe tolerable limits of this pollutant.

The most comprehensive and authoritative publication on the health effects of nitrogen oxides is the summary compiled by the World Health Organization (WHO) Task Group on Environmental Health Criteria for Nitrogen Oxides, which is updated periodically [95]. Other useful summaries are [96, 97]. The effects of exposure to high-

level NO_2 are of great interest to the military since high levels of NO_2 may be found in combat situations in the combustion products of propellants and explosives [98, 99]. It is also important to the civilian sector in occupational settings where accidents may occur, such as in silo filler accidents on agricultural farms. More information is needed on the chemistry of NO_2 interaction with body tissues, on the dosimetry of its uptake (isolated lung), on the biological effects of exposure *in vivo* in small animals (rats), large animals (sheep), and, finally, in the most relevant species, humans [100]. Most of these published studies are concerned with the lifelong, low-level inhalation of NO_x by the general population at large and not so much with the exceedingly rare accidental exposure of military personnel and rocket launch site or missile silo propellant-handling personnel to high levels of NO_2 [101]. Based on epidemiological studies, clean air legislation limiting the amount of allowable NO_x in the air in population centers can have a significant impact on economics and energy use patterns, both for stationary power plants and mobile power plants in automobiles and airplanes. Overly restrictive air pollution regulations, such as in California, may cause some industrial activities to leave the state and relocate to areas with less restrictive air pollution regulations, such as south of the border.

5.1 Inhalation Toxicity of Nitrogen Dioxide and Dinitrogen Tetroxide

Since the first documented fatal poisoning caused by NO_2 in 1804, several hundred more accidental poisoning deaths due to NO_2 have occurred worldwide [102].

Because of the relatively low water solubility of NO_2 and N_2O_4 , it is only slightly irritating to the mucous membranes of the upper respiratory tract. Therefore, at low concentrations where the red color of fumes is not visible, the warning power of NO_2 and N_2O_4 is low, and dangerous amounts of the vapor may be inhaled before the worker notices any real discomfort. The odor threshold is often assumed to be 0.2 ppm. Higher concentrations (60 to 150 ppm) cause immediate irritation of the nose and throat with coughing and burning in the throat and chest. Symptoms often clear after breathing fresh air, and the worker may feel well for several hours. After a relatively symptom-free 5- to 72-h period, pulmonary edema gradually develops, causing fatigue, restlessness, coughing, difficulty in breathing, frothy expectoration, mental confusion, lethargy, cyanosis, and a weak, rapid pulse. Inflammation of the lungs causes exudation into alveolar spaces interfering with gas exchange in lungs. The fluid lost from the blood also results in severe hemoconcentration. Unconsciousness and death by asphyxiation can result, usually within a few hours following the onset of pulmonary edema. Some patients who recover from the acute effects later may develop chronic pulmonary disease. The minimum lethal and maximum tolerated (survivable) human exposures (time $\times$ concentration product) to NO_2 and N_2O_4 have not been exactly established. Concentrations of 100 to 150 ppm are dangerous to humans for short exposures of 30 to 60 min. Concentrations of 200 to 700 ppm may be fatal after even very

short exposures. Data collected in a 1976 literature review by ACGIH suggest that a 60-min exposure of humans to 100 ppm leads to pulmonary edema and death, 50 ppm leads to pulmonary edema with possible subacute or chronic lesions in the lungs, and 25 ppm leads to respiratory irritation and chest pain.

Inhalation of brown fumes from the evaporation of N_2O_4 is a serious health threat and must be avoided. The exact composition of the brown fumes varies, but one cannot differentiate between the toxic effects of undissociated, colorless N_2O_4 and its dissociation product, the distinctly colored red-brown NO_2 . The red color of NO_2 becomes visible only in warm air at temperatures above 293 K (20 °C). There may be an invisible N_2O_4 toxicity hazard at lower temperatures.

The distinct odor threshold for NO_2 is at 10 ppm by volume. Larger concentrations can be recognized by their intense red-brown color and their tendency to linger along the ground since the vapors are heavier than air. The density of NO_2 at 294 K (21 °C) is 3.3 g/L, so it is about three times heavier than air. Nitrogen dioxide clouds are observed not only where N_2O_4 is used as a rocket propellant, but also when the gas space above red fuming nitric acid (RFNA) is vented or during the startup or shutdown of rocket engines operating with nitric acid as the oxidizer.

Inhalation of nitrogen dioxide in high concentrations may result in acute bronchospasm, delayed pulmonary edema, and late *bronchiolitis obliterans*, in that sequence. Low concentrations induce pulmonary fibrosis with chronic exposure [103]. See also [104–107].

NO_2 is a free radical and powerful oxidant that is reduced to nitrite ion NO_2^- in the lung; NO_2^- is then oxidized to nitrate ion NO_3^- in the blood. NO_2 in the presence of O_3 in a polluted atmosphere produces N_2O_5 and NO_3 (a free radical), both of which are more toxic than NO_2 . A potentiating effect that is observed in the toxicity of NO_2 plus O_3 (compared to effects of NO_2 or O_3 alone) may be explained on the basis of N_2O_5 and NO_3 formation [108].

The vapors escaping from RFNA at room temperature are essentially N_2O_4 and NO_2 , and the inhalation toxicity is the same as that of N_2O_4 without any nitric acid present [109].

To investigate the effects of anisodaminum and dexamethasone on the changes of blood gas of N_2O_4 -poisoned test animals, 224 male Wistar rats were divided randomly into four groups: **(1)** N_2O_4 blast-poisoned combined injury group; **(2)** anisodaminum-treated group; anisodaminum (3 mg/kg) was given *ip* immediately, 15 min, and 2 h after the injury; **(3)** dexamethasone-treated group; dexamethasone (10 mg/kg) was given *ip* immediately, 15 min, and 2 h after the injury; **(4)** anisodaminum and dexamethasone combination-treated group; anisodaminum (3 mg/kg) and dexamethasone (10 mg/kg) were given *ip* immediately, 15 min, and 2 h after the injury. Each group was subdivided into a control group and six treatment groups, which were necropsied 3, 6, 12, 24, 48, or 72 h after the injury for blood gas analysis. Measurements showed that in the N_2O_4 blast-poisoned group, PaO_2 and pH of the plasma were significantly decreased, while PaCO_2 was increased. The combined use of anisodaminum and dexamethasone in the

early stage significantly ameliorated the disorders of the blood gas of the injury. It was suggested that the combined use of anisodaminum and dexamethasone in the early stage is effective in the treatment of blast injury caused by explosion of dinitrogen tetroxide [110].

The PaO_2 of rats in three groups, especially that of the blast-poisoned group, was significantly decreased 3–6 h after the injury, and several died from respiratory failure. Each group underwent pathomorphologic changes in the main organs, and the change in the blast-poisoned group was the worst [111].

5.1.1 Chronic Exposure to Nitrogen Dioxide

Chronic exposure to nitrogen dioxide is usually associated with atmospheric pollution and urban smog. It is less likely to occur at rocket test sites or rocket launch sites [112]. Lung damage can be caused by long-term exposure to as little as 2 ppm [113]. Rats exposed continuously to 2 ppm NO_2 in air survived their ordinary lifetimes with persistent tachypnoea and usually died of non-pulmonary diseases, but they showed a reduced cleansing function of the periphery of the lung.

5.1.2 Olfactory Threshold

It is strange that for a common chemical that is so widely used whose toxicity has been thoroughly examined it is difficult to find reliable data on the olfactory threshold for this toxic compound. The odor threshold was once assumed to be 0.2 ppm. The distinct odor threshold for NO_2 is 10 ppm by volume. In a human volunteer test, one-fourth of the subjects ($N = 59$) tested could detect NO_2 at 0.9 ppm. With 1 ppm NO_2 , 8 of 59 (13.6%) subjects experienced irritation of the nasal mucosa [114]. It would be important to know whether the olfactory threshold at which NO_2 vapors can be reliably identified by their odor is above or below the Immediately Dangerous to Life or Health (IDLH) concentration of 20 ppm. Also, at what concentration do NO_2 vapors become visible in air near a leak? N_2O_4 vapors are invisible but just as toxic as visible NO_2 vapors.

The odor threshold levels for NO_2 have been generally quoted at 5 ppm by volume. Seven years of field experience by propellant loading personnel have indicated that the actual odor thresholds are considerably below these literature values [115]. Since odor threshold levels are used by safety and operating personnel at Kennedy Space Center as an indication of exposure, it was considered appropriate to evaluate this field experience. On the basis of these data and the results of some controlled studies, it was concluded that the actual odor thresholds are 0.5 ppm or less for NO_2 .

5.2 Maximum Allowable Workplace Concentrations for Nitrogen Dioxide

The maximum allowable workplace concentration as established by the US Occupational Safety and Health Administration has remained constant for a relatively long time, compared to the several-orders-of-magnitude changes that occurred during the same time for hypergolic hydrazine-based fuels. The American Conference of Governmental Industrial Hygienists (ACGIH)-recommended maximum allowable concentration, time-weighted average TWA for an 8-h workday at one time was 5 ppm until 1990, when it was lowered to 3 ppm. The current guidelines for limits on exposure to $\text{NO}_2/\text{N}_2\text{O}_4$ vapors are listed in Table 4.

Table 4: Maximum exposure limit guidelines for nitrogen dioxide

ACGIH TLV	OSHA PEL	NIOSH IDLH	NIOSH REL
STEL: 5 ppm; TWA: 3 ppm	(vacated) STEL: 1 ppm (1.8 mg/m ³) Ceiling: 5 ppm (9 mg/m ³) PEL: Ceiling 5 ppm	IDLH: 20 ppm; STEL: 1 ppm; STEL: 1.8 mg/m ³	ST: 1 ppm

STEL Short-term exposure limit

PEL Permissible exposure limit

OSHA Occupational Safety and Health Administration

NIOSH National Institute for Occupational Safety and Health

REL Recommended exposure limit

The same exposure guidelines would apply to military and space agency personnel, although the likelihood of accidental exposure to high concentrations of NO_2 is much higher for those groups than for the population at large [116].

The National Ambient Air Quality Standard (NAAQS) for NO_2 , initially established in 1971, is 0.053 ppm (annual average). Ambient concentrations monitored in urban areas in the United States are approximately 0.015 ppm, as an annual mean, i.e., below the current NAAQS. Short-term (1-h peak) NO_2 concentrations outdoors are not likely to exceed 0.2 ppm, and even 1-h periods exceeding 0.1 ppm are infrequent. Inside homes, 1-h NO_2 peaks, typically arising from gas cooking, can range between 0.4 and 1.5 ppm. See also [117] for acute and chronic inhalation toxicity studies with NO_2 and other propellants.

5.3 Emergency Exposure Limits for Nitrogen Dioxide

The original NIOSH Standard Completion Program (SCP) IDLH was 50 ppm. The originally chosen IDLH was based on earlier publications that stated that concentrations above 50 ppm are considered dangerous to humans for short exposures. Other

sources cited a rat 4-h LC50 of 68 ppm. The IDLH was later revised to 20 ppm [118, 119]. In September 2017, the IDLH was lowered further to 13 ppm [120]. Short-Term Public Emergency Guidance Levels (SPEGLs) proposed by the National Research Council are summarized in Table 5.

Table 5: Historical Short-Term Public Emergency Guidance Levels for nitrogen dioxide

Organization	Exposure duration	Maximum concentration, ppm
American Industrial Hygiene Association (1964) [121]	5 min	35
	15 min	25
	30 min	20
	60 min	10
National Research Council, Committee on Toxicology (1985) [122]	1 h	1
	2	0.5
	4	0.25
	8	0.12
	16	0.06
	24	0.04

Emergency exposure limits for NO₂ for military personnel, typically young, healthy males under close medical supervision, were established by the US National Research Council, Committee on Toxicology as follows: 10 min: 30 ppm; 30 min: 20 ppm; 60 min: 10 ppm [123].

5.4 Symptoms of NO₂ Inhalation Poisoning

Because NO₂ is not very soluble in water and body fluids, it can penetrate deeply into the respiratory system before a cough reflex is triggered. Coughing is triggered only at concentrations of 60 to 100 ppm, a relatively high concentration if one considers that 100 to 150 ppm can lead to acute poisoning within 30 to 60 min and that exposure to 200 to 700 ppm can be deadly even after short periods of inhalation.

The heinous aspect of NO₂ poisonings is that the damaging toxic effect often becomes apparent only several hours, possibly up to 24 h, after the incident [124]. The first symptoms are dizziness, headache, nausea, and weakness. At the next level of severity of poisoning, the victim will have difficulty breathing, experience shortness of breath, and struggle for air. This struggle may lead to death. If a poisoning incident progresses to this point, it is usually too late for medical help. If the symptoms are recognized early enough, oxygen inhalation is recommended as a first aid measure until professional medical help arrives.

The physiologically adverse action of NO_2 occurs through absorption in the lungs and into the bloodstream, where it disproportionates into nitrous acid and nitric acid, dropping the pH of blood below the point where it can effectively transport oxygen. Nitrate is not the main culprit. It is mostly the toxicity of nitrite that interferes with life-sustaining chemical reactions. Even after less serious nitrite poisoning incidents, the poisoning victim remains in an anemic state. Cases of acute NO_2 poisoning may lead to emphysema, accumulation of fluid in the lungs. This effect may take several hours to develop to its full level of severity.

5.5 Results of Laboratory Animal Exposure Tests

Chronic exposure of rats, mice, and guinea pigs to NO_2 (fumes from RFNA) for a duration of up to 4 h/day, 5 d/week, 6 months total showed that exposure to 4 ppm NO_2 caused no permanent detectable adverse effects [125]. At 9 to 14 ppm NO_2 lung damage was detected after only 6 weeks of testing. In another test series with male albino rats, the LC50 was 138 ppm after 30 min of inhalation, and 67 ppm after 4 h of inhalation [126, 127].

Most tests of animal exposure to toxic rocket propellants are conducted with only the oxidizer or only the fuel present. In real-life situations, where a missile or a launch vehicle with storable propellants malfunctions, there may be clouds of mixtures of nitrogen dioxide with fuel vapors that have not completely reacted because one component or another may be in excess. Spills very rarely happen at stoichiometric ratios of the offending propellants, and spilled propellants may not ignite instantly. Often the attempt to extinguish the flames of burning propellants releases clouds of incompletely burned intermediate reaction products.

Tests have been conducted in which animals were exposed to the clouds of partially reacted NTO and UDMH simulating a propellant spill and explosion. A “blast tube” was designed in which the propellants are injected simultaneously and allowed to react partially, simulating a propellant spill [128, 129]. The test animals were then exposed to the products of the incomplete reaction. A total of 168 healthy male rats were randomly divided into 3 groups and exposed to blast tube products for 10 min. The rats inhaling an excess of UDMH were designated the BU group, the rats inhaling an excess of N_2O_4 were designated the BN group, and the rats inhaling both UDMH and N_2O_4 were designated the BUN group. The clinical symptoms of the rats in the BUN group were aggravated progressively, the pulmonary alveoli were diffusely filled with pink exudate and large patchy hemorrhage, and pneumorrhagia and pneumoedema were aggravated. Cloudy swelling or hyaline degeneration occurred in the cardiac muscle cells in different degree and individual myocardial fiber was broken. The myocardial mesenchyme was loose and hemorrhage, and edema occurred. The pathologic change of the myocardium was aggravated. Dilation of the hepatic sinusoid and cloudy swelling in the hepatic cells were observed. The blood oxygen saturation in

all three groups decreased significantly at 3–12 h after injury and reached its lowest point at 3–6 h after injury. In addition to acute toxicity effects, the exhaust products from the blast tube may also be carcinogenic. After studying the immediate adverse effects, mostly on the lungs and dissolved gases in the blood system, additional tests looked at the presence of carcinogenic compounds, as indicated by their ability to create precancerous genes.

In another blast tube test, the animals were necropsied 3, 6, 12, 24, 48, and 72 h after exposure to observe the changes in pathomorphologic manifestation, blood gases, and gene expression [130]. The arterial oxygen saturation values of animals in all three groups decreased significantly at 3–6 h after exposure, and some of the animals died from respiratory failure.

In a similar test, 40 healthy mice, weighing from 18 to 22 g, were divided into 4 groups [131]. The mice were put into a 112-L cabinet and inhaled the partially reacted NTO/UDMH vapor mixture for 2 h. The exposure was repeated three times a day for 4 d, and then the mice were necropsied on the fifth day. The content of malondialdehyde (MDA) in serum and lipofuscin in liver homogenate and the activity of T superoxide dismutase (SOD) in serum were measured and it was found that **(1)** the content of serum MDA of 300-ppm group decreased significantly compared to that in the control ($P0.05$), **(2)** serum T SOD activity of the 60-ppm group and 300-ppm group decreased significantly compared to the control ($P0.01$), **(3)** the content of liver lipofuscin in the 9-ppm group increased significantly compared to the control ($P0.05$). It was concluded that low and moderate doses of liquid propellant mixtures can produce an abundance of free radicals but no oxidative damage.

It is difficult to find a common denominator in NO_2 inhalation pulmonary toxicity testing done with different animal species. Attempts were made to eliminate nasal variations among species and dermal absorption by administering the 200 ± 5 ppm ($376 \pm 9 \text{ mg/m}^3$) NO_2 -containing air directly to the lungs of rats for 15 min [132]. While most of the animal exposure tests were done with rodents, and it is difficult to extrapolate from rodent toxic effects to human exposure to this chemical, fewer animal exposure tests have been conducted with larger mammals, which would be more relevant to human NO_2 inhalation. Testing was done with 15- to 20-min exposures to either air (control) or 500 ppm NO_2 in sheep [133, 134]. Nose-only and lung-only routes of exposure were compared for effects on NO_2 pathogenesis. Histopathologic examinations of lung tissues were performed 24 h after exposure. Nose-only and lung-only routes of exposure were compared for effects on NO_2 pathogenesis. Bronchoalveolar lavage fluids from air- and NO_2 -exposed sheep were analyzed for biochemical and cellular signs of NO_2 insult. The influence of breathing pattern on NO_2 dose was also assessed. Five hundred ppm NO_2 exposure of intubated sheep (lung-only exposure) was marked by a statistically significant, albeit small, blood methemoglobin increase. The exposure induced an immediate tidal volume decrease and an increase in both breathing rate and inspired minute ventilation. Pulmonary function, indexed by lung resistance and dynamic lung compliance, progressively deteriorated after exposure.

Groups of rats were exposed to NO₂ for 3, 6, 12, 24, 48, and 72 h, and the long-term effects were studied during the post-exposure observation period of 2 months [135].

The comparative acute toxicity of NO₂ was studied in five species: mice, rats, guinea pigs, rabbits, and dogs [136]. Fifty ppm NO₂ was a critical concentration; below this value mortality rarely occurred with exposures of up to 8 h. A study was made of the sequential development of pathologic changes in the lung with grading of edema, congestion, interstitial irritation, bronchiolitis, and interstitial fibrosis. Acute deaths were characterized by marked bronchiolitis, desquamated bronchial epithelium, infiltration by polymorphonuclear cells, and edema fluid in the alveoli. Interstitial fibrosis occurred in about one-third of the surviving animals at 30 d and persisted in some for periods up to 6 months. Stress induced by exercise following exposure, by adrenalectomy, or by high levels of CO₂ increased mortalities.

Other tests were conducted in dogs and in rabbits [137]. In rabbits, after NO₂ exposure for 10 min, the observed pulmonary effects became more pronounced with increasing NO₂ concentrations (0, 125, 175, 250, 400, 600, or 800 ppm) (1 ppm NO₂ is equivalent to 1.88 mg/m³). The effects in rabbits were found to be broadly comparable to those in rats. See also [138].

5.5.1 Hematological Effects of NO₂ Inhalation on Blood Chemistry

Blood nitrite and nitrate of mice exposed to 5–40 ppm NO₂ were determined using naphthylethylenediamine and a Cu-Cd reduction column [139]. When mice were exposed to 40 ppm NO₂, nitrite became constant in 10 min. Nitrite declined rapidly, with a half-life of several minutes, after exposed mice were removed to fresh room air. Nitrate showed changes similar to those of nitrite; however, the concentration in the blood was higher and the half-life was longer. Dose-effect relationships were also determined at concentrations ranging between 5 and 40 ppm for 1 h of exposure. No increase of methemoglobin was observed at these concentrations. The addition of fresh mouse blood to sodium nitrite *in vitro* indicated a rapid conversion of nitrite to nitrate with an increase of methemoglobin, whereas addition to sodium nitrate caused no changes. The fate of inhaled NO₂ in the living body remains to be studied. Nitrogen dioxide inhalation affected red blood cells of rats and mice and caused changes in components of red cell membranes during *in vivo* exposure to NO₂ [140, 141].

5.5.2 Pulmonary Effects of NO₂ Inhalation

The relationship between respiratory function and morphological changes in 10 dogs exposed for 6 h to 69 ppm NO₂ was studied based on functional assessments of breathing pattern, breathing mechanics, forced expiration, gas exchange, and acid-base status [142]. Gross, microscopic, and ultrastructural evaluations were made of lung tissues from dogs killed at 0.1, 1.0, 2.0, 3.0, 7.0, and 14.0 d after exposure. Functional changes were similar to those reported for humans. The principal dysfunction was gas-exchange impairment, apparently resulting from foam in the

airways. Breathing-pattern alterations appeared to result from stimulation of neural receptors. Gas-exchange measurements provided the most useful indicators of the pulmonary damage observed in this study. See also [143, 144].

Quite often NO_2 inhalation toxicity studies in animals were conducted in parallel with or in combination with ozone exposure since both gases are constituents of atmospheric smog in polluted areas [145].

Table 6 is a summary of LC50 values obtained in animal tests, in comparison to the minimum concentration that resulted in human fatalities after only 1 min of inhalation. Some Safety Data Sheets (MSDSs) give the LC50 by inhalation in rats as 115 ppm/h.

Table 6: Median lethal NO_2 concentrations for inhalation in animals.

Animal	Inhalation LC50, ppm	Exposure duration
Mouse	1000	10 min
Rat	88	4 h
Guinea pig	30	1 h
Rabbit	315	15 min
Human	200 ^a	1 min

^aLowest published lethal concentration

Data source: [146]

It is already extremely hazardous for living beings to be exposed to NO_2 by itself or UDMH by itself, but the combination of the two poisons, as it may be encountered at launch sites after launch vehicle catastrophic failures, may aggravate the situation. The oxidative damage parameters of mice poisoned by inhaling gas mixtures containing NO_2 (N_2O_4) and UDMH were studied by exposing groups of mice, rats, or rabbits to simulated reacting hypergolic propellant spills [131, 147, 148] or to simulated launch site disasters with hypergolic fires and explosions and N_2O_4 releases [147, 149].

5.6 Human Volunteer Exposure Studies

Twenty human subjects with asthma and chronic bronchitis and 10 normal, healthy adults were exposed to 0.5 ppm NO_2 for 2 h in an environmental chamber [150]. Seven of the 13 subjects with asthma experienced breathing difficulty symptoms with exposure, while only one each of the subjects with chronic bronchitis and the healthy, normal group experienced symptoms. Exposure to NO_2 caused significant pulmonary function changes in decreased quasistatic compliance for both the 10 normal subjects and the 20 subjects with asthma and chronic bronchitis. In addition, functional residual capacity increased significantly for the 20 subjects with asthma and chronic bron-

chitis. It was concluded that exposure of subjects with asthma and chronic bronchitis to 0.5 ppm NO₂ for 2 h does not produce a significant decrement in their pulmonary function.

Ten healthy volunteers were subjected to six repeated exposures with 4 ppm NO₂ (7 mg/m³) for 20 min every other day [151]. Analysis of the recovered bronchoalveolar lavage fluid demonstrated that repeated exposures to NO₂ caused a lung cell response different from that reported after a single exposure. Amounts of lavaged alveolar macrophages, B-cells, and natural killer cells were decreased. Lymphocyte numbers in peripheral blood were reduced after exposure. These results suggested that repeated exposure to NO₂ adversely affects the immune defense and leaves inhalation victims to increased susceptibility to respiratory infections.

Eighteen non-smoking normal subjects (mean age = 25 ± 4 years) were exposed to filtered air or 2 ppm NO₂ gas for 1 h in a 30-m³ environmental chamber on different days, typically 1 week apart, in a double-blind randomized test [152]. Lung function tests included forced vital capacity, forced expiratory volume in 1 s, partial expiratory flow at 40% of vital capacity, functional residual capacity, and specific airway conductance and were measured before and after exposure. No significant changes were noted in the lung function tests after NO₂ exposure. These findings indicated that normal non-smokers exposed to 2 ppm NO₂ for 1 h develop an increase in airway reactivity to aerosol, which is not associated with changes in lung volumes, flow rates, or respiratory symptoms [153].

Fifteen subjects were exposed to nitrogen dioxide or air for 3 h in a double-blind, randomized fashion in a 45-m³ environmental chamber, with intermittent exercise sufficient to quadruple ventilation [154]. Pulmonary function was measured during and after exposure, and airway reactivity to carbachol was assessed before and after exposure. The 15 subjects were exposed to continuous 1.5 ppm NO₂ and underwent bronchoalveolar lavage 3.5 h after exposure. No significant symptomatic or pulmonary function changes could be detected in response to any of the NO₂ exposures.

Twenty-one healthy volunteers were exposed on separate occasions to air and 0.6 and 1.5 ppm NO₂ for 3 h [155]. Phlebotomy and bronchoscopy were performed 3.5 h after each exposure, and recovered cells were challenged with respiratory viruses *in vitro*. Blood studies revealed a 4.1% NO₂ dose-related decrease in hematocrit ($P = 0.003$). Circulating total lymphocytes ($P = 0.024$) and T lymphocytes ($P = 0.049$) decreased with NO₂ exposure. In healthy subjects, exposures to NO₂ at levels found indoors caused mild airway inflammation, effects on blood cells, and increased susceptibility of airway epithelial cells to injury from respiratory viruses. A no-effect level was established between 0.2 and 0.6 ppm NO₂ [156].

5.7 Eye and Skin Effects of Nitrogen Dioxide and Dinitrogen Tetroxide

If N_2O_4 is splashed into the eyes, rinse the eyes immediately with water and seek medical help for further treatment. Concentrations of 10–20 ppm NO_2 are mildly irritating to the skin and eyes.

Splashes of liquid N_2O_4 on the unprotected skin cause only a mild irritation because it will evaporate at typical body temperatures. If the liquid is allowed to remain in contact with skin for a longer time, it will cause acid burns comparable to those caused by 60 mass-% nitric acid. The affected area should be rinsed immediately with copious amounts of water and then neutralized with 1% sodium carbonate or sodium bicarbonate solution.

5.8 Prophylaxis Against NO_2 Poisoning

Ascorbic acid (vitamin C), glutathione, and/or α -tocopherol (vitamin E) may have a prophylactic effect against acute NO_2 inhalation toxicity [153, 157, 158].

Herbal medicine, like extracts from salvia roots, may alleviate some of the adverse effects caused by accidental inhalation of NO_2 . Groups of rats were exposed to 0.19 g/m^3 NO_2 for 10 min. Following inhalation, half of the rats were treated immediately with 9 g/kg salvia root extract by intravenous (i.v.) injection and 3 g/kg salvia root extract by intraperitoneal (i.p.) injection 3 h after the first injection. The treated group was less affected by the NO_2 inhalation, based on tissue examination and enzyme activity. The antioxidant activity of salvia root extract may be responsible for the protective effect [159].

5.9 Therapy for NO_2 Poisoning

Post-accident treatment with hyperbaric oxygen (HBO) improved the survival rates of rats exposed to near-fatal concentrations and durations of NO_2 in air [160]. In this experiment, 36 Wistar rats were divided into 3 groups: a control group (12), an NO_2 -exposed group (12), and an NO_2 -exposed plus hyperbaric oxygenation (HBO) treatment group (12). Blood gas changes were measured before and after HBO therapy. The arterial pH, $P_a\text{CO}_2$ (mm Hg), and $P_a\text{O}_2$ (mm Hg) of the HBO group (7.25 ± 0.20 , 52.4 ± 0.30 , 67.0 ± 3.0) had changed significantly from the NO_2 poisoning group (7.15 ± 0.19 , 83.2 ± 0.4 , 50.0 ± 2.0) and approached the values of the comparison group (7.32 ± 0.21 , 42.30 ± 0.20 , 75.0 ± 3.0). The survival ratio of the NO_2 group was 25.0%, but the survival rate of the HBO group was 50.0%.

Propellant-handling personnel should undergo routine periodic health examinations, and their medical records need to be reviewed for slow changes in body functions. Considerable information that is useful in evaluating the adequacy of control measures can be obtained by compiling and analyzing clinical laboratory results, physical findings, and subjective complaints. A detailed treatment procedure for acute exposures to hypergolic fuels or oxidizers was described [161].

Nineteen victims with pulmonary edema induced by accidental nitrogen dioxide poisoning in a rocket test site had to seek clinical care [162].

Dinitrogen tetroxide may cause acute lung injury and acute respiratory distress syndrome through the respiratory tract, skin, or inhalation. The acute lung injury has the characteristics of alveolar capillary membrane injury and pulmonary interstitial edema, and the clinical manifestations are acute respiratory distress and non-cardiac pulmonary edema. N-acetic acid cysteine, *salvia miltiorrhiza* extract, baicalin, ulinastatin, and penethyclidine hydrochloride combined with dexamethasone, which can remove free radicals, inhibit the inflammatory response or have strong activity against lipid peroxidation and may be able to prevent and control acute lung injury caused by N_2O_4 [163].

5.10 First Aid Administered to N_2O_4 Accident Victims

Prompt and effective decontamination is the most important first step in counteracting contamination by N_2O_4 to reduce the degree of injury and mortality significantly [164].

5.11 Nitrogen Dioxide Poisoning from Dinitrogen Tetroxide Accidents

Accident reports and case studies of nitrogen dioxide inhalation at sites of dinitrogen tetroxide spillage are discussed in the chapter on dinitrogen tetroxide.

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Nitrogen Fluorides

Nitrogen can form four binary fluorides: nitrogen trifluoride (NF_3 , CAS RN [7783-54-2]); dinitrogen tetrafluoride (tetrafluorohydrazine, N_2F_4 , CAS RN [10036-47-2]); difluorodiazene (N_2F_2 , CAS RN [10578-16-2]); and azine fluoride (fluorine azide, FN_3 , CAS RN [14986-60-8]). There are numerous other ternary nitrogen fluorine compounds containing a third type of atom, the most significant of which are nitrosyl fluoride and nitryl fluoride.

Only nitrogen trifluoride, NF_3 , and dinitrogen tetrafluoride, N_2F_4 , are of interest as oxidizers for rocket engines. Nitrogen–oxygen fluorides will be discussed in a subsequent chapter on ternary fluorides, so the existence of nitrosyl fluoride (NOF), nitryl fluoride (NO_2F), and nitroxyl fluoride (“fluorine nitrate”; FONO_2) shall simply be mentioned here since they are relatives of the nitrogen fluorides. Nitryl fluoride, NO_2F , is a potentially useful oxidizer for high-energy rocket propellants. As indicated by the number of publications, all of these compounds received a lot of attention in the 1960s when the search for high-energy storable propellants was in full swing [1]. Since then, things have calmed down, and in the twenty-first century very little work is being done on these chemicals, mostly for non-rocket applications.

Dinitrogen tetrafluoride (“tetrafluorohydrazine”) was discovered in 1958 and has been in the center of attention for fluorine rocket propellant chemists for a decade or two.

Looking at the list of potential nitrogen fluorides, one wonders why the fluoride of pentavalent nitrogen has not yet been discovered. Nitrogen pentafluoride would make a good rocket propellant oxidizer. After all, if nitrogen can form a pentavalent oxide, why not form a pentavalent fluoride? Or is N_2O_5 a peroxide with O–O bonds? Theoretical chemists have calculated the orbital energies of higher bonding states of nitrogen, but it appears that NF_5 is not a possibility at this time. But, of course, that is what was said about noble gas fluorides prior to the 1950s. Up to this time, all attempts to synthesize NF_5 have been unsuccessful, although the attempts have been going on for a long time [2–4]. Radioactive tracer experiments using ^{18}F have been conducted but failed to show the ability to synthesize even a trace of NF_5 , and the failure was blamed mainly on steric reasons [5–7].

Nitrogen fluorides are not very active fluorinating agents, but they can be used for the synthesis of organic difluoroamino compounds. They are weaker oxidizers than ClF_3 or BrF_5 . Most rocket fuels do not ignite hypergolically with either NF_3 or N_2F_4 .

When comparing the boiling points of nitrogen hydrides and nitrogen fluorides (NF_3 , boiling point (b.p.) 144 K [–129 °C]; NH_3 , b.p. 240 K [–33 °C]; N_2F_4 , b.p. 200 K [–73 °C]; N_2H_4 , b.p. 386 K [113 °C]), one will notice that despite their higher molecular weights, all nitrogen fluorides boil much lower than their nitrogen hydride counterparts. The higher boiling points of the hydronitrogens are due to the hydrogen bonding between molecules.

The chemical N–F bond in NF_3 is a very strong bond, and NF_3 is much more stable than its other nitrogen halide counterparts such as NCl_3 or even NI_3 , which are notoriously sensitive and explosive nitrogen halides. Among the nitrogen trihalides it is the only one that has a negative enthalpy of formation. NF_3 is stable enough that, when released into the atmosphere, it diffuses up into the stratosphere and becomes a global-warming and ozone-depleting environmental hazard.

The following publications summarized in Table 1 provide summaries of the physical and chemical properties of nitrogen–fluorine compounds, including HNF_2 and ClNF_2 .

Table 1: Summary of literature on nitrogen fluorides.

Topic	Author	Year	Pages	References
Nitrogen fluorides	Hoffman and Neville	1960	32	[8]
Nitrogen fluorides	Hoffman and Neville	1962	18	[9]
Inorganic nitrogen fluorides	Pankratov	1963	8	[10]
Nitrogen fluorides	Colburn	1963	24	[11]
Inorganic nitrogen fluorides	Pankratov	1968	26	[12]
Nitrogen fluorides	Kuznetsova et al.	1968	6	[13]
Soviet research	Markov	1969	11	[14]
Nitrogen fluorides	Constenla	1971	17	[15]
Fluorine and nitrogen	Jaeger et al.	1986	239	[16]
Nitrogen fluorides and related compounds	Emeleus, Shreeve, and Verma	1989		[17]
Non-metal fluorine chemistry	Crawford and Klapötke	1999	30	[18]
Fluorine compounds	Henderson and Woytek	2000		[19]
Nitrogen–fluorine compounds	Klapötke	2006	18	[20]

Understanding the nature of the electron cloud of nitrogen–fluorine and nitrogen–nitrogen bonds in nitrogen fluorides allows us to predict the thermal stability of yet unknown nitrogen fluorides and oxyfluorides of nitrogen [21–23]. The upcoming section on the molecular structure of N_2F_4 will provide more information on bond strengths and dissociation energies of N_2F_4 .

Hydrogen-containing nitrogen fluorides such as fluoroamine FNH_2 and difluoroamine F_2NH (Section 9) might be of interest as monopropellants were it not for their extreme sensitivity to explosions. It is even difficult to produce them in the pure state, and they are typically isolated in a matrix of a solid inert gas. The same applies to the chlorofluoroamines.

A substantial amount of effort has been devoted to the development of organic difluoroamino (“DOMINO”) compounds as monopropellants, plasticizers, and solid propellant binders. Difluoroamino compounds contain the $-\text{NF}_2$ group attached to an organic alkyl or aryl skeleton, making them more energetic but also more sensitive.

Many of these compounds are shock sensitive, similar to nitro compounds. These compounds are discussed in detail in *Encyclopedia of Oxidizers*, chapter “Difluoroamino Compounds.”

1 Nitrogen Trifluoride

Nitrogen trifluoride, also known as NF_3 , trifluoroamine, trifluoramine, nitrogen fluoride, trifluoroammonia, perfluoroammonia, perfluoroamine, CAS RN [7783-54-2], is a colorless gas that condenses at 144 K (-129°C) to a colorless liquid. With a formula weight of 71 g/mol, it contains 80.27 mass-% F and 19.73 mass-% N. Anyone who has ever worked with nitrogen trichloride or even nitrogen triiodide will be surprised how stable nitrogen trifluoride is in comparison to the other nitrogen halogenides.

Nitrogen trifluoride is the only second-period–element non-metallic fluoride that is currently still commercially available in compressed gas cylinders in the United States. Even the U.S. Department of Defense, Defense Logistics Agency lists it in its inventory to make it available to the Armed Forces for (sometimes classified) applications. The main reason for the commercial availability of NF_3 is that it is finding industrial applications in semiconductor chemical vapor deposition (CVD) equipment cleaning [24, 25] and as etchant for micromachining of silicon and silicon carbide by deep reactive ion etching [26]. The NF_3 is activated by passing it through a glow discharge. The destruction efficiency of NF_3 in the discharge as determined by mass spectrometry is typically 100%. The Si removal rates for NF_3 obtained at optimum settings of O_2 addition and microwave power are significantly higher than those for perfluorocarbon gases, which had been used before the advantages of NF_3 for this application were advertised. It has also been used as the oxidizer with thin metal wires in high-intensity flash bulbs for flash photography.

1.1 Preparation of Nitrogen Trifluoride

Nitrogen trifluoride was first prepared by Ruff in 1928. Of all the non-metallic fluorides, nitrogen trifluoride is the only one blessed with a string of patent applications for its production by electrochemical and non-electrochemical methods, so there seems to be an economic incentive to be in the NF_3 business. There appears to be a good industrial market for this chemical other than its prospective use as a rocket propellant or chemical rare gas–halide excimer laser reactant. See also [27].

1.1.1 Preparation of Nitrogen Trifluoride by Electrolysis of Ammonium Bifluoride

In all electrochemical NF_3 production processes, selection of the anode material is the most critical choice to make. This is a very corrosive environment, and few materials stand up to atomic fluorine without degradation. Candidate materials are graphite,

LiF-impregnated carbon, nickel, copper, Monel, and boron-doped diamond (BDD). A relatively high corrosion rate and passivation of nickel anodes are critical problems in this method. Deposition of nickel sludge consisting of NH_4NiF_3 on the cell bottom is another problem to be solved. Carbon (graphite) as an anode is free from corrosion and passivation, but it has problems such as the occurrence of anode effect, the breakdown of the anode, and the contamination of the product by CF_4 . Nitrogen trifluoride was first prepared by Ruff and coworkers in 1928 by electrolysis of molten anhydrous ammonium hydrogen fluoride NH_4HF_2 with a copper cathode and a graphite anode [2, 28, 29]. This method for production of NF_3 was eventually even patented, but the NF_3 yields were very poor [30]. The yields depended strongly on the type of electrode materials, and it appeared to be difficult to find the correct type of graphite. Instead of graphite, nickel has also been used as the anode material [31, 32]. All electrolytic methods for production of NF_3 may result in the formation of difluorodiazine (N_2F_2) and/or difluoroamine (F_2NH), potentially explosive by-products that need to be removed before they have a chance to accumulate in one of the cold traps. If the electrolyte is not absolutely dry, other by-products may be oxygen, nitric oxide, and nitrous oxide. Purification methods for crude NF_3 will be discussed in an upcoming section later in this chapter. In a divided cell drawing a current of 3000–4000 A having nickel anodes, extensive dilution of the gas streams with GN_2 was used to prevent explosive reactions between NF_3 and H_2 [33].

It is important that the NH_4HF_2 electrolyte be as water-free as possible to start with. In the presence of moisture, no NF_3 is formed initially, and the first NF_3 shows up only after days of operating the cell [34]. An electrolyte composition ranging from $\text{NH}_3 \cdot 2.2\text{HF}$ to $\text{NH}_3 \cdot 2.8\text{HF}$ gives good results. Nickel electrodes are preferred over graphite electrodes. The electrode voltage should be kept between 5.6 and 5.9 V. Other investigators producing NF_3 by electrolysis have observed the opposite, where the yield dropped off with time [35].

Substantial amounts of HF are carried out of the electrolyte with the NF_3 and H_2 evolved and need to be separated from the product stream. It would be best if the HF could be recycled into the process and not adsorbed on NaF, as is often done for small-scale operations. In order to minimize the HF carryout, the HF vapor pressure as a function of NH_4HF_2 /HF melt composition and temperature must be known [36].

Copper is often used as an electrode material, but in a melt of NH_4HF_2 during the production of NF_3 it does not survive very well. The electrochemical behavior of copper in anhydrous $1.37\text{HF} \cdot \text{NH}_4\text{HF}_2$ mixtures was investigated at 298 K (25 °C) using voltammetric and electrochemical impedance spectroscopic techniques [37]. The reaction mechanisms are complex, and the experimental results can be interpreted by considering the occurrence of adsorbed species and fluoride and oxide compounds of copper at oxidation states Cu(I) and Cu(II). Passivation does not protect the metal from further attack.

A very systematic study of different electrolyte compositions based on NH_4F with varying amounts of HF and the addition of other fluorides was done. The composition of the anode gas was analyzed by gas chromatography, and the performance of nickel anodes was also compared with that of carbon anodes [38]. With nickel anodes and the basic $\text{NH}_4\text{F} \cdot 2\text{HF}$ electrolyte, typical current efficiencies were 49.2% NF_3 , 20.1% N_2 , 9.26% O_2 , 4.83% N_2F_4 , 1.47% N_2F_2 , and 7.18% N_2O . When the current efficiency for NF_3 production on a nickel electrode versus current density was plotted, the efficiency leveled off at 70% for current densities above 100 mA/cm^2 ; 2.5% of the coulombs flowing were lost due to nickel anode corrosion. Four different anode metals were tested and the metal loss measured: The mass loss rate in $\text{g h}^{-1} \text{cm}^{-2}$ for the four metals was 1.94×10^{-5} , 2.27×10^{-5} , 2.12×10^{-4} , and 1.74×10^{-3} for Ni, Fe, Monel, and Cu, respectively. A skirt of Monel separating the anode and cathode space actually caused some hydrogen evolution on the wrong side of the diaphragm and explosions in the gas space. It was replaced with a polytetrafluoroethylene spacer. To avoid future problems, both anode and cathode gas spaces were purged with nitrogen during electrolysis from then on. The addition of KF to the $\text{NH}_4\text{F} \cdot 2\text{HF}$ lowered the vapor pressure of HF but increased the electric conductivity and viscosity of the melt. Besides KF, LiF, CsF, and NaF were also tested as electrolyte additives, but without measurable improvement of NF_3 yield.

Electrolysis of the melts of $\text{NH}_4\text{F} \cdot 2\text{HF}$ with and without metal fluorides such as LiF, NaF, KF, CsF, MgF_2 , or AlF_3 was conducted with a nickel anode [39]. The addition of LiF into the melt was most effective for increasing the NF_3 current efficiency and for minimizing the consumption of nickel anode. In contrast, KF in the melt decreased the current efficiency for NF_3 and other constituents in the anode gas as well as hydrogen generated at the cathode. It also worsened the consumption of the Ni anode. The concentration of nickel ion in the molten $\text{KF}/\text{NH}_4\text{F}/\text{HF}$ system was low compared with that in the melts of $\text{NH}_4\text{F} \cdot 2\text{HF}$ with and without alkali metal fluorides such as LiF and CsF because KNiF_3 was deposited on the cathode and the cell bottom.

Different anode metals were compared in the electrolytic formation of NF_3 from molten salts (NH_4FHF , KFNH_4HF , and CsFNH_4FHF) [40]. The current efficiencies for NF_3 formation on a Ni anode and a LiF-impregnated carbon (LiF/C) anode in the NH_4FHF melt increased with an increase of the current density and became constant at current densities higher than 120 and 50 mA/cm^2 , respectively. Current efficiencies on the Ni anode were greater than those on the LiF/C anode in the range of current density higher than 30 mA/cm^2 . On the other hand, the presence of KF in the melt reduced the NF_3 current efficiency on both the Ni and the LiF/C anodes, and the NF_3 current efficiency on the LiF/C anode in the KFNH_4FHF melt decreased with an increase of the current density. Product gases obtained with an LiF-doped carbon anode contained CF_4 , but only less than 1 vol-% CF_4 . Surface analysis methods showed that the oxide film on the Ni anode polarized in the NH_4FHF melt was composed of nickel difluoride with a small amount of nickel oxides such as NiO and Ni_2O_3 , some highly oxidized $\text{Ni}^{>2+}$ nickel fluoride, and oxyfluoride having plural

valences [41]. Consequently, nickel metal not only serves as a purveyor of electrons, but highly oxidized nickel fluorides on the Ni anode function as mediators of the electrochemical fluorination of ammonium ion. This effect would not be found with carbon electrodes.

The corrosion of nickel electrodes can be minimized by pre-saturating the electrolyte with Ni^{2+} ions [42]. Although the addition of complexes such as NiNH_4F_3 and $(\text{NH}_4)_3\text{FeF}_6$ in the melt was effective for minimizing the Ni or Fe anode consumption, the NF_3 formation was seriously affected [43]. Therefore, the allowable contents of Ni^{2+} or Fe^{3+} in the melt should be no more than 0.06 and 0.03 mol-%, respectively. Water in the melt retarded not only the anode consumption but also the current efficiency for NF_3 formation.

Instead of using plain nickel anodes, oxidized nickel anodes or composites pressed from nickel powder and NiO powder have performed well in the electrolysis of $\text{NH}_4\text{F} \cdot 2\text{HF}$ melts for the production of NF_3 [44]. The electrodes can be pre-treated by heating them in air [45].

A nickel electrode having 0.07 mass-% or less of Si content and containing a transition metal other than nickel has been patented [46]. The electrolyte must also contain a transition metal other than nickel.

Nickel/nickel oxide composite electrodes can be prepared from a mixture of Ni and NiO powders at 1173 K (900 °C) under 2000 atm pressure for 2 h by hot isostatic pressing (HIP). In electrolysis of molten $\text{NH}_4\text{F} \cdot 2\text{HF}$ at 373 K (100 °C) and at 25 mA/cm², the anode gas generated at the Ni-NiO composite anode was composed of NF_3 , N_2 , O_2 , N_2F_2 , N_2F_4 , and N_2O , and its composition was almost the same as that of a Ni sheet anode [47]. The best current efficiency for NF_3 formation was about 53% on the Ni/5 mol-% NiO composite anode, and it was almost the same as that of the Ni sheet anode. The anode consumption of the Ni-NiO composite was much smaller compared with that of the Ni sheet electrode.

Other nickel/metal oxide composites such as Ni/ Co_3O_4 , Ni/ MnO_2 , Ni/ Ag_2O , Ni/ Y_2O_3 , Ni/ La_2O_3 , Ni/ Nd_2O_3 , and Ni/ Sm_2O_3 systems were prepared by HIP and tested as electrodes in the $\text{NH}_4\text{F} \cdot 2\text{HF}$ electrolyzer [48]. Percentages of metal oxides in the nickel/metal oxide composite electrodes were 2, 5, and 10 mol-%. Composition of the anode gas evolved at every nickel-based composite electrode was almost the same as that on a nickel sheet electrode. Current efficiencies for NF_3 formation on Ni/ Y_2O_3 and Ni/ La_2O_3 composite anodes were almost the same as that on the nickel anode, whereas that on Ni/ Co_3O_4 composite anode was very small compared with that on the nickel sheet anode. In the cases of the Ni/ Co_3O_4 , the Ni/ MnO_2 , and the Ni/ Ag_2O composite anodes, the current efficiency for NF_3 formation decreased with an increase in the oxide concentration in the composite anodes. Current losses of the Ni/ Co_3O_4 composite anode were very large compared with the nickel sheet anode.

Nickel-based alloys, such as Ni/Co, Ni/Mn, Ni/Ag, Ni/Cu, Ni/Al, and Ni/Si, prepared by HIP at 1000 °C under 2×10^8 Pa pressure for 2 h, were employed as the anodes

for electrolytic production of NF_3 , but current efficiencies for NF_3 formation were not much better than that of the nickel sheet anode baseline, and the anode consumptions were almost the same or smaller compared with those of Ni sheet and hot isostatic-pressed Ni electrodes [49].

BDD thin-film electrodes combine electrical conductivity with chemical inertness and corrosion resistance. They can be prepared by a hot-filament CVD method on a carbon substrate using $\text{CH}_4/\text{H}_2/\text{B}(\text{OCH}_3)_3/\text{Ar}$.

The best current efficiency (72.4%) using BDD anode in $\text{NH}_4\text{F} \cdot n\text{HF}$ melts was obtained at 40 mA/cm^2 and an NH_4F -concentration of 33.3 mol% (the $\text{NH}_4\text{F} \cdot 2\text{HF}$ melt) [50]. An evaluation of electrolytic production of NF_3 using BDD anodes in molten $\text{NH}_4\text{F} \cdot 2\text{HF}$ showed that the current efficiency for NF_3 production was independent of the current density in the range of $200\text{--}1000 \text{ mA/cm}^2$ [51]. The average values of NF_3 current efficiencies on BDD anodes with boron concentrations of 2500 ppm were 32.3% at 80°C , 63.3% at 100°C , and 59.7% at 120°C . Galvanostatic polarization curves of BDD anodes with boron concentrations of 2500, 5000, 7500, 10000, and 12500 ppm in molten $\text{NH}_4\text{F} \cdot 2\text{HF}$ and a carbon anode in a molten $\text{NH}_4\text{F} \cdot \text{KF} \cdot 4\text{HF}$ were measured for comparison. The best current efficiencies for NF_3 production (70%) were obtained with BDD anodes containing 5000 ppm B. Electrode performance was measured during 1000-h tests, and there was little change in electrode performance. The mechanism on electrochemical fluorination seems to be as follows: At potentials higher than about 4 V, fluoride ion can be discharged to form $\text{F}^\bullet$ on an anode. The fluorine radical reacts with ammonia adsorbed on an anode and/or ammonium cation in the melt near the anode to produce $\text{NH}_2^\bullet$. The amino radical then reacts with fluorine radicals to form NF_3 . When current density and electrolyte temperature were varied, best yields (70%) were obtained with a current density of 450 mA/cm^2 at 100°C .

Metal fluoride (MgF_2 and CaF_2)-doped carbon anodes treated by pre-electrolysis were investigated for electrolytic production of NF_3 in molten $\text{NH}_4\text{F} \cdot \text{KF} \cdot 4\text{HF}$ at 373 K (100°C) [52]. The highest critical current density was 290 mA cm^{-2} . One anode was successfully used in the electrolysis at 100 mA cm^{-2} for 290 h, and the maximum NF_3 current efficiency was 55%. The metal fluoride-doped carbon anodes treated by pre-electrolysis have a high potential for improvement of the electrolytic production of NF_3 at higher current densities.

It is very important to separate the anode and cathode gas streams to prevent explosions. Purging with an inert gas will prevent explosions [53]. See also [54].

In the mid-1960s, while working at the DVL Institute for Rocket Propellants in Stuttgart, Germany, the author evaluated three different methods for the preparation of NF_3 . The best results were obtained by electrolysis of molten ammonium hydrogen fluoride ($\text{NH}_3 \cdot 2.5\text{HF}$) on nickel anodes [55]. Other processes for the preparation of NF_3 or N_2F_4 evaluated experimentally at DVL Stuttgart were the electrofluorination of urea or guanidine in anhydrous H_2F_2 at $258\text{--}253 \text{ K}$ (-15 to -20°C), but this resulted only in a mixture of reaction products, including COF_2 . At the attempt to purify the mixture of

reaction products by passing them through granulated activated charcoal, the charcoal ignited and combusted along with the polytetrafluoroethylene spacer that was meant to hold the charcoal in place.

At other organizations, instead of working with a melt of ammonium bifluoride at high temperatures, it was attempted to electrolyze ammonium bifluoride NH_4HF_2 in a large excess of H_2F_2 (anhydrous hydrogen fluoride [AHF]) as the solvent and electrolyte and operate at lower temperatures, but the only product was difluorodiazine $\text{FN}=\text{NF}$ [56–58]. Polarization curves of Monel electrodes in solutions of NH_4HF_2 in AHF did not show any diffusion-limited regions indicative of a potential-dependent stepwise reaction. The results indicated that the fluorination of NH_4HF_2 in AHF occurs by a radical mechanism involving anodically generated fluorine. Chronopotentiometric data, current-potential curves, and product yields versus time curves indicated that the fluorinating agent, during electrolysis, is a “loose” complex between $\cdot\text{F}$ and NiF_2 and/or CuF_2 . *Trans*- N_2F_2 was the only N-F product formed from the electrolysis of NH_4HF_2 in AHF.

The production of NF_3 by electrolysis of molten NH_4HF_2 was tested in a pilot plant that already bore some similarity to an industrial-scale production facility [59]. The composition of gases produced at the anode was analyzed as a function of current density, temperature, and electrolyte composition. The anode was made of the same carbon material that was also used for electrochemical production of elemental fluorine.

Nickel anodes used during production of NF_3 are heavily corroded, and dissolved nickel ends up in the spent electrolyte, but it can be recovered in the form of NiCO_3 for its metal value and purification of the electrolyte before it is recycled [60]. The recovery rate of nickel reached 97%.

1.1.2 Preparation of Nitrogen Trifluoride by Electrofluorination of Other Amino or Amido Compounds

Electrofluorination of organic compounds is a widely used method for synthesis of N–F compounds [61]. Some NF_3 is obtained by electrofluorination of urea dissolved in anhydrous hydrogen fluoride, but it is difficult to separate NF_3 from a host of unwanted byproducts (CF_4 , CO_2 , N_2 , COF_2 , N_2O , N_2F_2 , and OF_2) [62–65]. The mixture can barely be separated by fractionated distillation, but the distillate fraction may still contain about 1% CF_4 .

The electrofluorination of urea to nitrogen trifluoride at a carbon anode, in the system $\text{KHF}_2/\text{HF}/\text{CO}(\text{NH}_2)_2$, and the effect of current density, concentration of urea, and anode potential on the composition of the anodic product gas have been investigated [66]. By-products were N_2 , CO_2 , CO , O_2 , OF_2 , CF_4 , and F_2 . At optimum conditions (0.1–1 A/dm^2 ; 5.0–5.5 V, 2–3 mol-% of urea), the current efficiency of NF_3 production was 55%, whereas in $\text{KHF}_2/\text{HF}/\text{NH}_4\text{F}$ 75% may be achieved, and a better purity product would be obtained.

In the fluorination of urea, the main products were NF_3 , N_2 , COF_2 , and CO_2 , and small amounts of CF_4 , N_2O , and N_2F_2 were also found in the product [67]. The molar ratio of NF_3 to N_2 depended strongly upon electrolysis conditions and was found to increase with a decrease in the concentration of urea and with an increase in current density. In the fluorination of 1,1-dimethylurea, NF_3 , N_2 , CF_4 , CHF_3 , COF_2 , and CO_2 were mainly formed, with a small amount of CH_2F_2 and C_2F_6 .

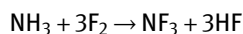
Adding urea to a working NH_4F - HF - KF electrolysis system did not improve the yield of NF_3 [68].

Instead of urea, one can also subject guanidine to electrofluorination [69]. Electrolytes containing up to 40 mass-% guanidinium fluoride were still not saturated; they remained liquid and were good conductors of electrical currents. The partial pressure of HF above the electrolyte was very low, reducing carryover into the product cold trap. The crystal structure of dry guanidinium fluoride was studied by X-ray diffraction (XRD) as a measure of quality control to ensure purity of the ingredients used for NF_3 production. The current yield of all fluorinated products was 66% and that of NF_3 alone was 47%. The resulting mixture of NF_3 and CF_4 had an average molecular mass of 76, which corresponds to a molar ratio $\text{NF}_3 : \text{CF}_4$ of 2.5 : 1. Because the boiling points of the two gases are very similar, the mixture cannot be separated by fractionated condensation, but it can be separated by gas chromatography.

The electrofluorination of acetamide (CH_3CONH_2) or formamide (HCONH_2) in molten KH_2F_3 at 393 K (120 °C) produced a mixture of N_2 , O_2 , NF_3 , CF_4 , C_2F_6 , N_2O , CO_2 , and COF_2 [70]. The addition of 1.0 mass-% LiF into the electrolyte decreased the yield of NF_3 . Amorphous carbon was used as the anode and a Pt-rod as the reference electrode. It was suggested that CH_3CONH_2 or HCONH_2 would react chemically with atomic fluorine produced on the carbon anode film by the discharge of fluoride ions.

1.1.3 Preparation of Nitrogen Trifluoride by Direct Ammonia Fluorination

Nitrogen trifluoride and/or tetrafluorohydrazine can also be prepared by direct fluorination of ammonia:



However, the yield is very poor [71, 72]. The yield of NF_3 in an unpacked reactor was initially only 6% based on fluorine consumed but could be improved to 39–60% when the reaction was performed in a T-shaped packed copper reactor. With an excess of ammonia, some tetrafluorohydrazine was formed. One must perform this reaction in very dilute media if one does not want to chance ignition, such as in a rocket engine operating on fluorine and ammonia. The direct combustion of ammonia with an excess of fluorine does not give NF_3 [73].

Most patented processes for the production of NF_3 by direct fluorination of ammonia or ammonium salts operate in a melt phase instead of in the gas phase. There are only a few publications and patents about operating in the gas phase. Nitrogen tri-

fluoride can be prepared by reacting fluorine gas with ammonia gas in the gas phase, where the reaction is performed at 203 K (70 °C) or less in the presence of a diluting gas [74]. The concentration of fluorine gas in the diluent gas is 3 mol-% or less, and the concentration of ammonia gas fed is 6 mol-% or less. The fluorine gas is fed in portions from two or more gas inlets, or the ammonia gas is fed in portions from two or more gas inlets.

If an excess of ammonia with diluent gas is used in a gas/gas reactor, the solid NH_4F salt will clog the reactor. A reactor has been described with a scraper that continuously removes the deposits from the wall of the reactor [75].

All the following patents perform the reaction of fluorine and ammonia in a melt of ammonium bifluoride instead of in the gas phase. One of the first patents in this category was [76], which described a process for the production of NF_3 by the direct fluorination of ammonium bifluoride at temperatures above 260 °F and below 400 °F. The HF/NH_3 ratio was maintained at 2.0 to 2.5. Diluted fluorine gas and ammonia were bubbled through the stirred melt at opposite locations. In a similar vein, [77] patented the synthesis of NF_3 from elemental fluorine gas and a source of ammonia in a gas-liquid phase reaction where the HF/NH_3 ratio is at least 2.55 and the reaction melt is agitated with a mixing apparatus. The source of nitrogen can be either NH_3 bubbled into the melt or an ammonium salt added in the form of NH_4F or NH_4HF_2 .

If the process is carried out continuously, the loss of HF from the melt and the generation of waste-melt products constitute expensive waste-disposal problems. The process can be optimized to minimize the amount of hazardous waste generated [78]. A stripping gas can be used to carry HF and reaction products from the melt.

An ammonium bifluoride melt can be suspended in an inert, heated perfluorocarbon bath while ammonia and elemental fluorine are injected continuously at separate locations into the agitated melt, producing NF_3 in yields up to 90% (based on converted fluorine) [79].

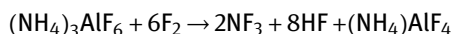
Nitrogen trifluoride can be produced by rapidly ejecting a jet of fused ammonium fluoride salt into a reactor through a nozzle while aspirating fluorine gas into the stream (similar to an aspirator vacuum pump) and recirculating the melt from the bottom of the reactor [80].

The direct fluorination of molten ammonium bifluoride can be carried out in two stages, first at low temperature and then in a second reactor at higher temperature with an excess of fluorine, which removes all unwanted by-products [81]. The fluorine feed stream can be diluted with hydrogen fluoride [82]. The momentum of the injected hydrogen fluoride carrier gas that carries the fluorine can also serve to stir the reacting ammonium bifluoride melt and ensure uniform mixing in the reaction zone [83].

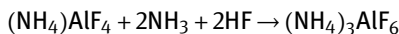
In another variant of the same process, the molten NH_4HF_2 and fluorine are co-injected at the inlet of a packed reactor operating at lower temperature, and the gaseous products are subsequently finished in a second reactor at higher temperature [84].

Instead of mechanical agitation, the gaseous reactants can be mixed by static mixing elements as they push the molten salt through the reactor [85]. Gaseous ammonia and gaseous fluorine are introduced on opposite sides of the first static mixing element. The reaction is conducted at a temperature only 5°C higher than the melting point of the ammonium bifluoride/hydrogen fluoride mix.

Instead of fluorinating molten ammonium fluoride, diluted fluorine can be reacted in a batch process with a packed bed of a solid, granular ammonium metal fluoride, such as ammonium cryolite $(\text{NH}_4)_3\text{AlF}_6$, and NF_3 emerges at the other end of the reactor [86, 87]. Ammonium cryolite $(\text{NH}_4)_3\text{AlF}_6$ is prepared in such a way that it has a large surface area to interact with the fluorine [88, 89].



The $(\text{NH}_4)\text{AlF}_4$ is then reconverted to $(\text{NH}_4)_3\text{AlF}_6$ and recycled:



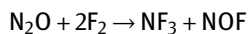
1.1.4 Preparation of Nitrogen Trifluoride by Combined Electrochemical Processes

Combined electrochemical processes are essentially ammonia direct-fluorination processes, except the fluorine does not arrive at the factory in compressed-gas bottles but is produced in an electrolytic cell that is adjacent to and combined with the ammonia fluorination reactor. In this case, the fluorination is carried out by bubbling ammonia and fluorine in a melt of a low-melting ternary mixture of $\text{HF/KF/NH}_4\text{HF}_2$. If ammonia is fluorinated in a reactor separately from an electrolysis unit, the hydrogen fluoride formed in the reaction is an unwanted process waste. It would have to be collected and trucked back to the fluorine factory. If ammonia is fluorinated in a molten bath containing a ternary flux of hydrogen fluoride, ammonium fluoride, and potassium fluoride that is part of the fluorine electrolyzer, the HF formed in ammonia fluorination is absorbed into the bath and can be sent (pumped) to the adjacent electrolyzer to be converted back to fluorine [90]. The flux circulating in the electrolyzer and the NF_3 reactor has the same three ingredients, but in different proportions. Ammonia gas is bubbled through the molten $\text{NH}_4\text{F/HF/KF}$ bath to replenish what has been consumed. HF is added prior to entering the fluorine electrolysis cell. In the reactor, an excess of fluorine is maintained and the apparatus is under pressure, which minimizes the by-products difluorodiazine and tetrafluorohydrazine.

1.1.5 Preparation of Nitrogen Trifluoride by Other Non-Electrochemical Processes

Other methods for preparation of NF_3 were reported in the literature, but none of these alternative methods has gained any significance, such as the reaction of azine fluoride (“fluorine azide”) N_3F with oxygen difluoride [91] or nitrosyl fluoride or chlorine trifluoride [92].

The fluorination of N_2O at $>373\text{ K}$ ($>100^\circ\text{C}$) gives a mixture of NF_3 and NOF [93]:



Small amounts of NF_3 (besides NF_2H and N_2F_2) are detected if one passes dilute fluorine gas over sodium amide powder [94].

If one replaces the sodium amide with metal nitrides (Li_3N , Be_3N_2 , Mg_3N_2 , BN , Si_3N_4 , TiN , VN), the NF_3 yield decreases to below 1%, but more difluorodiazine can be found in the reaction products [95–97]. All of the substances fluorinated gave predominantly nitrogen as a volatile product. No nitrogen trifluoride was observed in the case of the metallic type nitrides, TiN and VN . Small quantities of nitrogen trifluoride were observed in the other experiments. Nitrous oxide and carbon tetrafluoride were detected in all of the runs as the result of impurities in the fluorine and possibly in the nitrides.

It has also been possible to synthesize NF_3 directly from the elements in a glow discharge at 76 K (-197°C) and $20\text{--}40\text{ mm Hg}$. A 15-kV , 30-mA luminous tube transformer was used as the power source for the discharge. Starting with a mix of 25% N_2 and 75% F_2 , the yield was up to 30% [98]. The synthesis of nitrogen trifluoride from the elements appears analogous to the synthesis of oxygen fluorides from the elements under essentially the same conditions. However, unlike the polyoxygen fluorides, variations of the stoichiometry of the fluorine/nitrogen mixtures did not lead to other nitrogen-fluorine compounds such as N_2F_2 .

Nitrogen trifluoride was obtained from nitrogen and fluorine in a barrier discharge with 1.5–2% yield by using a circulation system [99]. The reverse reaction, the decomposition of the nitrogen trifluoride into the elements in the barrier discharge, reached 98%.

The degree of conversion of stoichiometric fluorine/nitrogen mixtures to nitrogen trifluoride increased monotonically with increasing specific energy at current strengths of 8, 12, and 25 mA and specific energies up to $200\text{--}450\text{ W}\cdot\text{h/L}$ [100]. The dependence of the degree of conversion on the current strength was extreme: A current strength of 12 mA was most favorable for the synthesis of nitrogen trifluoride. The absence of tetrafluorohydrazine in the reaction product of fluorine with nitrogen was explained by the low stability of tetrafluorohydrazine in a glow discharge. Argon is an inert additive in the synthesis of nitrogen trifluoride.

If pure NF_3 is passed through a glow discharge under conditions similar to its formation from the elements, it decomposes into the elements [101]. It is obvious that the yield of NF_3 in the synthesis from the elements by this method is limited by the reverse reaction unless the NF_3 is continuously and immediately removed from the discharge zone by condensing it.

Operating at much higher temperatures in an electric arc discharge, reminding one of the Birkeland process for production of HNO_3 from air and water, passing nitrogen and CF_4 or SF_6 through the hot zone, and quenching the reaction products quickly

thereafter gave only a very poor yield of NF_3 , CF_3NF_2 , or any other useful product [102, 103]. Only 1% of the nitrogen fed to the arc was converted to a product.

Passing a mixture of nitrogen and fluorine gas through an arc discharge reactor and immediately quenching the effluent in liquid nitrogen results in the formation of a mixture containing NF_3 and N_2F_4 [104]. By varying the $\text{F}_2:\text{N}_2$ ratio, NF_3 can be produced to the exclusion of N_2F_4 .

NF_3 can be prepared by chemical fluorination of urea in a solution of anhydrous H_2F_2 at temperatures from 253 to 273 K (-20 to 0°C) and molar ratios of fluorine to the starting compounds of not over 3 [105].

1.1.6 Purification of Nitrogen Trifluoride

For many industrial applications, the quality of NF_3 produced by electrolysis or other methods may not be adequate. The main contaminant in NF_3 produced by electrolysis with carbon electrodes is CF_4 , which is very difficult to separate from NF_3 because the physical properties of the two compounds are so similar. The two gases can be separated by gas chromatography, but preparative gas chromatography on an industrial scale would be impractical. Therefore, a number of alternative separation and purification methods have been developed and patented. Other unwanted contaminants are tetrafluorohydrazine, difluorodiazine, and nitrous oxide. The purity requirements for NF_3 to be used as rocket propellant or laser propellant are less stringent than the purity requirements for NF_3 to be used in the semiconductor industry. The need for purification methods such as those described in this chapter was driven mostly by the semiconductor etching and CVD equipment-cleaning applications.

Separation of nitrous oxide from nitrogen trifluoride is possible by fractionated distillation (condensation) or filtration of the solid N_2O from the liquid NF_3 at very low temperatures (78 K [-195°C]) [106, 107].

A continuous method for separation of NF_3 from CF_4 and C_2F_6 contaminants is based on column absorption of the organic compounds in a trickle tower fed with chilled chloroform or tetrachloromethane [108]. The less soluble NF_3 accumulates in the gas phase. Preparation and purification of NF_3 has its own set of hazards and potential for accidents [109].

A **safety warning** must be issued to anyone who might consider removal of contaminants in NF_3 by adsorption on activated charcoal, which in at least one case has resulted in an explosion with severe personal injuries [110, 111]: 600 g of activated, granulated charcoal had been dried at 393 K (120°C) and was placed in a steel cylinder and cooled to 173 K (-100°C). About 25 g of NF_3 were condensed into the cylinder within 10 min, and shortly after it all condensed, the cylinder **exploded**, throwing glowing charcoal all over the place and setting the methanol/dry ice cold bath on fire. In order to retain both N_2F_2 and N_2O , the active charcoal has to be cooled to at least 193 K (-80°C). At 273 K (0°C) only N_2O is absorbed. The adsorption of contaminated

NF₃ on charcoal is an exothermic process and caused temperature increases of 40–70 °C, which may be enough to ignite the mixture.

Difluorodiazene N₂F₂ contamination in NF₃ must be removed before NF₃ is further purified by adsorbing other contaminants on zeolites because N₂F₂ may react exothermically with aluminosilicates and cause explosions. Dinitrogen difluoride contamination present in nitrogen trifluoride gas can be removed by heating the nitrogen trifluoride gas to 423–873 K (150–600 °C) in a metallic vessel, the inner wall of which is lined with a solid fluoride, and then cooling the gas and passing it through a gas washing flask with a solution of potassium iodide or sodium sulfite [112]. A reactor made from nickel and coated on the inside with nickel fluoride is the preferred equipment for this process [113].

Difluorodiazene, F–N=N–F, formed as a contaminant during NF₃ synthesis, may accumulate in cold traps and is detonable, which is why it has to be removed. The gas to be purified by removal of dinitrogen difluoride can be passed through a packed bed of nickel spheres heated to 422–811 K (300–1000 °F) [114].

Nitrogen fluoride that is purified by condensing and by fractionated distillation can be freed from dioxygen or dinitrogen contamination if the condensation and distillation are carried out in the presence of helium, neon, or argon as a purge gas [115]. Purification of nitrogen trifluoride and removal of N₂F₂ and N₂F₄ by passing it through activated charcoal is a dangerous process, even if the adsorbent is wetted with water. The patent fails to warn users of this method about the explosive hazard [116].

Difluorodiazene N₂F₂ contamination in NF₃ can be removed from the crude NF₃ gas by passing the gas through an aqueous solution containing both an alkali metal iodide and an alkali metal sulfite or alkali metal hydrogen sulfite [117].

Tetrafluoromethane is difficult to separate from NF₃ because the boiling points are so similar. Separation is possible by adsorbing the mixture on a desiccated erionite synthetic zeolite at 243 K (–30 °C), pumping off the CF₄ or purging it out with an inert gas, and desorbing and condensing the purified NF₃ [118]. Nitrogen fluoride thus purified contained no more than 10 ppm CF₄.

A low-temperature two-column distillation with an extractive cryogenic liquid countercurrent stream of an inert cryogenic liquid in the first trickle column can effectively free NF₃ from more volatile and less volatile contaminants. The extractive distillation in the first column allows more volatile contaminants to pass. The NF₃ and less volatile contaminants dissolved in the auxiliary fluid from the bottom of the first column are fed to the second column, where NF₃ is withdrawn from the top of the column and thereby separated from the auxiliary fluid and less volatile contaminants [119].

A two-step purification method is to first remove unreacted F₂ and HF without forming oxygen difluoride or nitrogen oxides, and then to remove nitrogen oxides by adsorption on a molecular sieve [120]. One must remember that N₂F₂ and NF₃ may react explosively with SiO₂ and silicates.

NF_3/CF_4 mixtures can be separated by bringing them into contact with a polyacrylonitrile-based carbon molecular sieve so that at least a portion of one or more impurities are adsorbed by the molecular sieve without a significant adsorption of the NF_3 [121].

The pure and mixed gas permeabilities of Teflon AF2400, Teflon AF1600, and Hyflon AD60 membranes toward NF_3 and CF_4 were measured to determine whether membrane gas separation can be applied to purify NF_3 of CF_4 [122]. It was shown that thermal annealing of the solution cast films was necessary to reach optimum performance, wherein all membranes studied had a preferential permeation of NF_3 rather than CF_4 . The Teflon AF and Hyflon AD60 membranes displayed rather high pure and mixed gas selectivities ($\alpha(\text{NF}_3/\text{CF}_4)$) considering the high free volume of the polymers. Hyflon AD60 displayed the highest NF_3/CF_4 pure and mixed gas selectivity of just above 12, albeit with a rather low NF_3 permeability index of about 1.9 Barrer.

A high-purity nitrogen trifluoride with an impurity content of <10 ppm can be obtained by ultraviolet (UV) or infrared (IR) radiation to cause the dissociation of chemical bonds in the impurities to form dissociation products and thereby make the subsequent removal of the contaminants from the NF_3 easier [123]. The wavelength of the UV or IR light is selected such that one or more chemical bonds of the contaminants dissociate to form more reactive dissociation products.

1.2 Physical Properties of Nitrogen Trifluoride

The physical properties of nitrogen trifluoride are well characterized and are summarized in Table 2.

Table 2: Physical properties of nitrogen trifluoride.

Property	SI units	MKS units	References
Molecular mass	71.0019 g/mol	14.0841 mol/kg	
Boiling point	144.15 K	−129.0 °C	[31]
	144.1 K	−129 ± 0.3 °C	[124]
	144.14 K	−129.01 °C	[125]
Melting point	66.49 K	−206.67 °C	[31]
	64.6 K	−208.5 °C	[126]
	71.019 K	−202.13 °C	[125]
Triple point	66.373 or 66.361 K	−206.79 °C	[32]
	66.46 K	−206.69 °C	[127]
	66.36 K	−206.79 °C	[125]

Solid NF_3 undergoes a phase transition at 56.62 K. The heat capacity of nitrogen trifluoride has been measured from 12 to 144 K. The heat of transition was +1.514 kJ/mol (361.8 cal/mol) [128]. With its low melting entropy (1.43 eu) and high molecular mobility, solid NF_3 in its high-temperature phase can be classified as a plastic crystal.

The melting point of pure NF_3 was reported as 64.6 K (−208.5 °C) [126]. See also [8, 13, 129, 130].

1.2.1 Density of Nitrogen Trifluoride

The density of liquid NF_3 in the range from 78 to 170 K (−195 to −103 °C) can be expressed by the following polynomial equation [31]:

$$\rho = 2.103 - 3.294 \times 10^{-3}T - 4.675 \times 10^{-6}T^2$$

where ρ is the density in g/cm^3 and T is the temperature in kelvin. The estimated uncertainty in these values is $\pm 0.1\%$. The raw data are tabulated in Table 3.

Table 3: Density of liquid nitrogen trifluoride.

Temperature, K	Density, g/cm^3
78.05	1.819
79.44	1.812
87.23	1.780
92.22	1.760
97.01	1.740
101.79	1.720
109.91	1.683
119.47	1.643
124.50	1.621
131.06	1.593
135.35	1.574
139.94	1.552
144.66	1.530
153.93	1.484
158.53	1.461
164.16	1.434
169.54	1.406
144.16	1.539

Data source: [31]

1.2.2 Vapor Pressure of Nitrogen Trifluoride

The vapor pressure of NF_3 has been measured by several investigators. The data obtained between 86 and 144.5 K can be expressed by the following equation [128]:

$$\log p_v = 1.869858 \log T - \frac{673.5828}{T} - 0.0078335T + 4.64615$$

where p_v is the vapor pressure in mm Hg and T is the temperature in kelvin. Similar measurements led to a slightly different equation, related to the data in Table 4 [31]:

$$\log p_v = 6.77966 - \frac{501.913}{T - 15.37}$$

where p_v is the vapor pressure in mm Hg and T is the temperature in kelvin. Another equation covers the higher pressure range up to the critical pressure:

$$\log p_v = 4.27264 - \frac{613.33}{T}$$

where p_v is the vapor pressure in atm and T is the temperature in kelvin.

Table 4: Vapor pressure of nitrogen trifluoride.

Temperature, K	Vapor pressure, mm Hg
89.33	1.00
98.99	5.92
108.58	24.79
113.70	47.39
123.16	132.83
131.95	297.96
140.17	573.08
144.18	764.26
Temperature, K	Vapor pressure, atm
148.97	1.388
153.80	1.884
158.67	2.558
163.52	3.374
168.40	4.326
173.36	5.551
178.27	6.912
183.16	8.544
188.03	10.380
198.06	15.006
203.14	17.796
208.02	20.925
217.94	28.272
222.96	32.830

Data source: [31]

1.2.3 Viscosity of Nitrogen Trifluoride

The viscosity and velocity of sound of gaseous nitrogen trifluoride in the temperature range 225–375 K and up to 3.4 MPa were measured using a Greenspan acoustic viscometer [131]. The velocities of sound measured up to 3.4 MPa were fitted by a virial equation of state that predicted gas densities within the uncertainties of the equations of states available in the literature (Figure 1).

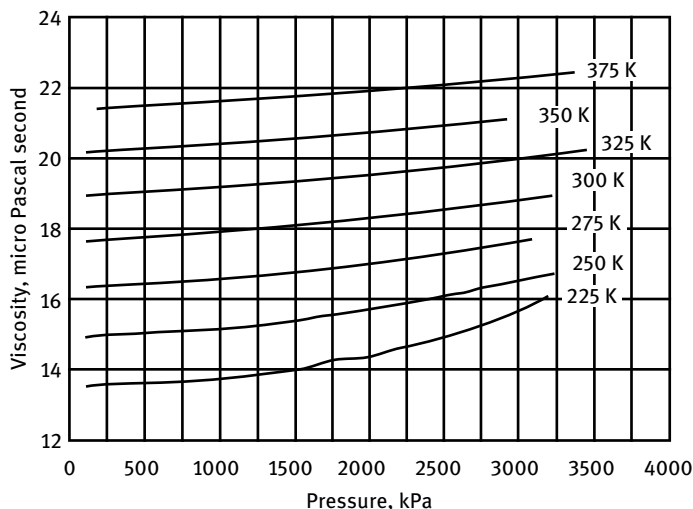


Figure 1: Viscosity of gaseous nitrogen trifluoride. (Graph created by Schmidt 2020, based on data from [131].)

1.2.4 Thermal Conductivity of Gaseous Nitrogen Trifluoride

The thermal conductivity of gaseous nitrogen trifluoride was estimated from other physical properties as listed in Table 5, in comparison to viscosity data obtained by similar computational methods.

1.2.5 Solubility of Nitrogen Trifluoride

NF₃ is slightly soluble in water without undergoing hydrolysis chemical reaction. The solubility in water at 101 kPa is 1.4×10^{-5} mol NF₃/mol H₂O.

NF₃ dissolved in anhydrous H₂F₂ without reaction or compound formation. The solubility of NF₃ in H₂F₂ was measured for pressures up to 1.2 MPa (12 atm) and followed Henry's law [133]. The slope of the solubility curve showed that F₂ was about half as soluble in H₂F₂ as NF₃. Simultaneously compressing mixtures of NF₃ and F₂ into H₂F₂ did not result in compound formation.

Table 5: Estimated thermal conductivity and viscosity of gaseous nitrogen trifluoride.

Temperature, K	Thermal conductivity, $\text{mW m}^{-1} \text{K}^{-1}$	Viscosity, $\mu\text{Pa s}$
200	10.50	11.70
210	11.29	12.28
220	12.10	12.84
230	12.92	13.40
240	13.76	13.95
250	14.62	14.49
260	15.48	15.02
270	16.36	15.56
280	17.24	16.08
290	18.12	16.60
300	19.02	17.11
310	19.91	17.62
320	20.80	18.12
330	21.70	18.62
340	22.59	19.11
350	23.48	19.59
360	24.37	20.07
370	25.25	20.60
380	26.13	22.22
390	27.00	22.70
400	27.87	23.18
410	28.73	23.65
420	29.59	24.11
430	30.44	24.57
440	31.28	25.03
450	32.12	25.48
460	32.95	25.93
470	33.77	26.37
480	34.59	26.81
490	35.41	27.25
500	36.21	27.68
550	40.20	29.77
600	44.17	31.79
650	48.25	33.73
700	52.61	35.59
750	57.46	37.40

Data source: [132]

Liquid NF_3 in a molar ratio of 1 : 1 is completely miscible with LOX or OF_2 at 77 K, with Ar at 85 K, with LOZ at 90 K, and with CF_3Cl or CF_4 at 90 K, but it forms two separate layers with O_2F_2 at 130 K, ClF_3 at 140 K, H_2F_2 at 140 K, and ClF at 150 K [134].

1.2.6 Critical-Point Properties of Nitrogen Trifluoride

Critical-point data of nitrogen trifluoride are listed in Table 6.

Table 6: Critical-point data of nitrogen trifluoride.

Property	SI units	MKS units
$t_{\text{crit.}}$	$233.89 \pm 0.10 \text{ K}$	$-39.26 \pm 0.10 ^\circ\text{C}$
$P_{\text{crit.}}$	$4.517 \pm 0.017 \text{ MPa}$	$44.72 \pm 0.17 \text{ atm}$
$V_{\text{crit.}}$		$123.8 \text{ cm}^3/\text{mol}$

Data source: [31]

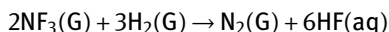
1.2.7 Thermodynamic Properties of Nitrogen Trifluoride

Thermodynamic properties of nitrogen trifluoride are listed in Table 7.

Table 7: Thermodynamic data of nitrogen trifluoride.

Property	SI units	Other units	References
Standard enthalpy of formation, gas, $(\Delta H)_{298}$	$-124.3 \pm 7.5 \text{ kJ/mol}$	$-29.7 \pm 1.8 \text{ kcal/mol}$	[135]
	-132.09 kJ/mol	-31.57 kcal/mol	[132]
	$-127.2 \pm 5.0 \text{ kJ/mol}$	$-30.4 \pm 1.2 \text{ kcal/mol}$	[136]
	-123.58 kJ/mol	-29.536 kcal/mol	[137]
Standard enthalpy of formation, liquid $(\Delta H)_{298}$	-142.6 kJ/mol	-34.08 kcal/mol	[137]
Standard entropy of formation, gas $(S)_{298}$	$260.77 \text{ J mol}^{-1} \text{ K}^{-1}$	$62.32 \text{ cal mol}^{-1} ^\circ\text{C}^{-1}$	[132]
Entropy, gas, at 144 K	$228 \text{ J mol}^{-1} \text{ K}^{-1}$	$54.50 \text{ cal mol}^{-1} ^\circ\text{C}^{-1}$	[128]
Heat of vaporization $(\Delta H)_{\text{evap}}$ (at 144 K [$-129 ^\circ\text{C}$])	11.58 kJ/mol	2.769 kcal/mol	[31]
	11.58 kJ/mol	2.769 kcal/mol	[128]
Heat of vaporization $(\Delta H)_{\text{evap}}$ (at normal boiling point)	11.59 kJ/mol	2.77 kcal/mol	[38]
Heat of fusion $(\Delta H)_{\text{melt}}$ (at 66.3 K [$-206.8 ^\circ\text{C}$])	398 J/mol	95.11 cal/mol	[128]
Heat of fusion	398 J/mol	95.12 cal/mol	[38]

The heat of reaction of



is $-834.7 \pm 0.9 \text{ kJ/mol}$ ($-199.49 \pm 0.22 \text{ kcal/mol}$) NF_3 [138]. It is difficult to derive the enthalpy of formation of NF_3 from this test because of the uncertainty of the heat of solution of HF.

A calorimetric method gave the enthalpies of formation $\Delta H^\circ_{\text{f}298}$ of several nitrogen fluorides, based on their reaction with aqueous KI solutions in a calorimeter in which gases were bubbled through the liquid [139]. The values of $\Delta H^\circ_{\text{f}298}$ recommended for NF_3 , N_2F_4 , *cis*- N_2F_2 (identical for *trans*- N_2F_2), NF_2Cl , NF_2H , FNO, and FNO_2 were listed, although the values for N_2F_4 , FNO, NF_2NO , and FNO_2 were provided with a caution of being uncertain, with the need for further experimental verification. From the $\Delta H^\circ_{\text{f}298}$ and $\Delta S^\circ_{\text{f}298}$ values, the thermodynamic bond energies for the nitrogen fluorides were calculated.

The heat of formation of NF_3 was measured by two different methods [140]. The heat of dissociation measurements gave $\Delta H_{\text{f}} = -31.44 \pm 0.3 \text{ kcal/mol}$, and the heat of reaction of NF_3 and sulfur gave $\Delta H_{\text{f}} = -31.75 \pm 0.2 \text{ kcal/mol}$. An average of -132.2 kJ/mol (-31.6 kcal/mol) NF_3 was employed to calculate values for $\text{HF}(\text{aq})$, which compared well with other work reported in the literature.

Literature values for the enthalpy and entropy of formation of NF_3 , N_2F_4 , NF_2Cl , *cis*- N_2F_2 , *trans*- N_2F_2 , F_2NN , FNO, and FNO_2 were collected and summarized, and expressions were derived for the temperature dependence of the free energy of formation of these substances [141]. The thermodynamics of several reactions for the synthesis of NF_3 , N_2F_4 , and FN_2F involving the substances listed above were examined.

The dissociation energy of difluorine and the heat of formation of hydrogen fluoride affect all methods for determining the heats of formation of fluorides. Methods used are fluorine bomb calorimetry at constant volume, fluorine flame calorimetry at constant pressure, explosion (decomposition) calorimetry, solid-state calorimetry, and solution calorimetry [142].

For additional thermodynamic properties of NF_3 , see also [143, 144].

The heats of formation of NF_3 , the hypothetical NF_5 , NFO, NFO_2 , NF_3O , N_2F_2 , N_2F_4 , N_3F , NF_3BF_3 , NFOBF_3 , NFO_2BF_3 , and NF_3OBF_3 were calculated using atomization reaction and formation reaction quantum mechanical computation methods, and the thermodynamic functions of these compounds were calculated [145]. Results showed that formation reaction quantum mechanical computation methods in conjunction with the G3 theory can accurately evaluate the heats of formation of these compounds. The results agreed well with experimental data.

1.2.7.1 Heat Capacity of Nitrogen Trifluoride

The heat capacity of gaseous NF_3 as a function of temperature can be calculated from the Shomate equation:

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + \frac{E}{\tau^2}$$

where C_p is the heat capacity in $\text{J mol}^{-1} \text{K}^{-1}$; A, B, C, D, and E are constants; and τ is the absolute temperature in kelvin divided by 1000. The coefficients are listed in Table 8. The same coefficients (and others) are used for formulas expressing the standard enthalpy of formation and the standard entropy of the vapor. These equations were curve-fitted from data covering ranges from 298 to 1000 K and from 1000 to 6000 K.

Table 8: Constants for vapor-phase thermodynamic properties of nitrogen trifluoride.

Temperature, K	298–1000	1000–6000
A	26.45610	82.54781
B	142.2606	0.345728
C	−137.6134	−0.071941
D	47.68505	0.005089
E	−0.404491	−4.482487
F	−146.5375	−169.6763
G	253.7876	340.7860
H	−132.0893	−132.0893

Data source: [132]

The saturation heat capacity C_σ of liquid NF_3 from the triple point to near the critical point can be calculated by the following formula [127]:

$$C_\sigma = A + BT + CT^2 + DT^3 + ET/(T_c - T)^{1/2}$$

The subscript σ , which in Greek stands for the letter s, refers to property values for the saturated liquid. The parameters A through E are listed in Table 9 and are also

Table 9: Heat-capacity parameters for liquid nitrogen and liquid nitrogen trifluoride.

	N_2	NF_3
A	$\text{JK}^{-1} \text{mol}^{-1}$	$\text{JK}^{-1} \text{mol}^{-1}$
B	$\text{JK}^{-2} \text{mol}^{-1}$	$\text{JK}^{-2} \text{mol}^{-1}$
C	$\text{JK}^{-3} \text{mol}^{-1}$	$\text{JK}^{-3} \text{mol}^{-1}$
D	$\text{JK}^{-4} \text{mol}^{-1}$	$\text{JK}^{-4} \text{mol}^{-1}$
E	$\text{JK}^{-1.5} \text{mol}^{-1}$	$\text{JK}^{-1.5} \text{mol}^{-1}$

Data source: [127]

shown in comparison for data for LN_2 . There is a shallow minimum in C_p of NF_3 at a temperature of about 110 K. T_c is 234 K.

The velocity of sound was measured in gaseous NF_3 using a highly precise acoustic resonance technique [146]. The measurements spanned the temperature range 200–425 K and reached pressures up to the lesser of 1500 kPa or 80% of the sample vapor pressure. The data were analyzed to obtain the constant-pressure ideal-gas heat capacity C_p as a function of temperature. The values of C_p were in agreement with those determined from spectroscopic data. The velocity-of-sound data were fitted by virial equations of state to obtain temperature-dependent density virial coefficients. Two virial coefficient models were employed, one based on square-well intermolecular potentials and the other based on a hard-core Lennard-Jones intermolecular potential. The resulting virial equations reproduced the velocity-of-sound data to within $\pm 0.02\%$ and may be used to calculate vapor densities with relative standard uncertainties of 0.1% or less.

1.2.7.2 Enthalpy of Formation of Nitrogen Trifluoride

The vapor-phase excess enthalpy above the standard enthalpy of formation $\Delta H^\circ_{f,298}$ of NF_3 can be calculated from the Shomate equation:

$$H^\circ - H^\circ_{298.15} = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{\tau} + F - \Delta H^\circ_{f,298}$$

where A, B, C, D, E, and F are constants and τ is the absolute temperature in K divided by 1000. The coefficients are the same as those listed in Table 8. The same coefficients (and others) were used for a formula expressing the heat capacity of the vapor (Section 1.2.7.1). These equations were curve-fitted from data covering a range from 298 to 6000 K from [147].

Thermodynamic functions of NF_3 were derived from spectroscopic data for the temperature range 200–2000 K [148]. Earlier investigations of the molecular constants were less accurate or were outright incorrect.

The enthalpy of $\text{NF}_4^+(\text{G})$ can be extrapolated from the other (N, F) and (N, O, F) compounds. The enthalpies of solid NF_4^+ salts are close to those of corresponding NO_2^+ salts, and from this an exothermic heat of formation for NF_4^+F^- was predicted [149]. This compound NF_5 is not expected to be stable at room temperature.

1.2.7.3 Enthalpy of Dissociation of Nitrogen Trifluoride

The enthalpies of explosion of mixtures of hydrogen and excess NF_3 were measured in a bomb calorimeter [150]. From the measurements, the enthalpy of dissociation of an excess (10 or 100% excess NF_3) of NF_3 was derived, and the enthalpy of formation was calculated to be $-131.5 \pm 1.2 \text{ kJ/mol}$ ($-31.44 \pm 0.30 \text{ kcal/mol}$).

1.2.8 Optical Properties of Nitrogen Trifluoride

Spectra of NF_3 in all regimes of the electromagnetic spectrum have been measured for several reasons: NF_3 is a very symmetrical molecule in the shape of a spinning top, similar to ammonia, and thus is easy to model. Spectroscopic studies were done to measure the inertia moments of the spinning top-shaped molecule and compare it to that of ammonia. Spectroscopy is needed to identify contaminants in NF_3 and verify its purity, an important property for its applications in the semiconductor processing industry. NF_3 is a greenhouse gas that may accumulate in the upper atmosphere and cause global warming or destruction of the ozone layer. For this reason, its spectra and its photolysis have been studied by many chemists. Spectra of NF_3 and its decomposition products and potential reaction products with F_2 would also be of interest in the search for the so-far unknown NF_5 , which would be an even more energetic oxidizer for rocket propellants. Also, if NF_3 is used as a source of fluorine atoms in rare gas halide excimer laser systems, its spectra and vibrational energy states must be known. All of these causes together explain why there are several hundred publications on NF_3 spectra, but only a few of those are referenced here.

1.2.8.1 Infrared Absorption Spectra of Nitrogen Trifluoride

The structure and the IR spectra of NF_3 and PF_3 are very similar. The IR spectra of NF_3 and PF_3 were investigated with a prism instrument in the range of 250–5000 cm^{-1} [151]. The fundamental frequencies for NF_3 were reported as $\nu_1(\text{A}_1) = 1032 \text{ cm}^{-1}$, $\nu_2(\text{A}_1) = 647 \text{ cm}^{-1}$, $\nu_3(\text{E}) = 905 \text{ cm}^{-1}$, and $\nu_4(\text{E}) = 493 \text{ cm}^{-1}$. From these numbers, the force constants as well as thermodynamic functions could be calculated for both molecules.

The IR spectrum of gaseous nitrogen trifluoride has been investigated with prism instruments in the range of 400–3000 cm^{-1} , and the Raman spectrum of liquid nitrogen trifluoride has been investigated in the range of 400–2000 cm^{-1} , [152]. The fundamental frequency assignment made from the infrared data is as follows: $\nu_1(\text{A}_1) = 1031 \text{ cm}^{-1}$, $\nu_2(\text{A}_1) = 642 \text{ cm}^{-1}$, $\nu_3(\text{E}) = 907 \text{ cm}^{-1}$, and $\nu_4(\text{E}) = 497 \text{ cm}^{-1}$. The corresponding Raman shifts in the liquid were $\nu_1(\text{A}_1) = 1050 \text{ cm}^{-1}$, $\nu_2(\text{A}_1) = 667 \text{ cm}^{-1}$, $\nu_3(\text{E}) = 905 \text{ cm}^{-1}$, and $\nu_4(\text{E}) = 515 \text{ cm}^{-1}$. The interpretation of the overtone and combination bands in the IR spectrum may differ from that of earlier interpretations.

An intensive study has been made of the degenerate bands of NF_3 , to verify the theory that a Beer-Lambert-type law should hold for spectrometer tracings of IR bands in an intermediate-pressure range, providing a number of conditions are fulfilled [153]. It was found that the Beer-Lambert law held for T and T_0 at every frequency in the P and R branches of ν_4 and across the whole ν_3 band when sufficient NF_3 had been added to pressure-broaden the lines. Values for the N–F bond dipole moment were derived from the IR data.

The absolute IR intensities of the fundamental vibrations of NF_3 have been measured [154]. The results were interpreted in terms of the N–F bond moment (μ), its derivative ($\partial\mu/\partial r$), and the unshared pair moment on the N atom ($\mu_{\text{u.p.}}$). The bond mo-

ment obtained from the A_1 bending mode was found to be in the vicinity of 1 D. $\mu_{u.p.}$ was in the vicinity of either 1.2 or 1.7 D, depending on the sign assumed for the molecular dipole moment. There was a striking difference in the values of $(\partial\mu/\partial r)$ from the two symmetry species, with $(\partial\mu/\partial r)(A_1)$ in the range of 1.5–2 D/Å and $(\partial\mu/\partial r)(E)$ in the vicinity of 4.5 D/Å.

An approximate potential function has been determined for NF_3 by using the four fundamental frequencies, the experimentally determined rotational distortion constant DJ , and physical arguments based on the absolute intensity results [155]. The rotational distortion constants have been calculated as a function of the force field. Using the approximate potential function, values of the valence type force constants and the rotational distortion constant DK were then calculated.

The IR spectrum of nitrogen trifluoride was measured over the range 400–3500 cm^{-1} , and the rotational fine structure of a number of bands was resolved [156]. The nature of this rotational structure was of special interest because few such studies had been done with oblate symmetric top-shaped molecules. From the parallel-type bands, estimates have been made of the coefficients α_B relating different vibrational states, and a detailed study of the perpendicular-type bands associated with ν_3 and ν_4 has made it possible to derive the Coriolis coefficients $\zeta_3 = +0.81$ and $\zeta_4 = -0.90$ and other coefficients α_A . A number of other bands due to overtones, harmonics, and difference transitions have been recorded and assigned.

The ν_4 perpendicular band of NF_3 was measured at a resolution of about 0.035 cm^{-1} [157]. At this resolution, the appearance of the band was extremely sensitive to the effect of ℓ -type resonance and unambiguously shows that the ℓ -type doubling constant q_4 is positive. Matching calculated spectra with the observed one resulted in $\nu_0 = 493.43 \text{ cm}^{-1}$ and $\alpha_4^c = -5.3 \times 10^{-4} \text{ cm}^{-1}$.

The high-resolution ν_4 and $(\nu_4 + \nu_2)$ IR bands of NF_3 and the ν_6 IR band of CF_3H (another spinning top) have been investigated in detail using an ℓ -type resonance calculation computer program [158]. By means of the computer simulation technique, the shapes of the observed P, Q, and R branches could be accurately reproduced and the frequencies of all the fine structure “lines” in the P and R branches precisely matched. The analysis provided accurate values of all the band constants whose determination was not possible from the microwave spectra. A band structure investigation showed that the observed P and R branch “lines” arise primarily from clusters of closely spaced PPK(J) and RRK(J) lines of a given J and that in these bands the peaks of these P and R “lines” generally correspond to the $K \equiv J$ components of the PP(J) and RR(J) clusters, respectively.

The IR spectrum of a typical NF_3 sample was measured as part of an effort to develop a military specification and analysis methods for NF_3 [159] (Figure 2). At the same time, the IR spectrum of a synthetic mixture of seven likely contaminants with known concentrations was recorded. Poor sensitivity at the test conditions that were used and overlap of absorption bands allowed only NO_2 , CF_4 , and N_2O in a mixture with NF_3 to be determined by IR without scale expansion.

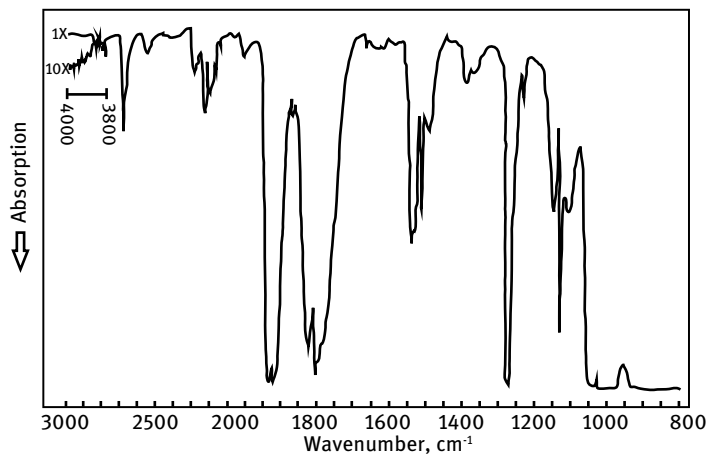


Figure 2: IR spectrum of nitrogen trifluoride. (Reproduced and modified from [159].)

The IR spectrum of dissolved NF_3 was measured in liquid-argon solution [160]. Because the sample of NF_3 used for the experiments was contaminated with N_2O , it was also necessary to measure the spectrum of N_2O in liquid-argon solution so that the impurity bands could be identified unambiguously. In the observed spectrum of NF_3 , it was possible to identify 29 overtone and combination bands in addition to the vibrational fundamentals. The wave numbers of the NF_3 bands were compared with the corresponding numbers determined from the gas-phase spectrum.

The intensities of the binary overtone and combination bands in the IR spectrum of NF_3 have been measured both in the gas phase and in liquid-argon solution and compared [161]. The observed intensities were interpreted in terms of a simple model that ascribed all the intensity of the binary overtones and combinations to anharmonic coupling with the fundamentals; i.e., a model in which the second derivatives of the dipole moment with respect to the normal coordinates were assumed to be zero. The agreement between the observed intensities and the calculated ones was very good for the bending modes but less satisfactory for the stretching modes.

High-resolution (0.004 cm^{-1}) IR spectra of all of the fundamental bands of nitrogen trifluoride have been obtained, and rotational analysis of these bands produced better band constants than had previously been reported [162].

The microwave and far-IR rotational spectrum in the ground vibrational state of $^{14}\text{NF}_3$ has been observed and analyzed up to $J=60$ using a tunable sideband spectrometer in the far-IR region [163]. The resulting molecular constants were (in MHz) $B_0 = 10681.092679(39)$, $D_J = 14.61109(11) \times 10^{-3}$, $D_{JK} = -22.77154(71) \times 10^{-3}$, $H_J = 0.019529(95) \times 10^{-6}$, $H_{JK} = -0.09847(96) \times 10^{-6}$, $H_{KKJ} = 0.1490(10) \times 10^{-6}$, $L_{JK} = -0.00072(12) \times 10^{-9}$, and $(eQq)_N = -7.0854(18)$. The millimeter-wave spectrum of $^{15}\text{NF}_3$ has also been observed and analyzed, providing the following slightly different

values of the rotational constants: $B_0 = 10629.47940(23)$, $D_J = 14.3234(12) \times 10^{-3}$, $D_{JK} = -22.2093(33) \times 10^{-3}$.

As part of an international spectroscopy effort, several accurate experimental values of the α^C and α^B rotation–vibration interaction parameters and ω_i , χ_{ij} , and g_{ij} vibrational constants were extracted from high-resolution Fourier-transform infrared spectroscopy (FTIR), millimeter wave, and centimeter wave investigations of the spectra of the oblate symmetric top–shaped molecule $^{14}\text{NF}_3$ [164–167]. The band-centers used were those of the four fundamentals, overtones, combinations, and hot bands identified in the region between 400 and 2000 cm^{-1} . Comparison of obtained constants with the ones measured previously, by IR spectroscopy at low resolution, revealed orders-of-magnitude higher accuracy of the new values, with wave numbers accurate to six places after the decimal point. The agreement between recent values and those determined by *ab initio* calculations employing the TZ2Pf basis was excellent.

The $\nu_1 + \nu_4$ (E, $\nu_0 = 1523.0407 \text{ cm}^{-1}$) IR absorption band of the oblate symmetric spinning top–molecule $^{14}\text{NF}_3$ has been studied by FTIR spectroscopy with a resolution of $2.5 \times 10^{-3} \text{ cm}^{-1}$, and in total, 1885 rovibrational transitions up to $K_{\text{max}} = 70 = J_{\text{max}}$ have been assigned [168]. Assuming the $\nu_1 = \nu_4 = 1$ vibrational state as isolated, the non-zero weighted experimental data were fitted to 26 free parameters with a standard deviation better than the spectral resolution. The experimental anharmonicity constant $\chi_{1,4}$ was determined as $-2.383249(49) \text{ cm}^{-1}$.

Laboratory measurements of NF_3 IR spectra gave an integrated IR absorption cross-section of $7.04 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$ over the spectral region 200–2000 cm^{-1} [169]. The radiative efficiency was calculated to be $0.21 \text{ W m}^{-2} \text{ ppbv}^{-1}$, and the 100-year global warming potential, relative to carbon dioxide, was predicted to be 17200. These values were approximately 60% higher than previously published estimates, primarily reflecting the higher IR absorption cross-sections reported.

The IR spectra of NF_3 in the range of 900–4500 cm^{-1} were calculated by the model Hamiltonian and seemed to describe the N–F stretching modes accurately with only four numbers of parameters. It only predicted the higher overtones but also showed good agreement with the few observed data [170]. See also [171].

1.2.8.2 Raman Fluorescence Spectra of Nitrogen Trifluoride

In the Raman spectrum of gaseous nitrogen trifluoride, all four fundamentals have been observed at 500 cm^{-1} (E), 649 cm^{-1} (A_1), 910 cm^{-1} (E), and 1035 cm^{-1} (A_1) [172]. The molecular vibrations were assigned on the basis of polarization data and line shape.

The Raman spectrum of gaseous NF_3 was recorded, and the band contours of ν_3 (E) and ν_4 (E) were analyzed to determine the intensity ratio between the contributions of $\gamma \pm 1$ and $\gamma \pm 2$ [173]. The Raman profiles were studied in the crystal and in the liquid between 60 and 185 K. The intense IR lines $\nu_1(A_1)$ and $\nu_3(E)$ showed complex structures made up of two peaks at low temperature, similar to the structures of the intense IR lines of crystals and which are due to a particularly strong transition dipole coupling.

The NF_3 molecules rotate more easily about the main axis, with a ratio between the mean angles of rotation about the main axis and the other axis, respectively, equal to ~ 3 at 78 K. The Coriolis perturbation was found to reduce the contribution of the spinning motion to the line width of ν_4 , by a factor of 3 owing to the large value of the Coriolis constant.

1.2.8.3 Ultraviolet Absorption Spectra of Nitrogen Trifluoride

Because of the suspected contributions of NF_3 as a greenhouse gas to global warming and atmospheric chemistry, the UV absorption spectra and their photolysis have been investigated extensively.

In the electronic absorption spectrum of NF_3 at low pressures, the long wavelength limit of absorption was at about 960 Å in agreement with the lowest ionization potential of the molecule (939 Å) [174]. Quantitative intensity measurements showed a smooth decrease of the absorption coefficients to effectively zero at about 1800 Å, with no indication of even partly resolved electronic transitions.

The absorption spectra of liquid NF_3 or N_2F_4 have been measured at low temperatures in the near UV region of the spectrum [175]. It was shown that the liquid-phase absorption spectra did not differ much from the spectra in the gaseous phase. Therefore, the elementary absorption event was characterized by the cross-section of photon absorption by an individual molecule. The absorption cross-sections of these molecules were represented in the liquid phase, which did not differ significantly from absorption cross-sections of these molecules in the gaseous phase.

The absorption coefficient of nitrogen trifluoride at 147 nm was determined using two Pyrex cells in series. The absorption coefficient of nitrogen trifluoride was found to be $k = 136 \pm 3 \text{ (atm at 298 K)}^{-1} \text{ cm}^{-1}$ (base e) [176].

Nitrogen trifluoride is an atmospherically persistent greenhouse gas that is primarily removed by UV photolysis and reaction with $\text{O}(^1\text{D})$ atoms. Therefore, the NF_3 gas-phase UV absorption spectrum, $\sigma(\lambda, T)$, was measured at 16 wavelengths between 184.95 and 250 nm at temperatures between 212 and 296 K [177]. A significant temperature dependence was observed in the wavelength region most relevant to atmospheric photolysis (200–220 nm), with a decrease in $\sigma(210 \text{ nm}, T)$ of $\sim 45\%$ between 296 and 212 K. Atmospheric photolysis rates and global annually averaged lifetimes of NF_3 were calculated, giving lifetimes from 610 to 762 years and global lifetimes from 484 to 585 years. The NF_3 global warming potential is of the order of 13300 to 19700.

1.2.9 Microwave Spectra of Nitrogen Trifluoride

The microwave absorption spectrum of NF_3 molecules trapped in an argon matrix in the region of 18–50 GHz was measured, but no microwave absorption in excess of 1 db was observed, 1 db being the smallest signal that could be detected by the microwave spectrometer used in this experiment [178].

The microwave spectra of two isotopic species of the NF_3 molecule were investigated in the excited vibrational states [179]. The vibration–rotation interaction constants α_v^B for the ν_1 , ν_2 , ν_3 , and ν_4 states were found to be -43.45 , $+38.65$, $+78.81$, and $+4.48$ MHz for $^{14}\text{NF}_3$, and -38.41 , $+40.14$, $+75.67$, and $+4.64$ MHz for $^{15}\text{NF}_3$, respectively. The equilibrium rotational constant, B_e , was then derived to be 10761.91 ± 0.2 MHz for $^{14}\text{NF}_3$ and 10710.63 ± 0.2 MHz for $^{15}\text{NF}_3$, from which the equilibrium bond length was determined to be $r_e(\text{N}-\text{F}) = 1.365 \pm 0.002$ Å and the bond angle $\alpha_e(\angle \text{FNF}) = 102^\circ 22' \pm 2'$. A set of linear relations was derived between cubic potential constants from the observed α_v^B and ℓ -type doubling constants.

The microwave spectra for the $J=2 \leftarrow 1$ and $J=3 \leftarrow 2$ transitions in NF_3 were measured and analyzed for two isotopic species of NF_3 in the excited vibrational states [180]. The ν_4 and $\nu_2 + \nu_4$ satellites showed spectral patterns characteristic of the ℓ -type resonance, with the splitting of the center lines amounting to more than 80 MHz. The ζ_4 was found to be -0.895 for $^{14}\text{NF}_3$ and -0.888 for $^{15}\text{NF}_3$. The ν_3 satellites also showed the pattern of the ℓ -type resonance, but slight discrepancies were found between the calculated and the observed spectra and cannot be accounted for unless third-order terms are taken into consideration.

The ν_4 band of NF_3 , $\nu_0 = 493.423 \text{ cm}^{-1}$, has been studied by FTIR spectroscopy with a resolution of $3 \times 10^{-3} \text{ cm}^{-1}$. Strong intensity perturbation by $\ell(2, 2)$ resonance was revealed. The more than 5000 IR assignments were complemented by 132 millimeter-wave measurements in the regions 140–250 and 340–470 GHz, by seven new or formerly reported $J=1-0$ and $3-2$ microwave frequencies and by 134 $\Delta J=0$, $\Delta k=\Delta \ell=\pm 2$ direct ℓ -type centimeter-wave transitions in the region 8–26 GHz with $J_{\text{max}}=22$ and $(k-\ell)_{\text{max}}=15$ [181]. The rotational data enabled detection of splittings caused by $\ell(2, -4)(t)$ and $(0, 6)(h_3)$ interactions in excess of those by $\ell(2, 2)(q)$ effects. The sets of molecular constants obtained from the merged data reproduced the IR observations with $\sigma = 0.24 \times 10^{-3} \text{ cm}^{-1}$, the millimeter-wave data with $\sigma = 29 \text{ kHz}$, and the centimeter-wave measurements with $\sigma = 3 \text{ kHz}$.

The submillimeter-wave spectrum of $^{14}\text{NF}_3$ has been measured, and the ground state rotational spectrum has been reanalyzed, including the $K=3$ splittings [182]. The quadratic, cubic, and semi-diagonal quartic force field has been calculated at the CCSD(T) level of theory, employing a basis set of at least polarized valence triple-zeta quality. This force field has been used to predict the spectroscopic constants, including the parameters specific to the doubly degenerate vibrational states. The calculated values were found to be in good agreement with the available experimental data. See also [183, 184].

1.2.10 Photoelectron XPS Spectra of Nitrogen Trifluoride

The He(I) resonance photoelectron spectra of gaseous nitrogen trifluoride and nitrogen oxide trifluoride were recorded and compared to those of boron trifluoride and carbon tetrafluoride [185, 186]. The first band in the He-I photoelectron spectrum of

NF₃ was obtained at sufficiently high resolution to reveal vibrational structure [187]. The bifurcated nature of the band was interpreted as a transition from pyramidal NF₃ to pyramidal NF₃⁺, the latter having a lower barrier to inversion since one of the lone electrons is missing. The span of the Franck-Condon region in the transition was sufficient to surmount the barrier, whose magnitude can be estimated from the spectrum to be ~0.75 eV. This is one of the very few cases for which an accurate experimental measurement of an inversion barrier is known.

The interaction of NF₃ with elemental silicon surfaces has been investigated using X-ray photoelectron spectroscopy (XPS) [188]. Si(100) surfaces were subjected to plasmas created by NF₃ gas mixtures and ion bombardment from NF₃-generated ion beams as a means of reproducing the ion component of semiconductor plasma etching under controlled conditions. NF₃ plasma impingement on Si led to the appearance of a high binding-energy component in F1s XPS spectra, possibly as a result of neutral interstitial fluorine being incorporated into the Si lattice as a result of an ion-damage mechanism.

1.2.11 Electrical Properties of Nitrogen Trifluoride

The dielectric breakdown voltage of NF₃ in comparison to SF₆ and air was measured with two 25-mm (1-in)-diameter copper sphere electrodes spaced 0.76–10.2 mm (0.03–0.4 in) apart with voltages applied from 10 to 70 kV AC [35]. SF₆ is widely used as a dielectric in transformers and high-voltage switches. NF₃ is a much better dielectric than either SF₆ or air, but concerns about its reactivity prevented its use in high-voltage electrical equipment. With a 10.2-mm (0.4-in) gap, the breakdown voltage for NF₃ was 70 kV, for SF₆ was 58 kV, and for air was 26 kV.

1.2.12 Magnetic Properties of Nitrogen Trifluoride

1.2.12.1 Nuclear Magnetic Resonance Spectra of Nitrogen Trifluoride

Direct comparisons between ¹⁹F nuclear magnetic resonance (NMR) spectra of liquid and gaseous F₂, OF₂, and NF₃ had not been reported prior to 1966 [189]. Previous sources had listed the chemical shift of liquid NF₃ as -145 ± 1 ppm (in relation to CFCl₃). The chemical shifts of liquid and gaseous F₂, OF₂, and NF₃ are listed in Table 10.

Table 10: ¹⁹F NMR shifts in liquid and gaseous F₂, OF₂, and NF₃.

	¹⁹ F NMR shifts ^a		
	F ₂ (ppm)	OF ₂ (ppm)	NF ₃ (ppm)
Liquid at 77 K	-422 ± 1	-249 ± 1	-142 ± 1
Gas	-419 ± 1	-248 ± 1	-138 ± 1
Difference gas–liquid	3	1	4

^aIn relation to CFCl₃ reference.

Data source: [189]

As can be seen in Table 10, the chemical shifts for liquid F_2 , OF_2 , and NF_3 were all lower than the corresponding shifts in the gas. This downfield shift due to liquefaction is similar to that observed in the proton magnetic resonance studies of the first-row hydrides

A combined nuclear quadrupole resonance (NQR) and NMR study has been made of solid NF_3 . The quadrupole coupling constant and asymmetry parameter of ^{14}N have been determined and the low-temperature torsional oscillation frequencies of the molecule in the solid calculated by fitting the temperature dependence of the resonance frequencies to Bayer theory [190]. The constants obtained were as follows: $3e^2q_0Q/4h = 5.3012 \pm 0.0005 \times 10^6 \text{ s}^{-1}$, $\eta_0 = 0.00112 \pm 0.00002$, $\nu_x = 1.505 \pm 0.005 \times 10^{12} \text{ s}^{-1}$, and $\nu_y = 1.003 \pm 0.003 \times 10^{12} \text{ s}^{-1}$, respectively, where the first two parameters are for the rigid lattice at 0 K. Above about 35 K, and particularly near the phase transition at 56.6 K, Bayer theory is inadequate to explain the observed temperature dependence. The line width decreased from 42 kHz at about 35 K to 1 kHz at 65 K, just below the melting point, but did not exhibit any noticeable discontinuity at a phase transition (56.62 K). The line width became very narrow before the solid melted, which was suspected to be due to the onset of hindered rotation of the NF_3 molecule about its triad axis below the transition temperature and the occurrence of additional large-amplitude motions above the transition. The data were reanalyzed in terms of a one-motion process and a two-motion process [191]. Although the data showed no apparent discontinuity at the phase transition, the two-motion analysis gave much better agreement with experimental data. See also [192].

The ^{14}N NMR shift in NF_3 at 143 K was +238 ppm in relation to the shift in aqueous nitrite ion [193].

The difluoroamino $\bullet NF_2$ free radicals, having a lone electron, of course are paramagnetic, but based on measurements with doublet rotational Zeeman spectroscopy, there is a modest contribution of diamagnetism in the molecule that should not be neglected [194].

1.2.13 Molecular Structure of Nitrogen Trifluoride

The molecular structure of NF_3 is often compared to that of ammonia on the one side and to that of N_2F_4 on the other side. The decomposition of NF_3 and N_2F_4 produces difluoroamino $\bullet NF_2$ free radicals that are relatively stable. The heat of formation of the difluoroamino free radical was found to be $37.2 \pm 10.5 \text{ kJ/mol}$ ($8.9 \pm 2.5 \text{ kcal/mol}$) [22]. The NF_2-F bond in NF_3 is the weakest bond in NF_3 , in contrast to ammonia, in which the NH_2-H bond is the strongest bond:

Bond energy

NF_2-F	238.91 kJ/mol
$NF-F$	297.06 kJ/mol
$N-F$	297.06 kJ/mol

The strength of the $\text{NF}_2\text{—F}$ bond is $239 \pm 10.5 \text{ kJ/mol}$ ($57.1 \pm 2.5 \text{ kcal/mol}$), while the average NF bond strength in NF_2 and N_2F_4 is 297 kJ/mol (71 kcal/mol). For comparison, the strength of the N—N bond in N_2F_4 , as determined from appearance potential data, is 86.6 kJ (20.7 kcal), which is in excellent agreement with the value 82.8 kJ (19.8 kcal) found by thermal measurements. Compared to other fluoroamines, the N—F bond in NF_3 is relatively short.

A separation of the effects of substituent groups into distinct σ and π contributions and the influence of the σ and π contributions on Hamiltonians and wave functions of various cores have proved useful for describing several diverse phenomena in N—F compounds [23]:

- (1) the “anomalous” difference in bond strengths in NF_3 and NF_2 where the N—F bond in NF_3 is weaker than that in NF_2 ;
- (2) the non-constancy of the δ_K value for F in ionization potentials of NF_3 and CF_3 , whereas other substituent group effects were constant;
- (3) the similarity between the effect of F on ionization potentials of $\bullet\text{NF}_2$ and of $\bullet\text{CF}_3$.

The repulsion between an atom and a lone pair of electrons, such as may exist on nitrogen atoms, affects properties of ammonia and nitrogen trifluoride. The repulsion force constants were estimated using a one-electron theory [195]. A new derivation was shown for the method of introducing forces by the lone pair and subtracting lone-pair motion from the vibrational secular equation. The vibrational force constants for NF_3 were examined with this model in mind.

General valence force-field constants for NF_3 have been calculated using very accurate frequency data, Coriolis coupling constants (ζ), and centrifugal distortion constants [148]. The calculated constants were in excellent agreement with the experimental data. Mean amplitudes of vibration were calculated by several different methods, and thermodynamic functions were derived from spectroscopic data for the temperature range 200–2000 K. Earlier investigations of these molecular constants were less accurate or incorrect.

The anharmonic force constants and electric dipole fields of NF_3 can be predicted from *ab initio* computations [196].

Much has been written about the difference in basicity and proton affinity of ammonia NH_3 versus nitrogen trifluoride NF_3 . Nitrogen trifluoride is not a base and has a very low, if any, proton affinity. Ion cyclotron resonance has been used to detect even traces of proton affinity of NF_3 in the gas phase [197].

1.2.14 Dipole Moment of Nitrogen Trifluoride

Nitrogen trifluoride is non-basic with a low dipole moment of 0.2340 D. By contrast, ammonia is basic and highly polar (1.47 D). The dipole moment of NF_3 is lower than the dipole moment of NH_3 , which can be explained by the reversed polarity of nitrogen. This difference arises from the fluorine atoms acting as electron-withdrawing groups, attracting essentially all of the lone-pair electrons on the nitrogen atom and reducing

its basicity. NF_3 has a positively polarized nitrogen atom, and the dipole moment of the lone pair is in the opposite direction to the dipole moment along the same axis associated with the three N—F bonds. In ammonia, the polarities are reversed, and the moments due to the N—H bonds and the lone pair operate in the same direction. The intrinsic moment of the N—F bond in NF_3 is 1.24 or 1.60 D, whereas it is 1.29 D in N_2F_4 [198].

When calculating the dipole moment of NF_3 , some investigators have neglected to consider the ionic character of the N—F bond. The bond may have 42% ionic character [199].

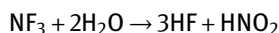
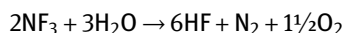
1.3 Chemical Properties of Nitrogen Trifluoride

Compared to the other nitrogen halogenides NCl_3 and NI_3 , which explode at the slightest stimulus, NF_3 is remarkably stable. Accidents have happened during the production of NF_3 when unstable by-products accumulated in cold traps, but these accidents were later blamed on unstable intermediates [28]. Contrary to the reactivity of fluorine or oxygen fluoride, NF_3 does not react with water at room temperature. It is somewhat soluble in water. It does not react with dilute caustic or acids, it does not hydrolyze, and it does not form salts in aqueous solutions as ammonia does (but it will form NF_4^+ salts with strong Lewis acids in anhydrous hydrogen fluoride).

Although initial thermodynamic and molecular orbital calculations let the stability of NF_4^+ salts appear unlikely [200, 201], skilled experimenters did succeed in synthesizing several NF_4^+ salts that might even be useful as oxidizers in solid rocket propellants or chemical lasers.

Nitrogen trifluoride is resistant to chemical attack by water and aqueous acids. The compound can be recovered quantitatively after 1 week in contact with excess dilute acid (HNO_3 , H_2SO_4 , HClO_4) or water at 406 K (133 °C) [202, 203]. In the presence of aqueous base, however, slow hydrolysis occurs at 373 K (100 °C). When boiled with hot caustic above 373 K (100 °C), NF_3 eventually hydrolyzes and decomposes to nitrite and fluoride. The unstable HONF_2 may be an intermediate in the hydrolysis. This differs from the hydrolysis of nitrogen trichloride, which gives ammonia and hypochlorite under similar conditions. While NF_3 is stable toward aqueous HCl, it reacts readily with hot, neutral sodium chloride solutions. The active species is the Cl^- anion, not the OH^- anion.

Mixtures of NF_3 and water steam can be made to burn in a slow flame reaction



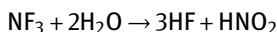
when ignited by an electric spark. Mixtures of NF_3 with combustible gases such as NH_3 , H_2 , CH_4 , C_2H_4 , CO , or H_2S combust explosively when ignited by a flame or

a capacitor discharge over a spark gap. Alkali metals as well as zinc, boron, and arsenic will ignite when heated in NF_3 . Copper and silver react only superficially with NF_3 at $\sim 600\text{--}800\text{ K}$ ($\sim 350\text{--}550\text{ K}$). Reactions of NF_3 with metals often lead to N_2F_4 as the reaction product [204].

It is known that the reaction of NF_3 with metal wire in a flash bulb produces a very bright light, suitable for flash photography. The reaction of NF_3 with other metals has been studied as well [205].

Unlike NH_3 , NF_3 does not react with diborane. The basicity of NF_3 is much lower than that of NH_3 .

In order to study the hydrolysis of NF_3 , a 300-mL borosilicate glass bulb was evacuated and filled with 23 mL of water and 0.40 g of NF_3 . The bulb was then heated to 373 K (100°C) and held at that temperature for 7 d. The partial pressure of NF_3 at that temperature was calculated to be 470 mm Hg. The reaction was assumed to be

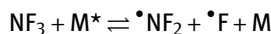


The amount of acid that was formed was found by titration with sodium hydroxide. The percentage of nitrogen trifluoride that had reacted was calculated on the basis of this equation and was 1.5% [35]. Additional information on chemical properties of NF_3 and other nitrogen fluorides can be found in [10, 11, 206].

1.3.1 Thermal Decomposition of Nitrogen Trifluoride

It appears that most experiments on the thermal decomposition of NF_3 were done in shock tubes, often in parallel with studies of the dissociation of N_2F_4 , which also leads to the relatively stable $\bullet\text{NF}_2$ free radical. It is probably difficult to study the homogeneous thermal decomposition of NF_3 gas by conventional methods in a static reactor or in a flow reactor because the gas would attack the walls and destroy the apparatus.

The rate of dissociation of nitrogen trifluoride in excess argon has been determined by measuring the rate of formation of $\bullet\text{NF}_2$ in the temperature range 1050–1390 K using a shock tube coupled with a spectrophotometric analysis technique [207]. In the range of 0.273–0.606 MPa (2.7–6.0 atm) total pressure, the reaction was found to be first order in both NF_3 and Ar concentrations. The reaction may be represented by



where M is a third-body gas. and for small conversions, other reactions were shown to be unimportant. The temperature dependence of the bimolecular rate constants can be described by

$$k = 10^{10.10 \pm 0.002} \exp\left(\frac{E_a}{RT}\right)$$

where E_a is the activation energy of -126 ± 9.6 kJ/mol (-30.1 ± 2.3 kcal/mol), k is the rate constant in $\text{mol}^{-1} \text{s}^{-1}$, and T is the temperature in kelvin. It was noted that the apparent activation energy is significantly lower than the bond dissociation energy, $D(\text{NF}_2-\text{F})$.

The proposed use of NF_3 and N_2F_4 as reagents in premixed HF or DF chemical lasers or rare gas halide excimer laser systems is one of the reasons why the dissociation of NF_3 and N_2F_4 has been investigated, as well as in combination with rapid thermal reactions of these substances with H_2 . Although flames of NF_3 and H_2 have been reported, these gases may be pre-mixed up to 373 K (100 °C) without reaction. In contrast, $\text{N}_2\text{F}_4/\text{H}_2$ mixtures without an inhibitor are spontaneously explosive near room temperature. Measurement of the UV absorption by $\bullet\text{NF}_2$ near 260 nm is the commonly used analytical method.

Shock waves in gas mixtures containing >94% Ar were combined with time-resolved spectrometry of $\bullet\text{NF}_2$ absorption at 260 nm and HF emission at $2.7\mu\text{m}$ in a study of rapid thermal reactions of NF_3 and mixtures of H_2 with NF_3 or N_2F_4 [208]. NF_3 decomposition between 1100 and 1500 K produced maximum $\bullet\text{NF}_2$ concentrations accountable by the equilibrium



followed by slower, irreversible $\bullet\text{NF}_2$ removal. NF_3/H_2 mixtures were inert for 2.2 ms below 1000 K and reacted in 550 ps above 1500 K, exhibiting complete HF yield, preceded by IR emission, no resolvable $[\text{NF}_2]$ transient, and copious $\text{NH}(\text{A}^3\Pi - \text{X}^3\Sigma^-)$ chemiluminescence at 336 nm during the reaction. Delayed and dynamically unstable gas reactions occurred over the $1000 < T < 1500$ K range. Pyrolytic dissociation and subsequent bimolecular reactions of the intermediates in the mechanism of stoichiometric formation of HF and N_2 may play a role in this process. Early attempts to observe 260-nm absorption during the $\text{NF}_3 + \text{H}_2$ reaction revealed instead the presence of strong UV chemiluminescent emission. Some of the tests required an inhibitor such as butene-1 to prevent premature ignition. This study was done in support of the planned use of $\text{N}_2\text{F}_4/\text{H}_2$ mixtures in lasers.

The thermal decomposition of NF_3 was reinvestigated behind incident shock waves in dilute (1%) NF_3/Ar mixtures over the temperature range 1150–1530 K and at 80.8–183 kPa (0.80–1.81 atm) total pressure, monitoring $\bullet\text{NF}_2$ radical concentrations in UV absorption at 260 nm or IR emission at $5.17\mu\text{m}$ [209]. The low-pressure-limit second-order rate constant was found to be

$$k_1 = 10^{16.61} \pm 0.13 \exp\left(\frac{E_a}{RT}\right)$$

where k_1 is the rate constant in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$, E_a is the activation energy $E_a = -201 \pm 3.3$ kJ/mol (-48.0 ± 0.8 kcal/mol), and T is the temperature in kelvin.

Although different investigators agreed that the dissociation reaction is unimolecular, there was still a considerable spread in the activation energy and Arrhenius rate parameter proposed for this reaction.

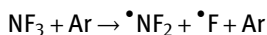
The decomposition of 0.25, 0.5, and 1.0% NF_3 in argon was studied in a reflected shock wave [210]. In these dilute mixtures, the unimolecular decomposition pathway could be studied independently of other modes of decomposition. The temperature range of the study was 1500–2400 K, and the total pressure range was 0.8–60 atm. The total gas concentration behind the reflected shock ranged from 5×10^{-6} to 3.6×10^{-4} mol/cm³. Kinetic measurements were made by following the decay of emission of the $\nu_3 + \nu_1$ combination band of NF_3 at 5.18 μm . The unimolecular rate constants were obtained from the emission decay data and were converted to second-order rate constants by dividing by the total gas concentration. The Arrhenius parameters calculated by a least-squares analysis of the second-order rate constants were given as

$$k = 10^{14.7} \exp\left(-\frac{56300}{RT}\right)$$

where k is the second-order rate constant in cm³ mol⁻¹ s⁻¹ and T is the temperature in kelvin. The activation energy for the reaction was very close to the first N–F bond energy of 238 kJ/mol (57 kcal/mol). The results suggested that under the reported conditions, vibrational equilibrium was not maintained during the shock-wave reaction.

Repeating some of the measurements with both IR emission at 5.18 μ and UV absorption at 270 m μ to analyze the $\bullet\text{NF}_2$ concentration, a rate constant of 2.5×10^4 s⁻¹ was derived from the IR emissions curve [211].

The kinetics of thermal dissociation of NF_3 in argon has been studied over the temperature range between 1461 and 2026 K using shock-tube heating [212]. The rate of formation of the reaction product NF_2 was monitored by following the absorption of a characteristic NF_2 band at 2600 Å. The total sample pressure of the experiment was between 0.98 and 1.47 atm, and the NF_3 concentration in Ar was between 1 and 5%. The reaction was found to be first order in both NF_3 and Ar and may be represented by

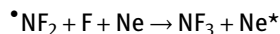


The second-order rate expression was found to be

$$k_{\text{Ar}} = 10^{(10.02 \pm 0.06)} \exp\left(-25.7 \pm 0.6 \frac{\text{kcal}}{RT}\right) \text{mol}^{-1} \text{s}^{-1}$$

The thermal dissociation rate of NF_3 in mixtures of 5 and 10% NF_3 in Ar has been measured behind incident shock waves over the temperature range 1330–2000 K [213]. Dissociation rates were determined from post-shock density gradients measured by laser beam deflection. The second-order rate coefficient determined for NF_3 -Ar collisions was $k = 2.31 \times 10^{15} \exp(-20500/T) \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$.

Dissociation is always limited by the reverse reaction due to recombination, which might limit the laser light output. The recombination reaction



has been investigated experimentally in electron beam-excited Ne/Xe/NF₃ mixtures [214]. The results obtained were in excellent agreement with theoretical predictions from knowledge of the dissociation forward reaction.

Prior to dissociating, the NF₃ molecule rotates and vibrates internally as it is being heated. It may also lose an electron and become an ion, which has a different lifetime than the parent molecule. The excited states of NF₃ and NF₃⁺ as a function of their initial internal-energy state have been studied by a photoelectron-photoion coincidence technique [215]. The fragments, products of dissociation, may leave in excited states and lase.

The rate constant of NF₃ dissociation in a helium mixture near the low-pressure limit was directly measured in a shock tube by a UV absorption method in the temperature range 1050–1600 K [216, 217]. The rate constant in the temperature range $T = 1050\text{--}1600\text{ K}$ may be expressed as

$$k = 10^{14.38 \pm 0.07} \exp\left(\frac{E_a}{RT}\right)$$

where k is the rate constant in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$, E_a is the activation energy $E_a = -153 \pm 8.8 \text{ kJ/mol}$ ($-36.6 \pm 2.1 \text{ kcal/mol}$), and T is the temperature in kelvin. Levels of the NF₃ stationary dissociation fraction were also measured as a function of the initial temperature of the mixture behind the shock wave. It increased monotonically with temperature and reached 50% of the value at 1600 K, which corresponded to high $\bullet\text{NF}_2$ concentrations of up to $2 \times 10^{17} \text{ cm}^{-3}$. Rates of NF₃ thermal decomposition in the temperature range 1950–2050 K and pressure range 1.2–4.2 atm were also measured. The bimolecular rate constant of the NF₃ decomposition reaction depended strongly on the pressure.

Rates of NF₃ thermal decomposition in the temperature range 1450–2050 K and pressure range 121–424 kPa (1.2–4.2 atm) were measured by a shock-tube technique [218]. NF₃ decomposition was monitored by UV absorption of the produced $\bullet\text{NF}_2$ radicals. The bimolecular rate constant of the NF₃ decomposition reaction depends on the pressure. An empirical formula was obtained from the experimental data that correctly expressed the dependence of the measured rate constant of decomposition upon the temperature and pressure of the reacting mixture behind the shock wave.

NF₃ that is used for etching silicon wafers or for cleaning CVD equipment has to be pre-dissociated in a plasma discharge, creating atomic fluorine free radicals. A radiofrequency (RF) plasma system can be used for decomposing NF₃. NF₃ was almost completely decomposed (>99%) at an input power of 30 W. However, allowing traces of O₂ to the system inhibited NF₃ decomposition [219]. The products detected in the NF₃/O₂/Ar plasma system were NO₂, NO, N₂O, SiF₄, N₂, and F₂.

Plasma excitation of NF_3 is not only useful for silicon etching and CVD equipment cleaning but, with the addition of some hydrogen gas as a reductant, can also be used for the destruction of unwanted NF_3 waste gases venting from other industrial processes. Low-power arc plasma discharges are characterized by extremely high enthalpy and temperature and are easy to generate and control, so thermal decomposition processes based on the plasma torch are receiving a lot of attention for decomposing non-degradable greenhouse gases. The effects of input power, waste gas flow rate, and additive gases on the destruction and removal efficiency of NF_3 have been examined [220]. Specific energy density decreased as the flow rate increased, and, accordingly, the destruction efficiency was reduced. The destruction efficiency is determined by the specific energy density. The highest destruction efficiency of NF_3 was 97% for a waste gas flow rate of 100 L/min at a low input power level of 2 kW with the help of hydrogen additional gas. The inlet and outlet concentration of NF_3 was analyzed using FTIR. See also [221].

1.3.2 Catalytic Decomposition of Nitrogen Trifluoride

Catalytic decomposition of nitrogen fluoride would facilitate the disposal of surplus NF_3 from industrial processes now that these gases may no longer be vented to the atmosphere. The NF_3 decomposition products would be more reactive than NF_3 itself and would then be easier to remove by reaction with a caustic washing fluid and calcium chloride.

The decomposition of NF_3 in the absence of water over Al_2O_3 , Fe_2O_3 , Co_3O_4 , and NiO and transition metal oxide (Fe_2O_3 , Co_3O_4 , and NiO)–coated Al_2O_3 reagents was investigated [222, 223]. The results showed that Al_2O_3 is an active reagent for NF_3 decomposition, with 100% conversion lasting for 8.5 h at 400 °C. Fe_2O_3 , Co_3O_4 , and NiO -coated Al_2O_3 reagents were superior to bare Al_2O_3 , and 5% $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ had a high reactivity, with NF_3 full conversion maintained for 10.5 h.

1.3.3 Photolysis of Nitrogen Trifluoride

It was hoped that photolysis of NF_3 or N_2F_4 in the presence of an excess of fluorine would produce higher fluorides of nitrogen ($\text{NF}_5?$), but that has not yet been shown. The other reason that the photolysis of NF_3 was studied in detail is that NF_3 may be used as a source of fluorine atoms in chemical lasers with D_2 .

One method to study the strength of chemical bonds is to attempt to break them by photolysis at different wavelength of light, using shorter and shorter wavelength until some dissociation is observed. Photolysis of NF_3 or N_2F_4 forms $\bullet\text{NF}_2$ free radicals that are comparatively long-lived [224].

Irradiation of an equilibrium mixture of N_2F_4 and $\bullet\text{NF}_2$ at room temperature gave NF_3 and N_2F_2 , along with N_2 and other products involving N_2F_2 decomposition products [225]. Coupling of fluoronitrene NF can give rise to N_2F_2 , a reaction that other ni-

trenes undergo, and $\bullet\text{F}_2$ and $\bullet\text{NF}_2$ may combine to make NF_3 . Photolyzed NF_3 or N_2F_4 can enter into all kinds of new reactions that would not take place in the dark [226].

With the rapid growth of the semiconductor and thin-film liquid crystal display manufacturing industries, large quantities of the potent greenhouse gas NF_3 are used and are accidentally or negligently leaked to the atmosphere. Similar to perfluorocarbons, NF_3 is very stable because of its molecular structure. Therefore, in the atmosphere on Earth, NF_3 is difficult to oxidize by O_3 , NO , NO_2 , or OH radicals, except by excited oxygen atoms $\text{O}(^1\Delta)$ that can react with it to form NF_2 or other products. In the upper atmosphere, anthropogenic NF_3 is a suspected greenhouse gas and ozone-layer depletion agent similar to CF_4 and SF_6 . The photolysis reactions of NF_3 in the upper atmosphere under the influence of UV light from the sun have therefore been investigated.

If the wavelength of UV radiation is varied, coming from the long-wavelength end of the spectrum until first ionization is detected, the photolysis/mass spectrometry method can be used to determine the bond strengths of the bonds being broken. Photoionization yield curves for the NF_3^+ , NF_2^+ , and NF^+ ions of NF_3 were measured from the threshold to 600 Å [227]. The ionization energies were used to calculate heats of formation of the ions, ionization energies of radicals, and bond dissociation energies. For NF_3 , the bond dissociation energies were $D(\text{NF}_2-\text{F}) = 2.39 \text{ eV}$, $D(\text{NF}-\text{F}) = 3.4 \text{ eV}$ and $D(\text{N}-\text{F}) = 2.4 \text{ eV}$.

The UV photodissociation of NF_3 and NF_2 has been investigated from 240–270 nm, using tunable UV radiation from a frequency upconverted YAG pumped dye laser system [228]. The absorption cross-section of NF_2 and the photolysis quantum yield for the fragment $\text{NF}(a^1\Delta)$ were measured with 0.25-cm^{-1} resolution. The $\text{NF}(a^1\Delta)$ quantum yield decreased at longer wavelengths and was only 1% at 260 nm. This suggested that the first long-wavelength band in NF_2 leads primarily to ground state $\text{NF}(X^3\Sigma)$ and that the existence of a new, higher-lying NF_2 electronic state is responsible for the $\text{NF}(a^1\Delta)$ production.

Nitrogen trifluoride was found to be stable toward photo-oxidation reactions that limit the atmospheric lifetimes of many detrimental gaseous species. Reactions with species such as $\bullet\text{OH}$ and $\bullet\text{OOH}$ are thermodynamically unfavorable. The reaction with O_3 , while thermodynamically favorable, was found to be too slow to be of atmospheric importance [229]. Measurements of the NF_3 absorption cross-sections from 180 to 250 nm yielded values that were smaller than those previously reported and indicated an atmospheric lifetime against photodissociation in the stratosphere of about 700 years. In addition, the IR band strengths were determined in order to enable estimates of greenhouse-warming potentials.

Although NF_3 , a trace gas of purely anthropogenic origin with a large global-warming potential, is accumulating in the Earth's atmosphere, little photochemical data existed from which to calculate its atmospheric removal rate. Photodissociation quantum yields, Φ_1 , were derived following 193.3-nm laser photolysis of NF_3 and

quantitative conversion of the F-atom photoproducts to OH, which was detected by laser-induced fluorescence [230]. Values of $\Phi_1(P,T) = (1.03 \pm 0.05)$ were determined at pressures between 28 and 100 mbar of He or N₂ and at either room temperature or 255 K. Absorption cross-sections, σ , obtained between 184 and 226 nm were combined with the values of $\Phi_1(P,T)$ to confirm a long (~700-year) photolysis lifetime for NF₃. No evidence for reaction of OH with NF₃ was found, indicating that this process makes little or no contribution to NF₃ removal from the atmosphere. These results underpin recent calculations of an NF₃ atmospheric lifetime of $\tau \sim 550$ years, largely controlled by photolysis in the stratosphere.

Photochemical processes were evaluated for the destruction of unwanted NF₃ in the waste gases from industrial processes at 5 mm Hg partial pressure of NF₃ and 600 mm Hg total pressure, with buffer gas of argon in a reactor based on controlled release of radicals [231]. The results indicated that reductive double bonds and allyl radicals, slowly released from polyisoprene irradiated by a UV lamp emitting 185 and 253.7 nm of light, could achieve NF₃ degradation. The NF₃ degradation efficiency was significantly affected by O₂ and was almost independent of N₂ and reached 96% with a kinetic rate constant $k \sim 1.77 \times 10^{-4} \text{ s}^{-1}$ after 300 min of UV irradiation.

1.3.4 Radiolysis of Nitrogen Trifluoride

The main industrial use of NF₃ is in silicon etching and cleaning of CVD equipment in the semiconductor industry. In these applications, NF₃ has to be activated by passing it through a glow discharge before directing the molecular beam at the surface to be cleaned or eroded. In a glow discharge, a stream of fast electrons knocks one or two atoms out of the NF₃ molecule. Ionization of NF₃ by fast electrons also takes place in the inlet of mass spectrometers and in the high atmosphere (where NF₃ is an unwanted contaminant). In the synthesis of tetrafluoroammonium salts, NF₃ and the other reactants are passed through a glow discharge and are excited so that they will perform reactions that cannot take place at room temperature in the absence of an electron beam. Fast electrons are sometimes called β -radiation.

Low-energy electron impact on NF₃ caused continuous UV emissions in the range of 2000–3400 Å [232]. It produced a structured emission with maxima at 2880, 3005, and 3130 Å and an onset energy of $8.5 \pm 2 \text{ eV}$ superimposed on a continuous feature from 2500 to 3500 Å with an onset at about 30 eV, which has been attributed to the NF₂ fragment. UV emission can be used to monitor the proper operation of semiconductor etching equipment.

Depending on the accelerating voltage, the electron beam may knock off one or two fluorine atoms from the NF₃ molecule. In the latter case, the NF²⁺ ion is formed once its appearance energy ($43.8 \pm 1.0 \text{ eV}$) in the electron impact ionization of NF₃ is exceeded [233].

The absolute cross-sections for the electron-impact ionization of NF₃ from threshold to 200 eV were obtained independently in two different laboratories using two

different experimental techniques, and the agreement was better than $\pm 8\%$ [234]. At 70 eV, the absolute parent NF_3 ionization cross-section was $0.35 \pm 0.06 \text{ \AA}^2$. Absolute cross-sections for the formation of the fragment ions NF^{2+} and NF^+ were found to be, respectively, 1.05 ± 0.20 and $0.7 \pm 0.15 \text{ \AA}^2$ NF^+ at 70 eV.

Close-coupling calculations were made for low-energy electron-collision processes involving NF_3 to obtain cross-sections for (dissociative) excitation of the lowest singlet and triplet electronically excited states [235].

Absolute elastic cross-sections for electron impact on NF_3 have been measured for impact energies from 1.5 to 100 eV and scattering angles from 20 to 130° [236]. Vibrational excitation function measurements showed a 2-eV-wide resonance at 3-eV impact energy. Vibrational loss spectra were measured near this resonance and were resolved into their vibrational components.

The electron collision cross-section of NF_3 is of interest for modeling plasma-enhanced etching of materials. Measurements of the absolute dissociative ionization cross-sections of NF_3 were compared with previous data in the literature for electron attachment, momentum transfer, vibrational excitation, and dissociative excitation [237].

The partial cross-sections creating NF_x^+ ($x = 0, 1, 2, 3$), F^+ and NF_x^{2+} ($x = 1, 2, 3$) during the ionization and dissociative ionization of NF_3 by electron impact were measured by Fourier transform mass spectrometry [238]. The total ionization cross-section grew to a maximum value at 140 eV. Estimates of the total single ionization cross-section using *ab initio* energies with the binary encounter models were roughly twice the measured values.

Absolute total cross sections for 0.5–370-eV electrons scattered by NF_3 molecules have been measured employing the transmission method in a linear configuration [239]. It was found that the total cross-section energy function for NF_3 is dominated by two pronounced enhancements: one resonant-like centered between 2 and 3 eV with the maximum value of $28 \times 10^{-20} \text{ m}^2$ followed by a minimum at around 7–12 eV, $17 \times 10^{-20} \text{ m}^2$, and the second much broader enhancement located around 40 eV ($19 \times 10^{-20} \text{ m}^2$ in the maximum). The maximum, resonant in character, is centered between 2.2 and 3 eV and is superimposed with weak features located at 1.8, 2.2, and 2.8 eV. With low-energy (“thermal”) electrons, one ionization step might be a simple electron attachment, forming NF_3^- ions. The rate constant for the dissociative attachment of thermal electrons (300–350 K) to NF_3 has been measured using a flowing afterglow technique [240].

Total cross-sections of electron impact scattering by NF_3 molecules were measured over electron impact energies from 1 eV to 5 keV and compared to predicted values from *ab initio* calculations [241]. Electronic excitation, rotational excitation, and differential cross-sections were calculated at low incident energies. Resonances were detected at 5.6 and 6.2 eV, indicating the probability of anion formation by the electron attachment process and further decay to neutral and negative ion fragments.

Gamma irradiation of NF_4AsF_6 has created trapped $\bullet\text{NF}_3^+$ free radicals that have a trigonal pyramid structure and could be identified by electron paramagnetic resonance (EPR) [242].

Exposure of liquid NF_3 at 77, 100, or 134 K to intense X-ray radiation from a 3-MeV X-ray source with dose rates up to 100 Mrad/h resulted in the formation of a mixture of N_2 , F_2 , *cis*- N_2F_2 , and *trans*- N_2F_2 and very little N_2F_4 [243, 244]. No higher fluorides of nitrogen (NF_5 ??) were detected.

1.3.5 Decomposition of Nitrogen Trifluoride in a Glow Discharge

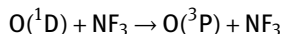
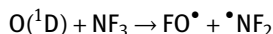
In an attempt to synthesize higher (higher than N(III)) fluorides of nitrogen, nitrogen trifluoride was mixed with fluorine and other gases and subjected to a glow discharge [101]. Instead of forming a higher nitrogen fluoride like NF_5 , NF_3 decomposed in the glow discharge into its elements. Additions of F_2 , N_2 , or O_2 had little effect on the decomposition [245]. Fluorine slowed down the decomposition of nitrogen trifluoride, whereas nitrogen and oxygen accelerated it. Trifluoroamine oxide was obtained with a yield of ~15% from an equimolar mixture of nitrogen trifluoride with oxygen in a discharge tube, cooled with liquid nitrogen.

1.3.6 Reactions of Nitrogen Trifluoride with Inorganic Substances

The reaction of NF_3 with crystalline elemental boron was carried out in a bomb calorimeter, and the heat of reaction was measured [136]. The heat of reaction was $-1003 \text{ kJ/formula weight}$ ($-239.7 \pm 1.2 \text{ kcal/formula weight}$), and the heat of formation of gaseous NF_3 derived from this number was $-127.2 \pm 5.0 \text{ kJ/mol}$ ($-30.4 \pm 1.2 \text{ kcal/mol}$).

For a better understanding of the lifetime of NF_3 and the mechanisms for its destruction in the upper atmosphere, where it acts as a greenhouse gas, the mechanism of the reaction of NF_3 with atomic oxygen $\text{O}(^1\text{D})$ has been thoroughly investigated.

The reactions of $\text{O}(^1\text{D})$ atoms with NF_3 were investigated by time-resolved laser magnetic resonance [246]. $\text{O}(^1\text{D})$ atoms were produced by the dissociation of ozone with an excimer laser (KrF, 248 nm). $\text{O}(^1\text{D})$ reacts with NF_3 by two competitive processes:



The rate constant for total removal of $\text{O}(^1\text{D})$ by NF_3 at 298 K was $(1.2 \pm 0.25 \times 10^{-11} \text{ cm}^3/\text{s})$, and the reaction rate constant for NF_3 was $(1.0 \pm 0.3 \times 10^{-11} \text{ cm}^3/\text{s})$. It was attempted to back up these experiments by theoretical computations [247, 248].

Absorption of infrared radiation from a continuous wave (CW) CO_2 laser in nitrogen fluorides initiated a number of reactions between NF_3 or N_2F_4 and nitric oxide (NO), nitrous oxide (N_2O), nitrogen dioxide (NO_2), or nitrosyl chloride (ClNO) [249]. In all cases, the major product was FNO , and when N_2O or NO_2 was used, some FNO_2

was also produced. No higher states of oxidation of nitrogen were detected. The laser-induced reactions probably proceeded through a non-equilibrium thermal process rather than a true multi-photon dissociation, but some data were not totally consistent with this interpretation.

The crystal structures of protective films of FeF_2 and NiF_2 formed on Fe and Ni surfaces in NF_3 and SF_6 at 1473 K (750 °C) were examined by electron diffraction [250]. In NF_3 at 473–573 K (200–300 °C), a phase transformation of $\text{FeF}_2 \rightarrow \text{FeF}_3$ was observed.

The reaction of NF_3 with metal powders was evaluated as a method to remove NF_3 trace from process gases. Of the three metals (Ti, Si, Sn) evaluated as NF_3 -getters, Ti powder performed best. The reaction of NF_3 with Ti started at 433 K (160 °C), and the conversion was 99.8% when the metal was heated to 598 K (325 °C) [251].

That NH_3 forms a hydrate with water has been long known, but that NF_3 can also form a clathrate hydrate with a P_{m3n} cubic unit cell dimension of 11.91 Å at 110 K came as a surprise [252]. NF_3 hydrate samples were prepared by condensing NF_3 at low temperatures into a pressure vessel containing degassed H_2O or D_2O ice and several stainless steel rods and allowing NF_3 and water to react. During the reaction period, the pressure vessel was rolled so as to subject the solid sample to continuous grinding. Hydrate formation was monitored by the decrease in gas pressure, which was normally complete in 24 h. The dissociation pressure of NF_3 hydrate was 16.5 ± 0.2 atm at 273 K (0 °C) and 3.7 ± 0.2 atm at 233 K (–40 °C). This hydrate is therefore more stable than the hydrates of CH_4 or CF_4 , whose dissociation pressures at 273 K (0 °C) are 26.0 and 41.5 atm, respectively.

Fluorine reacts with most other compounds spontaneously at room temperature, and those that do not sometimes need a little help in the form of an electric discharge or UV illumination or high temperature and high pressure. This may lead to compounds in higher states of oxidation, but in the case of NF_3 it did not work for the synthesis of NF_5 [253, 254].

One of the main applications of NF_3 , and one of the main reasons why there is now such a high demand for NF_3 , is the deep reactive ion etching of silicon wafers in the production of semiconductors and masks for color television displays. The NF_3 is activated in a plasma discharge in an ion gun, and as it impinges on the solid elemental silicon, it forms SiF_4 gas, which is carried away with the carrier gas. The reactions of NF_3 with Si and SiC have been studied using X-ray photoelectron spectroscopy–electron spectroscopy for chemical analysis (XPS-ESCA) [255]. This was done to study and differentiate the role of ions and neutrals in NF_3 plasma etching of Si. Both ion-beam and plasma experiments indicated that etching, nitridation, and fluorination of Si occurred simultaneously. Density functional theory (DFT) calculations were performed to test the validity of the qualitative electronegativity approach in interpreting the XPS results [256]. The DFT calculations confirmed the expected changes in atomic charge and the direction of binding energy shift for $\text{F}\bullet\text{N}\bullet\text{Si}$ moieties.

The effects of rf power and NF_3 pressure on the etching rate of SiC and the surface morphology were investigated by means of scanning electron microscopy (SEM) and

atomic force microscopy [26]. A procedure for getting a smooth and residue-free etched surface of SiC with a high etching rate of 87 nm/min was developed under the conditions such as rf power of 100 W and NF_3 pressure ranging from 0.5 to 1 Pa. A smooth surface within the scale of ~ 300 nm can be obtained.

1.3.7 Reactions of Nitrogen Trifluoride with Organic Substances

Nitrogen trifluoride is not nearly as reactive as tetrafluorohydrazine when one is looking for a method to prepare organic difluoroamino compounds. It can be used as an additive in the hydrofluorination reactions of chlorocarbons with anhydrous hydrogen fluoride and chromium catalysts [257]. Nitrogen trifluoride does not add to the double bond in olefins as readily as N_2F_4 does. Perfluoroalkyldifluoroamines can be made from perfluoroolefins (hexafluoropropene or tetrafluoroethylene) and NF_3 in moderate yields [258]. Sometimes the reacting mixtures of NF_3 and organic compounds that one intends to fluorinate ignite prematurely.

1.3.8 Analytical Methods

1.3.8.1 Analysis of Nitrogen Trifluoride Traces in Air

With increasing industrial use of NF_3 , there is a need for automated monitoring of workroom air in semiconductor processing facilities. The threshold limit value (TLV)–maximum allowable concentration (MAC) of NF_3 was established by the American Conference of Governmental Industrial Hygienists (ACGIH) in 1993–1994 as 10 ppm (29 mg/m^3) time-weighted average (TWA), so the instruments have to be sensitive to at least that level in air.

In order to test the sensitivity of NF_3 detection by IR, an existing IR monitor intended for the detection of Otto Fuel II was modified for use in the 900-cm^{-1} region [259]. The optical path length was 17.2 m by multiple reflection. There was strong interference by HNO_3 and several other vapors. The instrument was capable of detecting down to 1 ppm NF_3 in air.

Other than the occupational hygiene concern about the presence of NF_3 in parts-per-million levels in workroom air, there is concern about the environmental impact of NF_3 in the atmosphere. Highly sensitive methods have been developed to analyze NF_3 in ambient air and are sensitive down to the parts-per-trillion level. There is no natural source for NF_3 , so all NF_3 in the atmosphere is man-made (“anthropogenic”). A preconcentration gas chromatography/mass spectrometry (GC/MS) technique of gas separation and chromatography after initial preconcentration was used to conduct *in situ* measurements of NF_3 in the air above La Jolla, California, and as of December 2011, NF_3 measurements ranged from ~ 0.85 to 1.18 ppt, with a gradual rise in the baseline concentration [260]. NF_3 and CF_4 were separated from more abundant gases before detection by the mass spectrometer. In the mass spectrometer, CF_4 was identified at $m/e = 69^+$, and NF_3 was identified at $m/e = 52^+$.

1.3.8.2 Analysis of Contaminants in Nitrogen Trifluoride

Nitrogen trifluoride, in accordance with the military specifications listed in Table 11, must be analyzed to verify the purity of the chemical because contaminants might interfere with operation of a chemical laser.

1.3.8.3 Military Specification for Nitrogen Trifluoride

The military specification for nitrogen trifluoride was issued for NF_3 intended as a chemical laser propellant. The specification has gone through several revisions over the past several decades (Table 11).

The military-specification purity requirements for NF_3 are listed in Table 12.

Total reactive fluoride is determined by slowly bubbling 4.5 L of NF_3 through 40 mL of 0.1-N NaOH in an impinger and analyzing the solution for fluoride with an ion-selective electrode.

Table 11: Military specifications for nitrogen trifluoride.

Designation	Date
MIL-P-87896	Oct 1982
MIL-P-87896 Amendment-1	Oct 1987
MIL-P-87896 Notice 1	Dec 1997
MIL-P-87896 Notice 2	Oct 2005
MIL-PRF-87896A	Jan 2011

Table 12: Purity requirements for nitrogen trifluoride according to military specifications.

Composition	Limit per MIL-P-87896	Limit per MIL-P-87896, Amendment 1	Limit per MIL-PRF-87896A
Assay, (purity), nitrogen trifluoride (NF_3), %-vol, min	98.0	98.0	99.0
Tetrafluoromethane (CF_4), %-vol, max	1.0	1.0	0.5
Carbon monoxide (CO) + oxygen (O_2) + nitrogen (N_2), %-vol, max	0.5	1.5	—
Oxygen + argon, %-vol, max	—	—	0.1
Carbon monoxide (CO), %-vol, max	—	—	0.1
Carbon dioxide (CO_2), %-vol, max	0.1	0.1	0.1
Nitrogen	—	—	0.1
Nitrous oxide (N_2O), %-vol, max	0.2	0.2	0.1
Sulfur hexafluoride (SF_6), %-vol, max	—	—	0.1
Difluorodiazine (N_2F_2), percent by vol, max	0.1	0.1	—
Total reactive fluoride (as HF, hydrogen fluoride), ppm by vol, max	0.1	10	1000
Water (H_2O), ppm by vol, max	5	5	5

1.3.8.4 Analysis of Nitrogen Trifluoride by Gas Chromatography

Mixtures of NF_3 with OF_2 , CF_4 , SiF_4 , N_2 , or O_2 can be analyzed by GC on a silica gel column that has been dried and desorbed by first heating to 1173 K (900 °C) and then coated with 30% halocarbon oil. They proved to be sufficiently resistant to very aggressive gases, while still giving good separations. The retention volumes of a series of inorganic gases on this column were measured, and the height equivalent of a theoretical plate (HETP) retention volumes were calculated [261].

The more difficult task is a complete separation of NF_3 from CF_4 because the boiling points of the two gases are nearly identical. Complete separation was achieved on a 12-m silica gel column cooled to 273 K (0 °C) as well as on a 3-m activated charcoal column cooled to 252 K (–21 °C) [55, 262]. Other gas chromatographic techniques for the separation of NF_3 from contaminants are described in [263, 264] and [265, 266].

In support of the development of a military propellant specification for NF_3 , a gas chromatographic analysis method was developed by the Air Force Research Laboratory (AFRL) [267, 268]. Because the specification represents the portion of a procurement contract that defines the quality of the product, it was necessary that all quality tests be reliable and, at the same time, as simple as possible so that a reproducible and high-quality product could be assured without unnecessarily high analytical costs for routine analysis. Nitrogen trifluoride is a relatively inert compound at ambient temperature; however, the possible impurities can vary from highly reactive (e.g., HF , F_2 , N_2F_4 , COF_2 , N_2F_2) to very inert (e.g., N_2 , O_2 , CF_4 , CO_2 , N_2O). Also, impurities of intermediate reactivity (e.g., NO , NO_2 , CO) can be present. Analysis of such a potentially complex mixture required some compromise with respect to specificity in order to maintain reasonable analysis costs. The impurities can be grouped into several categories: (1) those that lower performance by dilution, (2) those that lower performance by interference with the fuel/oxidizer reaction, and (3) those that affect the storability of the propellant. Active fluoride was determined by a wet chemistry method in which the gas sample was bubbled through 40 mL of 0.1N NaOH . A total active fluoride determination will provide a greater penalty for N_2F_4 contamination than for HF on a mol-for-mol basis. An active fluoride scrubber (4 in of 40/50 mesh KI followed by 4 in of 40/50 mesh $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) was inserted between the gas source and the gas chromatograph to protect the instrument from corrosion. Nitrogen trifluoride was analyzed both with and without the active fluoride scrubber in place. Good separation was achieved with a 20-ft $\times$ 1/8-in-outer-diameter stainless steel column packed with 80/100 mesh Chromosorb 102 (Johns Manville) baked at 473 K (200 °C) and operated at 308 K (35 °C) with a thermoconductivity detector and helium carrier gas. This is the GC method adopted for MIL-P. The component elution order is H_2 , N_2 , $\text{CO}(\text{O}_2)$, NO , CF_4 , NF_3 , N_2F_2 , CO_2 , N_2O , and SF_6 . NO_2 may appear as a tailing peak between NO and CF_4 . A typical gas chromatogram with a real sample and a sample spiked with all contaminants is shown in Figure 3.

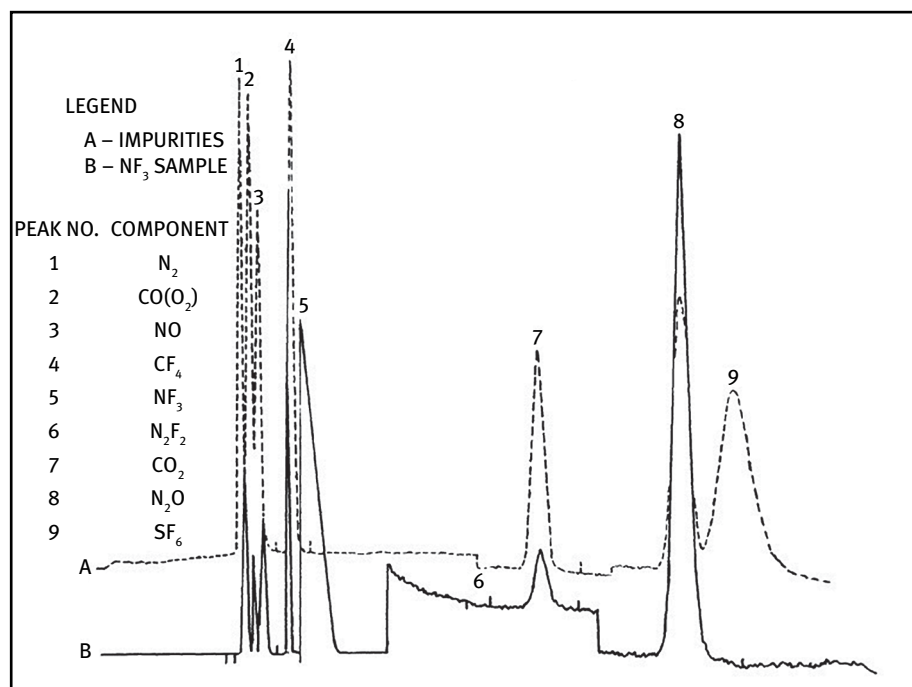


Figure 3: Gas chromatogram of NF₃ and a sample spiked with contaminants. (From MIL-P-87896.)

IR spectra were measured with a 100-mm path length micro gas cell with BaF₂ windows in an IR spectrophotometer. The outlet line of the gas valve was fed into an air/propane burner to destroy the excess NF₃. For IR analysis, poor sensitivity at the test conditions used will likely allow only NO₂, CF₄, and N₂O to be determined without scale expansion. GC fractograms and IR spectra were measured of a calibration mix with six contaminants at known concentrations and retention times and were compared to the analysis of a typical NF₃ sample (Figure 2 in Section 1.2.8.1).

A dual-column back-flush gas chromatograph was used to analyze impurities in NF₃ [269]. The impurities that were analyzed at the low mg/L levels included dioxygen (O₂), dinitrogen (N₂), carbon dioxide (CO₂), carbon monoxide (CO), sulfur hexafluoride (SF₆), methane (CH₄), and nitrous oxide (N₂O). Carbon tetrafluoride (CF₄) was also present in the product at levels of 20–400 mg/L. Good separation was achieved by using a dual-channel gas chromatograph with single-column back-flush switching on one channel for the determination of O₂, N₂, CH₄, and CO, with column-sequence reversal on a second channel for the determination of CO₂, N₂O, SF₆, and CF₄. A similar system using a combination of dual-column back flush and heart-cut configurations worked equally well. Pulsed-discharge helium ionization detectors were used on both channels in both configurations.

A dual-channel gas chromatographic method can be used for quantitation of NF_3/CF_4 mixtures with a thermal conductivity detector on one channel for the quantitation of high-concentrations and a pulsed-discharge helium ionization detector on a second channel for the quantitation of low concentrations [270]. It was shown that adequate separation can be achieved on both channels with this dual single-column setup in which column switching as used for NF_3/CF_4 analysis in industrial chromatographic methods is not required, thus yielding an effective analysis method for laboratory-scale investigations. The use of packed columns with purified divinylbenzene-styrene co-polymers as the sole stationary phase yields satisfactory resolution between NF_3 and CF_4 at isothermal conditions of 303 K (30 °C), with elution times of less than 8 min on the thermal conductivity detector (TCD) channel and less than 4 min on the pulsed-discharge helium ionization detector (PDHID) channel.

1.3.8.5 Analysis of Nitrogen Trifluoride by Mass Spectrometry

Electron impact ionization and dissociation of NF_3 in a mass spectrometer provided data on the relative abundances and appearance potentials of the NF_3^+ , NF_2^+ , NF^+ , N^+ , F^+ , F^- , and F_2^- ions [271]. The heat of formation of the NF_3 molecule can be used to determine the probable processes of formation of the N^+ and F^+ ions and to calculate the ionization potentials of the $|\text{NF}$ and $^*\text{NF}_2$ radicals.

Gases passing through the inlet of a mass spectrometer are usually ionized by electron bombardment, but they can also be ionized by UV radiation. If the wavelength of the UV radiation is varied, coming from the long-wavelength end of the spectrum until first ionization is detected, this photolysis/mass spectrometry method can be used to determine the bond strengths of the bonds being broken. Photoionization yield curves for the NF_3^+ , NF_2^+ , and NF^+ ions of NF_3 and the ONF_3^+ , ONF_2^+ , and NO^+ ions of NF_3O were measured from the threshold to 600 Å [227]. The ionization energies were used to calculate heats of formation of the ions, ionization energies of radicals, and bond dissociation energies. For NF_3 , the bond dissociation energies were $D(\text{NF}_2-\text{F}) = 2.39 \text{ eV}$, $D(\text{NF}-\text{F}) = 3.4 \text{ eV}$, and $D(\text{N}-\text{F}) = 2.4 \text{ eV}$.

1.4 Handling of Nitrogen Trifluoride

Nitrogen trifluoride was evaluated as the most promising near-term replacement for elemental difluorine F_2 in a DF chemical laser. Safety and compatibility characteristics of NF_3 have been scattered through the literature since the gas was first prepared by Ruff in 1928.

Summaries of the data to outline the general chemical behavior of NF_3 , critical safety, compatibility, and environmental were compiled in 1976 [259]. This was done as part of a System Safety Program Plan for the U.S. Department of Defense High En-

ergy Laser Program and included reactivity/materials compatibility, health effects, inhalation reactions, injection reactions, and effects on plants.

Guidelines for the safe handling of compressed gas nitrogen trifluoride are available from the Compressed Gas Association [272].

1.4.1 Disposal of Nitrogen Trifluoride

The disposal of nitrogen trifluoride waste gas has become a problem for the semiconductor and TV/computer display industry where NF_3 is used to etch masks and micro-machine silicone chips and to clean CVD equipment and remove unwanted deposits from the walls of the CVD chambers. In all of these applications it would be desirable not only to destroy the effluent NF_3 but to eventually capture, separate, purify, and recycle it, but that requires more effort. Surplus NF_3 can be disposed of by combustion with hydrogen, methane, propane, or butane in a caged flare stack, but then the HF combustion product needs to be washed out in a scrubber. Oddly enough, the chemical stability of NF_3 makes it more difficult to dispose of it through a chemical reaction. It does not dissolve in water and does not react quickly enough with water at room temperature. In all cases, one of the reaction products is HF, which needs to be scrubbed from the exhaust gas and then neutralized with lime or caustic.

The NF_3 concentration in effluents from semiconductor processing is much lower than NF_3 concentrations in pressurant gases vented from a liquid NF_3 tank following a rocket engine or laser test. The waste-gas treatment methods may be different but similar.

Metal oxides, manganese oxides, metals, and mixed systems were tested in the design of an effective, cost-efficient system with microwave heating to eliminate or recycle unreacted effluent NF_3 [273]. Interaction of microwaves and materials has proven to be an efficient method for material synthesis. Manganese oxides were chosen because they are known to absorb microwave radiation, indicating that synthesis of manganese oxides in a microwave field might lead to more efficient NF_3 absorbers.

The NF_3 can be recycled by passing the effluent gas mixture through a series of membrane separators, where the first membrane is more permeable to NF_3 and the second membrane is more permeable to the diluent gas at increased pressure, followed by pressure-swing adsorption, condensation, and fractionated distillation of the NF_3 [274].

A tandem packed-bed plasma and adsorbent hybrid gas cleanup system consisting of a BaTiO_3 packed-bed plasma reactor and a CaCO_3 adsorbent filter was used to study the removal of NF_3 from semiconductor-process effluent gases [275]. Plasma-chemical kinetics of $\text{N}_2/\text{NF}_3/\text{O}_2/\text{H}_2$ gas mixtures were studied to predict possible by-products. The laboratory-scale system demonstrated NF_3 removal at atmospheric pressure. Typically, 100% NF_3 abatement was achieved with an inlet concentration of 5000 ppm and a gas dwell time in the reactor of less than 10 s.

The CF_4 , C_2F_6 , or NF_3 waste gas used to be vented to the atmosphere, but environmental concerns about ozone-layer depletion and global warming now dictate a more controlled method of disposal [276].

Unwanted NF_3 waste gases venting from industrial processes can be destroyed by passing them through low-power arc plasma discharges with the addition of some hydrogen gas [220]. The destruction efficiency is determined by the specific energy density. The highest destruction efficiency of NF_3 was 97% for a waste-gas flow rate of 100 L/min at a low-input power level of 2 kW with the help of additional hydrogen gas.

1.5 Materials of Construction for NF_3 Systems

All materials that are found to be compatible with elemental fluorine can also be used for the design of NF_3 systems. NF_3 can be handled in glass apparatus and has even been used in flash bulbs.

A welding torch for welding refractory metals has been developed using NF_3 and H_2 , and several materials have been tested as candidates for this application because at the tip of the torch the temperatures are very high, similar to the injector of a rocket engine [277].

The chemical compatibility of nitrogen trifluoride was determined with 29 metallic materials and 22 non-metallic materials subjected to immersion tests [278]. Twelve types of tests were used in this determination: cleaning and passivation, static exposure, fracture mechanics/toughness, gaseous flow at high temperatures, adiabatic compression, water hammer, mechanical impact, liquid flow impact, screening, disposal, nitrogen trifluoride chemical analyses, and passivation film evaluation. Five common contaminants were included in the tests in order to determine their effect on chemical compatibility. Static exposure conditions ranged in temperature from 195 to 344 K and in pressure from 3.4 to 17.2 MPa. None of the metals tested exhibited corrosion penetration rates of greater than 1 mil (1/1000th of an inch) per year during a 270-d exposure period when exposed to the NF_3 . However, the presence of HF or H_2O enhanced the corrosion rates significantly. Of the non-metals investigated, the fluorocarbons exhibited the best compatibility with NF_3 . Under load conditions, several of the metals were found to be susceptible to stress corrosion cracking. Under dynamic conditions, nickel, Inconels, and the 300-series stainless steels were found to be suitable metals for use with NF_3 .

Additional tests were conducted to evaluate the compatibility of NF_3 with 15 different materials when compressed suddenly in a U-tube apparatus in which a slug of liquid was rammed into dead-ended passage with high-pressure helium push pressures up to 17.3 MPa (2515 psia) [279]. Mechanical impact tests were conducted with Teflon and Kel-F in nitrogen trifluoride/helium atmospheres and in pure nitrogen trifluoride at pressures up to 17.3 MPa (2515 psia).

At room temperature, NF_3 appears to be inert toward polymers. Even polyethylene film has been reported to show no observable deterioration after more than a month of exposure to NF_3 [259]. Samples of polyethylene, polypropylene, polystyrene, Lucite, and silicone grease were examined both visually and by differential scanning calorimetry (DSC) after 6 days of exposure to 5 atm of NF_3 at 408 K (135°C). All but Lucite and silicone grease showed a mild surface reaction. In another study, samples of Kel-F valve packing, Teflon, Viton, Neoprene, silicone rubber, Buna-N, butyl rubber, and ethylene propylene were heated for 6 weeks at 423 K (150°C) under 1.03 MPa (150 psi) of NF_3 . Similar samples were also heated under N_2 for comparison. No changes were observed in the Teflon, Viton, or Kel-F. Silicone rubber exposed to NF_3 was noticeably deteriorated; although still flexible, it was covered with cracks, was less elastic, and appeared softer. Its Shore hardness had dropped from 57 to 40. Neoprene had become considerably stiffer, harder, and brittle, and the other polymers showed extensive deterioration.

Nitrogen trifluoride is not as aggressive as elemental fluorine, yet it may cause accidental ignition if it is compressed rapidly. A strong mechanical impact shock may not always be required to initiate reactions of fluorine compounds with metals. Sudden gas-pressure increases may cause adiabatic heating and ignition. Accidental ignitions have been observed in industrial applications of nitrogen trifluoride for cleaning of semiconductor processing equipment [280].

Compatibility data of materials with NF_3 are limited and have been addressed only by companies that routinely handle NF_3 . Even more limited is the ability to conduct configuration testing of components in NF_3 to evaluate ignition-chain and reaction effects. In NF_3 systems, the cylinder valve is subjected to severe operating conditions and is known to have experienced fires in service. A new testing approach was developed to positively ignite the non-metallic seat of a cylinder valve pressurized with NF_3 [281]. The goal of the work was to investigate whether the ignition of the seat would kindle the surrounding sub-components of the valve and, ultimately, whether a kindling reaction would develop that could breach the valve body. The ignition concept of the test method consisted of electrically heating a thin section of wire positioned across the seat to act as a promoter. The concept required minimal modifications to the valve, and the overall valve design remained consistent with normal operation. The assembled valves were tested at a pressure of 10.3 MPa (1500 psig), and no burn-through was observed during any of the tests. The post-test valve disassembly and inspection confirmed that the wire fused and successfully ignited the seat, but the seat retainer and surrounding subcomponents did not burn. All of the other parts of the valve were unaffected by the ignition and consumption of the non-metallic seat. The test provided a new approach for evaluating the propagation propensity of NF_3 components containing non-metallic materials.

1.6 Toxicity of Nitrogen Trifluoride

1.6.1 Inhalation Toxicity of Nitrogen Trifluoride

Already the discoverer of NF_3 , Ruff reported in 1931 that this gas is very toxic: 1% NF_3 in air proved to be fatal to a group of mice within 40 min. Lower concentrations (0.2% NF_3) were tolerated without visible effects. A cat that was forced to inhale 1% NF_3 for 20 min died after 4 h. Nitrogen trifluoride is not a lung poison but a blood poison. The color of the blood changes in the presence of NF_3 , but the suspected formation of methemoglobin could not be confirmed. Unlike PF_3 or CO, NF_3 does not form a complex with hemoglobin. Some industry brochures recommend a MAC of 100 ppm and list a lower limit of toxic effects at 300 ppm, but they do not provide the foundation for such recommendations.

Single-exposure episodes of rats to concentrations in excess of 1000 ppm NF_3 caused methemoglobinemia [282]. Concentrations of 2500 or 1000 ppm NF_3 caused death after 4 h of exposure. Exposures to higher concentrations resulted in shorter survival times. The recovery of survivors appeared rapid, although enlarged spleens were seen in many of the surviving animals. Repeated exposures 7 h/d, 5 d/week of male and female rats to 100 ppm NF_3 for 4.5 months resulted in slight to moderate pathologic changes in the livers and kidneys of rats of both sexes. An increase in the average weight of the liver, kidneys, and spleen of the male rats was also found. Microscopic examination of liver and kidney tissues showed degenerative changes in rats of both sexes, but damage was more pronounced in female rats. No evidence of fluorosis of the teeth or deposition of fluorine in the teeth or bone was observed, although a very slight increase in total fluorine in the urine was detected. The concentration of NF_3 in work areas where repeated human exposure is likely should be limited to well below 100 ppm until more adequate information is available. Nitrogen trifluoride does not possess warning properties adequate to prevent excessive exposure; therefore, monitoring of work spaces by instruments is recommended. Analysis by IR absorption is extremely sensitive to this material and with a suitable gas cell should provide a method suitable for continuous monitoring.

Nitrogen trifluoride exposures of groups of rats were made in an $18 \times 18 \times 27$ -in aluminum chamber fitted with transparent Kel-F view ports and lined with Teflon-surfaced glass cloth [283, 284]. Groups of 10 rats were exposed to 15–1000 ppm NF_3 . The reaction of NF_3 with hemoglobin *in vitro* has been studied in a closed system in which the amount of NF_3 utilized and methemoglobin formed during each reaction was varied. The behavior of blood or suspensions of erythrocytes in dynamic atmospheres of NF_3 was studied in a small exposure chamber. Each mol of NF_3 oxidized more than 1 mol of heme. Animals exposed to 10000 ppm NF_3 showed very definite respiratory distress as well as generalized depression to the extent that they were non-responsive to external stimulation. The methemoglobin formed was superficially detectable in eye color and in the coloring of the mucous membranes and extremities. The LD50 of

NF₃ gas injected intraperitoneally was about 8.25 mL (0.37 mmol)/kg. Each animal observed at the terminal stages of NF₃ poisoning was found to be suffering from 60–70% conversion of hemoglobin to methemoglobin, which is presumably a lethal level.

Blood samples of rats exposed to high concentrations of NF₃ were analyzed for concentrations of serum glutamic oxalacetic transaminase, serum isocitric dehydrogenase, blood lactate, and methemoglobin [285]. Inhalation of 10000 ppm NF₃ for 45 min resulted in the conversion of 37% of the total rat hemoglobin to methemoglobin and a sixfold increase in blood lactate at the end of exposure. Both parameters had returned to normal 4 h later. Serum isocitric dehydrogenase did not change detectably as a result of the exposure. Serum glutamic oxalacetic transaminase was unchanged at 1 h but was increased twofold to threefold by 6 h post exposure and remained elevated for as long as 24 h after the exposure.

Rats were exposed for 1 min to tracheal inhalation of NF₃ gas to determine its toxic effects on the cardiovascular system [286]. The exposed rats had a definite decrease in diastolic pressure, systolic pressure, and heart rate. Similarly, rats that pre-breathed oxygen for 5 min before exposure had the same changes in the cardiovascular system as those breathing only NF₃. However, animals that inhaled oxygen for 5 min immediately after exposure to NF₃ showed a temporary increase in diastolic pressure, systolic pressure, and heart rate.

The distribution of fluoride in rat tissues has been studied over periods of 20–48 h following acute intoxication with NaF, NF₃, N₂F₄, ClF₃, and BrF₅ [287]. The data do not suggest the existence of any fluoride-bearing degradation products that behave differently from fluoride ion. NF₃ and N₂F₄ intoxication resulted in persistently high concentrations of fluoride in erythrocytes.

The stoichiometry of the reaction of hemoglobin with NF₃ *in vitro* and *in vivo* was measured. In examining the nature of this reaction, the ratio of mols of NF₃ utilized/equivalents of methemoglobin formed was measured in aqueous solutions of hemoglobin and in acetone solutions of crude ferroprotoporphyrin, as well as in intact anesthetized dogs [288]. Results suggested that 1 mol NF₃ mediates or participates in the oxidation of 3 heme equivalents.

Short-term exposures of rats, mice, dogs, and monkeys to acute concentrations of NF₃ were performed, and median lethal concentrations were determined for rats and mice [289]. It appeared that the immediate effects of acute exposure to NF₃ were caused by extensive methemoglobin formation and the resulting anoxia. Dogs surviving exposure to 9600 ppm for 60 min exhibited a Heinz body anemia, with red blood cell count, hemoglobin, and hematocrit decreasing 33% to minimum values by the end of the second week post exposure. Recovery of hematologic values to pre-exposure levels was attained in 40 d. In dogs, the anemia caused by a dose level of 120000 ppm-min was severe enough to invalidate that dose as an emergency exposure limit (EEL). At 30000 ppm-min, however, no detectable anemia occurred, and no other toxic effects were discernible. The results of experiments conducted at sub-acute levels jus-

tified recommending an upward revision of the EEL to 30000 ppm-min from the proposed U.S. National Academies of Science, Engineering, and Medicine National Research Council value of 3000 ppm-min.

The acute toxicity of nitrogen trifluoride has been shown to be due to massive formation of methemoglobin, with death ensuing from the resulting anoxia. Previous studies did not quantitate the acute toxicity of NF_3 by determination of LC50 values. Additional investigations were undertaken to evaluate the LC50 at 15, 30, and 60 min in rats, mice, beagle dogs, and rhesus monkeys (Table 13) [290]. The LC50 for a 50-min exposure would be 7500 ppm in mice, 6700 ppm in rats, 9600 ppm in dogs, and 10000 ppm in monkeys. There were no detectable physiologic changes in dogs or monkeys at 1000 ppm/30 min or 500 ppm/1 h. The gaseous NF_3 was introduced into the chamber air stream after passage through a sodium fluoride trap to remove any hydrogen fluoride that might have been present in the NF_3 .

Table 13: Nitrogen trifluoride lethal toxicity levels for four different types of test animals.

Time, min	Rats	Mice	Dogs	Monkeys
15	26700	19300	38800	24000
30	11700	12300	20200	14100
60	6700	7500	9600	9200

Data source: [290]

Additional experiments were conducted to determine which short-term exposure levels of NF_3 would have no significant effects on all species tested. The latter series of tests was carried out to aid in setting up realistic EELs. EEL values for NF_3 at one time proposed by the U.S. National Academies of Science, Engineering, and Medicine Committee on Toxicology were 100 ppm for 30 min and 50 ppm for 60 min, corresponding to a dose level of 3000 ppm-min. It was later recommended to raise the EEL to 30000 ppm-min, but the Committee eventually settled on an EEL of 22500 ppm-min.

As of 2014, the ACGIH TLV-TWA was 10 ppm. The National Institute for Occupational Safety and Health (NIOSH) Immediately Dangerous to Life and Health (IDLH) limit for NF_3 was originally 2000 ppm and was revised in 1995 to 1000 ppm for a 10-min exposure [291, 292].

The Committee on Toxicology has recommended the following EELs for spills of NF_3 on or around rocket launching sites or in the testing of rocket motors or lasers: 10 min, 2250 ppm; 30 min, 750 ppm; and 60 min, 375 ppm [293]. See also [294].

1.7 Environmental Effects of Nitrogen Trifluoride

1.7.1 Atmospheric Effects of Nitrogen Trifluoride

If accidentally released into the atmosphere, nitrogen trifluoride will diffuse to the upper stratosphere and absorb energy from the incoming solar radiation. Gradual hydrolysis will convert it to hydrogen fluoride, which, of course, is a very unpleasant environmental pollutant. The global-warming potential (GWP) of NF_3 on a 100-year time scale was calculated to be 16800 times that of CO_2 , although other kinetic studies suggested a slightly lower GWP due to a shorter stratospheric lifetime. Regardless of small uncertainties in its calculated lifetime, NF_3 is a stronger greenhouse gas than the compounds it replaced in some industrial applications (such as CF_4 and C_2F_6). Of the Kyoto Protocol-listed gases, its GWP is second only to that of SF_6 (which has a 100-year GWP of 22800).

Nitrogen trifluoride was included in the group of Kyoto-recognized greenhouse gases only with effect from 2013 and the start of the second commitment period of the Kyoto Protocol. It has an estimated atmospheric lifetime of 740–550 years [295]. NF_3 production has grown from 1992, when less than 100 metric tons were produced, to an estimated 4000 metric tons in 2007 and continues to increase. World production of NF_3 was expected to reach 8000 tons a year by 2010. It was predicted that the maximum atmospheric NF_3 concentration is less than 0.16 parts per trillion (ppt) by volume, which would provide less than 0.001 Wm^{-2} of IR forcing [169].

The mean global tropospheric concentration of NF_3 has risen quasi-exponentially from about 0.02 ppt at the beginning of the record in 1978 to a 2008 value of 0.454 ppt, with a rate of increase of 0.053 ppt/year, or about 11% per year, and with an interhemispheric gradient that is consistent with these emissions occurring overwhelmingly in the northern hemisphere [296]. This rate of increase corresponds to about 620 metric tons of current NF_3 emissions globally per year, or about 16% of the global NF_3 production estimate of 4000 metric tons/year.

The amount of NF_3 emitted from the electronics industry around the world in 2006 was estimated to be between 3.6 and 56 metric tons [297]. Although the cumulative amount of NF_3 in the atmosphere currently would be negligible based on the predicted ratio (the order of 10^{-6} to 10^{-7}) of equivalent CO_2 emission from NF_3 to total equivalent CO_2 emissions from other industries and consumers, it was deemed to be necessary to adopt the available abatement and also to monitor the concentration of NF_3 in workplaces in order to reduce the overall environmental and health impacts of various semiconductor processes [298].

It was estimated that the global emissions of NF_3 in 2011 were $1.18 \pm 0.21 \text{ Gg/year}$, or $\sim 20 \text{ Tg CO}_2\text{-eq/year}$ (CO_2 -equivalent emissions based on a 100-year GWP of 16600 for NF_3). The 2011 global mean tropospheric dry-air mol-fraction of NF_3 was $0.86 \pm 0.04 \text{ ppt}$, resulting from an average emissions growth rate of $0.09 \text{ Gg} \cdot \text{year}^{-2}$ over the prior decade. In terms of CO_2 equivalents, current NF_3 emissions represent between 17 and 36% of the emissions of other long-lived fluorinated compounds from electronics

manufacturing. There is a continuing need for improvements in NF_3 emissions-reduction strategies to keep pace with its increasing use and to slow its rising contribution to anthropogenic climate forcing.

It has been argued that the contribution of NF_3 emissions to overall global warming is overestimated and that the contribution of nitrogen trifluoride to the CO_2 budget of thin-film solar cell production is compensated by the fossil fuel-burning savings potential of the photovoltaic technology. Amorphous-silicon and nanocrystalline-silicon thin-film photovoltaic modules are made in high-throughput manufacturing lines that necessitate quick cleaning of the reactor. Using and emitting NF_3 as the cleaning agent has triggered concerns by environmentalists, but industry quantified the life-cycle emissions of NF_3 in photovoltaic manufacturing on the basis of actual measurements at the facilities of a major producer of NF_3 and of a manufacturer of photovoltaic end-use equipment [299]. But, of course, that leaves all the NF_3 emitted during the production of flat-screen TVs, which has no environmental benefit.

1.7.2 Biospheric Effects of Nitrogen Trifluoride

The effects of NF_3 or N_2F_4 on seeds and seedlings of bean, corn, pea, squash, and Sudan grass were measured by exposing dry seeds to a gaseous 100% NF_3 atmosphere for 1 to 8 h, which caused inhibition of subsequent germination [300]. Exposure of seeds to a 10% N_2F_4 atmosphere for 1 h completely inhibited germination of all five species of seeds. Concentrations of N_2F_4 or NF_3 up to 10000 ppm in air were required to cause visible damage of plant seedlings after a 30 to 60-min exposure period. The exposed seeds and seedlings were analyzed for fluoride content.

1.8 Applications of Nitrogen Trifluoride

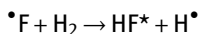
1.8.1 Semiconductor Industry

Significant use of NF_3 began with the replacement of perfluorocarbons in the 1990s in the semiconductor industry for chemical etching because of better process performance and a supposed reduction in carbon dioxide-equivalent greenhouse-gas emissions and ozone-depletion potential. It is used for cleaning of CVD reactors and, more recently, in the manufacturing of liquid crystal flat-panel displays and thin-film photovoltaic cells. Prior to that, gases that were in use for the various processing steps associated with semiconductor device fabrication included CF_4 , CF_4/O_2 , and SF_6 . But then it was found that NF_3 worked better than any of those chemicals, and so its use increased for a while [301], but only until NF_3 was also identified as environmentally damaging because of its high GWP. It could then no longer be vented above-roof to the atmosphere. CVD chamber cleaning is now done with elemental difluorine gas generated on site by electrolysis of molten KHF_2 .

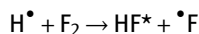
1.8.2 Lasers

There are two types of lasers in which NF_3 might be used: electric discharge-pumped KrF lasers and chemical fluorine-hydrogen or fluorine-deuterium lasers. Because these lasers involve reactions between an NF_3 oxidizer and hydrogen-containing fuels, these reactions should be discussed under rocket propellant combustion headings in a future volume on bipropellant combinations, but we preferred to summarize the laser applications here since they are not truly a rocket propulsion application.

In a pulsed $\text{NF}_3 + \text{H}_2$ hydrogen fluoride laser, the reaction is initiated by a short-duration electric discharge. The pulsed laser was chosen in an attempt to obtain short-duration, high-intensity pulses for laser fusion. In the $\text{NF}_3 + \text{H}_2$ laser, the electric discharge dissociates a fraction of the NF_3 to give F atoms and other species that do not participate in laser action. The chemical reaction

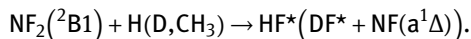


creates vibrationally and rotationally excited HF^* , which lases. It is also possible to build a pulsed CW laser using a mixture of F_2 and H_2 so that the chemical reaction

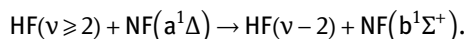


produces additional excited HF^* , and it also creates a new $\text{F}^{\cdot}$ atom to replace the one consumed in the first reaction, sustaining a chain reaction [302]. Typically, in a combustion-driven chemical laser, an excess of atomic fluorine is produced in the combustor by burning a fuel, and the combustor products, including the atomic fluorine, are expanded at supersonic speed into a cavity with parallel mirrors. Hydrogen or deuterium fuel is introduced into the cavity and reacts with the atomic fluorine to form the lasing species HF^* or DF^* . Decay of the lasing species to ground level produces laser emission at 2.6–2.9 μm for HF and 3.6–4.0 μm for DF. Cavity pressures vary from about 0.13 to 2.67 kPa (1–20 mm Hg) and cavity temperatures from about 300 to 900 K. The spent reactants must be removed from the cavity at supersonic speeds since the ground-state species will quench the lasing reaction.

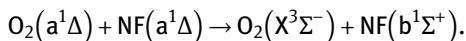
A mixture of NF_3 and Ar was passed through an RF discharge in a flow system to produce, among other species, $\cdot\text{F}$ and $\cdot\text{NF}_2$ [303]. When H_2 , D_2 , or CH_4 was added downstream, reactions with $\cdot\text{F}$ atoms produced vibrationally excited HF or DF together with $\cdot\text{H}$, $\cdot\text{D}$, or $\cdot\text{CH}_3$. The latter free radicals can react with NF_2 to produce electronically excited NF:



A vibrational-to-electronic energy-transfer process between the products of this reaction then produced the next higher state of NF:



A similar transfer process has also been found between the electronically excited $a^1\Delta$ states of O_2 and NF:



The $H^\bullet$ or $D^\bullet$ atoms, but not the $\bullet CH_3$ radicals, were found to react with either $NF(a^1\Delta)$ or $NF(X^3\Sigma^-)$ to produce electronically excited $N(^2D)$ atoms, which in turn reacted with the $NF(a^1\Delta)$ molecules to produce $N_2(B^3\Pi_g)$. Some emission was observed at 3344 Å, which was attributed to $NF(A^3\Pi)$ that had not been previously reported.

A peak density of the electronically excited free-radical species $NF(a^1\Delta)$ of $2.4 \times 10^{-9} \text{ mol cm}^{-3}$ has been chemically produced in a subsonic laser device operating on hydrogen and nitrogen trifluoride [304]. This high concentration confirmed previous analyses and predictions of the chemical system. This was a concentration scale-up by a factor of 10^4 from previous flow-tube results.

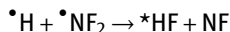
The reaction (1) of $H(^2S)$ atoms with $\bullet NF_2$ radicals forms metastable excited $NF(a^1\Delta)$ molecules with a branching ratio greater than 0.9 [305]:



Subsequent reactions also form the $b^1\Sigma^+$ state of NF. The strong 0,0 bands of the a,X and b,X transitions of NF are near 874 and 528 nm, and their emission intensities were used to follow the excited-state concentrations.

The reaction of hydrogen atoms with $\bullet NF_2$ was studied in a flow tube using pulsed KrF laser initiation of $H_2/NF_2/Ar$ mixtures at 440 K [306]. The quantum yield for $NF(a)$ production from the 249-nm photolysis of NF_2 was 0.10 ± 0.05 . Several important reactions in this system were investigated, and rate coefficients were determined at 440 K. A value of $(1.03 \pm 0.20) \times 10^{-30} \text{ cm}^6/\text{molecule}^2$ was obtained for the three-body recombination of F atoms with $\bullet NF_2$ and Ar. Rate constants for the relaxation of $HF(v=2)$ and $HF(v=3)$ by $\bullet NF_2$ are $(9.7 \pm 1.0) \times 10^{-14}$ and $(2.5 \pm 0.5) \times 10^{-13} \text{ cm}^3/\text{molecule}$, respectively. Study of the quenching of $NF(a)$ by $\bullet NF_2$ yielded a rate coefficient of $(2.7 \pm 1.0) \times 10^{-16} \text{ cm}^3/\text{molecule}$. That indicates that the disproportionation of $NF(a)$ is three orders of magnitude slower than that of ground-state NF. Modeling results were presented that agreed well with experimental data.

The reaction of $\bullet H$ atoms with $\bullet NF_2$ radicals produces metastable $NF(a^1\Delta)$ radicals and vibrationally excited HF as primary products [307]:



Reactions in a photolytically excited HF chemical laser based on a NF_3/H_2 gas mixture were modeled using known kinetic rates [308].

A flowing afterglow method was used to study a number of reactions of importance in KrF lasers using NF_3 as the fluorine donor, and total rate constants for $Kr^*(^3P_2) + NF_3$ and $Kr^+ + NF_3$ were reported [309]. The thermal energy attachment

coefficient has been measured for NF_3 , and the cross-section for the electron excitation process $\text{Kr}^*(^3\text{P}_2) + \text{e} \rightarrow \text{Kr}^*(^3\text{P}_1) + \text{e}$ has been estimated.

Based on an urgent requirement for NF_3 , in October 2002 the U.S. Defense Energy Support Center/Defense Logistics Agency awarded an emergency contract to Advanced Specialty Gas in Dayton, Nevada, for 1000 lb of NF_3 [310]. Delivery to White Sands Missile Range in New Mexico was required no later than November 2002. Arrangements were made to fill a government-provided trailer coming from Amarillo, Texas, to the contractor's plant in Nevada, and then to transport it to White Sands Missile Range, and all arrangements were accelerated to ensure delivery by the required delivery date. White Sands Missile Range received the 1000 lb of NF_3 on 3 November 2002. Another solicitation for procurement of another 1000 lb of NF_3 was issued in 2003. It is not known whether this effort still continues. NF_3 is still listed in the propellant inventory.

1.8.3 Photography Flash Bulbs

The reaction of NF_3 with metals (zirconium or aluminum) creates a very hot flame with a bright light, similar to daylight in color and suitable for flash bulbs for photography (prior to the invention of the electronic strobe light) [311–313]. The use of such chemical flash bulbs was abandoned after more efficient electric strobe tubes became available, which are now found on every digital camera.

2 Tetrafluoroammonium Salts

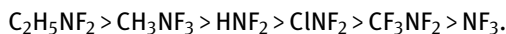
Although initial thermodynamic and molecular orbital calculations let the stability of NF_4^+ salts appear unlikely [200, 201], skilled experimenters did succeed in synthesizing several NF_4^+ salts that might even be useful as oxidizers in solid rocket propellants or fluorine gas generators.

The chemistry of tetrafluoroammonium salts was pioneered by Christie and colleagues at Rocketdyne, at that time a division of Rockwell International in Canoga Park, California. The list of NF_4^+ publications and patents from that group fills several pages, and only the most remarkable topics are discussed here to the extent that they relate to their potential use as oxidizers in rocket propellants or as gas generants for fluorine generators in chemical lasers.

Close to 100 tetrafluoroammonium salts have been synthesized since NF_4^+ was first discovered, and there are some good summary reviews of the work that has been performed, including [314–316].

The lone electron pair in ammonia as well as nitrogen trifluoride makes both of these molecules a Lewis base, where they can share that electron pair with Lewis acids. The resulting adducts can have saline character. Nitrogen trifluoride and other

compounds carrying the difluoroamino group can form Lewis adducts with a variety of Lewis acids, such as BF_3 , BCl_3 , PF_5 , and SO_2 , which are stable at low temperatures [317]. The relative base strengths of difluoroamines decreased in the order



IR spectra have shown that where complex formations occur, the intermolecular binding was through donation of the nitrogen lone-pair electrons to the Lewis acid.

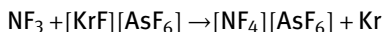
2.1 Preparation of Tetrafluoroammonium Salts

The first tetrafluoroammonium, or tetrafluoronitronium(V) as it was once called, salt was $[\text{NF}_4]^+[\text{AsF}_6]^-$, prepared by Christe, Guertin, and Pavlath in 1966 [318, 319]. When NF_3 , AsF_5 , and F_2 in a 1:1:1 mol ratio were subjected to a low-temperature glow discharge, a white crystalline powder formed that was stable and non-volatile at 298 K. In differential thermal analysis (DTA) it decomposed at about 540 K. The compound was very hygroscopic and easily hydrolyzed to an initially blue solution with the evolution of gas. XRD showed the cation to have a tetragonal structure with unit cell dimensions of $a = 7.70 \text{ \AA}$ and $c = 5.73 \text{ \AA}$, with two molecules per unit cell [320].

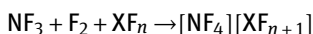
The reaction of nitrogen trifluoride, difluorine, and Lewis acids such as AsF_5 or SbF_5 in an autoclave at high pressures (50–200 atm) and high temperatures between 373 and 473 K (100 and 200 °C) leads to the corresponding tetrafluoroammonium salts [321–323].

Complex fluoro cations are generally prepared through fluorine abstraction from the parent molecule by means of a strong Lewis acid. This was first demonstrated in 1949 for BrF_3 . In the case of NF_4^+ salts, this approach was impossible because the parent molecule NF_5 is unknown and is unlikely to exist owing to the validity of the octet rule for first-row elements such as nitrogen and fluorine. The synthesis of NF_4^+ from NF_3 and F^+ is preempted by the fact that fluorine is the most electronegative element; hence, F^+ should be extremely difficult, if not impossible, to prepare by chemical means.

Many reactions previously requiring the use of the prohibitively expensive PtF_6 may now be carried out at reasonable expense by the use of Lewis acid–promoted activated fluorine. Two direct methods for the synthesis of $[\text{NF}_4]^+$ salts are now available, based on the reaction of NF_3 with either $[\text{KrF}]^+$ salts

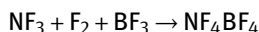
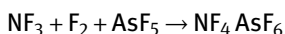


or the reaction of NF_3 with F_2 and a strong Lewis acid in the presence of an activation energy source



Four different activation energy sources have been used for the direct syntheses of $[\text{NF}_4]^+$ salts: heat, UV light, glow discharge, and X-ray bremsstrahlung. Of these, the thermal synthesis is most convenient and provides the starting material required for the syntheses of other $[\text{NF}_4]^+$ salts by indirect methods. For the syntheses of pure $[\text{NF}_4]^+$ salts on a small scale, low-temperature UV photolysis is preferred.

When gaseous mixtures of NF_3 , F_2 , and the strong Lewis acids SbF_5 , AsF_5 , or BF_3 were exposed to unfiltered UV irradiation, the corresponding $[\text{NF}_4]^+$ salts were formed rapidly and reproducibly. Using AsF_5 or BF_3 and sapphire reactor, the following reactions occurred:



However, the yield of the NF_4 salt was less than 1%. This low yield appeared not to be caused so much by a slow reaction rate but by deposition of the solid product on the reactor walls, thereby preventing further irradiation of the reactants. In the case of SbF_5 and a quartz reactor, all of the SbF_5 starting material was consumed in less than 3 d [324].

Exposure of $\text{NF}_4^+ \text{AsF}_6^-$ and $\text{NF}_4^+ \text{SbF}_6^- \cdot 0.8 \text{SbF}_5$ to ^{60}Co γ rays at 77 K gave two paramagnetic centers, one of which was shown by electron spin resonance (ESR) spectroscopy to contain one nitrogen atom and three equivalent fluorine atoms. Based on its magnetic properties, it was identified as pyramidal $\cdot\text{NF}_3^+$, a radical cation [325].

One of the intermediates in the synthesis of NF_4^+ salts may be $\cdot\text{NF}_3^+$. UV photolysis of both the $\text{NF}_3\text{-F}_2\text{-AsF}_5$ and the $\text{NF}_3\text{-F}_2\text{-BF}_3$ systems produced an intensely violet species that exhibited the ESR signal typical for $\cdot\text{NF}_3^+$ cation free radical [326]. The observation of identical signals for both the BF_3 -containing and the AsF_5 -containing systems proved that the signal must be due to a species not containing boron or arsenic.

Many tetrafluoroammonium salts have been prepared by metathetical reactions where the equilibrium between four different salts can be shifted in the desired reaction only if one of the products is insoluble and precipitates, such as AgCl or AgI . A better method is to load the $[\text{NF}_4]^+$ cation onto a cation exchange resin or load the anion onto graphite acting as an anion exchange medium [327]. See also [328].

2.2 Molecular Structure of Tetrafluoroammonium Salts

Although NF_4 salts had been known for 20 years, the exact structure of the NF_4^+ cation was not known for several years. From ^{19}F NMR spectra it was known that in solution NF_4^+ is an ideal tetrahedron. Vibrational spectra of many NF_4^+ salts indicated that in the solid state, the NF_4^+ cations are also essentially tetrahedral. From the general va-

lence force field, the bond length in NF_4^+ was been estimated to be $\sim 1.31 \text{ \AA}$. This value was supported by *ab initio* calculations, which resulted in a value of $1.32 \text{ \AA}$. ^{19}F NMR, IR, and Raman spectra confirmed the ionic structure of NF_4^+ in the solid state and in HF solution. The $[\text{NF}_4]^+$ cation has four equivalent fluorine atoms in a tetrahedral configuration (space group T_d) [329, 330].

The ESR spectra of the $^{14}\text{N}^+\text{F}_3$ and $^{15}\text{N}^+\text{F}_3$ radical cations were observed over the temperature range 15–340 K [331]. The radical cations were generated either by γ -irradiation of NF_4^+ salts or by low-temperature UV photolysis of NF_3/F_2 /Lewis acid mixtures. An analysis of the observed spectra was supported by computer simulations and the observed ^{15}N isotopic data. The spin-density distributions indicated that $\text{NF}_3^{+\bullet}$ is pyramidal but that within the isoelectronic series BF_3^- , $^+\text{CF}_3$, and NF_3^+ , the planarity of the radicals increases from BF_3^- toward NF_3^+ .

The molecular structure of fluoronitrogen cations and π - and σ -fluoro effects were studied by ^{14}N and ^{15}N NMR spectroscopy of N–F cations in comparison to N–H cations [332]. These shifts in the NMR spectra were described as σ fluoro effects and were explained, at least in part, by the decrease in electron density on nitrogen.

The estimate of the bond length in NF_4^+ from the published general-valence force field was revised, and a value of $1.31 \text{ \AA}$ was suggested [333].

The room-temperature tetragonal structure of $\text{NF}_4^+\text{BF}_4^-$ has been determined by a combination of single-crystal XRD and vibrational spectroscopy [334]. This compound crystallizes in the tetragonal space group $P4_21m$, with $Z=4$ and unit cell dimensions of $a = 9.92(1) \text{ \AA}$ and $c = 5.23(1) \text{ \AA}$. The structure is made up from an approximately tetrahedral NF_4^+ cation with a bond length of $1.30 \text{ \AA}$ and a BF_4^- anion that rotates or oscillates around a threefold axis along one of its bonds.

2.3 Thermodynamic Properties of Tetrafluoroammonium Salts

Even before the first tetrafluoroammonium salts were synthesized and characterized, speculation about their potential stability had already started [200, 201]. Calculations were made of the predicted enthalpies of formation and decomposition of tetrafluoroammonium salts. A highly desirable rocket propellant oxidizer would be tetrafluoroammonium perchlorate, which has yet to be made and stabilized. The lattice energy of that salt would be 486 kJ/mol (116 kcal/mol), and the heat of formation was predicted to be somewhere between $+88$ and $+234 \text{ kJ/mol}$ ($+21$ and $+56 \text{ kcal/mol}$).

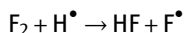
The decomposition, solid-phase change, and formation enthalpies for NF_4BF_4 , NF_4PF_6 , NF_4AsF_6 , NF_4SbF_6 , NF_4GeF_5 , and $(\text{NF}_4)_2\text{GeF}_6$ were determined by differential scanning calorimetry (DSC) [335]. The enthalpies of reaction with water of NF_4BF_4 , NF_4PF_6 , NF_4AsF_6 , and NF_4SbF_6 were measured and used to obtain an alternate set of formation enthalpies for these NF_4 compounds. Recommended values for ΔH_f° in the solid state are as follows: $\text{NF}_4\text{BF}_4 - 1410 \pm 10 \text{ kJ/mol}$, $\text{NF}_4\text{SbF}_6 - 1669 \pm 12 \text{ kJ/mol}$, $\text{NF}_4\text{AsF}_6 - 1538 \pm 1 \text{ kJ/mol}$, $\text{NF}_4\text{PF}_6 - 1841 \pm 7 \text{ kJ/mol}$, $\text{NF}_4\text{GeF}_5 - 1473 \pm 1 \text{ kJ/mol}$, and

$(\text{NF}_4)_2\text{GeF}_6 - 1606 \pm 5 \text{ kJ/mol}$. The thermally most stable salt in this group was NF_4SbF_6 , with an onset of exotherm at 578 K (305 °C). The thermally least stable salt was NF_4GeF_5 , with beginning decomposition at 374 K (101 °C).

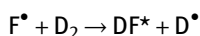
DSC study of the thermal decomposition of $(\text{NF}_4)_2\text{NiF}_6$ and NF_4SbF_6 gave standard enthalpies of formation of -1033 and -1649 kJ/mol , respectively [336].

2.4 Applications of Tetrafluoroammonium Salts

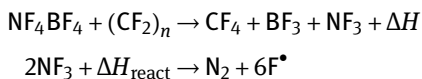
Tetrafluoroammonium salts were initially only of academic interest, and it was not until 1971 when, with the advent of chemical HF-DF lasers, the interest in storable NF_3 -F sources was renewed [337]. It became rapidly obvious that NF_4 salts were the most promising oxidizers for solid-propellant NF_3 -F₂ gas generators for combustion-driven chemical lasers. The concept of such a gas generator was conceived by Pilipovich at Rocketdyne [338]. These propellants consist of a highly over-oxidized grain using NF_4^+ salts as the oxidizer. Burning these propellants with a small amount of fuel, such as aluminum powder, generates sufficient heat to thermally dissociate the bulk of the oxidizer and generate fluorine atoms. This technology was further developed for several years at Rocketdyne [339]. It offers significant logistics and safety advantages over cryogenic or storable liquid fluorine oxidizers. In a chemical HF-DF laser, F atoms are generated by burning F₂ in a pre-combustor with a fuel, such as hydrogen:



The F atoms are subsequently reacted with a cavity fuel, such as D₂, to produce vibrationally excited DF* as the active lasing species:

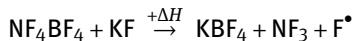


In the original solid F atom generator concept, the F atoms were directly generated by burning the solid propellant grain, thus eliminating the need for a pre-combustor. This concept was demonstrated for NF_4BF_4 with a small percentage of Teflon serving both as a fuel and a binder. The heat of reaction $(\Delta H)_{\text{react}}$ is sufficient to dissociate most of the NF_3 and F₂ to F atoms and N₂:



From a practical point of view, however, such a direct generation of F atoms was not desirable, since it did not allow the necessary flow controls and flexibility required for on-off operation. Consequently, the concept was modified to that of an NF_3 -F₂ molecule generator, using a gas catch tank for interim storage. Further modification of this concept became necessary when system analysis data revealed that gaseous by-products of high molecular weight and low C_p/C_v significantly degraded the per-

formance of a laser. Consequently, an $\text{NF}_3\text{-F}_2$ gas generator was desired that would produce no gases other than NF_3 and F_2 . The latter objective can be achieved by a so-called clinker system in which the BF_3 by-product is converted by an alkali metal fluoride to a non-volatile BF_4 salt:



Whereas the feasibility of such a clinker system approach has been well demonstrated, the addition of KF lowered the $\text{NF}_3\text{-F}_2$ yield per mass of solid propellant, and the possibility always exists of having incomplete clinkering. Realizing these limitations, Rocketdyne developed “self-clinkering” NF_4 salts. Such self-clinkering formulations contain $(\text{NF}_4)_2\text{SnF}_6$, NF_4SnF_5 , $(\text{NF}_4)_2\text{TiF}_6$, $\text{NF}_4\text{Ti}_2\text{F}_9$, $\text{NF}_4\text{Ti}_3\text{F}_{13}$, or $\text{NF}_4\text{Ti}_6\text{F}_{25}$ [340–342]. These are salts derived from anions that will yield NF_4^+ salts which are the key ingredients for solid-propellant $\text{NF}_3\text{-F}_2$ gas generators. The reaction leaves behind non-volatile fluorides, such as SnF_4 or TiF_4 after thermal decomposition. Test firings of these salts in formulations, however, revealed problems. The “non-volatile” fluorides were found to be not so non-volatile after all, and they either sublimed or were blown as fine dust throughout the system. Furthermore, very high fuel levels were required to burn these formulations. To be able to fire these formulations, it was necessary to add some alkali metal fluorides as burning aids and to develop burning-rate modifiers. It was possible to increase the fluorine yields by using the lighter LiF instead of KF in some of these formulations and to use less than the stoichiometric amount. The NF_4^+ salt with the highest theoretical fluorine yield (64.6 mass-% before burning) was $(\text{NF}_4)_2\text{NiF}_6$ (Table 14).

However, this salt had the disadvantage of being of limited thermal stability and did not completely meet long-term storability requirements. An alternate salt with high fluorine yield was $(\text{NF}_4)_2\text{MnF}_6$, a compound that approached the fluorine yield of the nickel salt but was thermally more stable [343].

The thermal decompositions of NF_4BF_4 and NF_4AsF_6 were studied in a sapphire reactor at different temperatures by total-pressure measurements, at 455, 462, and 464 K (182, 189, and 191 °C) for NF_4BF_4 and 473, 491, 500, and 511 K (200, 218, 227, and 238 °C) for NF_4AsF_6 [344]. It was found that the rates are those of a 3/2 order reaction. From the temperature dependence of the decomposition rates, the global activation energies of NF_4BF_4 and NF_4AsF_6 decomposition were calculated as $E_{\text{act}} = 153 \pm 3.3 \text{ kJ/mol} = 36.6 \pm 0.8 \text{ kcal/mol}$ and $187 \pm 17.6 \text{ kJ/mol} = 44.7 \pm 4.2 \text{ kcal/mol}$, respectively. The following reversible reaction mechanism was proposed:

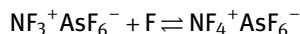
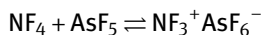
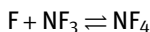


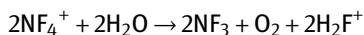
Table 14: Theoretical fluorine yields of NF₃-F₂ gas generator compositions.

System	Usable F content (mass-%) before burning	Comments
(NF ₄) ₂ XeF ₈	71.7	Requires no clinkering agent; difficult to synthesize; hydrolyzes to shock-sensitive XeO ₃ ; expensive
(NF ₄) ₂ BeF ₄	71.7	Unknown
(NF ₄) ₃ AlF ₆	69.3	Unknown
(NF ₄) ₂ NiF ₆	64.6	Marginal long-term storability
NF ₄ XeF ₇	62.9	Same as for (NF ₄) ₂ XeF ₈
(NF ₄) ₂ MnF ₆	59.9	Requires burning aid
(NF ₄) ₂ SiF ₆	59.0	Requires clinkering agent
(NF ₄) ₂ TiF ₆	55.6	Requires burning aid
NF ₄ BF ₄	54.0	Requires KF as clinkering agent
(NF ₄) ₂ GeF ₆	51.8	Requires clinkering agent
NF ₄ AlF ₄	49.2	Requires burning aid
NF ₄ Be ₂ F ₅	46.8	Very toxic; requires burning aid
(NF ₄) ₂ SnF ₆	46.0	Requires burning aid
NF ₄ PF ₆	40.4	Requires clinkering agent
NF ₄ GeF ₅	36.9	Requires clinkering agent
NF ₄ AsF ₆	34.1	Requires clinkering agent; toxic
NF ₄ SnF ₅	31.3	Requires burning aid
NF ₄ SbF ₆	29.2	Requires clinkering agent
NF ₄ BiF ₆	23.0	Requires clinkering agent

Data source: [337]

The tendency to form NF₄ salts by thermal activation strongly decreases with decreasing Lewis acid strength in the order SbF₅ > AsF₅ > PF₅ > BF₃. Consequently the thermal stability of the formed salts decreases in the same order. The heat of formation of NF₄BF₄ was known from previous experiments, and the heat of formation of NF₄⁺AsF₆⁻ was predicted to be about 372 kcal/mol.

The NF₄⁺ content of complex tetrafluoroammonium salts can be determined by hydrolysis of very small (500–1000 mg) samples using gasometric and gas chromatographic methods [345, 346]. The hydrolysis of tetrafluoroammonium salts according to



can sometimes proceed explosively and has to be carried out gradually at low temperatures, with intermittent cooling in liquid nitrogen or in an inert diluent. The O₂ + NF₃ gas mixture evolved can then be analyzed by GC or by fractional condensation. Examples were given for NF₄BF₄, NF₄SbF₆, NF₄BiF₆, and NF₄SnF₅, with NF₃ contents ranging from 17 to 40%.

2.5 Tetrafluoroammonium Salts with Different Anions

2.5.1 Tetrafluoroammonium Salts with Fluorine-Containing Anions

The discovery of tetrafluoroammonium salts opened up a new branch of fluorine chemistry with potential applications for rocket propellants [318, 347] and fluorinating agents. The tetrafluoroammonium cation NF_4^+ is one of the strongest fluorinating agents known.

Sometimes it is desirable to exchange the easy-to-prepare tetrafluoroborate anion with other ions with better oxidizing power or stabilizing effectiveness. Metathetical reactions work only if one of the products is either insoluble or volatile. Ion exchange can also be achieved with ion-exchange media. Traditional ion exchange resins with organic polymers would not be stable in NF_4^+ solutions in H_2F_2 . Instead, graphite can be used as an ion-exchange medium. An improved process for the production of advanced NF_4^+ salts used graphite salts as an HF-resistant and oxidizer-resistant anion-exchange medium [348].

One of the more easily prepared tetrafluoroammonium salts with all volatile constituents is tetrafluoroammonium fluorosulfonate $\text{NF}_4^+\text{SO}_3\text{F}^-$ [349]. This salt can be prepared by metathetical reaction between NF_4SbF_6 and CsSO_3F in anhydrous HF solution at 195 K (−78 °C). In HF solution, it is stable at room temperature. Removal of the solvent produces a white solid that is stable at 273 K (0 °C) but slowly decomposes at 283 K (+10 °C) to produce FOSO_2F and NF_3 in high yield.

2.5.2 Tetrafluoroammonium Salts with Complex Group 4 Transition Metal Anions

Group 4 metals include Ti, Zr, and Hf. Tetrafluoroammonium hexafluorotitanate $(\text{NF}_4)_2\text{TiF}_6$ is a potential ingredient for fluorine gas generators in chemical lasers.

Bis-perfluoroammonium hexafluorotitanate $(\text{NF}_4)_2\text{TiF}_6$ can be prepared by a metathetical reaction between Cs_2TiF_6 and NF_4SbF_6 in HF solution [350]. $(\text{NF}_4)_2\text{TiF}_6$ is a white crystalline solid and is stable to about 473 K (200 °C). It was characterized by elemental analysis and IR, Raman, ^{19}F NMR spectroscopy, and XRD. $(\text{NF}_4)_2\text{TiF}_6$ crystals have a tetragonal structure with $a = 10.715 \text{ \AA}$, $c = 11.114 \text{ \AA}$. Heating of NF_3 , F_2 , and TiF_4 to 463 K (190 °C) for 50 d at an autogenous pressure of 163 atm produced a polymeric salt of the approximate composition $\text{NF}_4\text{Ti}_6\text{F}_{25}$. $(\text{NF}_4)_2\text{TiF}_6$ has the highest usable fluorine content of any presently known NF_4^+ salt.

Improved NF_4^+ compositions for solid-propellant NF_3 - F_2 gas generators have been patented that produce NF_3 and F_2 free of volatile Lewis acids and do not require clinker-forming additives for their complexing. These self-clinkering compositions contain $(\text{NF}_4)_2\text{SnF}_6$, NF_4SnF_5 , $(\text{NF}_4)_2\text{TiF}_6$, $\text{NF}_4\text{Ti}_2\text{F}_9$, $\text{NF}_4\text{Ti}_3\text{F}_{13}$, and $\text{NF}_4\text{Ti}_6\text{F}_{25}$ [340].

The use of self-clinkering formulations based on $(\text{NF}_4)_2\text{TiF}_6$ has previously been proposed as a means of increasing the theoretically obtainable NF_3 - F_2 yield relative to that of the state-of-the-art $\text{NF}_4\text{BF}_4 \cdot 1.2\text{KF}$ formulations. However, test firings of $(\text{NF}_4)_2\text{TiF}_6$ -based formulations showed that the relatively high volatility of TiF_4

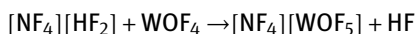
(boiling point 284 °C) resulted in the deposition of TiF_4 throughout the whole gas generator system. Such self-clinkering formulations contain $(\text{NF}_4)_2\text{SnF}_6$, NF_4SnF_5 , $(\text{NF}_4)_2\text{TiF}_6$, $\text{NF}_4\text{Ti}_2\text{F}_9$, $\text{NF}_4\text{Ti}_3\text{F}_{13}$, or $\text{NF}_4\text{Ti}_6\text{F}_{25}$ [340].

The problem of obtaining a Lewis acid-free NF_3 - F_2 gas stream from NF_4^+ compositions without clinker-forming additives is overcome by using NF_4^+ salts derived from the polymeric non-volatile Lewis acids SnF_4 (subliming at 704 °C) or TiF_4 (1 atm vapor pressure at 284 °C). The lack of acidity of SnF_4 at temperatures at which NF_4^+ salts can be formed and exist was demonstrated by heating mixtures of NF_3 , F_2 , and SnF_4 to temperatures up to 573 K (300 °C) at autogenous pressures of about 15.2 MPa (150 atm); no evidence was shown of NF_4^+ formation.

Improved compositions were patented for solid-propellant NF_3 - F_2 gas generators using $(\text{NF}_4)_2\text{TiF}_6$ and clinkering agents derived from LiF , KF , and NaF , either alone or in mixtures [351]. A sample composition of 81.44 mass-% $(\text{NF}_4)_2\text{TiF}_6$, 14.71 mass-% LiF , and 3.83 mass-% Al was fired in a typical gas generator; the residue was a clinker, and no dust had deposited in the cold trap.

2.5.3 Tetrafluoroammonium Salts with Complex Group 5 or 6 Transition Metal Anions

Group 5 metals include V, Nb, and Ta. Group 6 metals include Cr, Mo, and W. Tetrafluoroammonium pentafluorooxotungstate(VI) can be prepared by



Tetrafluoroammonium pentafluorooxotungstate(VI) is a white crystalline solid that is stable at 328 K (55 °C) but slowly decomposes at 358 K (85 °C) to yield NF_3 , OF_2 , WF_6 , and $[\text{NF}_4][\text{W}_2\text{O}_2\text{F}_9]$ [352].

2.5.4 Tetrafluoroammonium Salts with Complex Group 7 Transition Metal Anions

Group 7 metals include Mn and Re. Bis(tetrafluoroammonium) hexafluoromanganate(IV), $(\text{NF}_4)_2\text{MnF}_6$, is a compound that approached the fluorine yield of the nickel salt but was thermally more stable [343, 353]. The $(\text{NF}_4)_2\text{MnF}_6$ salt is a yellow crystalline solid that is highly soluble in anhydrous HF. At 297 K (24 °C), its solubility exceeded 1.30 g per gram of HF. It is stable at room temperature and up to 65 °C, and in the absence of fuels, it is not shock sensitive. With water, a violent reaction occurs. By analogy with the other known NF_4^+ salts, the hydrolysis was found to result in quantitative NF_3 evolution and, therefore, is a useful analytical method. At 338 K (65 °C), $(\text{NF}_4)_2\text{MnF}_6$ appears to be stable, but at about 373 K (100 °C) it starts to slowly decompose. The calculated XRD density was 2.64 g/cm³. NMR and IR spectra provided information about the molecular structure.

2.5.5 Tetrafluoroammonium Salts with Complex Groups 8, 9, 10 Transition Metal Anions

Groups 8, 9, and 10 include the iron, nickel, and cobalt transition metals. Tetrafluoroammonium hexafluoronickel(II)ate, $(\text{NF}_4)_2\text{NiF}_6$ is a powerful oxidizer, potentially useful for solid-propellant formulations and NF_3 - F_2 gas generators. $(\text{NF}_4)_2\text{NiF}_6$ can be prepared by combining Cs_2NiF_6 and $(\text{NF}_4)_2\text{SbF}_6$ in a mol ratio of 1:2.0–2.30 in anhydrous HF and removing the CsSbF_6 precipitate by filtration at -78°C [354].

DSC study of the thermal decomposition of $(\text{NF}_4)_2\text{NiF}_6$ and NF_4SbF_6 gave enthalpies of decomposition for $(\text{NF}_4)_2\text{NiF}_6$ and NF_4SbF_6 of 134.7 ± 13.0 and 245.6 ± 28.9 kJ/mol, respectively [336]. The corresponding standard enthalpies of formation were found to be -1033 and -1649 kJ/mol, respectively.

$(\text{NF}_4)_2\text{NiF}_6$ was prepared from Cs_2NiF_6 and NF_4SbF_5 by metathesis in HF as a solvent and was characterized by elemental analysis, vibrational spectroscopy, and its XRD pattern [355]. The reaction of $(\text{NF}_4)_2\text{NiF}_6$ with water is very violent and can result in explosions. The decomposition rates of $(\text{NF}_4)_2\text{NiF}_6$ were determined over the temperature range 353–401 K (80 – 128°C). The evolved gas was shown by IR and MS to be a mixture of NF_3 and F_2 in a mol ratio of about 2:3. On thermal decomposition, 1 cm^3 of solid $(\text{NF}_4)_2\text{NiF}_6$ is capable of producing 12% more useful fluorine values, i.e., in the form of F_2 and NF_3 , than liquid F_2 at 86 K (-187°C). The calculated XRD density of $(\text{NF}_4)_2\text{NiF}_6$ was 2.61 g/cm^3 . $(\text{NF}_4)_2\text{NiF}_6$ is a deep red hygroscopic solid that is stable at room temperature. In DSC it showed a very slow endothermic, irreversible decomposition between 383 and 403 K (110 and 130°C), which became rapid above 473 K (200°C). The rate constant of decomposition was

$$k = 4.840 \times 10^{14} \exp\left(\frac{E_{\text{act}}}{RT}\right)$$

$$E_{\text{act}} = 147 \frac{\text{kJ}}{\text{mol}} = 35.161 \frac{\text{kcal}}{\text{mol}}$$

The heat of formation of solid $(\text{NF}_4)_2\text{NiF}_6$ was estimated to be somewhere near or below -962 kJ/mol (-230 kcal/mol).

2.5.6 Tetrafluoroammonium Salts with Complex Group 13 Element Anions

Group 13 elements include B, Al, and Ga. Of all the anions NF_4^+ can be combined with to make a rocket propellant, BF_4^- is one of the most desirable due to its low molecular weight and the high heat of combustion of boron compounds [3]. The crystalline compound $\text{NF}_4^+\text{BF}_4^-$ has been prepared by exposing the heterogeneous ternary system $\text{NF}_3/\text{BF}_3/\text{F}_2$ to 3-MeV bremsstrahlung at 77 K. The compound is stable at room temperature in dry air. It decomposes above 523 K (250°C) to the reactants in a reversal of its formation reaction. It reacts rapidly with moisture and with organic substances. The ionic structure was confirmed by IR and Raman spectroscopy. The XRD powder pattern could be indexed on the basis of a tetragonal unit cell with $a = 7.01\text{ \AA}$ and $c = 5.22\text{ \AA}$.

Tetrafluoroammonium tetrafluoroborate, $\text{NF}_4^+\text{BF}_4^-$, is an important starting reagent for the preparation of other energetic oxidizers. One of the first steps in the preparation of NF_4BF_4 is the preparation of NF_4SbF_6 as an intermediate. For this purpose, NF_3 , F_2 , and SbF_5 in a 2:2:1 mol ratio are heated in a Monel cylinder to 523 K (250 °C) for 72 h. The size of the cylinder is chosen in such manner that at the completion of the reaction, the autogenous pressure is about 70 atm. The product is extracted from the Monel cylinder with anhydrous HF using about 50 mL of liquid HF per 100 g NF_4SbF_6 . NF_4BF_4 salt can be prepared either directly from NF_3 , F_2 , and BF_3 using glow discharge, bremsstrahlung, or UV, or indirectly from NF_4SbF_6 using a metathetical reaction. Of these, the metathetical process is the one most amenable to the larger-scale production of NF_4BF_4 utilizing existing technology. The original metathetical NF_4BF_4 process involved several steps but did not deliver a pure product. NF_4BF_4 of at least 97 mol-% purity can be prepared by a simpler process using anhydrous HF at different temperatures as the only solvent, and the last step of purification is the recrystallization from BrF_5 as the solvent [356].

NF_4BF_4 can be prepared by reaction of NF_4SbF_6 in 0–15 mol-% excess, with CsBF_4 in anhydrous HF [357]. NF_4SbF_6 in turn is prepared by heating SbF_5 in the presence of an excess of NF_3 and F_2 to 250 °C until conversion of the SbF_5 to NF_4SbF_6 is complete.

A very clean method for preparation of NF_4BF_4 and other NF_4^+ salts is by UV illumination at low temperatures. It was found that low-temperature UV photolysis is ideally suited for preparing NF_4BF_4 . A large number of reaction parameters were studied to maximize the yield [358]. Maximum yields of NF_4BF_4 were obtained at close to boiling point of liquid nitrogen temperatures (77 K [–196 °C]) using unfiltered UV radiation, a short path length to avoid recombination of F atoms to molecular F_2 , and the periodic addition of fresh starting materials to the UV cell to avoid coating of the surface of the condensed reactants by solid NF_4BF_4 . The highest yield of NF_4BF_4 achieved to date with a 900-W mercury arc lamp was in excess of 3 g/h. The quantum yield for the formation of NF_4BF_4 at a rate of 3 g/h was only 0.015. Based on XRD measurements, the calculated density of solid NF_4BF_4 is 2.27 g/cm³. Three new NF_4^+ salts, NF_4PF_6 , NF_4GeF_5 , and $(\text{NF}_4)_2\text{GeF}_6$, have also been prepared by UV photolysis and displacement reactions.

A controversy about the structure of the NF_4^+ cations in NF_4BF_4 could not be resolved based on vibrational spectra and XRD alone [359]. Only a redetermination of the crystal structure and solid-state ¹⁹F NMR spectra of NF_4BF_4 showed that, in accord with the vibrational spectra and contrary to a previously published crystal structure, the NF_4 cations in this salt are indeed tetrahedral [360]. These results resolved a long-standing controversy regarding vibrational spectroscopy and XRD crystallography.

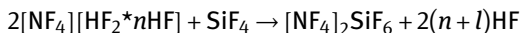
The goal of the tetrafluoroammonium salt investigations was to come up with compounds with very high available fluorine content. The NF_4^+ salts derived from BeF_2 and AlF_3 would have a usable fluorine content of 71.7 and 69.3 mass-%, respectively, which is one of the best available. $\text{NF}_4\text{Be}_2\text{F}_5$ and NF_4AlF_4 were prepared from concentrated NF_4HF_2 solutions and BeF_2 and AlF_3 , respectively [361]. Tetrafluoroam-

monium tetrafluoroborate(III) is a hygroscopic white crystalline solid that is stable up to about 423 K (150 °C). It is highly soluble in anhydrous HF.

Both $(\text{NF}_4)_2\text{BeF}_4$ and $(\text{NF}_4)_3\text{AlF}_6$ have very high theoretical fluorine yields, but efforts to prepare these two compositions have been unsuccessful. Investigators succeeded partially in that NF_4AlF_4 and $\text{NF}_4\text{Be}_2\text{F}_5$ were prepared.

2.5.7 Tetrafluoroammonium Salts with Complex Group 14 Element Anions

Group 14 elements include Si, Ge, and Sn. Bis(tetrafluoroammonium) hexafluorosilicate(IV) can be made by reaction of tetrafluoroammonium hydrogen fluoride with tetrafluorosilicon [362]:



Bis(tetrafluoroammonium) hexafluorosilicate(IV) is a white crystalline solid that is stable at 298 K (25 °C) but slowly decomposes at 363 K (90 °C) to NF_3 , F_2 , and SiF_4 .

Bis(tetrafluoroammonium) pentafluorostannate(IV) $(\text{NF}_4)_2\text{SnF}_5$ can be prepared by a metathetical reaction between Cs_2SnF_6 and NF_4SbF_5 in HF solution [363]. It is a white solid and is stable at room temperature up to above 473 K (200 °C). Based on XRD, it crystallizes in the tetragonal system. Its composition was established by elemental analysis, and the presence of tetrahedral NF_4^+ and octahedral SnF_6^{2-} ions in the solid state and in BrF_5 solution was demonstrated by vibrational and ^{19}F NMR spectroscopy. The salt NF_4SnF_5 was obtained in quantitative yield from the displacement reaction between equimolar amounts of NF_4BF_4 and SnF_4 in HF solution. When a large excess of NF_4BF_4 was used, the main product was still the same NF_4SnF_5 , and only a small amount of $(\text{NF}_4)_2\text{SnF}_6$ was formed. The calculated XRD density of $(\text{NF}_4)_2\text{SnF}_6$ is 2.73 g/cm³. The NF_4SnF_5 salt was characterized by elemental analysis, vibrational and ^{19}F NMR spectroscopy, and XRD. The hydrolysis of $(\text{NF}_4)_2\text{SnF}_6$ and NF_4SnF_5 proceeds, as previously established for other NF_4^+ salts, with quantitative NF_3 evolution. This reaction can be used for elemental analysis of the compounds. An F_2 - NF_3 gas generator based on $(\text{NF}_4)_2\text{SnF}_6$ has the potential to form a self-clinkering residue in the combustion chamber and to produce very little dust.

2.5.8 Tetrafluoroammonium Salts with Complex Group 15 Element Anions

Group 15 elements include N, P, As, Sb, and Bi. Tetrafluoroammonium hexafluorophosphate, NF_4PF_6 , can be prepared by ultraviolet photolysis of a mixture of NF_3 , F_2 , and PF_5 at 77 K (−196 °C) [364].

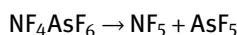
Tetrafluoroammonium salts with more desirable anions can be prepared from the easy-to-obtain tetrafluoroborates through metathetical reactions if one of the products is insoluble or at least less soluble than the other. Tetrafluoroammonium hexafluorophosphate, NF_4PF_6 , can be prepared by a displacement reaction between NF_4BF_4 and PF_5 [365].

Tetrafluoronitrogen(V) hexafluoroarsenate(V), NF_4AsF_6 , can be prepared by reaction of NF_3 , AsF_5 , and F_2 in a 1:1:1 mol ratio in a glow discharge at low temperatures [320, 329]. It was the first tetrafluoroammonium salt to be discovered. This complex is considered a derivative of hypothetical NF_5 . The white crystalline powder is stable and non-volatile at 298 K (25 °C). Differential thermal analysis indicated incipient decomposition at about 543 K (270 °C). The compound was very hygroscopic and easily hydrolyzed to an initially pale blue solution with the evolution of gas. The XRD powder diffraction pattern could be indexed in the tetragonal system with unit cell dimensions $a = 7.70 \text{ \AA}$ and $c = 5.73 \text{ \AA}$.

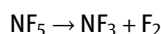
NF_4AsF_6 has also been prepared by the glow discharge reaction of NF_3 , F_2 , and AsF_5 at 193 K (−80 °C) [366]. NF_4AsF_6 decomposed smoothly at 448 K (175 °C) and above to the starting materials NF_3 , F_2 , and AsF_5 [367, 368]. The decomposition has been followed by total pressure measurements and was found to obey the equation

$$P^{\frac{3}{2}} = At + B$$

This has been interpreted in terms of an equilibrium dissociation step



followed by irreversible decomposition of the unstable NF_5



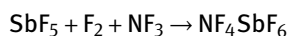
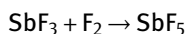
The latter step was taken to be a 3/2-order reaction

$$\frac{dP}{dt} = k_1 P_n P_a$$

where P_n is the partial pressure of NF_5 and P_a that of AsF_5 . An attempt to identify NF_5 in the products by matrix isolation methods yielded, besides the expected NF_3 and AsF_5 , an unknown minor product that appeared not to contain any nitrogen.

Samples of both $^{14}\text{NF}_4\text{AsF}_6$ and $^{15}\text{NF}_4\text{AsF}_6$ were prepared by low-temperature UV-photolysis, and their vibrational spectra were recorded [369]. The observed spectra were in agreement with space group $P_{4/n}$ for NF_4AsF_6 and site symmetries of S_4 and C_4 , for NF_4^+ and AsF_6^- , respectively. The observed ^{14}N - ^{15}N isotopic shifts were used to compute a general valence force field for NF_4^+ .

Since most of the advanced NF_4 salts can be prepared from NF_4SbF_6 as a starting material, it was also important to simplify its synthesis as much as possible. The previous best synthesis involved the following two steps:



NF_4SbF_6 is prepared by heating SbF_5 in the presence of an excess of NF_3 and F_2 to 523 K (250 °C) until conversion of the SbF_5 to NF_4SbF_6 is complete [357]. This synthesis

was simplified to a one-step process according to [370]



Similar perfluoroantimonate complexes can be prepared starting with N_2F_4 instead of NF_3 (Section 3.3.2).

Tetrafluoroammonium hexafluoroantimonate(V) is a hygroscopic white crystalline solid that is stable up to about 543 K (270 °C). It is highly soluble in anhydrous HF (259 mg per gram of HF at 195 K [−78 °C]).

Tetrafluoroammonium hexafluorobismuthate(V) NF_4BiF_6 can be prepared by several methods, but depending on the method used, it may sometimes contain excess BiF_5 [371]. Similar to NF_4SbF_6 , it can be used for the synthesis of other NF_4^+ salts.

2.5.9 Tetrafluoroammonium Salts with Group 17 (Halogen) Anions

Ammonium perchlorate is the main oxidizer for solid propellants and some explosives. In an effort to increase the oxidizing power of AP, it has been attempted to replace the hydrogen in the ammonium ion by fluorine and, furthermore, to replace the oxygen in the perchlorate ion with fluorine as well. The result is tetrafluoroammonium tetrafluorochlorate NF_4ClF_4 , a stable compound and very powerful oxidizer.

Although the majority of tetrafluoroammonium salts are paired with fluoro complex anions, there are a few salts of interest that do not contain fluorine in the anion.

One of the salts of interest as a rocket propellant would be tetrafluoroammonium perchlorate, $\text{NF}_4^+\text{ClO}_4^-$, but it is very unstable. Its potential advantage is that it contains oxidizing groups both in the cation and in the anion. The same is true for tetrafluoroammonium nitrate, $\text{NF}_4^+\text{NO}_3^-$, but it has not yet been prepared [372].

The possibility of synthesizing NF_4XO_4 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) salts by metathetical reactions between NF_4SbF_6 , and CsXO_4 in anhydrous HF solution at 195 K (−78 °C) was studied [373]. Of these NF_4 salts, only $\text{NF}_4^+\text{ClO}_4^-$ was isolated and characterized by vibrational and ^{19}F NMR spectroscopy. $\text{NF}_4^+\text{ClO}_4^-$ is an unstable white solid decomposing at 298 K (25 °C) to give NF_3 and FOClO in high yield. If this chemical were used as an oxidizer in a cryogenic propellant, this would give a specific impulse much higher than any conventional solid propellant with ammonium perchlorate.

Other salts investigated were tetrafluoroammonium tetrafluorobromate $\text{NF}_4^+\text{BrF}_4^-$ and tetrafluoroammonium tetrafluorooxobromate $\text{NF}_4^+\text{BrF}_4\text{O}^-$ [374].

2.5.10 Tetrafluoroammonium Salts with Perfluoro Group 18 (Noble Gas) Anions

It is unlikely that salts of tetrafluoroammonium cation with noble gas anions would ever be used as rocket propellants, but we add them here just for speculation and curiosity. The perfluoroammonium salts of the heptafluoroxenon anions NF_4XeF_7 and $(\text{NF}_4)_2\text{XeF}_8$ can be prepared by reacting NF_4HF_2 with XeF_6 and exposing NF_4XeF_7 to blue 4880 Å laser light. The NF_4XeF_7 salt was prepared from XeF_6 and NF_4HF_2 and was converted to $(\text{NF}_4)_2\text{XeF}_8$ by selective laser photolysis. These new salts and the

already known CsXeF_7 and CsXeF_8 were characterized, and their vibrational spectra were reported. Evidence was presented for the existence of a stable NaXeF_7 salt [375–377], but it is doubtful that it can ever be used as a rocket propellant or gas generant for chemical lasers due to the limited availability of xenon (although much xenon is now used in ion and Hall thrusters). Irradiating the yellow NF_4XeF_7 with blue 4880 Å light causes disproportionation:



NF_4XeF_7 is of particular interest due to its exceptionally high energy content. The thermal decomposition of NF_4XeF_7 proceeds according to



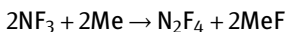
The decomposition enthalpy of $\text{NF}_4\text{XeF}_7(\text{S})$ is $\Delta H_{\text{dec}} = 64.6 \pm 5 \text{ kJ/mol}$, and the enthalpy of formation is -490.7 kJ/mol [378]. A comparison of this value with those previously found for a series of NF_4^+ salts containing other complex fluoro anions showed that NF_4XeF_7 is by far the most energetic of these salts.

3 Tetrafluorohydrazine

Tetrafluorohydrazine, also known as N_2F_4 , F_2NNF_2 , 1,1,2,2-tetrafluorohydrazine, tetrafluorohydrazine, dinitrogen tetrafluoride, perfluorohydrazine, CAS RN [10036-47-2] is a colorless gas with a very unpleasant, fluorine-like odor. It is more reactive than NF_3 . With a formula weight of 104.01, it contains 73.06 mass-% F and 26.94 mass-% N. Nitrogen fluorides containing several nitrogen atoms in the molecule are difficult to synthesize and were not evaluated as rocket propellants until the mid-1960s.

3.1 Preparation of Tetrafluorohydrazine

Tetrafluorohydrazine was first prepared by reduction of NF_3 with metals at 573–773 K (300–500 °C) [204, 379]:

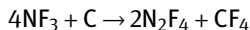


Me: 1 equivalent metal

Iron, copper, arsenic, antimony, and bismuth have been tested as the reducing metals. The yield can be up to 62% (based on the consumption of NF_3). The reaction of NF_3 with As, Sb, Bi, or Cu can be carried out in a fluidized bed or packed-bed reactor [380].

During the reaction of NF_3 with arsenic to produce N_2F_4 , small amounts of difluoroamine were obtained as by-product and identified by its mass spectrum and IR spectrum [381].

Instead of using metals, NF_3 can also be reacted with carbon to produce N_2F_4 [382, 383]:



If the reaction is carried out with activated charcoal dust in a fluidized bed, the contact time can be shortened from several minutes to 3 s at 673–773 K (400–500 °C). The N_2F_4 yield is up to 75% at a 75% NF_3 conversion. Hexafluoroethane is a by-product.

The controlled direct fluorination of ammonia with diluted fluorine in a copper tube can be modified by suitable adjustment of the mixture ratio to yield 11% N_2F_4 (based on F_2 consumption) [71]. Attempts to fluorinate $\text{N}_2\text{H}_4 \cdot 2\text{HF}$ with BrF_3 or BrF_5 were not successful [62]. Traces of N_2F_4 can be found as by-products if one adds BF_3 , AlF_3 , or PF_3 to the molten NH_4HF_2 electrolyte during the conventional NF_3 production [384].

Reaction of NF_3 with mercury at low pressure in a glow discharge leads to formation of N_2F_2 and N_2F_4 , which can then be adsorbed on silica gel and then separated by preparative gas chromatography [385, 386]. Instead of excitation in a glow discharge, the thermal reaction of NF_3 with mercury at 593–603 K (320–330 °C) leads also to N_2F_4 [387]. Small amounts of N_2F_4 are formed during the thermal decomposition of difluoroamine, a very unstable compound.

A mixture of N_2F_4 and NOF is obtained if one passes a mixture of NF_3 , NO , and/or N_2O through a nickel tube at high temperature [388, 389]. Tetrafluorohydrazine can be obtained by hydrolysis of *N,N*-difluorourea [390].

Very pure samples of N_2F_4 can be obtained by preparative gas chromatography [391]. These high-purity samples are suitable to determine physical and spectroscopic properties.

A continuous method for separation of N_2F_4 or NF_3 from carbon-containing contaminants is based on column absorption of the organic compounds in a trickle tower fed with chilled chloroform or tetrachloromethane [108]. The less soluble N_2F_4 accumulates in the gas phase. After the first pass, the N_2F_4 concentration can be 88% and can be improved by repeated passage through a trickle tower.

The application of N_2F_4 as a rocket propellant has been slowed by its high price and limited availability [392]. In the United States, Air Products Inc. has been supplying NF_3 and N_2F_4 since the 1960s.

Tetrafluorohydrazine can be synthesized from NF_3 using iron powder at a temperature of 673 K (400 °C) [393]. Iron(II) fluoride, as reducing agent, showed similar results in synthesizing N_2F_4 from NF_3 . The reaction of ClF_3 or ClF_5 with fluoroamine produced a 1 : 1 mixture of N_2F_4 and ClNF_2 [394].

A process based on the oxidation of difluoroamine by ferric ion was developed for the preparation of tetrafluorohydrazine and for pilot-plant scale-up [395]. Difluoroamine, made by hydrolysis of aqueous difluorourea, was passed through aqueous ferric chloride to effect the oxidation, and the product was passed through aqueous caustic to eliminate carbon dioxide, through aqueous ferrous chloride to remove nitric

oxide, and finally through Drierite to remove water. Only minor amounts of impurities remained in the product.

The process for the continuous production of N_2F_4 by the oxidation of HNF_2 by aqueous ferric ions was demonstrated on a pilot-plant scale [396]. The reactions were carried out at low pressures (34–103 kPa [5–15 psig]) and moderate temperatures (294–373 K [70–220 °F]), which facilitated system design and operation. Purification of the product was accomplished without cryogenic fractionation. Production rates of 0.8 kg/h (1.8 lb/h) with 98.5% pure N_2F_4 were routine. Scale-up of this process to much higher production rates appeared to be safe and technically feasible.

Several synthesis methods for N_2F_4 depend on the availability of difluorourea that can be made by direct fluorination of urea [397–399].

The reaction of NF_3 with elemental silicon, similar to reactions with carbon or certain metals, reduces NF_3 to NF_2 , which then recombines to N_2F_4 [400]. In the reaction products, the N_2F_4 has to be separated from SiF_4 by a series of wash baths and cold traps.

3.2 Physical Properties of Tetrafluorohydrazine

Some physicochemical constants of tetrafluorohydrazine (vapor pressure variation with temperature, normal boiling point, melting point, critical temperature and pressure, and heat of vaporization measurements between 112 and 306 K [–161 and +33 °C]) were measured and are considered the most reliable data at this time [401]. See also [8, 13, 130].

3.2.1 Freezing Point, Boiling Point, and Phase Diagrams of Tetrafluorohydrazine

The physical properties of tetrafluorohydrazine are summarized in Table 15, 16, and 17.

Table 15: Physical properties of tetrafluorohydrazine.

Property	SI units	MKS units	References
Molecular mass	104.0070		[132]
Boiling point	199 K	–74.1 °C	
Boiling point	198.9 ± 0.1 K	–74.2 ± 0.1 °C	[401]
Melting point (triple point)	104 K	–169 °C	
Melting point	111.6 ± 0.5 K	–161.5 ± 0.5 °C	[401]
Density, liquid, ρ (at 200 K [–73 °C])		1.652 g/cm ³	
Critical-point data			
$t_{\text{crit.}}$	309 K	+36 °C	
$t_{\text{crit.}}$	309.3 ± 0.1 K	+36.2 ± 0.1 °C	[401]
$P_{\text{crit.}}$	7.77 MPa	77 atm	
P_{crit}	3.70 ± 0.08 MPa	36.6 ± 0.8 atm	[401]

3.2.2 Vapor Pressure of Tetrafluorohydrazine

The vapor pressure of N_2F_4 can be represented by the following equations, one dating back to 1958 [204]:

$$\log p = 6.33 - \frac{692}{T}$$

where p is the pressure in mm Hg and T is the temperature in kelvin. The other dates to 1962 [391]:

$$\log p_V = 7.2163 - \frac{862.9}{T}$$

where p_V is the vapor pressure in mm Hg and T is the temperature in kelvin. See also Figure 4.

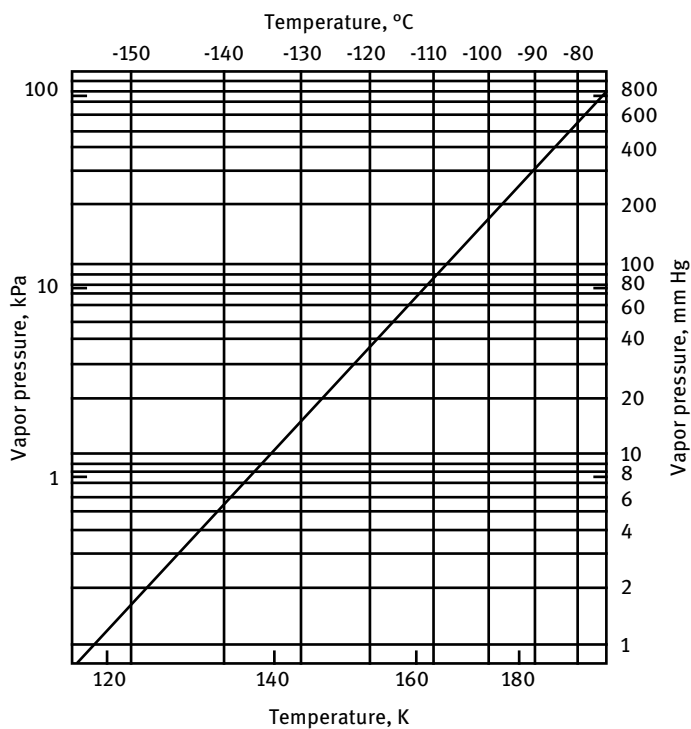


Figure 4: Vapor pressure of tetrafluorohydrazine. (Reprinted and modified from [391], with permission from © 1962 Elsevier; permission conveyed through RightsLink.)

More recent measurements gave the following equations to calculate the vapor pressure, one for the range between the triple point and the normal boiling point, and another for the range between the boiling point and the critical point, with accuracies from 1.25 to 1.5% [401]. Between the triple point and normal boiling point:

$$\log p_V = 7.0051 - 820.75/T$$

Between the boiling point and critical point:

$$\log p_V = 7.1950 - 861.57/T$$

where p_V is the vapor pressure in mm Hg and T is the temperature in kelvin.

3.2.3 Viscosity of Tetrafluorohydrazine

The viscosity of tetrafluorohydrazine as a liquid under pressure is 0.002 N s m^{-2} at 311.4 K (0.20 cPs at -38.3°C).

3.2.4 Thermal Conductivity of Tetrafluorohydrazine

The thermal conductivity of gaseous tetrafluorohydrazine is $0.150 \text{ W m}^{-1} \text{ K}^{-1} = 3.6 \times 10^{-4} \text{ cal s}^{-1} \text{ cm}^{-1} ^\circ\text{C}^{-1}$.

3.2.5 Solubility, Miscibility, Mixtures, and Solutions of Tetrafluorohydrazine

Liquid N_2F_4 in a molar ratio of 1:1 is completely miscible with CF_3Cl at 110 K or CCl_2F_2 at 130 K, but it forms two separate layers with O_2F_2 at 130 K [134].

A Henry's law constant of $0.00085 \text{ mol kg}^{-1} \text{ bar}^{-1}$ for the solubility of N_2F_4 in water that was shown in the NIST Chemistry WebBook is most certainly useless because N_2F_4 hydrolyzes in water and would not remain dissolved unreacted for any length of time.

3.2.6 Thermodynamic Properties of Tetrafluorohydrazine

Thermodynamic properties of tetrafluorohydrazine reported in the literature vary over a wide range, and it is difficult to decide which data are the most reliable. It is unclear whether the discrepancies were caused by insufficient purity of the samples, by deficiencies in the measurement techniques, or both. In some cases the sources – all second-hand sources – even failed to specify whether the data were for gaseous or liquid N_2F_4 . That lack of accuracy adds to the confusion. Most sources list only the enthalpy of formation of the gas, but if we were planning to use N_2F_4 as a liquid rocket propellant, then we would need the enthalpy of formation of the liquid the way it is stored in the propellant tank.

Table 16: Thermodynamic properties of tetrafluorohydrazine.

Property	SI units	Other units	References
Standard enthalpy of formation, gas (ΔH) ₂₉₈	-8.3 ± 10 kJ/mol	-2.0 ± 2.5 kcal/mol	[402]
	-8.368 kJ/mol	-2.0 kcal/mol	[403]
	-8.27 kJ/mol	-1.976 kcal/mol	[137]
	-19.66 ± 2.5 kJ/mol	-4.7 ± 0.6 kcal/mol	[404]
	-8.37 kJ/mol		[132]
	-22.2 ± 5.9 kJ/mol	-5.3 ± 1.4 kcal/mol	[405]
	$-14.22 \pm$	$-3.398 \pm$	[406]
	14.31 kJ/mol	3.378 kcal/mol	
Standard enthalpy of formation, liquid at 298 K = +25 °C	-21.7 kJ/mol	-5.2 kcal/mol	[407]
Heat of vaporization at normal boiling point	15.52 kJ/mol	3.71 kcal/mol	[408]
	15.69 kJ/mol	3.75 kcal/mol	[401]
	13.26 kJ/mol	3.170 kcal/mol	[204]
Heat capacity of the liquid at 298 K	79.7 J K ⁻¹ mol ⁻¹	19.06 cal °C ⁻¹ mol ⁻¹	[408]
Entropy of vaporization (ΔS) _{evap} at ___ K	66.5 J K ⁻¹ mol ⁻¹	15.9 cal °C ⁻¹ mol ⁻¹	
Standard entropy of formation, gas (ΔH) ₂₉₈	301.191 J K ⁻¹ mol ⁻¹	71.98 cal °C ⁻¹ mol ⁻¹	[409]
Standard entropy of formation, gas (ΔH) ₂₉₈	301.18 J K ⁻¹ mol ⁻¹		[132]

3.2.6.1 Heat Capacity of Tetrafluorohydrazine

The heat capacity of gaseous N₂F₄ as a function of temperature can be calculated from the Shomate equation:

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + \frac{E}{\tau^2}$$

where C_p is the molar heat capacity in J mol⁻¹ K⁻¹; A, B, C, D, and E are constants; and τ is the absolute temperature in kelvin divided by 1000. The coefficients are listed in Table 17. The same coefficients (and others) are used for formulas expressing the standard enthalpy of formation and the standard entropy of the vapor. These equations were curve-fitted from data covering ranges from 298 to 1000 K and from 1000 to 6000 K.

3.2.6.2 Enthalpy of Formation of Tetrafluorohydrazine

The vapor-phase excess enthalpy above the standard enthalpy of formation $\Delta H^\circ_{f,298}$ of N₂F₄ can be calculated from the Shomate equation:

$$H^\circ - H^\circ_{298.15} = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{\tau} + F - \Delta H^\circ_{f,298}$$

Table 17: Constants for vapor-phase thermodynamic properties of tetrafluorohydrazine.

Temperature range, K	298–1100	1100–6000
A	39.04848	132.1588
B	224.5360	0.488239
C	–205.0875	–0.098902
D	66.64526	0.006853
E	–0.925509	–8.286706
F	–31.41933	–71.53427
G	284.8057	424.8936
H	–8.368001	–8.368001

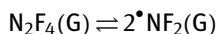
Data source: [132]

where A, B, C, D, E, and F are constants and τ is the absolute temperature in K divided by 1000. The coefficients are the same as those listed in Table 17. The same coefficients (and others) were used for a formula expressing the molar heat capacity of the vapor (Section 3.2.6.1). These equations were curve-fitted from data covering a range from 298 to 6000 K.

A calorimetric method was used to determine the enthalpies of formation ΔH°_{f298} of several nitrogen fluorides, based on their reaction with aqueous KI solutions in a calorimeter in which the gases were bubbled through the liquid [139]. The values of ΔH°_{f298} recommended for N_2F_4 were listed, although it was cautioned that the values for N_2F_4 were uncertain, with the need for further experimental verification.

Literature values for the enthalpy and entropy of formation of N_2F_4 and other nitrogen fluorides were collected and summarized, and expressions were derived for the temperature dependence of the free energy of formation of these substances [141]. The thermodynamics of several reactions for the synthesis of N_2F_4 involving the substances listed above were also examined.

The equilibrium dissociation of tetrafluorohydrazine via the reaction



has been studied behind incident shock waves over the temperature range 375–1500 K [209]. At temperatures above 500 K, the N_2F_4 is completely dissociated, and absorption measurements in this region yielded the absorptivity of $\bullet NF_2$ as a function of temperature. Absorption measurements in the temperature range 375–462 K yielded equilibrium constants for the above reaction. On the basis of second-law and third-law analyses of the data, a value of 87.4 ± 1.7 kJ/mol (20.9 ± 0.4 kcal/mol) for the heat of dissociation of N_2F_4 was obtained. In addition, previously reported measurements of the equilibrium constants for the reaction



have been reanalyzed, and a value of $239 \pm 4 \text{ kJ/mol}$ ($57.2 \pm 1.0 \text{ kcal/mol}$) was obtained for the heat of dissociation of NF_3 . The above results were then used to obtain revised values for the heats of formation of $\text{N}_2\text{F}_4 \Delta H^\circ_f(\text{G}) = -22.2 \pm 5.9 \text{ kJ/mol}$ ($-5.3 \pm 1.4 \text{ kcal/mol}$) and ${}^\bullet\text{NF}_2(\text{G}) = +32.6 \pm 4.2 \text{ kJ/mol}$ ($+7.8 \pm 1.0 \text{ kcal/mol}$).

3.2.6.3 Entropy of Tetrafluorohydrazine

The entropy of gaseous N_2F_4 at 298 K and 1 bar pressure is $S^\circ_{\text{gas}} = 301.18 \text{ J mol}^{-1} \text{ K}^{-1}$ (NIST Chemistry WebBook [132]). The entropy of gaseous N_2F_4 can be calculated from the polynomial equation

$$S^\circ = A \times \ln(\tau) + B \times \tau + \frac{C \times \tau^2}{2} + \frac{D \times \tau^3}{3} - E/(2 \times \tau^2) + G$$

where G is the integration constant in $\text{J mol}^{-1} \text{ K}^{-1}$, τ is the temperature in kelvin divided by 1000, and A , B , C , D , E , and G are constants listed in Table 17 for two different temperature ranges.

3.2.6.4 Heat of Dissociation of Tetrafluorohydrazine

The heat of dissociation of N_2F_4 into two ${}^\bullet\text{NF}_2$ free radicals is 83.2 kJ/mol (19.88 kcal/mol). Other sources (Evans and Tschuikow-Roux [405]) give $87.4 \pm 1.7 \text{ kJ/mol}$ ($20.9 \pm 0.4 \text{ kcal/mol}$).

3.2.7 Molecular Structure, Dipole Moment, and Molecular Orbital Calculations of Tetrafluorohydrazine

3.2.7.1 Molecular Structure of Tetrafluorohydrazine

The molecular structure of tetrafluorohydrazine F_2NNF_2 resembles that of hydrazine H_2NNH_2 . In the temperature range 123–193 K, the staggered (C_{2h}) and gauche (C_2) isomers of dinitrogen tetrafluoride are in equilibrium with each other, both in the condensed phase and the vapor phase. The staggered conformation is favored by about 2 kJ/mol , and a barrier of 12.5 kJ/mol hinders the free rotation of the NF_2 groups.

The structures of the difluoroamino free radical and tetrafluorohydrazine have been determined by electron diffraction [410]. The bond distances and bond angles determined by this method were as follows: $\text{N}-\text{F} = 1.363 \pm 0.008 \text{ \AA}$ and $\angle \text{FNF} = 102.5 \pm 0.9^\circ$ for NF_2 and $\text{N}-\text{F} = 1.393 \pm 0.008 \text{ \AA}$, $\text{N}-\text{N} = 1.53 \pm 0.02 \text{ \AA}$ and $\angle \text{FNF} = 103.7 \pm 0.9^\circ$ for F_2NNF_2 . The dihedral angle is considerably less in N_2F_4 than in N_2H_4 .

The far IR ($60\text{--}350 \text{ cm}^{-1}$) and low-frequency Raman ($80\text{--}150 \text{ cm}^{-1}$) spectra of gaseous N_2F_4 revealed the fundamental vibrations and several excited state transitions of the torsional mode of the *gauche* conformer [411]. Variable-temperature ($213\text{--}183 \text{ K}$ [-60 to -90°C]) studies of the IR spectra of N_2F_4 dissolved in liquid xenon provided data from which the enthalpy difference could be determined to be $69 \pm 6 \text{ cm}^{-1}$ ($824 \pm 71 \text{ J/mol} = 197 \pm 17 \text{ cal/mol}$), with the *trans* conformer the more stable rotamer. *Ab initio* calculations were then carried out with several different basis

sets, from which the structural parameters, conformational stability, harmonic force constants, and IR and Raman spectra could be predicted and compared to the experimental values when appropriate. Some of the fundamentals had to be reassigned, and the potential function governing the conformer interchange has been determined.

3.2.7.2 Bond Lengths and Bond Energies of Tetrafluorohydrazine Molecule

Under conditions that prevail in the ionization section of mass spectrometers, dinitrogen tetrafluoride will be totally dissociated [412]. The dissociation energy was estimated as 80.3 kJ/mol (19.2 kcal/mol).

Bond dissociation energies of N_2F_4 and other molecules determined by kinetic methods were summarized in [413].

The interatomic distances, bond angles, and the proportions of *gauche* and *trans* isomers present in N_2F_4 have been determined by gas-phase electron diffraction [414]. The two rotamers are similar in structure except for the dihedral angle of $67.1 \pm 0.8^\circ$. The 47% *gauche*-53% *trans* mixture found at below room temperature indicated that the *trans* configuration is 1255–2092 J (300–500 cal) more stable than the *gauche* rotamer. The bond lengths N–N of $1.489 \pm 0.007 \text{ \AA}$ and N–F $1.375 \pm 0.004 \text{ \AA}$ are the same for both species, but the valence angles are slightly different ($\angle \text{FNF}$ *gauche* is $105.1 \pm 1^\circ$, $\angle \text{FNF}$ *trans* is $102.9 \pm 0.75^\circ$, $\angle \text{F}_1\text{NN}$ *gauche* is $100.1 \pm 1.0^\circ$, $\angle \text{F}_2\text{NN}$ *gauche* is $104.3 \pm 1.0^\circ$, $\angle \text{FNN}$ *trans* is $100.6 \pm 0.8^\circ$). The non-bonded mean-square amplitudes showed a strong angular dependence on the equilibrium geometry due to torsional motion about the N–N bond.

Analysis of electron-diffraction patterns from gaseous N_2F_4 at 298 K (25°C) has verified conclusions from earlier work that the material contains both *trans* and *gauche* conformers [415]. Assuming that these conformers have the same parameter values except for the torsion angle, the following principal results were obtained: 71.2 $\pm$ 8.1% *trans* configuration, $r_{\text{N}-\text{N}} = 1.492 \pm 0.007 \text{ \AA}$, $r_{\text{N}-\text{F}} = 1.372 \pm 0.002 \text{ \AA}$, $\angle \text{FNF} = 103.1 \pm 0.6^\circ$, $\angle \text{NNF} = 101.4 \pm 0.4^\circ$, θ (the dihedral angle $\angle \text{N}_2\text{N}_1\text{F}_4$, $\angle \text{N}_1\text{N}_2\text{F}_1 = 64.2 \pm 3.7^\circ$). The electron diffraction results indicated that the energy difference $E_{\text{gauche}} - E_{\text{trans}}$ is roughly less than 1.0 kcal but that the rotational barrier may be several kilocalories.

3.2.7.3 Dipole Moment of Tetrafluorohydrazine

The intrinsic moment of the N–F bond in N_2F_4 is 1.29 D, whereas it is 1.24 or 1.60 D in NF_3 [198].

3.2.7.4 Molecular Orbital Calculations of Tetrafluorohydrazine Molecule

Results from several *ab initio* method calculations were compared with local, hybrid, and gradient-corrected DFT methods for computing structures and energies of N_2F_4 rotamers [416]. The generated energies of *trans*- and *gauche*- N_2F_4 rotamers and their

dissociation energies to $\bullet\text{NF}_2$ free radicals were compared with experimental data. Suitable hybrid and gradient-corrected DFT methods for determining structures and energies for these and similar molecular systems were discussed.

3.2.8 Optical Properties of Tetrafluorohydrazine

3.2.8.1 Infrared Absorption Spectra of Tetrafluorohydrazine

The IR spectrum of N_2F_4 (Figure 5) can be used to calculate N—F and N—N bond strengths and determine the molecule conformation. Similar to hydrazine, there exists free rotation around the N—N axis at temperatures above 300 K. Recording the IR spectrum was complicated by reaction of N_2F_4 with the NaCl windows of the sample cell [391].

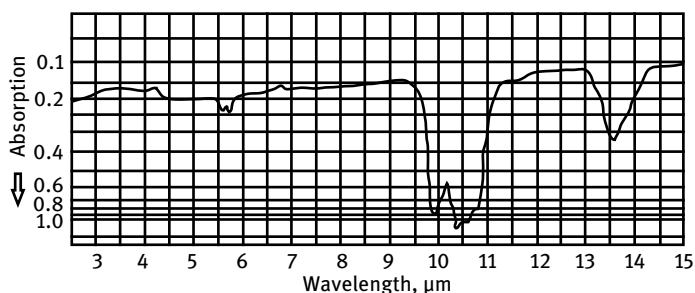


Figure 5: IR spectrum of tetrafluorohydrazine. (Reprinted and modified from [391], with permission from © 1962 Elsevier; permission conveyed through RightsLink.)

Because they are always in equilibrium with each other, it would be difficult to separate the IR spectra of N_2F_4 and $\bullet\text{NF}_2$, except the former dominates at low temperatures and the latter prevails at high temperatures [417]. When equilibrium mixtures of N_2F_4 and NF_2 are heated in a conventional IR cell to increase the proportion of NF_2 , profound changes in the IR spectrum are observed. The 1010 cm^{-1} band of N_2F_4 is found to decrease drastically, while smaller decreases are found at 960 and 740 cm^{-1} . A large increase is found between 940 and 910 cm^{-1} , with smaller increases at 990 – 970 and 735 – 730 cm^{-1} . It is not possible to distinguish the bands, however, because of severe overlapping by N_2F_4 bands at 1010 , 960 , and 735 cm^{-1} . To increase the resolution of the NF_2 spectrum, a compensating technique was used to cancel the N_2F_4 spectrum. A short cell (2 cm) was filled to a high pressure of N_2F_4 and placed in the reference beam, and a long cell filled to a low pressure was placed in the sample beam.

A complete vibrational analysis of the IR spectrum of N_2F_4 was carried out on the assumption that the molecule belongs to the point group C_2 [418]. The 12 normal vibrations of this point group have been assigned to observed bands. The band due

to the torsional vibration was observed at 122 cm^{-1} in the far-IR spectrum of the vapor. The band contours were consistent with a dihedral angle smaller than 90° .

When trying to identify bands in the $900\text{--}1000\text{ cm}^{-1}$ range of the IR absorption spectrum of N_2F_4 , it was assumed that N—F valency vibrations in N_2F_4 change in the same manner on transition from the gaseous to the solid state as those in NF_2Cl [419, 420]. Comparison of N_2F_4 spectra in the gaseous and solid states made it possible to isolate the following bands: **(1)** band with Q, P, and R branches and maxima at 934 , 911 , and 950 cm^{-1} , respectively; **(2)** with P and R branches, maxima at 950 and 965 cm^{-1} , respectively, and a minimum at 958 cm^{-1} ; **(3)** with P and R branches, maxima at 965 and 1010 cm^{-1} and a minimum at 1003 cm^{-1} ; and **(4)** with Q, P, and R branches and maxima at 1018 , 1010 , and 1034 cm^{-1} , respectively. The following correlation between fundamental frequencies of the IR spectrum of N_2F_4 at $120\text{--}1100\text{ cm}^{-1}$ and molecular vibrations was proposed on the basis of the experimental results obtained (frequency in cm^{-1}): 122 , $\text{F}_2\text{N--NF}_2$ rotational; 270 , NNF deformation; 379 , NNF deformation; 466 , NNF deformation; 517 , FNF deformation; 539 , FNF deformation; 587 , FNF deformation; 737 , N—N valency; 934 , NF symmetric valency; 859 , NF anti-symmetric valency; 1003 , anti-symmetric valency; and 1018 , symmetric valency. The normal vibration frequencies of N_2F_4 were calculated by using the same force constants for the NF_2 group as those that apply to this group in NF_2H , NF_2D , NF_2Cl , and NF_2Me molecules, giving satisfactory agreement between calculated and measured values.

The IR spectrum of liquid N_2F_4 at 153 K (-120°C) was found to be essentially identical to that of the solid and the vapor [421]. A comparison of these data with Raman results on the liquid indicated that a number of frequencies are mutually exclusive in the IR and Raman spectra. This was taken as evidence for the presence of the *trans* isomer in addition to the *gauche* one.

The IR spectrum of gaseous N_2F_4 was reanalyzed in the $4000\text{--}20\text{ cm}^{-1}$ region, and a number of new details on band positions and IR band contours were discovered [422]. The vibrational assignments, based on the new IR data and earlier reported Raman data, strongly supported the concept that N_2F_4 actually consists of an equilibrium mixture of two rotational isomers, *trans* (C_{2h}) and *gauche* N_2F_4 , differing very little in energy as suggested by NMR and electron diffraction data. The new vibrational assignment differed considerably from those offered in earlier investigations.

The IR spectra of N_2F_4 solutions in liquid argon and nitrogen have been recorded and reanalyzed in the $3300\text{--}3550\text{ cm}^{-1}$ region, and the fundamental absorption bands of NF-stretching modes of both the *gauche* and *trans* isomers and the bands of second-order transitions have been observed [423]. These IR data on the spectra of cryosystems and published Raman data allowed an unambiguous interpretation of the NF_2 -stretching vibrational bands for both the N_2F_4 conformers.

The far-IR ($60\text{--}350\text{ cm}^{-1}$) and low-frequency Raman ($80\text{--}150\text{ cm}^{-1}$) spectra of gaseous N_2F_4 revealed the fundamental vibrations and several excited-state transitions of the torsional mode of the *gauche* conformer [411].

IR spectra of N_2F_4 at higher temperatures are not those of the N_2F_4 molecule but those of the difluoroamino free radical $\cdot\text{NF}_2$ [424, 425]. IR spectra can be measured to determine the degree of dissociation of N_2F_4 as a function of temperature and pressure.

The decay of N_2F_4 in moist air was tracked by a sequence of IR spectra, as shown in Figure 6.

Raman Spectra of Tetrafluorohydrazine

The Raman spectra of liquid N_2F_4 at temperatures ranging from 193 to 123 K (-80 to -150°C) showed 17 pronounced Raman lines, whereas the C_2 isomer of N_2F_4 accounts for only 12 fundamentals [426]. The large number of Raman lines suggested the presence of more than one isomer at 153 K (-120°C). A comparison of the IR and Raman bands below 800 cm^{-1} showed that the mutual exclusion principle is operative, and it was concluded from this alternative forbiddenness that the *trans*- N_2F_4 isomer of C_{2h} symmetry gives rise to these mutually exclusive bands. Assignment of the observed frequencies based on depolarization values, band positions, and IR band contours were presented for the molecule in both the C_2 and C_{2h} configurations. It was shown that the data could be interpreted only in terms of an equilibrium mixture of the two isomers at both ambient and lower temperatures and that these isomers differ little in energy.

The Raman spectra of gaseous N_2F_4 at a pressure of 760 torr and of the solid at 18 K were recorded with a spectral slit width of 3 cm^{-1} [427]. Ten of the expected 11 fundamentals of the symmetric motions of both the *gauche* and *trans* rotamers gave rise to strongly polarized Raman lines. These new data required a reassignment of some of the fundamentals for both the C_2 and C_{2h} conformers. Both conformers were found in the solid even after annealing the sample for 9 h at a temperature of 101.6 K and for 3 h at a temperature of 106.8 K. Bands attributable to the *gauche* rotamer became more intense relative to those for the *trans* rotamer after several hours of annealing.

Microwave Spectra of Tetrafluorohydrazine

In the microwave spectrum of N_2F_4 , ten $J = 1$ lines with $J \leq 4$ have been assigned [428]. A number of Q-branch transitions at higher J numbers have also been identified.

The ground-state rotational microwave spectrum of *gauche*- N_2F_4 has been investigated between 8 and 200 GHz, including quantum states up to $J = 74$ and $K = 39$ [429]. Quadrupole coupling hyperfine structures were analyzed to give $\chi_{aa} = 2246(12)\text{ MHz}$ and $\chi_{cc} = -1792(5)\text{ MHz}$. The hypothetical ($e_Q = 0$) center frequencies were fitted using a rigid-rotor Hamiltonian function, including centrifugal-distortion terms up

to the eighth degree in (J , K). The rotational constants are $A = 55761995(1)$ MHz, $B = 318943277(8)$ MHz, and $C = 281316955(8)$ MHz. The electric dipole moment along the c axis was determined from field shifts of magic-doublet components to be $\mu_e = 0.256(4)$ D.

Ultraviolet Spectra of Tetrafluorohydrazine

In the course of flash-photolysis kinetic-spectroscopy experiments on NF-containing compounds, it was found necessary to examine the absorption of the NF_2 radical at 2600 Å at a higher dispersion than that used by previous authors [430].

An investigation of the photolysis of NF_2 was carried out by kinetic absorption spectroscopy in the UV vacuum [431]. A series of diffuse bands in the region of 126–140 nm were attributed to Rydberg transitions of NF_2 . A number of transient bands have also been observed and attributed to the species NF in more than one electronic state, and some collisional rate data for these bands were calculated.

3.2.9 Magnetic Properties of Tetrafluorohydrazine

When first measured, the ^{19}F nuclear magnetic resonance spectrum of tetrafluorohydrazine consisted of a single broad unresolved band at a field of approximately 75 ppm lower than that of the ^{19}F nuclei of trifluoroacetic acid [204]. Resolution of the expected triplet was not observed, probably because of the low symmetry of tetrafluorohydrazine.

The ^{19}F NMR spectrum of the *trans* and *gauche* rotamers of N_2F_4 was analyzed, and the *gauche* form was found to best be represented by the AA'BB' system [432]. The parameters of *gauche* N_2F_4 were $\delta = 688.6$ cps, $\text{JAB} \pm 489.6$ cps, $\text{JAB}' = \pm 13.4$ cps, $\text{JAA}' = \pm 58.8$ cps, and $\text{JBB}' = \pm 109.0$ cps.

3.3 Chemical Properties of Tetrafluorohydrazine

Tetrafluorohydrazine is a compound that easily decomposes similar to hydrogen peroxide or hydrazine. When the N_2F_4 gas is ignited with a hot wire, it decomposes completely to NF_3 and N_2 , but it usually does not detonate. Similar to NF_3 , N_2F_4 also dissolves in liquid OF_2 and is miscible with this oxidizer in all proportions. Such oxidizer mixtures might be useful as oxidizers for hydrocarbon fuels in rocket engines.

3.3.1 Reactions of Tetrafluorohydrazine

Tetrafluorohydrazine does not react hypergolically with most rocket fuels. It dissociates at room temperatures, and there are measurable numbers of NF_2 radicals similar to the dissociation of N_2O_4 .

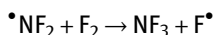
3.3.1.1 N₂F₄ Reactions with Inorganic Compounds

Tetrafluorohydrazine will react with elemental fluorine and form NF₃ [433], but no higher nitrogen fluorides (NF₅?) were found [253, 254].

Reactions of N₂F₄ with O₃, O atoms, NO₂, or NO did not result in the formation of a more powerful oxidizer like the hoped-for, yet-unknown F₂NO₂ or F₂NOONF₂ [434]. The reactions of tetrafluorohydrazine with Cl₂O₇ or ClF₃ did not result in the formation of new oxidizers, either.

Many of the reactions initially attributed to N₂F₄ are actually reactions of the difluoroamino free radical formed by dissociation of N₂F₄ [435]. The physical and chemical properties of the difluoroamino radical have been determined separately and independently of the properties of tetrafluorohydrazine from which it was formed.

The rate of the exothermic free radical reaction



has been directly determined by measuring the disappearance of fluorine and the initial rate of NF₃ formation in the temperature range 1100–1600 K by means of a shock tube coupled to a TOF mass spectrometer [436]. The Arrhenius expression

$$k_a = 4.8 \times 10^9 \exp(-14400/RT) \frac{\text{mol}}{\text{s}}$$

was obtained for the rate constant, which when extrapolated ($\sim 10^7$) to near room temperature was in reasonable agreement with corrected data.

Reactions of N₂F₄ with Lewis acids resulted in the formation of a wide variety of trifluorodiazinium N₂F₃⁺ and pentafluorodiazinium N₂F₅⁺ salts, which are discussed in a separate section to follow.

Tetrafluorohydrazine is more reactive than NF₃ and will hydrolyze with water at room temperature. In moist air, it will decompose under formation of NO₂, NOF, HF, and N₂.

The reaction of dinitrogen tetrafluoride with aqueous solutions of potassium iodide varies with pH but is temperature independent [437].

The reaction of N₂F₄ with sodium azide at 318–358 K (45–85°C) produced NF₃, dinitrogen, and NaF [438]. The yield of NF₃ is pressure dependent and increases almost linearly from 30% at 3 atm to 70% at 8.5 atm. Two reactions occurred simultaneously and competitively; one produced NF₃, dinitrogen, and NaF, and the other yielded only dinitrogen and NaF.

The atmospheric decay of N₂F₄ was studied in preparation for animal-exposure toxicity tests with this material [439]. An IR study of the degradation of N₂F₄ in air was undertaken and is illustrated in Figure 6. The sequence of spectra confirm the course of reaction elucidated by Dost et al. [283, 440, 441]. Figure 6a is the pure N₂F₄ spectrum before the addition of air. Figure 6b is the spectrum 8 min after the addition of air and is essentially a spectrum of NOF with a small amount of N₂O₄. In Figure 6c, 24 min after air addition, the concentration of NOF has decreased and that of N₂O₄

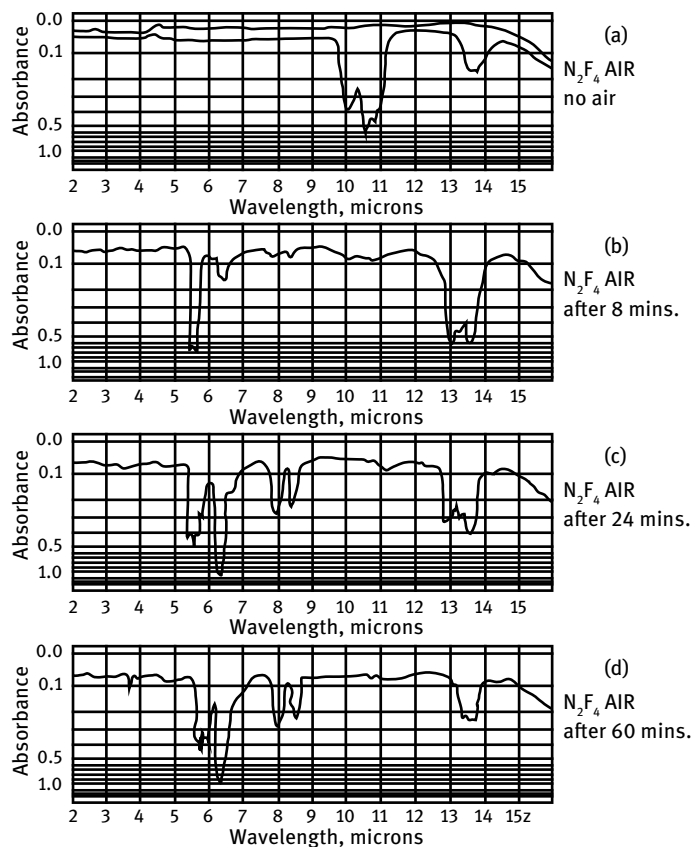
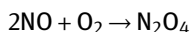


Figure 6: IR spectra showing degradation of research-grade N_2F_4 in room air. (Reproduced from MacEwen [439].)

has increased. In addition, new peaks at 3.5, 5.8, and 5.9 microns indicate the possible production of HF and NOCl (possibly from reaction of NOF with the AgCl cell windows). In the last spectrum, Figure 6d, 60 min after air addition, NOF has almost completely disappeared, the cell containing mostly N_2O_4 and possibly HF and NOCl. The same series of reactions apparently occurred with propellant-grade N_2F_4 but at a much faster rate than with the research grade. For example, it took 60 min for complete conversion of research-grade N_2F_4 to N_2O_4 , whereas the same conversion took place in about 5 min with the propellant grade, although the degradation time was quite variable and seemed to be subject to many influences (Figure 7). The presence of NO in the propellant-grade N_2F_4 may account for the increase in reaction rate with air, since it is known that the following reaction takes place readily in air:



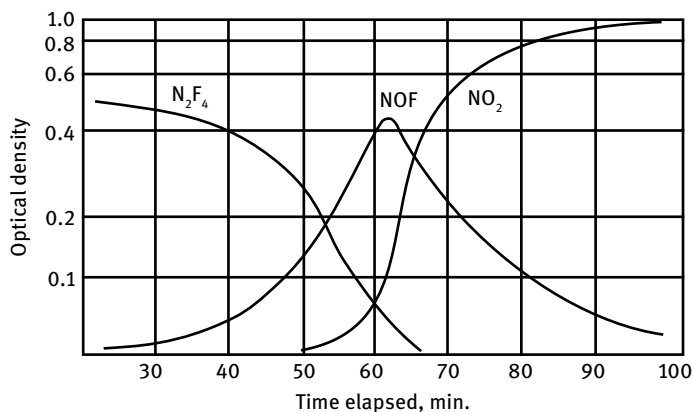
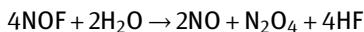
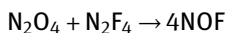
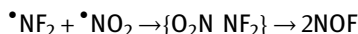


Figure 7: Degradation of research-grade N_2F_4 in room air. (Republished and modified from Dost et al. [284], with permission of © 1968 Elsevier Science Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

Since both NF_2 and NO_2 are free radicals, they could combine briefly to form O_2NNF_2 , which then decomposes to NOF

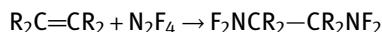


When small amounts of NO_2 were added to dilute N_2F_4 in dry air or nitrogen, NO_2 disappeared rapidly, with a simultaneous decrease in N_2F_4 and an increase in NOF. Thus, NO would be catalytic for the degradation of N_2F_4 in air. The combined use of IR spectrophotometry, mass spectrometry, and gas chromatography led to the successful characterization of the impurities present in propellant-grade N_2F_4 that affected its degradation in air. This degradation occurred at a much faster rate with propellant-grade N_2F_4 than with the research grade, possibly due to the presence of NO in the former material. See also [442].

One of the shortcomings of tetrafluorohydrazine as a storable propellant in combination with hydrazine, ammonia, or MMH is the lack of hypergolicity. It was attempted to hypergolize N_2F_4 by the addition of N_2O_4 or ClF_5 [443]. N_2O_4 reacted spontaneously with N_2F_4 with a luminous flame and could therefore not be used as an additive. ClF_5 did not react spontaneously with N_2F_4 . Chlorine trifluoride was not used in this test series because it was known that it would react with N_2F_4 at higher temperatures, forming NF_3 and ClF in an exchange of fluorine atoms. At temperatures above 373 K (100 °C), ClF_5 and N_2F_4 also began to react, but the reaction products could not be identified. The most likely products of that reaction are ClF , ClF_3 , and NF_3 .

3.3.1.2 N₂F₄ Reactions with Organic Compounds

Reactions of N₂F₄ with alkanes, alkenes, and alkynes lead to difluoroamino compounds of the R—NF₂ type, which have been evaluated as monopropellants and energetic plasticizers for solid propellants:



Addition reactions of N₂F₄ have been described with olefins, acetylenes, allyl chloride, diallyl ether, cyclic olefins, vinyl alcohol, and many other organic compounds. There are too many reactions and a wide variety of organic —NF₂ compounds to include them all in this chapter, e.g., [444–446]. There are several other sections in this book describing organic —NF₂ compounds and their proposed uses as monopropellants, energetic plasticizers, and energetic binders.

Tetrafluorohydrazine reacts with acetylenes to produce α -fluoro- α -difluoroamino fluorimines. These compounds appear to be the result of a rearrangement of the original adduct, α,β -bis(difluoroamino)ethylenes [447].

If N₂F₄ was irradiated at 2537 Å in the presence of alkanes, the major process was substitution of a hydrogen atom by an NF₂ group, photodifluoramination, reminiscent of photochlorination. Similar treatment of alkenes and alkynes resulted in addition of the elements of NF₂ to the multiple bond. Kinetic and stoichiometric information about the photodifluoramination process was obtained from a study of the photolysis of NF₂ with methane. Irradiation of N₂F₄ with propylene and isobutylene resulted not only in substitution of NF₂ for H but also in addition of F and NF₂ to the double bond. The F was found mainly on the terminal carbon atom [448].

HF-stimulated emission has been observed from flash-photolyzed mixtures of N₂F₄ with a number of hydrogen sources: HCl, CH₄, CH₃F, CH₂F₂, CH₃Br, C₂H₆, C₂H₅F, and C₂H₅I [449].

Addition of N₂F₄ to alkenols or alkenyl esters gives bis(difluoroamino)alkanols, which can be nitrated to give difluoroamino-substituted alkyl nitrates, which are very energetic compounds [450].

3.3.2 Trifluorohydrazinium Salts Derived from Tetrafluorohydrazine

Similar to the large group of tetrafluoroammonium salts, there is a similar, less exhaustively examined group of salts derived from reaction of tetrafluorohydrazine with Lewis acids, such as SbF₅ or AsF₅.

The first reports on the formation of a stable adduct between N₂F₄ and a Lewis acid were published in 1965 and 1966 by Ruff [451, 452].

Boron trifluoride, which is a weaker Lewis acid than AsF₅ or SbF₅, did not form a stable adduct with N₂F₄ at temperatures as low as 195 K (–78 °C). Equimolar amounts of N₂F₄ and BF₃, when combined at 195 K (–78 °C) in a Teflon-FEP ampoule, did not form a solid. The liquid could be distilled at 195 K (–78 °C) to a colder trap without leaving any solid residue behind.

The reaction of tetrafluorohydrazine with arsenic(V) fluoride at 195 K (-78°C) produced a solid salt that was analyzed by IR, but it decomposed after a few days of storage under dry nitrogen at room temperature [453].

SbF_5 , when treated with an excess of N_2F_4 , produced either the 1:2 adduct $\text{N}_2\text{F}_4 \cdot 2\text{SbF}_5$ or the 1:3 adduct $\text{N}_2\text{F}_4 \cdot 3\text{SbF}_5$. The IR spectra from 4000 to 250 cm^{-1} and laser Raman spectra of solid $\text{N}_2\text{F}_3\text{AsF}_6$ and $\text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11}$ were measured to study the molecular structure and compare it to crystal structure information obtained from XRD [454]. N_2F_4 and SbF_5 reacted in anhydrous HF to produce $\text{N}_2\text{F}_3\text{SbF}_6$ [455, 456]. The reaction between N_2F_4 and AsF_5 can be achieved at room temperature quantitatively even without HF solvent. These salts are useful as a burn-rate modifier in NF_3 - F_2 gas generators. Trifluorohydrazinium pentafluorostannate $\text{N}_2\text{F}_3\text{SnF}_5$ is formed by reacting $\text{N}_2\text{F}_3\text{SbF}_6$ and Cs_2SnF_6 in the presence of HF as a solvent [341]. $\text{N}_2\text{F}_3\text{SnF}_5$ is useful as a component of NF_3 - F_2 gas-generating compositions.

3.3.2.1 Other Salts Derived from Tetrafluorohydrazine

The purported synthesis of $\text{N}_2\text{F}_5^+(\text{CF}_3)_3\text{CO}^-$, a salt containing the unknown pentafluorohydrazinium cation, would have been the first known example of a substituted NF_4^+ cation, i.e. an NF_4^+ cation in which a fluorine ligand is replaced by an NF_2 group [457]. Since such a heterolytic fission of $(\text{CF}_3)_3\text{COF}$ with F^+ formation is unlikely, the reported synthetic and spectroscopic evidence for $\text{N}_2\text{F}_5^+(\text{CF}_3)_3\text{CO}^-$ was critically reviewed [458]. The reexamination indicated that the reported white solid was not $\text{N}_2\text{F}_5^+(\text{CF}_3)_3\text{CO}^-$ but was most likely the known compound $(\text{NO}^+)_2\text{SiF}_6^{2-}$.

3.3.3 Analysis of Tetrafluorohydrazine

For the analysis of tetrafluorohydrazine in air, the compound was converted to fluoride ion by nitrogen dioxide and water [459]. The fluoride ion was detected continuously in a flow-through apparatus by a commercial fluoride ion electrode. A 30-mV change in electrode potential was obtained for 1 part per million of N_2F_4 in the air. Various factors affecting sensitivity, stability, interferences, and speed of the detection system were considered.

3.3.3.1 Mass Spectrometric Analysis of Tetrafluorohydrazine

The fragmentation process producing NF_2^+ is complex, and several pathways for its production have been proposed, based on the relative abundance of ions in the mass spectrum with an excitation voltage of 70 eV. It was the second most abundant ion after NF^+ . The ionization potential of NF_2 was calculated as 11.4 V [460].

Mass spectra and appearance potentials for dinitrogen tetrafluoride and its dissociation products NF_2 , NF_3 , and N_2F_2 were measured, and the activation energy of the dissociation reaction was determined from an Arrhenius plot [461, 462].

Appearance potentials have been measured for selected ions from NF_2 , NF_3 , N_2F_2 , and N_2F_4 [463]. Ionization-dissociation processes were identified, and bond dissociation

tion energies were calculated. The N—N bond dissociation energy, $D(\text{F}_2\text{N}-\text{NF}_2)$, was directly measured to be $5.14 \pm 0.38 \text{ kJ/mol}$ ($21.5 \pm 1.6 \text{ kcal/mol}$). The appearance potential of N_2F_4 was $12.0 \pm 0.1 \text{ eV}$.

During attempts to analyze N_2F_4 by mass spectrometry, reactive species often react prematurely in the inlet to a mass spectrometer before a clean mass spectrum can be obtained. Cooling the mass spectrometer inlet to 83 K (-190°C) will allow the sample to enter the ionization chamber unadulterated. Mass spectra of N_2F_4 and several other reactive fluorides were obtained by this method [464]. Operating at low temperatures will also allow one to examine the sample for dimer association in the vapor phase. The appearance potential of NF_2^+ from N_2F_4 was 12.63 eV .

3.3.3.2 Gas Chromatographic Analysis of Tetrafluorohydrazine

Tetrafluorohydrazine can be purified by preparative gas chromatography. In particular, it is important for this purification method to remove C_2F_6 , a contaminant that is otherwise difficult to remove [391].

Tetrafluorohydrazine can be analyzed by gas chromatography and IR spectrophotometry [465].

Mixtures of F_2 , HF , NF_3 , *trans*- N_2F_2 , and N_2F_4 can be analyzed by gas chromatography [266].

3.4 Thermal Decomposition and Radiolysis of Tetrafluorohydrazine

3.4.1 Thermal Decomposition of Tetrafluorohydrazine

The NF_2 free radical is formed not only as a result of photolysis of N_2F_4 but also as the result of simple thermolysis, i.e., thermal dissociation of N_2F_4 .

The enthalpy and entropy changes of the N_2F_4 dissociation were measured between 373 and 423 K by two independent methods, one a constant-volume pressure measurement and the other a spectroscopic method [466, 467]. The constant-volume method gave $\Delta H = 83.3 \text{ kJ/mol} = 19.9 \text{ kcal/mol}$ and $\Delta S = 39.9 \text{ e.u.}$ The spectroscopic method gave $\Delta H = 90.8 \text{ kJ/mol} = 21.7 \text{ kcal/mol}$ and $\Delta S = 45.0 \text{ e.u.}$

The EPR spectrum of the difluoroamino radical ($^*\text{NF}_2$) was observed as a function of temperature and found to be a single broad line at a pressure of $2.67\text{--}5.33 \text{ kPa}$ ($20\text{--}40 \text{ mm Hg}$) of N_2F_4 and a temperature of $340\text{--}435 \text{ K}$. The constant-volume dissociation energy of N_2F_4 was obtained directly from the slope of an Arrhenius plot and was 78.2 kJ/mol (18.7 kcal/mol). The enthalpy change ΔH was found to be 80.7 kJ/mol (19.3 kcal/mol). The N—N bond strength in N_2F_4 was evaluated by three methods, and the best value for the heat of dissociation of N_2F_4 was 82.8 kJ/mol ($19.8 \pm 0.8 \text{ kcal/mol}$) [468, 469]. The IR spectra and thermodynamic properties of $^*\text{NF}_2$ were measured, and the energy levels of the fragment and its electron orbitals were calculated from molecular orbital theories [425, 470].

The EPR spectrum of NF_2 was observed in the gas phase at approximately 40 mmHg pressure and over the temperature range 340–435 K [471]. The spectrum observed was a single broad line with a g -value of 2.010 and a peak-to-peak line width of 104 gauss. The spectrum of NF_2 in a matrix of solid argon showed some hyperfine structure, in particular, a center triplet arising from interaction with the ^{14}N nucleus (16 gauss) and corresponding to the NF_2 spin state in which the two fluorine nuclei spins are anti-parallel. Two side lines were also found about 47 gauss from the center line.

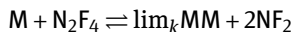
Difluoroamino radicals ($\cdot\text{NF}_2$) formed during dissociation of N_2F_4 can be trapped and stabilized on molecular sieves for further examination by EPR [472]. The other technique is to trap them in a solid matrix of frozen argon or neon at liquid helium temperatures [473].

The rate of dissociation of N_2F_4 in N_2 and Ar was determined at temperatures between 344 and 410 K and total pressures between 0.6 and 6.0 atm in a shock tube [474, 475]. The progress of the reaction behind the incident shock wave was followed by a time-resolved spectrophotometric technique. The absorption coefficient of NF_2 at $12602\text{ \AA}$ was determined between 350 and 571 K and found to be $537 \pm 10\text{ L mol}^{-1}\text{ cm}^{-1}$. The kinetics data indicated that the dissociation in 99% N_2 was quasi-unimolecular throughout the experimental pressure range, attaining its first-order limit at a total pressure not far above 6 atm and its second-order region below 0.6 atm. The observed pressure for the region of transition from first-order to second-order kinetics was reasonably consistent with the transition pressure obtained from classical theory on the basis of the estimated value ($2 \times 10^{15}\text{ s}^{-1}$) of the pre-exponential factor for the limiting high-pressure first-order specific rate. At approximately 2 atm, the observed specific rate for the nitrogen mixture was given by

$$k_2(\text{N}_2) = 10^{14.98} \pm 0.42 \exp \left[\left(-19.4 \pm 0.7 \frac{\text{kcal}}{\text{mol}} \right) / RT \right] \text{ s}^{-1}$$

between 344 and 407 K.

The equilibrium dissociation of $\text{N}_2\text{F}_4 \rightleftharpoons 2\text{NF}_2$ was studied in shock waves, yielding an equilibrium constant identical to those obtained previously in static measurements [476]. The thermal dissociation rate for N_2F_4 diluted with argon, helium, or SF_6 was studied between 523 and 623 K (350 and 450 °C) at total pressures of 0.058–0.27 MPa (0.58–2.7 atm). The reaction



was found to be first order in M and first order in N_2F_4 , indicating a bimolecular mechanism. The rate constant k_{Ar} for argon dilution could be expressed either by

$$k_{\text{Ar}} = 1.5 \times 10^{12} T^{0.5} \exp(-15200/RT)$$

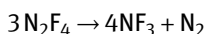
or

$$k_{Ar} = 2.96 \times 10^8 T^{0.5} \left(\frac{E_0}{RT} \right)^{4.0} \exp \left(-\frac{E_0}{RT} \right)$$

where k_{Ar} is the rate constant in $\text{L mol}^{-1} \text{s}^{-1}$, T is the temperature in kelvin, and E_0 is the dissociation energy of N_2F_4 , here taken to be 77 kJ/mol (18.4 kcal/mol). For the other diluent gases, the activation energy was unchanged.

A mass spectrometer with a collision-free modulated molecular beam sampling system was used to obtain the mass spectrum of N_2F_4 and to study ionization and dissociation processes in N_2F_4 and NF_2 [477]. Surprisingly, dissociation of N_2F_4 into NF_2 radicals at 300 K at very low pressures, for which the degree of dissociation should be almost 100% at equilibrium, was found to be a slow process, an N_2F_4 molecule readily surviving the order of 10^6 wall collisions without decomposing. To obtain substantial conversion of N_2F_4 into NF_2 , it was necessary to send the sample through a heated line at the inlet of the mass spectrometer. Appearance potentials were determined for selected ions from N_2F_4 and NF_2 and the relevant processes identified. The bond dissociation energy $D(\text{F}_2\text{N}-\text{NF}_2) = 0.94 \pm 0.1 \text{ eV} = 90.4 \pm 13.4 \text{ kJ/mol} = 21.6 \pm 3.2 \text{ kcal/mol}$ was directly obtained from the appearance potentials of the NF_2 ion from NF_2 and N_2F_4 . Other thermochemical energies were measured as follows: $D(\text{NF}-\text{F}) = 3.15 \pm 0.10 \text{ eV} = 304 \pm 9.6 \text{ kJ/mol} = 72.8 \pm 2.3 \text{ kcal/mol}$, ionization potential (N_2F_4) = $12.00 \pm 0.1 \text{ eV}$, ionization potential (NF_2) = $11.76 \pm 0.1 \text{ eV}$, and ionization potential (NF) = $12.24 \pm 0.1 \text{ eV}$.

At higher temperatures, N_2F_4 decomposes to a mixture of NF_3 and N_2 :



The pyrolysis of N_2F_4 has been studied from 578 to 791 K [478–480]. The reaction rates were measured, and the effects of surface area to volume, inert diluent gas pressure, and nitric oxide (a radical scavenger) addition have been examined. The reaction rate was found to exhibit good second-order behavior at temperatures above 678 K. The general rate expression is

$$k_1 = 10^{9.0 \pm 0.4} \exp \left(-36950 \pm \frac{500}{RT} \right)$$

where k_1 is the rate constant in s^{-1} and T is the temperature in kelvin.

The shock-initiated thermal dissociation of $\text{N}_2\text{F}_4 \rightleftharpoons 2\text{NF}_2$ in excess argon and nitrogen has been investigated over the temperature range 351–453 K at total pressures 1.0–9.4 atm in Ar and 0.69–12.0 atm in N_2 [481]. The progress of the reaction behind incident shock waves was followed by monitoring the NF_2 radical concentration in absorption at 260 nm using a time-resolved spectrophotometric technique. Assuming that the activation energy in the high-pressure limit may be approximated by the enthalpy of reaction, the high-pressure limiting rate constant was given by

$$k_{Ar} = 10^{15.37} \exp(-19800/RT)$$

where k_{Ar} is the rate constant in argon in s^{-1} and T is the temperature in kelvin. A similar value was obtained from the N_2F_4 - N_2 data. At pressures below 2 atm, the rate was essentially in the second-order region, and the bimolecular rate constants for the N_2F_4 -Ar data were found to be in good agreement with literature values. The combined data may be represented by

$$k_{\text{bi}}^{\circ} = 10^{13.56 \pm 0.1} \exp\left(-15300 \pm \frac{600}{RT}\right)$$

where k_{bi}° is the bimolecular rate constant in $\text{mol}^{-1} \text{s}^{-1}$ and T is the temperature in kelvin.

3.4.2 Photolysis of Tetrafluorohydrazine

It was hoped that photolysis of NF_3 or N_2F_4 in the presence of an excess of fluorine would produce higher fluorides of nitrogen ($\text{NF}_5?$), but that has not yet been shown. The other reason that the photolysis of N_2F_4 was studied in detail is that N_2F_4 may be used as a source of fluorine atoms in chemical lasers with D_2 . A pulsed CO_2 laser was used to initiate and sustain the dissociation of N_2F_4 by depositing energy directly in the vibrational degrees of freedom [482]. The photolytic dissociation proceeded at an initial rate that far exceeded the measured thermal dissociation rate.

Stimulated laser emission was obtained as a result of vibration-rotational transitions in HF and DF molecules in $\text{N}_2\text{F}_4 + \text{H}_2$ and $\text{N}_2\text{F}_4 + \text{D}_2$ mixtures [483]. The stimulated emission was initiated by CO_2 laser pulses of $\lambda = 10.3 - 10.6 \mu\text{m}$ wavelength. The peak output power of the HF laser was 500 W and that of the DF laser was 1000 W for pulses of 1.2 and 0.5- μs duration, respectively.

Tetrafluorohydrazine induced passive Q-switching in a CW CO_2 laser in both the P and R branches of the 10.4- μm system, showing comparable effectiveness on all the accessible lines [484]. At higher pressures, this gas forced the laser to oscillate in the 9.3- μm system in non-frequency-selective cavities.

The photodissociation of N_2F_4 by a strong nanosecond-duration CO_2 laser pulse was studied by probing the interaction volume with both UV and IR beams [485]. Up to 20% of the molecules were found to be dissociated into NF_2 during the first few nanoseconds following the passage of the pulse.

The dissociation of N_2F_4 by CO_2 laser radiation and the N_2F_4 fluorescence were measured at very low pressures from 5 $\mu\text{m Hg}$ down to the collision-free region [486, 487]. The products of thermal heating and collision-free multi-photon absorption were distinguished via the time-resolved UV absorption of NF_2 following the laser pulse. The rate constant for dissociation of vibrationally excited N_2F_4 was $k = (1.0 \pm 0.4) \times 10^6 \text{ LMW}^{-1} \text{ cm}^{-3} \text{ s}^{-1}$ at a N_2F_4 partial pressure of 0.28 mbar and argon diluent partial pressure of 1 mbar.

An online diagnostic system was used to investigate the kinetics of the $\text{N}_2\text{F}_4 = 2\text{NF}_2$ dissociation in a high-power pulsed CO_2 laser field [488]. It was found

that at N_2F_4 pressures of 3–15 mmHg and incident energy densities of 0.2–3 J/cm², collisions did not have a significant influence on the excitation and dissociation process, and its rate was governed by the rate of radiative activation of the molecules. The intramolecular relaxation time of N_2F_4 was estimated from the experimental results. The experiment was interpreted satisfactorily, assuming that the behavior of N_2F_4 molecules in the field is characterized only by the dependence of the stimulated transition cross-section on the molecular energy $\sigma(E)$ and by the dissociation energy that corresponds to the breaking energy of the weakest N–N bond. At low excitation levels (~1 photon/molecule), the process was in thermodynamic equilibrium, and its kinetics was governed by the condition for adiabatic dissociation [489]. An increase in the energy input to ~3 photons/molecule gave rise to a radiative dissociation stage that was independent of pressure. This was followed by non-equilibrium collisional dissociation involving additional activation with a radiative molecular energy distribution function.

Saturation parameters and absorption characteristics of N_2F_4 at 10.6 μm were studied using an intense 1.5-ns excitation pulse and a low-CW CO_2 laser-probe beam [490]. It was found that, for short-pulse interaction, a four-level model could describe satisfactorily the experimental results at pressure up to 120 mmHg. The main parameters of the model were a rotational-rotational exchange constant of 47 ns $\times$ mmHg, a fundamental radiative cross-section of 1×10^{-16} cm², a contribution of 1/60 of the ground-state population to absorption, and a residual absorption coefficient equal to 20% of the small signal absorption at low pressure.

The photolysis of N_2F_4 in the presence of bromine gives N_2F_2 [491, 492].

3.4.3 Radiolysis of Tetrafluorohydrazine

Exposure of liquid N_2F_4 at 77 or 105 K to intense X-ray radiation from a 3-MeV X-ray source with dose rates up to 100 Mrad/h resulted in the formation of a mixture of N_2 , F_2 , NF_3 , *cis*- N_2F_2 , and *trans*- N_2F_2 [243, 244]. The evolution of decomposition products was analyzed by online mass spectrometry. The F_2 concentration peaked after 10 min and then dropped to zero. No higher fluorides of nitrogen (NF_5 ??) were found.

3.5 Handling of Tetrafluorohydrazine

The odor of N_2F_4 is very irritating and similar to that of elemental fluorine. Very little information is available on short-term and long-term toxicity of N_2F_4 .

When N_2F_4 was still commercially available, it was stored and shipped in steel cylinders conforming to ICC-3 AA-2265 regulations at 6.8 atm (100 psi). At the point of manufacture, larger quantities were stored as a cryogenic liquid in copper vessels holding up to 10 kg of N_2F_4 .

3.6 Compatibility with and Corrosion of Materials in Tetrafluorohydrazine

Organic materials of construction, for instance glass-fiber reinforced plastics, are not suitable for operation with N_2F_4 . The oil in vacuum pumps connected to N_2F_4 systems must only be of the perfluorinated kind.

3.7 Handling and Safety Properties of Tetrafluorohydrazine

In 1986, the U.S. Air Force showed a renewed interest in N_2F_4 and initiated a summary of known test results and handling safety. Because only limited testing had been conducted initially on N_2F_4 , further tests were considered necessary. To further characterize N_2F_4 hazards, tests determining flammability, spontaneous ignition, incompatibility, and explosion hazards, as well as the toxicity and environmental effects, were recommended. Flame ignition and propagation tests were recommended using standard techniques for measurement of flammability limits, ignition energies, the maximum experimental safety gap, and burning velocity to determine flammability hazards. Incompatibility hazards should be assessed by corrosion studies performed on materials exposed to liquid and vapor N_2F_4 , in addition to shock-sensitivity tests performed on non-metallic materials after exposure.

3.7.1 Toxicity of Tetrafluorohydrazine

Rats and dogs were exposed to several concentrations of N_2F_4 below the previously determined rat 15 and 60-min LC50s to determine the intermediate, non-lethal level effects [493]. No histopathologic changes were observed in animals exposed to lethal or sub-lethal concentrations of N_2F_4 in the 15 and 60-min exposures. However, some pathologic changes involving the lungs, spleens, and livers were observed in animals exposed to lethal concentrations in the 4-h exposures. The toxic signs were cyanosis, hematologic changes, and eye and nasal irritation. Rats showed signs of eye and nasal irritation at concentrations causing no such effects in dogs. However, at these concentrations dogs had a greater increase in methemoglobin in the blood than did the rats.

Early on in preparing for animal-exposure studies, it was recognized that N_2F_4 was so unstable in the atmosphere that there was some doubt whether exposed animals would ever come into contact with the unadulterated parent compound. Studies of N_2F_4 poisoning were therefore paralleled by, and became dependent upon, chemical studies that were begun in an effort to identify the terminal products to be expected of the reaction of N_2F_4 with moist air. Inhaled N_2F_4 at concentrations of 1% (10000 ppm) in air was lethal to rats after about 25 min of exposure [283]. Thirty-minute exposures to 1% N_2F_4 were found to be lethal before the end of exposure in every case. Exposures at this concentration for 25 min usually resulted in death before removal from the exposure chamber or within 10 min after removal. Twenty minutes

in this atmosphere was not lethal. Lethally affected animals occasionally died within the few minutes after emergence from the chamber, but if they survived this period, they rarely died. The tests indicated that the acute lethal effect of N_2F_4 inhalation may be due to methemoglobin formation. N_2F_4 caused a localization of fluoride in red blood cells that persisted at least 24 h, and in these respects was similar to the effect of NF_3 .

Exposure to 10000 ppm N_2F_4 for 25 min or longer was lethal to rats [494]. If N_2F_4 did not decompose prior to inhalation, lethal concentrations caused oxidation to methemoglobin of as much as 65% of total hemoglobin. Decomposed N_2F_4 was approximately as lethal, however, with only moderate formation of methemoglobin. The LD50 of the gas injected intraperitoneally was about 0.5 mmol/kg, with limited methemoglobinemia. The chemistry of N_2F_4 decomposition in air was reviewed in the context of toxic atmospheres expected after accidental release of the agent. As long as intact N_2F_4 remains in an atmosphere, the principal degradation products present will be NO and HF. With the disappearance of N_2F_4 , NO_2 will accumulate. N_2F_4 exposure is thus to a mixture of N_2F_4 and hydrolysis products.

3.7.2 Detonability of Tetrafluorohydrazine

Tetrafluorohydrazine or nitrogen trifluoride is not detonable under most conditions of initiation, in contrast to other nitrogen halides such as nitrogen trichloride or nitrogen triiodide. In a steel pipe with a diameter of 1 in and length of 8 in initiated with booster charges consisting of two tetryl pellets with diameter of $1 \times 1\text{-}5/8$ in, a charge of liquid N_2F_4 was not detonable [495]. The temperature range was -196 to 100°C .

In another test with 2.5-cm (1-in.) internal-diameter charges initiated by 100-g tetryl boosters, no propagation was observed [496]. In adiabatic compression U-tube tests, none of the samples exploded under the conditions tested.

3.8 Environmental Effects of Tetrafluorohydrazine

Several inorganic fluorides were reviewed for their chemical, physical, toxicologic, and environmental effects properties [300]. Seeds and seedlings of bean, corn, pea, squash, and Sudan grass were exposed to air or water mixtures of these compounds. Exposure of dry seeds to a gaseous 100% NF_3 atmosphere for 1–8 h caused inhibition of subsequent germination depending on the seed species. Exposure of seeds to a 10% N_2F_4 atmosphere for 1 h completely inhibited germination of all five species of seeds. Concentrations of N_2F_4 or NF_3 up to 10000 ppm in air were required to cause visible damage of plant seedlings after a 30–60-min exposure period.

3.9 Applications of Tetrafluorohydrazine

3.9.1 Laser Applications of Tetrafluorohydrazine

Similar to chemical lasers using difluorine or nitrogen trifluoride to generate fluorine atoms that can then react with hydrogen or deuterium in a lasing cavity, tetrafluorohydrazine or its dissociation product difluoroamino free radical is a good source for fluorine atoms as well [303].

A laser emission spectrum was investigated of excited DF molecules produced by chemical reaction in mixtures of $D_2 + F_2$, $D_2 + NF_3$, $D_2 + N_2F_4$, and $D_2 + NO_2F$ at a pressure of ~ 133 Pa (~ 1 mm Hg) [497]. The largest number of laser lines (including those in the 1-0 band) was observed in the $D_2 + NF_3$ laser. The increase and decay behavior of the intensity of different lines elucidated peculiarities ascribed to a temperature increase of the mixture during the reaction and to cascade transitions.

4 Difluorodiazene

Difluorodiazene, N_2F_2 , is of no use as a rocket propellant. We mention it here only because it is a frequently observed undesirable, explosive contaminant of other more desirable nitrogen fluorides. Its properties must be known to be able to identify it as a contaminant and to eliminate it from improved preparation methods for NF_3 and N_2F_4 , which have industrial uses and have been evaluated as rocket and laser propellants. Difluorodiazene has been found to be an active polymerization initiator for fluoropolymers such as tetrafluoroethylene. It is an intermediate in the synthesis of fluoronitrogen salts, which are more stable than the N_2F_2 they are made from.

Difluorodiazene, N_2F_2 , (also called dinitrogen difluoride, 1,2-difluorodiazene, 1,2-difluorodiimide, or difluorodiazene) is a colorless gas. It exists in two stereoisomers, a *cis*- and a *trans*-difluorodiazene. The CAS RN of *cis*-difluorodiazene is [13812-43-6], and the CAS RN of *trans*-difluorodiazene is [13776-62-0]. The existence of an unsymmetrical isomer, 1,1-difluorodiazene, has been proven to be very unlikely.

4.1 Preparation of Difluorodiazene

Difluorodiazene was first obtained during the thermal decomposition of azidofluoride N_3F . N_2F_2 is also obtained as an unwanted by-product during the production of NF_3 by electrolysis of a NH_4HF_2 melt [498, 499].

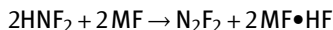
Products of the reaction of NF_3 with mercury in a glow discharge are tetrafluorohydrazine, difluorodiazene, mercury fluorides, and nitrogen [386]. The yield of a given product can be varied by changing the NF_3 pressure, discharge current density, and the temperature of the discharge tube. The NF_3 is separated from the tetrafluorohydrazine and difluorodiazene by fractional distillation from an 87-K (-186°C) trap

cooled with liquid argon to a 77-K (-196°C) trap. With parallel fractionating systems, the discharge tube can be operated almost continuously with a minimum of NF_3 . The reaction products are essentially free of contamination. Mass spectrometer analyses have shown them to contain 0.1% of nitrogen oxides or silicon tetrafluoride. Tetrafluorohydrazine and the two forms of difluorodiazene can be separated by gas adsorption chromatography using a 5-ft silica gel column at 233 K (-40°C).

Pyrolysis of NF_3 in an electric arc results in the formation of some difluorodiazene as the pyrolysis product, a very wasteful procedure [500]. Difluorodiazene can also be obtained if one allows elemental fluorine to react with sodium azide at 293–343 K (20 – 70°C) [96, 97, 501]. Reactions of N_2F_2 with SF_4 , SO_2 , NO , and SbF_5 have been described [502]. The reaction of N_2F_2 with SbF_5 forms a salt $[\text{N}_2\text{F}]^+[\text{SbF}_6]^-$. Difluorodiazene is an unwanted byproduct of the production of tetrafluorohydrazine by hydrolysis of *N,N*-difluorourea, mostly done at low temperatures and high concentrations of caustic [503]. Pure *trans*- N_2F_2 can be obtained by reaction of N_2F_4 with AlCl_3 [504].

The scaled-up preparation of both *trans*- and *cis*- N_2F_2 using the Hurst-Khayat method is described in detail in [505–507]. The apparatus used in the preparation of *trans*- N_2F_2 followed the design described by Hurst and Khayat. The reactor consisted of a glass U-trap (~ 250 mL volume) connected to a vacuum line by ball joints. In a typical run, 15–18 g of dry AlCl_3 was sublimed onto the walls of the reactor. The reactor was cooled to 193 K (-80°C) and evacuated. One arm of the glass reactor was connected to a storage bulb containing 30 mmol N_2F_4 . The bulb was cooled to 138 K (-135°C) in order to maintain a pressure of 15–20 mm Hg during the run. The other arm of the reactor led to a manometer, and a train of collecting traps opened to a vacuum pump. Between the reactor and set of collecting traps was a Teflon needle valve, with which the flow of N_2F_4 through the reactor could be controlled. To initiate the reaction, 15 mm Hg of N_2F_4 was introduced into the reactor with the needle valve closed and was kept in contact with the AlCl_3 for 20–30 min. After the reaction was initiated, the Teflon needle valve was opened partially to allow a slow leakage of gas out of the reactor. The condensable products, *trans*- N_2F_2 , NF_3 , Cl_2 , and any unreacted N_2F_4 , were collected at 77 K (-196°C). Separation of the *trans*- N_2F_2 was effected by fractionation through 138 K (-135°C) and 77 K (-196°C) baths. Two fractionations gave a sample collected in the 77 K (-196°C) trap, which showed no Cl_2 by mass spectral analysis. The 77 K (-196°C) fraction was then left open to a vacuum pump at 77 K (-196°C) to remove the bulk of the NF_3 . Final analysis by IR showed *trans*- N_2F_2 and less than 1% NF_3 . N_2F_4 was not observed. Yields of *trans*- N_2F_2 were of the order of 10–12 mmol, or 35–40%, based on the amount of N_2F_4 used. In order to prepare *cis*- N_2F_2 , approximately 10 mmol *trans*- N_2F_2 was distilled into a 500-mL CRES-316 stainless steel container (0.5 atm) and heated overnight at 348–353 K (75 – 80°C) according to the procedure described by Hurst and Khayat. The contents of the cylinder were then cooled to 77 K (-196°C), and the non-condensables were pumped off. IR analysis of the condensable portion showed *cis*- N_2F_2 (90%), *trans*- N_2F_2 (10%), and a trace of NF_3 . The total recovery yield of N_2F_2 was 80–90%.

Difluorodiazene can be prepared by reaction of difluoroamine with alkali metal fluorides [508, 509]:



The photolysis of N_2F_4 in the presence of bromine gives N_2F_2 [491, 492].

4.2 Physical Properties of Difluorodiazene

The boiling point of *cis*-difluorodiazene was estimated to be 167.5 K, a few degrees higher than that of *trans*-difluorodiazene. The boiling point of *trans*-difluorodiazene was found at 161.8 K, and the freezing point was at 101 K.

The isomers of N_2F_2 have been characterized in the past by their reactivity toward mercury. Investigation of the IR spectra showed that inactive N_2F_2 is *trans*-1,2-difluorodiazene and may be identified by the single strong band centered at 989 cm^{-1} [510]. The suggestion that active N_2F_2 resembles 1,1-difluorodiazene instead of a *cis*-isomer was later proven by other investigators to be in error.

In order to determine the molecular structure, the microwave spectra of the $\text{F}^{14}\text{N}^{14}\text{NF}$ and $\text{F}^{15}\text{N}^{14}\text{NF}$ isotopic forms of the “active” isomer of N_2F_2 were measured in the gas phase [511, 512]. From this information the structure could be derived as planar and *cis* with the following structural parameters: $d(\text{N}-\text{N}) = 1.214 \pm 0.005\text{ \AA}$, $d(\text{N}-\text{F}) = 1.384 \pm 0.01\text{ \AA}$, $\angle\text{FNN} = 114.5 \pm 0.5^\circ$. The dipole moment $0.16 \pm 0.01\text{ D}$ was derived from the rotational Stark effect. From relative intensity measurements of an excited vibrational, a vibrational frequency of $300 \pm 35\text{ cm}^{-1}$ was estimated.

The assignment of ^{19}F NMR spectra of the two isomers of N_2F_2 was consistent with the assumption of *trans* and *cis* 1,2-difluorodiazene structures for these molecules [513]. The qualitative features of the $^{19}\text{F} - \{^{14}\text{N}\}$ double-resonance spectra and a comparison of the ^{19}F NMR spectra at 56.4 and 40.0 MHz strongly favored a *cis* structure over a 1,1-difluorodiazene structure for the more reactive isomer. A comparison of the indirect N—F coupling constants for the two isomers indicated that the $\angle\text{FNN}$ angles are probably quite different for *cis* and *trans* N_2F_2 .

Initial assignments of fundamental vibrations in gaseous *trans*-difluorodiazene based on IR and Raman spectra were as follows: $\nu_{\text{NN}} = 1522\text{ cm}^{-1}$, $\nu_{\text{NF}} = 1010\text{ cm}^{-1}$, $s\delta_{\text{NF}} = 600\text{ cm}^{-1}$, $a\nu_{\text{NF}} = 990\text{ cm}^{-1}$, $a\delta_{\text{NF}} = 423\text{ cm}^{-1}$, and torsion = 363.5 cm^{-1} [514].

The Raman spectrum of *cis*- N_2F_2 has been measured, and the assignment of the in-plane fundamentals was established as follows: $\nu_1 = 1526\text{ cm}^{-1}$, $\nu_2 = 884\text{ cm}^{-1}$, $\nu = 341\text{ cm}^{-1}$, $\nu_6 = 945\text{ cm}^{-1}$, $\nu_{6'} = 729\text{ cm}^{-1}$ [515]. There was a weak feature in the Raman spectrum at $\sim 550\text{ cm}^{-1}$ that may be the torsional fundamental. The IR spectrum was then remeasured, and the 341 cm^{-1} vibration was located as a type-B band.

Two type-A bands of *trans*- N_2F_2 have been resolved and analyzed to yield estimates of the rotational constant $B_c = (B + C)$ of 0.14821 and 0.14876 cm^{-1} [516]. These values were consistent with the geometry previously obtained from electron diffrac-

tion measurements; i.e., $r_{\text{N-N}} = 1.224 \text{ \AA}$, $r_{\text{N-F}} = 1.397 \text{ \AA}$, $\angle \text{NNF} = 106.3^\circ$. Two type-B and two type-C bands have been partially resolved and aided in the description of the molecular structure.

The Raman spectrum of gaseous *trans*-N₂F₂ has been recorded and analyzed [517]. All three symmetric vibrations were obtained and assigned as follows: N—F symmetric stretch, 1018 cm^{-1} ; N—N stretch, 1523 cm^{-1} ; and N—N—F symmetric bend, 603 cm^{-1} . The IR and Raman spectra proved that the structure of *trans*-N₂F₂ belongs to point group *C*_{2h}. The Raman data also made possible a more complete assignment of the IR combination lines.

4.2.1 Molecular Structure of Difluorodiazene

Two planar isomers of N₂F₂ are known, the *cis* isomer (*C*_{2v}, melting point 78 K, boiling point 167.3 K, dipole moment 0.18 D) and *trans* isomer (*C*_{2h}, melting point 101 K, boiling point 161.8 K, dipole moment 0 D). The conversion of one form into the other can be achieved by warming, whereby the *trans* isomer is the more stable and less reactive form of the molecule. At 298 K the equilibrium has about 90% *cis* and 10% *trans*, and at about 342 K the *trans* isomer rearranges to the *cis* form. The unsymmetrical structural isomer F₂N=N could not be isolated and exists only on paper or as a short-lived transient during the decomposition of other fluorides.

The shortening of the N=N bond in the *cis* isomer, which is accompanied by a lengthening of the N—F bond, can be explained by negative hyperconjugation.

Synthesis of N₂F₂ by the electrolysis of ammonium bifluoride invariably leads to a mixture of the *cis* (85%) and *trans* (13%) isomers. Thermodynamically the *cis* form is favored over the *trans* form, the barrier being 134 kJ/mol (32 kcal/mol). Structure studies revealed that both molecules are planar, with an N—N distance of 1.25 Å and a *d* N—F of 1.44 Å in the *trans* form and *d* N—F of 1.384 Å in the *cis* form [518].

The decomposition of ¹⁵N₃F at 253 K (−20 °C) leads to a mixture of *cis*- and *trans*-¹⁵N₂F₂. The corresponding ¹⁹F NMR spectra were analyzed as [AX]₂ systems. ¹⁹F, ¹⁵N, and ¹⁴N NMR spectra were simulated using the DSYMPCD, DCYMPCD, and WIN-DAISY programs running under WIN-NMR [519]. Stereospecific coupling constants were obtained for both isomers. Comparison of the ¹⁹F NMR spectra from both ¹⁵N₂F₂ and ¹⁴N₂F₂ overcomes the inherent ambiguities of the analysis.

Isopropyl-*N,N*-difluorocarbamate is a stable liquid. Reaction of isopropyl-*N,N*-difluorocarbamate with potassium *tert*-butoxide gives a quantitative yield of difluorodiazene in a mix of 3 : 1 of *trans*:*cis* stereoisomers [520]. When isopropyl-*N,N*-difluorocarbamate is added to a chilled solution of aniline in methylene chloride, difluoroamine is obtained instead. Difluoroamine has been known to explode violently and must be handled using precautions. See also [521–525].

A semiempirical molecular orbital (MO) method (CNDO/2) with empirical constants adjusted to give agreement with ground-state geometries has been used to study

isomerization mechanism in the N_2F_2 system [526]. Calculated transition states did not correspond to the simple postulated transition states.

The isomerization of *trans*- N_2F_2 to *cis*- N_2F_2 going through $[\text{N}_2\text{F}^+][\text{AsF}_6^-]$ was unpredictable, erratic, required two steps, and consumed an equimolar amount of AsF_5 . It was found that catalytic amounts of SbF_5 at 303 K (30 °C) can achieve this isomerization, but they still result in substantial N_2F_2 losses due to $[\text{N}_2\text{F}^+][\text{SbF}_6^-]$ formation [527]. When the reaction was carried out at 333 K (60 °C), surprisingly, $[\text{NF}_4^+][\text{SbF}_6^-] \cdot n\text{SbF}_5$ was formed. AlF_3 was also studied as a catalyst for the N_2F_2 isomerization and was found to be an ideal catalyst, resulting in very high conversions of *trans*- N_2F_2 and high yields of *cis*- N_2F_2 . AlF_3 can be used repeatedly without loss of activity or N_2F^+ salt formation.

4.2.2 Thermodynamic Properties of Difluorodiazene

The thermodynamic properties of the two difluorodiazenes are summarized in Table 18.

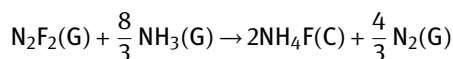
Table 18: Thermodynamic properties of difluorodiazenes.

Property	Units	<i>cis</i> -difluorodiazene	<i>trans</i> -difluorodiazene
$\Delta_f H^\circ_{\text{gas}}$	kJ/mol	+68.62	+81.17
$S^\circ_{\text{gas, 1 bar}}$	J mol ⁻¹ K ⁻¹	259.80	262.63

Data source: [132]

Once the IR absorption bands of a molecule are known, the vibrational frequencies and moments of inertia can be calculated, and from there the thermodynamic functions can be derived [528].

The heats of reaction associated with the reaction



were observed for two mixtures containing the *trans* and the “active” isomeric forms of difluorodiazene in different proportions [529]. From the observed heats of reaction of the two samples, the heat of isomerization ΔH_{298} of “active” to *trans*- N_2F_2 was found to be 12.5 kJ/mol (3.0 kcal/mol). With the use of known auxiliary data for NH_3 and NH_4F , the heats of formation $\Delta H_f^\circ_{298}$ were determined to be +81.1 and +68.6 kJ/mol (+19.4 and +16.4 kcal/mol) for the gaseous *trans* and the “active” isomers, respectively. A similar method had previously been used by the same authors to determine the enthalpy of formation of nitrogen trifluoride.

The energy barrier to isomerization is $k = 10^{14} \exp(-32.2 \text{ kcal}/RT) \text{ s}^{-1}$ [530]. In this study, *trans*-difluorodiazene, highly diluted in argon (1:70), was heated in a single-

pulse shock tube. The reaction mixture was heated by reflected shock waves to elevated temperatures, where it reacted for a short period of time.

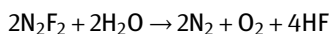
A calorimetric method was used to determine the enthalpies of formation ΔH°_{f298} of several nitrogen fluorides, based on their reaction with aqueous KI solutions in a calorimeter [139]. The values of ΔH°_{f298} recommended for *cis*-N₂F₂ (assumed to be identical for *trans*-N₂F₂) were listed. From the ΔH°_{f298} and ΔS°_{f298} values, the thermodynamic bond energies for the nitrogen fluorides were calculated.

4.3 Thermal Stability of Difluorodiazene

Difluorodiazene is unstable at room temperature and will decompose to nitrogen and nitrogen trifluoride. Difluorodiazene can be stored only at temperatures below 203 K (−70 °C). If it is heated rapidly to above 473 K (200 °C), decomposition may proceed with explosive speed. At 570 K, N₂F₂ dissociates to the elements.

4.4 Reactions of Difluorodiazene

Many investigators have commented on the differences in reactivity between *cis*- and *trans*-difluorodiazene. The two isomers react very differently. The *cis* form is more stable as well as more reactive. The *trans* form can be stored in glass vessels, whereas the *cis* form reacts slowly with glass to form SiF₄ and N₂O. However, *trans*-difluorodiazene is only slightly more resistant to chemical attack by water and aqueous acids than is *cis* isomer. Both are unaffected by water at 333 K (60 °C) for a period of 15 h [203, 504]. The *cis* isomer reacts slowly at 347 K (74 °C) (30% decomposed in 17 h), while the *trans* isomer reacts at a similar rate at 362 K (89 °C). In both cases, the hydrolysis products are nitrogen, oxygen, and hydrogen fluoride. The strong nucleophile OH[−] does not significantly accelerate the reaction, and very little N₂O is formed. This indicates that the hydrolysis does not proceed by nucleophilic attack on N₂F₂.



4.4.1 Salts of Difluorodiazene

The reaction of N₂F₂ with strong Lewis acids forms fluorodiazonium (fluorodiazonium) N₂F⁺ salts. The existence of solid adducts of N₂F₂ and Lewis acids, such as AsF₅ and SbF₅, is well known. In all cases an IR band at about 1060 cm^{−1} was observed that was attributed to the N—F stretching vibration of the N₂F⁺ cation. N₂F⁺ salts are important precursors in the synthesis of N₅⁺ compounds, and better production methods are needed for their larger-scale production. For the preparation of N₅⁺ salts on a larger scale, it was necessary to prepare the corresponding precursors in an efficient manner and in larger quantities [531].

cis-Difluorodiazine and arsenium pentafluoride react at or below room temperature to form a solid fluorodiazonium hexafluoroarsenate $[\text{N}_2\text{F}^+][\text{AsF}_6^-]$ that is stable up to 323 K (150 °C) and is soluble in anhydrous H_2F_2 [532, 533].

The existence of trifluorodiazyl ions in BrF_5 and in IF_5 was established by ^{19}F NMR and IR analyses. Solutions of $\text{N}_2\text{F}_3\text{AsF}_6$ in IF_5 treated with perchlorates showed absorptions of N_2F_3^+ and ClO_4^- in the IR [534]. Attempts to isolate trifluorodiazyl perchlorate from solution were not successful. An attempt to prepare N_3F_5 by reaction of $\text{N}_2\text{F}_3\text{AsF}_6$ with triphenyl fluoroaminomethane at 203 K (−70 °C) resulted in the formation of N_2F_4 and *trans*- N_2F_2 . Attempts to prepare new interhalogen oxides by the fluorination of $\text{Cl}_2\text{O}_2\text{AsF}_6$ and $\text{NOClO}_2\text{AsF}_6$ were unsuccessful.

The IR and Raman spectra for $[\text{N}_2\text{F}]^+[\text{AsF}_6]^-$ and $\text{N}_2\text{F}_2 \cdot 1.3\text{SbF}_5$ were reexamined, and previous assignments of the two stretching modes for N_2F^+ were confirmed, but the deformational mode was shown to occur at 390 cm^{-1} and not at 803 cm^{-1} [535]. Force constants were then calculated for N_2F^+ and compared to those of a series of isoelectronic molecules and ions.

A new, marginally stable N_2F^+ salt, $\text{N}_2\text{F}^+\text{Sn}_2\text{F}_9^-$, was prepared and characterized [536, 536]. A crystal structure was obtained for $\text{N}_2\text{F}^+\text{Sn}_2\text{F}_9^-$, resulting in the first observation of individual $\text{N}\equiv\text{N}$ and $\text{N}-\text{F}$ bond distances for N_2F^+ in the solid phase. The observed $\text{N}\equiv\text{N}$ and $\text{N}-\text{F}$ bond distances of 1.089 and 1.257 Å, respectively, are among the shortest experimentally observed $\text{N}-\text{N}$ and $\text{N}-\text{F}$ bonds. High-level electronic structure calculations showed that *cis*- N_2F_2 is more stable than *trans*- N_2F_2 by 1.4 kcal/mol at 298 K. The calculations also demonstrated that the lowest uncatalyzed pathway for the *trans-cis* isomerization of N_2F_2 has a barrier of 251 kJ/mol (60 kcal/mol) and involves rotation about the $\text{N}=\text{N}$ double bond. This barrier is substantially higher than the energy required for the dissociation of N_2F_2 to N_2 and 2F. Therefore, some of the N_2F_2 dissociates before undergoing an uncatalyzed isomerization, with some of the dissociation products probably catalyzing the isomerization. Furthermore, it was shown that the *trans-cis* isomerization of N_2F_2 is catalyzed by strong Lewis acids, involves a planar transition state of symmetry C_s , and yields a 9:1 equilibrium mixture of *cis*- N_2F_2 and *trans*- N_2F_2 . The increased reactivity of *cis*- N_2F_2 with Lewis acids and the exclusive formation of *cis*- N_2F_2 in the reaction of N_2F^+ with F^- can be explained through its electronic structure. Only *cis*- N_2F_2 and not *trans*- N_2F_2 forms N_2F^+ salts with Lewis acids. The geometry and vibrational frequencies of the $\text{F}_2\text{N}=\text{N}$ isomer have also been calculated and imply strong contributions from ionic $\text{N}_2\text{F}^+ \text{F}^-$ resonance structures, similar to those in F_3NO and FNO .

Solutions of N_2F_2 in SbF_5 are initially blue but fade rapidly to yellow. Electron magnetic resonance was used to determine whether the blue color originates from free radicals [537].

Raman spectra supplement the information that can be obtained from IR spectra. In particular, the existence of an N_2F^+ ion in the solid adduct obtained from N_2F_2 and AsF_5 could be proven by this method [538].

The $\text{N}_2\text{F}^+\text{AsF}_6^-$ salt was prepared from *trans*- N_2F_2 by thermal *trans-cis* isomerization in the presence of AsF_5 at 343 K (70 °C) [539]. The crystal structure of $\text{N}_2\text{F}^+\text{AsF}_6^-$ is monoclinic, space group $C2/m$ with $a = 9.184(5) \text{ \AA}$, $b = 5.882(2) \text{ \AA}$, $c = 5.160(2) \text{ \AA}$, $\beta = 90.47(4)^\circ$, $Z = 2$. The resulting N—F bond length of $1.217 \text{ \AA}$ is by far the shortest presently known N—F bond, while the N—N bond length of $1.099 \text{ \AA}$ is comparable to the shortest presently known $\text{N}\equiv\text{N}$ bond length of $1.0976 \text{ \AA}$ in N_2 . The surprising shortness of both bonds is attributed to the high s-character (sp hybrid) of the σ -bond orbitals on nitrogen and the formal positive charge on the cation. Upon going from sp^3 hybridized NF_4^+ ($1.30 \text{ \AA}$) to sp hybridized N_2F^+ , the N—F bond is shortened.

5 Other Nitrogen Fluorides

5.1 Nitrogen Pentafluoride

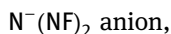
In the hope of replicating the synthesis of chlorine pentafluoride from the trifluoride and elemental fluorine under extreme conditions, 1:1 mixtures of nitrogen trifluoride and difluorine at very high pressures (8.1–9.5 MPa [80–94 atm]) were irradiated with fission fragments and neutrons created by fission of fully enriched $^{235}\text{UF}_6$ within the sample capsules [540]. Gas chromatography showed a new compound that was not identical to either *cis*- or *trans*- N_2F_2 or N_2F_4 and eluted at a retention time indicating a boiling point of 223 K (−50 °C). Mass spectrometry showed a peak at $m/e = 90$ that could be NF_4^+ or a fragment of the unknown F_3NNF_3 . This observation has not been repeated or confirmed by other investigators. If NF_5 existed, it would make a good rocket propellant oxidizer.

The structure, bonding, harmonic vibrational frequencies, and decomposition reactions of NF_5 were studied employing five different computational methods with single, double (CCSD), and perturbative triple excitations in conjunction with different basis sets. [541] The overall $\text{NF}_5 \rightarrow \text{NF}_3 + \text{F}_2$ reaction is exothermic with 176 kJ/mol (42 kcal/mol). The trigonal-bipyramidal form of $\text{NF}_5(D_{3h})$ was found to be a minimum at all levels of theory. A natural bond orbital comparison of NF_5 and PF_5 revealed the much greater polarity of the P—F than the N—F bonds. The weak ionic character and the relatively short $\text{F}\cdots\text{F}$ separations, within the sum of the van der Waals radii, are responsible for the metastable nature of NF_5 .

If NF_5 existed, it would be a violation of the octet rule that has governed chemical bond and molecular orbital theory for a long time, stating that the outer valence shell of second-row elements of the periodic table of elements (Li to Ne) cannot hold more than eight electrons [542].

5.1.1 Nitrogen Fluoride Anions

Nitrogen fluoride anions would be useful building blocks in the synthesis of catenated polynitrogen fluorides. It has been attempted to synthesize the dinitrogen fluoride anion N_2F^- or the trinitrogen difluoride anion N_3F_2^- by reaction of $(\text{CH}_3)_4\text{N}^+\text{F}^-$ with N_2F_2 , N_2F_4 , FNO , or FNO_2 , but no anions could be found [543]. One potential, still unknown nitrogen fluoride anion would be



which is analogous to the nitrite anion. A precursor for the synthesis of N_3F_2^- compounds is fluorine azide; this compound is extremely shock sensitive but can be safely used in solution.

5.2 Fluorine Azide

Fluorine azide, also known as azido fluoride, triazadienyl fluoride, N_3F , CAS RN [14986-60-8] is a very dangerous chemical. The very high heat of formation (about +544 kJ/mol [+130 kcal/mol]) of fluorine azide ($\text{N}\equiv\text{N}=\text{NF}$) makes it a candidate as an energetic material. It may be too sensitive to be used as a rocket propellant, but it can be used as a source of fluorine, fluoronitrene, and $\cdot\text{NF}$ free radicals in the study of fluorine laser reactions. It was speculated that it might be a precursor for the synthesis of the so-far unknown NF_5 or N_5F .

Fluorine azide was first prepared by reaction of hydrogen azide and difluorine [544, 545]. Good yields of FN_3 were obtained by reaction of 2 mol dry HN_3 with 1 mol F_2 gas at room temperature. The HN_3 was carried into the reaction chamber in a stream of dry N_2 at 45 cm³/min. Fluorine azide was characterized by its visible spectrum in GN_2 . In addition to a strong band at 410 mμ, weaker bands were observed at 378, 390, 397, 428, 439, and 444 nm. It was described as a greenish-yellow gas at room temperature, liquefying at 191 K (−82 °C) when diluted with nitrogen, and freezing to a yellow solid at 130 K (−143 °C). Evaporation of this solid generally resulted in a violent explosion. One drop of N_3F will pulverize any glass within a 5-cm distance. However, gaseous fluorine azide decomposed slowly at room temperature and very rapidly at 373 K (100 °C) without explosion, forming difluorodiazene (N_2F_2) and nitrogen. The thermal decomposition of gaseous N_3F into a mixture of *cis*- and *trans*- N_2F_2 and nitrogen at different temperatures was investigated quantitatively by IR spectroscopy [545]. At a pressure of 10–20 mbar and a temperature of 193 K (−80 °C), N_3F can be stored for several months without noticeable decomposition. The melting point of N_3F is 134 K (−139 °C) [546]. The vapor pressure can be expressed by the equation

$$\ln p = -(2.683 \times 10^3)/T + 17.958$$

where p is the vapor pressure in mbar and T is the temperature in kelvin. The extrapolated boiling point is 243 K (-30°C).

Microwave and IR spectra of FN_3 and its various ^{15}N -enriched isotopomers were recorded and analyzed, yielding data on molecular structure, dipole moment, and harmonic force constants [547]. The electronic and molecular structures of FN_3 and FONO_2 were calculated by using split-valence and d-orbital polarized basis sets and the GAUSSIAN 82 program [548].

Quantum chemical computations were used to describe the N_3F molecule and identify the energy levels and bond strengths [549]. The objective was to improve orbital optimization methods for different types of wave functions that could lead to substantial savings of computer time and memory and to predict new high-energy isomers for singlet and triplet states of N_3F and their kinetic stability with respect to isomerization and dissociation reactions. Additional studies also included the possibility of three-ring structured N_3F , a fluorotriazirine-type isomer [550]. The potential energy surfaces for the N_3F molecule have been studied using multi-configurational wave functions. Two new isomers were found, one on the singlet ($1\text{A}'$) and one on the triplet ($3\text{A}''$) surface. Both isomers have a three-numbered cyclic structure and C_s symmetry.

The low thermal stability of N_3F is apparent from its electronic structure determined by photoelectron spectroscopy [551].

Triazadienyl fluoride forms stable adducts with BF_3 and AsF_5 at low temperatures, as demonstrated by IR measurements [552]. The Lewis acids are bonded to the $\text{N}\alpha$ -atom of N_3F , as deduced from the data for ^{15}N -isotopically enriched N_3F . The basicity of N_3F is comparable to that of ethyne and ethene, according to the HF stretching frequency of the $\text{N}_3\text{F}/\text{HF}$ complex isolated in an argon matrix.

The burn rate of 5–80- μm -thick cryogenic films of fluorine azide was determined by schlieren photography to be $1.6 \pm 0.2 \text{ mm}/\mu\text{s}$ [553]. This rate was found to be strongly influenced by the presence of N_2F_2 , but less so by the presence of CO_2 . By analogy with the results from the gas-phase decomposition of fluorine azide, the nascent decomposition products were expected to be NF^* and N_2 . A thermal combustion mechanism driven by the energy released upon production and quenching of the excited NF^* species was proposed.

5.3 Other Nitrogen Fluorides

The possible existence of FN_5 was studied by *ab initio* electronic structure theory [554]. Calculations were carried out at various levels of theory for the $[\text{N}_5^+][\text{AsF}_6^-]$ ion pair and its decomposition to FN_5 and AsF_5 . Six possible vibrationally stable isomers of FN_5 have been identified. One of the possible structures is that of a linear 1-azido-2-fluorodiazene, CAS RN [610789-59-8]. These theoretical predictions were confirmed by an

experimental study of the thermolysis of N_5AsF_6 and $[N_5]_2SnF_6$ and the displacement of FN_5 from $[N_5]_2SnF_6$ with CsF using FTIR spectroscopy.

By way of definition, we call “binary fluorides” those that contain only one type of atom that is different from fluorine. Examples are ClF_3 and NF_3 . We call “ternary fluorides” those compounds that contain two different atoms other than fluorine. Examples are ClO_3F and NO_2F .

6 Nitrogen Oxygen Fluorides

Oxyfluorides of nitrogen, i.e., compounds containing the grouping $F-N-O$, have been known for many years in the form of simple compounds, such as nitrosyl fluoride ONF and nitryl fluoride O_2NF . Detailed studies of physical, structural, and chemical aspects of this class of compounds were conducted only after the potential of NF compounds as rocket propellants had been recognized. Several novel types of oxyfluorides of nitrogen, such as trifluoroamine oxide, F_3NO , have since been added to the list. The nitryl hypofluorite compound O_2NOF is also a potential rocket oxidizer [555, 556].

A summary of literature references on all nitrogen–oxygen–fluorine and chlorine–oxygen–fluorine compounds contains information on physicochemical properties (including spectral, structural, and thermodynamic properties) for NO_3F , FNO_2 , $ONOF$, FNO , F_2NNO , F_3NO , ClO_4F , ClO_3F , ClO_2F , $ClOF$, $ClF \cdot O_2F_2$, ClO_2F_3 , $ClOF_3$, and $ClOF_5$, along with reactivities with inorganic Lewis acids and bases [557]. It contains 159 references. Similar summaries are in [558].

6.1 Nitrosyl Fluoride

Nitrosyl fluoride (nitrosonium fluoride, NOF) is a colorless gas. It was first obtained by the addition of elemental fluorine to nitric oxide in a copper tube [559, 560]. It can also be obtained by reaction of $NOBF_4$ with NaF . The undiluted combination of nitric oxide and fluorine is a luminous flame reaction. The reaction proceeds with the emission of visible light [561]. Under different conditions, it may even produce some trifluoroamine oxide F_3NO .

Nitrosyl fluoride is not particularly suitable as a rocket propellant, and nobody has even patented it. It is interesting from a more academic point of view because of its close relationship with the more energetic nitryl fluoride and because it can form stable nitrosonium salts with Lewis acids that can be used to synthesize other energetic salts. NOF reacts with $NaOH$ to give NO , NaF , $NaNO_2$, and $NaNO_3$.

In a study of laser-induced reactions of tetrafluorohydrazine or nitrogen trifluoride with nitric oxide, nitrous oxide, nitrogen dioxide, or nitrosyl chloride, it was noted that absorption in the nitrogen fluorides of IR radiation from a CW carbon dioxide laser

initiated a number of reactions [562]. In all cases, the major product was FNO, and when nitrous oxide or nitrogen dioxide were used, FNO₂ was also produced.

The physical properties of nitrosyl fluoride are summarized in Table 19.

Table 19: Physical properties of nitrosyl fluoride.

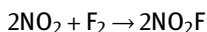
Property	SI units	MKS units	References
Melting point	140.6 K	−132.5 °C	[559]
Boiling point	213.2 K	−59.9 °C	[559]
Density, liquid		$d = 1.919 - 0.002787 \text{ g/cm}^3$	[559]
Enthalpy of formation at 298 K, gas	−66.1 kJ/mol	−15.8 kcal/mol	[563]

6.2 Nitryl Fluoride

Nitryl fluoride, also known as NO₂F, “nitronium fluoride,” nitrogen dioxygen fluoride, CAS RN [10022-50-1] is a colorless gas that was obtained by the discoverer of elemental fluorine, Moissan, in one of the first reactions performed with the newly isolated element.

6.2.1 Preparation of Nitryl Fluoride

Nitryl fluoride can be obtained by direct combination of NO₂ and F₂ in a copper vessel. The reaction is not very exothermic [559]:



The vapor–liquid fluorination of NO or NO₂ in a fluorothene vessel proceeded very smoothly to yield 90% nitrosyl fluoride, NOF, or 90% nitryl fluoride, NO₂F, respectively [564].

Passing a stream of NO₂Cl over AgF in a platinum tube at 513 K (240 °C) formed NO₂F in a yield of 5% [565, 566]. Equivalent quantities of dry HF and BF₃ introduced into a solution of N₂O₅ in nitromethane formed crystals of NO₂BF₄, which when heated with NaF at 513 K (240 °C) in a platinum tube formed NO₂F. If SiF₄ was substituted for BF₃, the intermediate was (NO₂)₂SiF₆, but it could also be used to make NO₂F. For example, about 70 mL MeNO₂ was added to 3 g N₂O₅ cooled to 223 K (−50 °C), and the substance was allowed to dissolve at 233 K (−40 °C). After the addition of 0.6 g HF and BF₃, a crystalline precipitate of [NO₂⁺][BF₄[−]] was formed. After removal of the excess reaction product and the solvent by distillation *in vacuo*, the dry substance was mixed with NaF in a platinum crucible and heated to 473 K (200 °C) *in vacuo*. NO₂F evolved and was condensed in a liquid-air-cooled cold trap.

The rate of reaction between NO_2 and F_2 to form NO_2F was measured at 300.8, 323.5, and 343.3 K (27.7, 50.4, and 70.2 °C) [567]. Light absorption by NO_2 was used to follow the reaction. The rate was found to be first order in each reactant, and it showed no dependence on the NO_2F present. The empirical second-order rate constant k_1 is that of an elementary bimolecular reaction with $A = 1.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $E = 44.0 \text{ kJ} = 10.5 \text{ kcal}$. It has been attempted to improve the yield of this method by modification of the conditions of reaction [568–571].

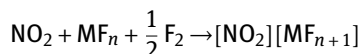
The reaction of OF_2 with NO_2 leads to a mixture of NO_2F , NO_3F , and O_2 , and the proportions of products depend on the operating pressure. At low pressure, this is a useful method for preparation of NO_2F . The thermal reaction between F_2O and NO_2 was studied at 333–353 K (60–80 °C) [572]. The reaction took place with a pressure decrease, 1 mol F_2O being used up for each 2 mol NO_2 . The reaction products varied with the total operating pressure and consisted of NO_2F , NO_3F , and O_2 . At very low pressure, only NO_2F and O_2 were formed in the mol ratio 4 : 1.

Nitryl fluoride can be prepared by first treating PF_5 with fuming HNO_3 , crystallizing the nitronium hexafluorophosphate, mixing nitronium hexafluorophosphate with pre-dried NaF in a platinum tube connected to three traps in series at 263, 193, and 83 K (–10, –80, and –190 °C), and heating the contents of the tube for 3 h at 473 K (200 °C) under a current of dry nitrogen [573]. Nitryl fluoride is a colorless gas, with boiling point 200.7 K (–72.4 °C) and melting point 107 K (–166 °C), and can be used as an oxidizer in rocket propellants.

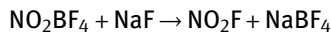
Nitryl fluoride NO_2F can be prepared by passing N_2O_4 over a stirred bed of CoF_3 at 573 K (300 °C) [574]. The condensate from the gaseous product must then be distilled from the mixture and usually gives a yield of 89%. The CoF_2 formed can be regenerated by treatment with F_2 to re-form CoF_3 . An attempt to prepare NOF by passing NO over heated CoF_3 failed because of complex formation.

Nitryl fluoride can be prepared by heating an excess of a metal fluoride with NO_2 in a reactor [575]. For example CoF_3 was placed in a reactor and heated to ~573 K (~300 °C) with stirring and passing NO_2 gas over the continuously heated bed for ~30 min. The CoF_2 remaining was later regenerated by treating it with F_2 at 523–573 K (250–300 °C), thereby quantitatively reconvertng the CoF_3 . Similarly, CeF_4 , MnF_3 , or AgF_2 were reacted with NO_2 to produce FNO_2 .

Simple nitronium salts, e.g., nitronium hexafluoroarsenate or nitronium tetrafluoroborate, were formed by adding nitrogen dioxide, a metal fluoride, and fluorine gas to a vessel held at a low temperature and allowing the vessel to warm until a reaction occurred [576]:



Small quantities of nitryl fluoride can be prepared in the laboratory by a metathetical reaction of nitryl tetrafluoroborate and sodium fluoride [93]:



It has also been attempted to circumvent the need for elemental difluorine in the preparation of nitryl fluoride and nitrosyl fluoride by electrofluorination of N_2O , NO , NO_2 , or HNO_2 between electrodes in anhydrous hydrogen fluoride [577–579]. The presence of traces of water in the electrolyte, either introduced initially as contaminants in the reactants or formed as by-product during the reaction, leads invariably to the same reaction products, namely a mixture of OF_2 , NO_2F , and NO_3F , and the yields are very poor. The H_2F_2 can be dried by electrolyzing it for a while before introducing any nitrogen oxide [580, 581].

Nitryl fluoride can be made by fluorination of alkali metal nitrates with COF_2 . The interaction of LiNO_3 or NaNO_3 with COF_2 at 358 K (85 °C) in a stainless steel reactor in the presence of 12 mol-% CsF , an HF scavenger, resulted in nearly quantitative yields of NO_2F . No reaction was observed between CsNO_3 and COF_2 either in the presence or the absence of CsF .

6.2.2 Physical Properties of Nitryl Fluoride

Physical properties of nitryl fluoride are summarized in Table 20.

Table 20: Physical properties of nitryl fluoride.

	SI units	MKS units	References
Molecular mass	65.008 g/mol		
Melting point	107 ± 0.5 K	-166 ± 0.5 °C	[559]
	107 K	-166 °C	[573]
Boiling point	200.7 ± 0.2 K	-72.4 ± 0.2 °C	[559]
	200.7 K	-72.4 °C	[573]
Density, liquid at 200 K (-73 °C)	1494 kg/m ³	1.494 g/cm ³	[558]
Density, liquid at 172 K (-101 °C)	1571 kg/m ³	1.571 g/cm ³	[582]
Viscosity, liquid at 200.6 K (-72.5 °C)		4.60 mPs	[583]
Viscosity, liquid at 172 K (-101 °C)		5.72 mPs	[583]
Surface tension at 168.6 K (-104.5 °C)		27.6 dyn/cm	[582]
Critical temperature	349.5 K	76.3 °C	[582]
Standard enthalpy of formation, gas (ΔH) ₂₉₈	+108.78 kJ/mol	+26.0 kcal/mol	[583]
Heat of hydrolysis in water	-129.7 kJ/mol	-31 kcal/mol	[583]

6.2.2.1 Density of Nitryl Fluoride

The temperature dependence of the density of liquid nitryl fluoride can be expressed by the following equation [582, 584].

$$\rho = 2.046 - 0.00276T$$

where ρ is the density in g/cm^3 and T is the temperature in kelvin.

6.2.2.2 Vapor Pressure of Nitryl Fluoride

The vapor pressure of nitryl fluoride can be calculated from the following equation from Ruff, Menzel, and Neumann [559]:

$$\log p_v = -(5692/4.573T) + 1.75 \log T - (0.051606T/4.573) + 7.3187$$

where p_v is the vapor pressure in mm Hg and T is the temperature in kelvin.

6.2.2.3 Optical Properties of Nitryl Fluoride

Infrared Absorption Spectra of Nitryl Fluoride

The IR spectrum of nitryl fluoride was studied between 400 and 5000 cm^{-1} , and the Raman spectrum of the liquid at 168 K (-95°C) and the polarization of the lines were determined [585]. Frequency assignments were made in terms of an assumed planar C_{2v} structure, and the following assignments of fundamentals were proposed: $\nu_1(A_1) = 1312\text{ cm}^{-1}$; $\nu_2(A_1) = 822\text{ cm}^{-1}$; $\nu_3(A_1) = 460\text{ cm}^{-1}$; $\nu_4(B_1) = 1793\text{ cm}^{-1}$; $\nu_5(B_1) = 570\text{ cm}^{-1}$; $\nu_6(B_2) = 742\text{ cm}^{-1}$. Initially, the model C_{2v} was for an asymmetrical top, approximating for NO_2F to an oblate symmetrical top.

High-resolution IR spectra of FNO_2 were measured in the region of $1750\text{--}1825\text{ cm}^{-1}$ to obtain rotationally resolved IR line positions for the identification of FNO_2 as an atmospheric pollutant [586]. The spectrum in this range displayed extensive rotational structure consisting solely of b-type transitions that were assigned to ν_4 , the NO_2 anti-symmetric stretching vibration. Over 1500 IR and 51 microwave transitions were fitted to generate rotational constants for the $\nu_4 = 1$ state and improved constants for the ground state.

Another set of high-resolution IR spectra of FNO_2 of the strong a-type absorptions corresponding to the ν_1 ($n_0 = 1310.75\text{ cm}^{-1}$) and ν_2 ($n_0 = 821.9387\text{ cm}^{-1}$) bands were analyzed, and the n_1 line positions exhibited extensive perturbations as a result of three nearly degenerate vibrational states ($\nu_1, \nu_3 + \nu_6$ and $\nu_5 + \nu_6$) that interact through strong Coriolis coupling [587]. Line positions, assignments, and relative intensities for the dominant transitions in both bands were established, although a comprehensive analysis of the perturbations requires a detailed understanding of the lower-frequency vibrational states.

The gas-phase IR spectra of the ν_5 , ν_3 , ν_6 , and ν_2 bands of FNO_2 were studied at resolutions ranging from 0.0023 to 0.0050 cm^{-1} [588]. These bands form an isolated tetrad that is coupled by a-, b-, and c-Coriolis resonances. The c-Coriolis interaction

between ν_3 and ν_5 is particularly strong. From a ground-state combination difference analysis, the ground-state rotational constants were then obtained.

In a continuation of this effort, the ν_4 , $2\nu_6$, $\nu_2 + \nu_3$, and ν_1 bands of the gas-phase mid-IR region of the FNO_2 spectrum at $1200\text{--}1900\text{ cm}^{-1}$ were measured again at a resolution of 0.003 cm^{-1} [589]. Improved ground-state rotational and centrifugal distortion constants were obtained from a simultaneous analysis of earlier data and the present data from ν_4 and ν_1 . The ν_4 and $2\nu_6$ bands were free from local perturbations, and upper-state spectroscopic constants were obtained from the conventional Watson Hamiltonian. The bands ν_1 and $\nu_2 + \nu_3$ were strongly perturbed by Coriolis interactions with the nearby dark levels $\nu_5 + \nu_6$, $\nu_3 + \nu_6$ and $\nu_2 + \nu_5$. Upper state constants for ν_1 and $\nu_2 + \nu_3$ were obtained from triad and tetrad models, respectively, including Coriolis resonances determined from the observed perturbation effects on ν_1 and $\nu_2 + \nu_3$.

Ultraviolet Spectra of Nitryl Fluoride

The UV absorption spectrum of nitryl fluoride was quantitatively studied over the near-UV/visible region at room temperature [590]. The absorption obeyed Beer's law and was a continuum, having photoabsorption cross-sections (σ) ranging from $(2.2 \pm 0.8) \times 10^{-18}\text{ cm}^2$ at 195 nm to $(3.0 \pm 2.8) \times 10^{-20}\text{ cm}^2$ at 300 nm. No appreciable absorption ($\sigma < (3 \pm 3) \times 10^{-20}\text{ cm}^2$) occurred at wavelengths longer than 300 nm.

6.2.2.4 Microwave Spectra of Nitryl Fluoride

Microwave spectra of isotopically labeled molecules of NO_2F ($^{14}\text{N}^{16}\text{O}_2\text{F}$, $^{14}\text{N}^{18}\text{O}^{16}\text{OF}$, and $^{15}\text{N}^{16}\text{O}_2\text{F}$) gave rotational constants from the three species, which could then be used to determine the structure in several ways, resulting in angle $\angle\text{ONO} = 136^\circ \pm 1.5^\circ$, N—O distance = $1.1798 \pm 0.0035\text{ \AA}$, N—F distance = $1.467 \pm 0.015\text{ \AA}$, and O—O distance = $2.1878 \pm 0.003\text{ \AA}$, dipole moment $0.466 \pm 0.005\text{ D}$ [591].

The millimeter microwave rotational spectrum of NO_2F has been measured in the frequency range 90–200 GHz, and a complete set of the ground-state moments of inertia was obtained [592]. Two different methods were used in order to determine the general quadratic force field by a combination of IR and microwave data. The first method was based on the complete consistency between force constants and vibration frequencies of the normal species and on the best fit of the rotational spectrum. The second method used the least-squares determination of the corrections on some starting set of force constants. The two methods gave very similar results. The agreement between observed and calculated rotational and vibration frequencies was satisfactory.

Microwave spectra of NO_2F in excited vibrational states in the $\nu_3 = 1$ and $\nu_6 = 1$ states were identified, and the rotational constants, vibrational-rotational interaction constants, and inertia defects in these states were determined [593]. Large inertia defects and large vibrational-rotational interaction constants indicated that the ν_3 and ν_6 state vibrations are nearly degenerate. See also [594].

6.2.2.5 Molecular Structure of Nitryl Fluoride

Nitryl fluoride O_2NF is an isomer of nitrosyl hypofluorite ONOF , CAS RN [96607-23-7]. Nitrosyl hypofluorite is an unstable molecule, and its existence was contested for a long time.

The stretching-force constants of FNO_2 and ClNO_2 that were obtained in two different systems of symmetry coordinates were shown to be physically incompatible and need to be reexamined [595].

A series of self-consistent field–molecular orbital (SCF-MO) calculations using the method of linear combination of Gaussian-type functions (GTF) were performed on the nitryl fluoride molecule, and a variable geometry was used in order to obtain an *ab initio* potential hypersurface [596]. This hypersurface was used to obtain harmonic force constants for a matrix calculation, from which the fundamental frequencies associated with the normal modes were then calculated.

The in-plane harmonic and some cubic force constants of FNO_2 calculated by *ab initio* methods were compared with experimental data [597]. One of the two sets of equivalent force fields was physically correct but still reproduced isotope shift data poorly. Therefore, a new force field was determined that agreed with the *ab initio* results. Total and orbital energies and the dipole moment of FNO_2 were also calculated.

SCF-MO calculations were performed on three FNO_x ($x = 1, 2, 3$) compounds to obtain dipole moments, ionization potentials, and geometries [598]. The predicted relative stability for FNO_2 isomers was $\text{FNO}_2 > \text{cis-FONO} > \text{trans-FONO}$. FONO_2 was predicted to only slightly prefer a planar configuration, in agreement with experiments. The FONO_2 isomer was more stable than FOONO by about 167 kJ/mol (40 kcal/mol).

Computational chemistry with local density functional theory can predict some of the properties of FNO_2 . It was shown that FNO_2 is 171 kJ/mol (40.8 kcal/mol) more stable than *cis*- ONOF , which in turn is 105 kJ/mol (25.2 kcal/mol) more stable than its *trans* isomer [599].

It was found that the second-order Møller-Plesset (MP2) level of theory for the molecule of FNO_2 significantly overestimated the N–F bond length, which is the geometric parameter most sensitive to the effects of basis set and electron correlation [600]. More accurate structures were obtained by using the Pople split valence rather than Dunning-Huzinaga basis sets, a result explained by the compactness of the Pople basis sets. However, the use of the Pople basis sets did not overcome the deficiencies of the MP2 method for determining the structure and force field of FNO_2 . See also [601].

6.2.2.6 Thermodynamic Properties of Nitryl Fluoride

The standard enthalpy of formation of NO_2F has been determined by several authors, but the data do not agree very well. The direct synthesis reaction for NO_2F yielded a heat of formation value for the gas of -107.9 ± 2.1 kJ/mol (-25.8 ± 0.5 kcal/mol) [570].

IR and mass spectra of nitryl fluoride have been measured and serve as analytical tools or can be used to calculate thermodynamic data. The following thermodynamic data of nitryl fluoride in Table 21 were calculated from its IR spectra [602].

Table 21: Thermodynamic properties of nitryl fluoride.

Temperature K	Molar heat capacity		Enthalpy function		Free-energy function		Entropy	
	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹
100	33.9	8.11	33.3	7.97	183.7	43.90	217.0	51.87
200	41.3	9.86	35.2	8.42	207.2	49.52	242.5	57.95
273	47.8	11.42	37.7	9.02	218.5	52.23	256.3	61.25
293	49.5	11.82	38.5	9.19	221.2	52.87	259.7	62.07
303	50.3	12.02	38.9	9.29	222.2	53.11	261.1	62.40
400	57.1	13.64	42.5	10.15	233.8	55.88	276.3	66.03
500	62.3	14.90	45.9	10.98	243.6	58.23	289.6	69.22
600	66.4	15.88	49.0	11.72	252.3	60.30	301.3	72.02
700	69.5	16.62	51.7	12.36	260.0	62.15	311.7	74.51
800	71.9	17.19	54.1	12.93	267.1	63.83	321.2	76.76
900	73.8	17.64	56.2	13.43	273.6	65.39	329.8	78.82
1000	75.2	17.98	58.0	13.87	279.6	66.83	337.6	80.70

Data source: [602]

These data agreed essentially with those reported by Tschuikow-Roux: The thermodynamic data of nitryl fluoride were calculated according to the rigid rotator harmonic oscillator approximation [603]. The bond energy of the N—O bond was 256 kJ/mol (61.3 kcal/mol), and the bond energy of the N—F bond was 187 kJ/mol (44.7 kcal/mol). See also [604].

The gas-phase heat capacity of NO₂F can be calculated by a Shomate equation

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + \frac{E}{\tau^2}$$

where C_p is the heat capacity in J mol⁻¹ K⁻¹; τ is the temperature in kelvin divided by 1000: $\tau = K/1000$; and A, B, C, D, and E are constants listed in Table 22 for two temperature ranges. According to the NIST Chemistry WebBook website, the standard enthalpy of formation of the NO₂F gas is ΔH_f^{298} gas (−108.78 kJ/mol). The enthalpy of formation of gaseous NO₂F as a function of temperature can be expressed by the equation

$$H^\circ - H_{298.15}^\circ = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{\tau} + F - H$$

where H° is the standard enthalpy in J mol^{-1} ; τ is the temperature in kelvin divided by 1000: $\tau = K/1000$; and A, B, C, D, E, F, and H are constants listed in Table 22 for two temperature ranges. The standard entropy of gaseous NO_2F as a function of temperature can be expressed by the equation

$$S^\circ = A \times \ln(\tau) + B\tau + \frac{C\tau^2}{2} + \frac{D\tau^3}{3} - E/(2\tau^2) + G$$

where S° is the standard entropy in $\text{J mol}^{-1} \text{K}^{-1}$; τ is the temperature in kelvin divided by 1000: $\tau = K/1000$; and A, B, C, D, E, and G are constants listed in Table 22 for two temperature ranges.

Table 22: Coefficients for thermodynamic property Shomate equations for nitryl fluoride.

Temperature range (K)	298–1100	1100–6000
A	25.78490	81.12650
B	112.9375	1.116488
C	-89.46061	-0.224392
D	26.17284	0.015461
E	-0.208291	-6.925650
F	-121.4527	-150.8014
G	260.3523	332.9213
H	-108.7840	-108.7840

Data source: [132]

6.2.3 Chemical Properties of Nitryl Fluoride

Nitryl fluoride is a potential intermediate in the photolysis and destruction of ozone layer-depleting fluorocarbons in the upper atmosphere; consequently, some work has been done on the photolysis and kinetics of atmospheric reactions of atomic oxygen and ozone involving FNO_2 [605].

Very few investigations have been reported on the hypergolic ignition of FNO_2 with amines and hydrazines, propellant combinations that deserve further study.

6.2.3.1 Thermal Decomposition of Nitryl Fluoride

At temperatures above 293 K (+20 °C), nitryl fluoride dissociates partially into nitrogen dioxide and difluorine. Therefore, it is difficult to measure IR spectra of the pure vapor without interference by NO_2 .

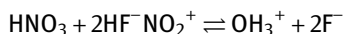
6.2.3.2 Reactions of Nitryl Fluoride with Inorganic Compounds

Nitryl fluoride is a strong oxidizer that will spontaneously ignite with iodine, antimony, arsenic, phosphorus, boron, silicon, and many organic compounds, and it reacts with hydrogen, sulfur, mercury, and charcoal only at elevated temperature.

Quartz glass will not be attacked by dry nitryl fluoride. Nitryl fluoride can be mixed with oxygen difluoride without reaction [606].

Instead of storing nitryl fluoride as a cryogenic liquid or compressed gas, it is more convenient to store it in the form of its stable, solid complex salts $[\text{NO}_2][\text{BF}_4]$ or $[\text{NO}_2][\text{PF}_6]$ and to release it on demand by reaction with sodium fluoride.

^{14}N or ^{15}N NMR and electrical conductivity measurements have indicated conclusively that NO_2F is completely dissociated into NO_2^+ and F^- ions when it is dissolved in liquid H_2F_2 [607]. The existence of the equilibrium



was demonstrated by the magnetic resonance shift of ^{14}N in HNO_3/HF mixtures.

The phase diagram of the system $\text{NO}_2\text{F}\text{-HF}$ showed the formation of the following four addition compounds: $\text{NO}_2\text{F}\cdot 3.50\text{HF}$, $\text{NO}_2\text{F}\cdot 4.00\text{HF}$, $\text{NO}_2\text{F}\cdot 5.25\text{HF}$, and $\text{NO}_2\text{F}\cdot 6.66\text{HF}$ [608]. The diagram, which contained five eutectics, resembled that of the system $\text{NOF}\text{-HF}$. An addition compound with the composition of $\text{NO}_2\text{F}\cdot 5\text{HF}$ is a water-like liquid with a freezing point below 195 K (-78°C).

6.2.3.3 Reactions of Nitryl Fluoride with Organic Compounds

Nitryl fluoride would be suitable as a hypergolic oxidizer because it ignites spontaneously with all amines and hydrazines. Experimental results have not been reported.

6.2.4 Toxicity of Nitryl Fluoride

Nitryl fluoride has a pungent odor and attacks the mucous membranes vigorously.

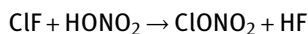
6.3 Nitroxyl Fluoride

Nitroxyl fluoride, NO_3F (also improperly called “fluorine nitrate”), CAS RN [7789-26-6], was discovered by Cady in 1934 when he reacted difluorine with 3-N nitric acid [609]. Frequent explosions occurred during its preparation and even more so during subsequent experiments to determine its physical and chemical properties [610]. The colorless liquid boils at 231 K (-42°C) and hydrolyzes rapidly, even with traces of moisture. Due to its explosive properties, this compound is not suitable as a rocket propellant, although it would probably ignite hypergolically with most commonly used fuels.

6.3.1 Preparation of Other Nitroxyl Halogenides

Halogen analogues of nitroxyl fluoride, chlorine nitrate, and bromine nitrate are more stable than nitroxyl fluoride but still need to be handled with caution.

Chlorine nitrate can be made from chlorine monofluoride and nitric acid [611]:



The reaction of BrF_5 with a large excess of LiNO_3 at 273 K (0°C) produced BrONO_2 , LiF , N_2O_5 , and O_2 as the principal products [612]. BrONO_2 has a planar structure. With N_2O_5 , the BrONO_2 molecule formed an unstable adduct, which was shown by Raman spectroscopy to possess the ionic structure $\text{NO}_2^+[\text{Br}(\text{ONO}_2)_2]^-$. A cesium salt $\text{Cs}^+[\text{Br}(\text{ONO}_2)_2]^-$ was also prepared, and its vibrational spectra were recorded and assigned. Bromine nitrate may play a role in atmospheric chemistry and ozone depletion.

6.3.2 Physical Properties of Nitroxyl Fluoride

Nitroxyl fluoride is a colorless liquid that boils at 231 K (-42°C).

6.3.2.1 Optical Properties of Nitroxyl Fluoride

The low-temperature IR and Raman spectra of $\text{I}(\text{NO}_3)_3$ and the Raman spectra of liquid ClONO_2 , FONO_2 , FNO_2 , and ClNO_2 have been recorded [613]. Comparison of the vibrational spectra within the series NO_2 , FNO_2 , ClNO_2 , FONO_2 , and ClONO_2 allowed unambiguous assignments for the halogen nitrate molecules. Raman polarization measurements showed that in halogen nitrates, the halogen atom is perpendicular to the ONO plane, contrary to previous assumptions, and to the known planar structure of HONO_2 and CH_3ONO_2 . The vibrational spectrum of $\text{I}(\text{NO}_3)_3$ is consistent with predominantly covalent nitrate ligands. However, the complexity of the spectrum suggests a polymeric structure with bridging nitrate groups.

The vibrational frequencies and corresponding normal mode assignments of nitroxyl fluoride were examined theoretically using the Gaussian 98 set of quantum chemistry codes [614]. All normal modes were successfully assigned to one of six types of motion utilizing the C_s symmetry of the molecule. Uniform scaling factors were derived for each type of motion. Predicted IR and Raman intensities agreed well with reported experimental measurements.

6.3.2.2 Molecular Structure of Nitroxyl Fluoride

The molecular structure of nitroxyl fluoride was the subject of lengthy disputes for several decades. Eventually the experts agreed that nitroxyl fluoride has a planar structure similar to nitric acid and methyl nitrate. It oscillates between two isomeric structures:



A general valence force field for FONO_2 was derived from frozen Ne-matrix IR spectra together with ^{15}N and ^{18}O isotopic shifts [615]. A gas electron diffraction study resulted in a planar structure with the following geometric parameters (distances and

angles with 3σ uncertainties in parentheses): N=O 1.184(2) Å, N—O 1.507(4) Å, O—F 1.409(5) Å, $\angle$ O—N=O_c 117.1(9)°, $\angle$ O—N=O_t 108.4(18)°, $\angle$ O_c—N=O_t 134.5(21)°, and $\angle$ N—O—F 106.0(11)°. O_c and O_t are the oxygen atoms *cis* and *trans* to the O—F bond. The N—O single bond in fluorine nitrate is about 0.1 Å longer than those in nitric acid and methyl nitrate (Figure 8).

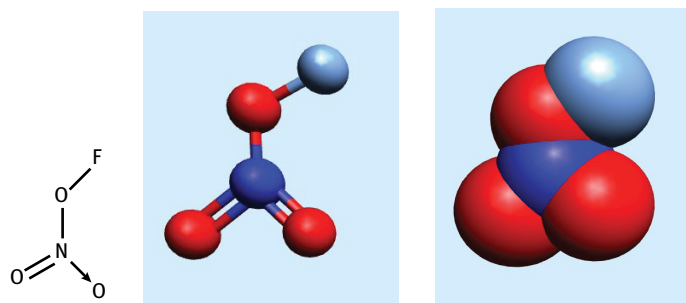


Figure 8: Molecular structures of nitroxyl fluoride.

The molecular structure of nitroxyl fluoride has been derived from IR and Raman spectra and discussed in terms of the adjacent charge rule [616].

6.3.2.3 Thermodynamic Properties of Nitroxyl Fluoride

The heat of formation of gaseous nitroxyl fluoride is $+10.46 \pm 2.1$ kJ/mol ($+2.5 \pm 0.5$ kcal/mol) [617, 618].

Another source reported the enthalpy of formation of gaseous nitroxyl fluoride at 294 K as -17.6 ± 3.8 kJ/mol (-4.2 ± 0.9 kcal/mol) [619, 620].

6.3.3 Chemical Properties of Nitroxyl Fluoride

Other known halogen nitrates are ClONO₂, and I(NO₃)₃. Nitroxyl fluoride is extremely shock sensitive. I(NO₃)₃ is a non-volatile residue in the form of a fluffy, light yellow solid that decomposes above 273 K (0 °C).

Nitroxyl fluoride decomposed explosively into NOF and O₂. The slow thermal decomposition over the range 353–380 K (80–107 °C) proceeded by a different stoichiometry [621]:



The first-order rate constant decreased with decreasing initial reactant pressure, showing a fall-off region characteristic of a unimolecular reaction. The rate constant was

$$k_\infty = 5.80 \times 10^{13} \exp(-29700/RT) \text{ s}^{-1}$$

See also [622, 623]. Nitroxyl fluoride reacted with tetrafluoroethylene to form carbonyl fluoride and trifluoronitromethane [610].

6.4 Trifluoramine Oxide

Trifluoramine oxide, also known as trifluoroamine oxide, F_3NO , nitrogen trifluoride oxide, nitrogen fluoride oxide, nitrogen oxide trifluoride, "AMOX", CAS RN [13847-65-9] was discovered in the early 1960s. In 1966 three research groups independently reported the synthesis of trifluoramine oxide, F_3NO [624–626], but the filing dates of some patents predate these publications. If nitrogen trifluoride is already a good rocket propellant oxidizer, then trifluoramine oxide should be an even better oxidizer because it contains additional oxygen. It would be much better if it were only more readily available. It has not yet flown in a rocket, and even static ground-level tests have not yet been reported.

6.4.1 Preparation of Trifluoramine Oxide

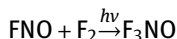
Trifluoramine oxide can be made by fluorination of nitric oxide or by pyrolysis of nitrosyl hexafluoronickelate(IV) or nitrosyl hexafluoroiridate(VI) [625]. At 760 mm Hg, 500 mL NOF gas and 2500 mL F_2 gas were condensed at 77 K (-196°C) into a reactor constructed of Ni or Monel, and the reactor was pressurized to 7.9 MPa (1150 psig) with N_2 and heated for 1 h at 623 K (350°C) as the pressure rose to 34 MPa (4950 psig) [627]. The reactor was then quickly chilled to 77 K (-196°C) and was vented, and the contents were fractionally distilled to give 97% F_3NO containing 1% NOF and some F_2 . Varying the conditions gave lower yields of F_3NO .

Trifluoramine oxide (nitrogen oxide trifluoride) was prepared in trace quantities by the reaction of nitric oxide and fluorine [628]. Low but improved yields were obtained when nitrosyl fluoride and fluorine were heated together at 493 K (220°C). It was found that $(\text{NO})_2\text{NiF}_6$ was formed by the reaction of the walls of the Monel reaction vessels with nitrosyl fluoride and fluorine and that pyrolysis of this salt (in 483 kPa [70 psi] fluorine at 623 K [350°C]) gave the new compound in good yield. The reactions of platinum and iridium hexafluoride with nitrosyl fluoride were also investigated as potential routes to ONF_3 . Trifluoramine oxide was colorless in the solid, liquid, and gaseous phases, melting at 112 K (-161°C) and boiling at 185.6 K (-87.5°). The vapor pressure was determined over the range 145–195 K (-128 to -78°C). Trifluoramine oxide was found to be only moderately reactive. There was no evidence that ONF_3 could be protonated by strong acids. A 1:1 adduct was formed with AsF_5 . The chemical behavior and IR spectrum of the adduct were consistent with the formula $[\text{ONF}_2^+][\text{AsF}_6^-]$.

The apparatus used for preparation of F_3NO was similar to that employed by Kirshenbaum for the low-temperature electric-discharge preparation of O_3F_2 [629]. In a typical run, an equimolar mixture (77 mmol each) of gaseous NF_3 and oxygen was

passed slowly at 10–15 mm pressure into the discharge tube (held at 77 K [–196 °C]) with continuous pumping on the exit side of the tube to remove non-condensable material and to maintain the reactor pressure in the desired range. During a run, which generally required 1–2 h, the discharge current varied from 30 to 50 mA at 5 kV. Upon completion of a run, the condensable material in the discharge tube was an amber solid–liquid mixture at 77 K (–196 °C) that became a reddish liquid on slight warming. Alternate warming to 195 K (–78 °) and cooling to 75 K (–198 °C) caused all color to disappear and produced considerable non-condensable off-gassing, suggesting that the colored materials were lower-oxygen fluorides (e.g., O_2F_2 or O_3F_2) that decomposed to O_2 and F_2 . Subsequent fractionation through traps at 140, 90, and 77 K (–130, –183, and –196 °C) yielded unreacted NF_3 (23.3 mmol, trapped at 77 K [–196 °C]), F_3NO (7.0 mmol, trapped at 90 K [–183 °C]), and an unresolved mixture (trapped at 140 K [–130 °C]) of NO_2 , N_2O_3 , and a white solid that was probably $(\text{NO})_2\text{SiF}_6$. From these data, the conversion of NF_3 was 71%, and the yield of F_3NO was 13%.

Trifluoramine oxide can be obtained readily by the photochemical fluorination of nitrosyl fluoride at ambient temperature and pressure [630, 631]:



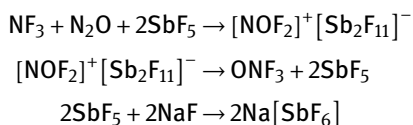
Although the direct fluorination of nitrosyl fluoride had been attempted before, F_3NO was produced only at high temperature and pressure where corrosive attack on the reactor was severe. Other methods for F_3NO synthesis required either relatively complex electric-discharge apparatus or the use of higher-valent transition metal fluorides (IrF_6 , OsF_6) that are difficult and inconvenient to prepare. The photochemical method produced 50% yields of F_3NO and required only simple apparatus and the readily available raw materials fluorine and nitric oxide.

The effluent from a F_2/NO flame contained traces of F_3NO , suggesting that the very exothermic initial reactions provided the energy necessary for further fluorination of NOF [632]. Rapidly quenching the energy-rich gas mixture in the flame by impinging on a cold surface increased the yield of F_3NO , and further enhancement resulted when F_2 in excess of that required for NOF formation was used. A convenient, continuous-flow process was developed for F_3NO synthesis in yields up to 20% by using the empirically optimized reactor geometry, reactant ratio, gas flow rates, and quench temperature conditions.

Trifluoramine oxide can be prepared by reacting air with fluorine or fluorine with nitrogen oxides in a glow discharge and quenching the reaction products on a cold finger [633]. Trifluoramine oxide can be prepared by reacting difluoramine with chlorine trifluoride and an oxygenated halogen compound such as ClO_2 , FClO_2 , or FClO_3 [634–636]. The reaction between difluoramine, chlorine trifluoride, and the oxygenated halogen compound is conducted in the gas phase. The gaseous reactants are cooled to a condensed phase in separate layers at temperature below 147 K (–126 °C). After the reactants are condensed, the temperature is raised to above 147 K (–126 °C), and the gas-phase reaction allowed to proceed at temperatures between 147

and 303 K (–126 and +30 °C). The product and by-products have to be separated by multiple fractionated condensation.

The formerly difficult synthesis of F_3NO has been facilitated by the direct chemical oxygenation of NF_3 . The interaction of NF_3 with N_2O in the presence of SbF_5 at 423 K (150 °C) leads to the quantitative formation of the previously known $[NOF_2]^+[Sb_2F_{11}]^-$ salt. Vacuum pyrolysis of $[NOF_2]^+[Sb_2F_{11}]^-$ at 463–503 K (190–230 °C) in the presence of excess NaF affords NOF_3 in high yield.



The operation of a microwave cavity and electrodeless discharge cell filled with mixtures of O_2 , N_2 , and F_2 and immersed in liquid nitrogen produced small amounts of ONF_3 [637]. Higher yields of ONF_3 were produced by a capacitor pulsed discharge between electrodes in a low-temperature cell, but yields were very low if a direct-current discharge was used.

At low temperatures and ambient pressures, $ClFO_3$ and HNF_2 react to form ONF_3 , $ClNF_2$, and HF [638]. Higher yields can be obtained at autogenic pressures. The reactor was evacuated and cooled to condense one of the reactants, the other reactant was added, and, as the cooling means was removed, the reaction proceeded. Thus, 30 cm³ $ClFO_3$ was condensed at 77 K (–196 °C). Then 29 cm³ HNF_2 was condensed in the same trap at 131 K (–142 °C), and the reaction was allowed to proceed. All of the HNF_2 was converted to a 2:2:1 mixture of NF_3O , $ClNF_2$, and N_2F_4 .

F_2 can react with N_2O in a glow discharge to form ONF_3 [639]. A mechanism of the reaction was proposed involving the formation of NO and atomic F as intermediates. At a $F_2:N_2:O_2 = 3:1:1$ concentration ratio, O_2F_2 formation would compete with ONF_3 formation. This was attributed to a faster reaction of atomic F with O_2 than that with NO and to O_2F_2 stabilization along the cold-reaction vessel walls. ONF_3 can be purified by filtering it through a bed of dry, solid KOH.

Equilibrium compositions of the N-O-F system were calculated as a function of temperature (200–1000 K) and pressure (20–760 mm Hg) [640]. Variation of concentrations was shown for 10 of 26 species present in this system. Optimum concentration of NF_3 occurred at 200–300 K. The concentration of ONF_3 decreased rapidly as the temperature increased. The yield of ONF_3 depends on the type of electrical discharge and the quenching conditions.

6.4.2 Physical Properties of Trifluoramine Oxide

Trifluoramine oxide has a melting point of 111.6 K (−161.5 °C) and a boiling point of 184 K (−89 °C). The vapor pressure of trifluoramine oxide can be expressed by the equation [629]

$$\log P = -A + \frac{B}{T} + \frac{C}{T^2} + D \log T$$

where P is the vapor pressure in mm Hg, T is the temperature in kelvin, and the constants A , B , C , and D are as follows: $A = 10.391602$, $B = 180.04119$, $C = 39443.176$, and $D = 6.0353102$. The normal boiling point from the equation is 185.5 K (−87.6 °C), Trouton's constant is 20.7, and the heat of vaporization is 16.1 kJ/mol (3.85 kcal/mol). The critical temperature is 302.6 K (29.5 °C), the critical density is 0.593 g/cm³, and the critical pressure is 63.5 atm. The temperature dependence of liquid density over the range 193–153 K (−80 to −120 °C) is

$$d = 1.237 - 0.003544t$$

where t is the temperature in degrees Celsius and d is the density in g/cm³. See also [13].

6.4.2.1 Optical Properties of Trifluoramine Oxide

Infrared Absorption Spectra of Trifluoramine Oxide

Trifluoramine oxide gas exhibits strong IR absorptions at 530, 743, 885, 1690, and 1771 cm^{−1}. The IR spectrum of F₃NO is shown in Figure 9.

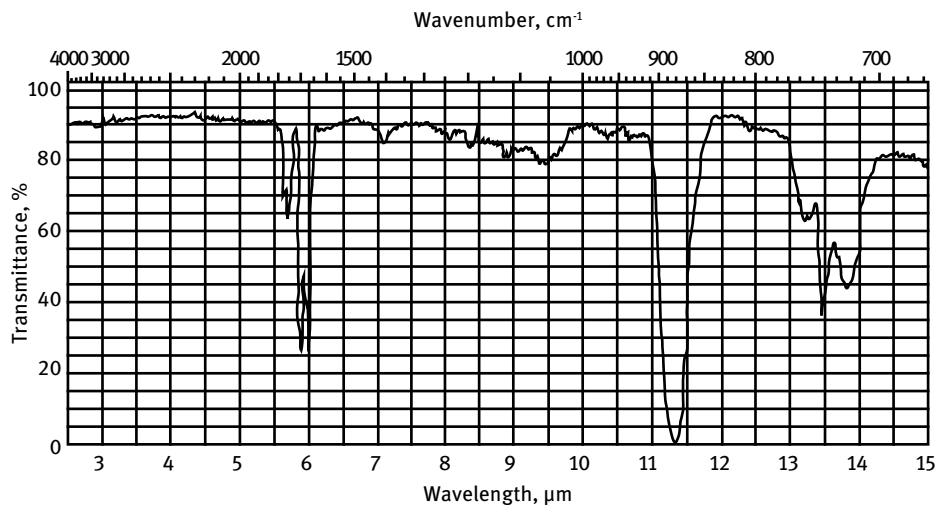


Figure 9: Infrared spectrum of trifluoramine oxide. (Reproduced and modified from [636].)

The general appearance of the IR spectrum established that the NF_3O molecule has C_{3v} symmetry [641]. The bands at 1691, 743, 528, 883, 558, and 400 cm^{-1} were assigned as the fundamental frequencies. The rotational spacing of ν_2 was used to determine the rotational constant, $B = 0.19\text{ cm}^{-1}$. Assuming tetrahedral angles and $r(\text{N}-\text{O}) = 1.15\text{ \AA}$ with this rotational constant gave an estimate of $r(\text{N}-\text{F}) = 1.48\text{ \AA}$.

The IR spectra of trifluoramine oxide and its ^{15}N analogue have been measured from 4000 to 260 cm^{-1} , and fundamental frequency assignments (based upon C_{3v} symmetry) were made from the ^{14}N spectrum as follows: $\nu_1(\text{a}_1) = 1689\text{ cm}^{-1}$, $\nu_2(\text{a}_1) = 740\text{ cm}^{-1}$, $\nu_3(\text{a}_1) = 528\text{ cm}^{-1}$, $\nu_4(\text{e}) = 880\text{ cm}^{-1}$, and $\nu_6(\text{e}) = 398\text{ cm}^{-1}$ [642]. Normal coordinate calculations support the assignment of the remaining fundamental $\nu_5(\text{e})$ to a band system appearing as a shoulder, about 558 cm^{-1} , on the intense $\nu_3(\text{a}_1)$ fundamental.

An investigation of the partially resolved IR bands of NOF_3 in the region 350 – 1800 cm^{-1} provided the rotational constant B_0 , the Coriolis constants, and integrated absorption intensities [643].

Raman Fluorescence Spectra of Trifluoramine Oxide

The Raman spectrum of a polycrystalline film of ONF_3 at 78 K was measured with displacements of 90 – 2500 cm^{-1} from the exciting line from a 60-mW helium-neon laser [644]. The vapor pressure of the solid sample at this temperature was 0.053 Pa ($8 \times 10^{-4}\text{ mm Hg}$), making the sample preparation rather difficult, which compromised the quality of the observed spectrum.

The main feature in the Raman spectrum of gaseous F_3NO was the band structure between 500 and 550 cm^{-1} [645]. The sharp bend occurring at 542 cm^{-1} was definitely polarized, while the band at 528 cm^{-1} was depolarized. These were therefore assigned as $\nu_3(\text{A}_1)$ and $\nu_3(\text{E})$, respectively, in conformance with earlier assignments. See also [646].

Raman spectra of ONF_3 were recorded from 118 to 300 K and, as predicted through group theory for C_{3v} mol, ONF_3 has six fundamental frequencies that are all Raman and IR active: three A_1 bands ($\nu_1 \sim 1680\text{ cm}^{-1}$, NO symmetric stretch; $\nu_2 \sim 740\text{ cm}^{-1}$, NF symmetric stretch; $\nu_3 \sim 540\text{ cm}^{-1}$, NF δ symmetry), and three E-type bands ($\nu_4 \sim 880\text{ cm}^{-1}$, NF asymmetric stretch; $\nu_5 \sim 530\text{ cm}^{-1}$, NOF deformation; $\nu_6 \sim 400\text{ cm}^{-1}$, NF δ symmetry) [647].

The rotational behavior of NOF_3 was derived from the band contour analysis of the Raman spectra in the liquid phase [648]. The angular momentum correlation times derived from the rotational diffusion model indicated that the molecule rotates almost isotropically. The band profiles were interpreted in terms of the rough hard-sphere model.

Ultraviolet Absorption Spectra of Trifluoramine Oxide

The UV spectrum of F_3NO showed an onset of very weak absorption at $2200\text{ \AA}$, the intensity increasing only slightly down to the limit of measurement at $2800\text{ \AA}$. Prolonged

photolysis of F_3NO gas in a nickel cell with BaF_2 windows with a 500-W high-pressure mercury lamp caused only minor decomposition, with traces of NO_2 , NO_2F , and NOF being formed.

Microwave Spectra of Trifluoramine Oxide

The microwave spectrum of ONF_3 cooled to 195 K (-78°C) gave a symmetric rotor pattern that was consistent with the point group C_{3v} assignment [649]. The dipole moment was very small, 0.0390 ± 0.0004 D, which made it difficult to record the microwave spectrum.

6.4.2.2 Magnetic Properties of Trifluoramine Oxide

The ^{14}N NMR shift in ONF_3 at 153 K was +376 ppm in relation to the shift in aqueous nitrite ion [193].

6.4.2.3 Molecular Structure of Trifluoramine Oxide

Several possible molecular structures for trifluoramine oxide are shown in Figure 10.

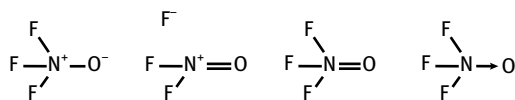


Figure 10: Possible molecular structures for trifluoramine oxide.

The nearly tetrahedral C_{3v} symmetry of F_3NO is clearly supported by the IR spectrum in which the required six fundamental bands have been assigned. The N—O stretching vibration at 1687 cm^{-1} in F_3NO is closer to that of an $\text{N}=\text{O}$ double bond than to that of the familiar amine N-oxides and, in fact, has nearly 75% double-bond character.

The molecular structure of trifluoramine oxide is illustrated in Figure 11.

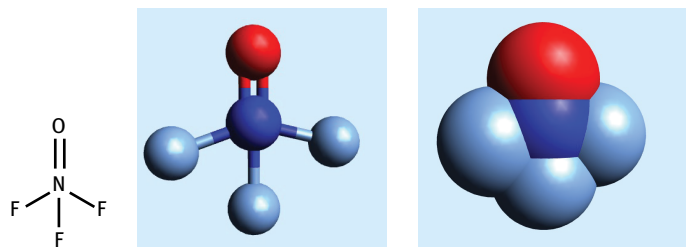


Figure 11: Molecular structures for trifluoramine oxide.

With the experience with organic amine N-oxides, one would first assume that nitrogen trifluoride oxide NF_3O is an amine N-oxide, but it behaves quite different from or-

ganic amine N-oxides. The bonds are highly covalent, and it has a low freezing point and low boiling point compared to organic N-oxides. Nitrogen trifluoride oxide, NF_3O , is a fascinating molecule that is isoelectronic with NF_4^+ . Its N—O bond possesses a high degree of double-bond character ($r_{\text{N—O}} = 1.159 \text{ \AA}$); therefore, it is not a typical amine oxide with a long, semipolar $\text{N} \rightarrow \text{O}$ bond and a negative charge on the oxygen atom.

Trifluoramine oxide does not contain an N—O—F bond as originally assumed. The N—F and N—O bond-lengths of 1.43 and 1.15 Å for this molecule are, respectively, longer than the N—F bonds of NF_3 and NF_4^+ (1.36 and 1.30 Å) and similar to the bond length (1.15 Å) for free NO. Resonance between several structures can account qualitatively for the lengthening of the N—F bond. Nitrogen difluoride hypofluorite (difluoroaminohypofluorite, CAS RN [14984-90-8]) F_2NOF is unstable and would rearrange itself to trifluoroamine.

Several values of force constants, mean amplitudes of vibration, and thermodynamic functions of ONF_3 were calculated [650]. The diagonal symmetry force constants, internal coordinate force constants, and mean vibrational amplitudes were listed in the report. The enthalpy per degree kelvin, the free enthalpy per degree, the entropy, and the heat capacity for the ideal gas at 1 atm pressure in $\text{cal } ^\circ\text{C}^{-1} \text{ mol}^{-1}$ are, respectively, as follows: at 273.16 K, 10.51, 54.42, 64.93, 15.40; at 298.16 K, 10.95, 55.36, 66.31, 16.22. Similar values were given for 19 other temperatures in the region 200–2000 K.

The molecular structure of trifluoramine oxide has been investigated by gaseous electron diffraction at a nozzle temperature of 293 K (20 °C) [651]. The results verified the expected C_{3v} symmetry for the molecule. The N—F bond is slightly longer than the sum of the single-bond radii corrected for electronegativity difference, but the N—O bond is very much shorter and must be regarded as essentially a double bond. The bond angles were not in themselves unusual. However, the positions of the four ligands corresponded with remarkable accuracy to the corners of a regular tetrahedron, a fact that strongly emphasizes the importance of non-bonded interactions. The five covalent bonds formed by the nitrogen atom may be understood in terms of a σ system of four bonds comprising 2s-2p hybrids and a π -bond obtained by utilizing an empty 3p π or 3d π nitrogen orbital with a filled 3p π oxygen orbital. The distances and amplitudes are r_a and l_a values. The electron-diffraction analysis led to the following values for the principal parameters: $r(\text{N}=\text{O}) = 1.158 \text{ \AA}$, $r(\text{N}-\text{F}) = 1.431 \text{ \AA}$, $r(\text{O}-\text{F}) = 2.214 \text{ \AA}$, $r(\text{F}\cdots\text{F}) = 2.206 \text{ \AA}$, $l(\text{N}=\text{O}) = 0.0289 \text{ \AA}$, $l(\text{N}-\text{F}) = 0.0507 \text{ \AA}$, $l(\text{O}\cdots\text{F}) = 0.0584 \text{ \AA}$, $l(\text{F}\cdots\text{F}) = 0.0551 \text{ \AA}$, $\angle \text{ONF} = 117.1^\circ$, and $\angle \text{FNF} = 100.8^\circ$.

The photoelectron spectrum of F_3NO showed evidence for four ionization potentials [652].

The electronic structure and conformation of ONF_3 were investigated based on complete neglect of differential overlap (CNDO) and intermediate neglect of differential overlap (INDO) approximations [653]. The minimization of the total energy with respect to the ONF angle occurred for a value that agreed perfectly with microwave

data. A bicentric energy partitioning showed that the variations of the total energy were completely reflected by the only variation of the N—F bond energy. The analysis of electronic density revealed the importance of the $2s(\text{N}) \rightarrow 2px(\text{O})$ transfer in the formation of the dative ($\text{N} \rightarrow \text{O}$) bond, the total transfer being equal to 0.33 electrons.

A normal coordinate analysis of the force field in ONF_3 gave good agreement between calculated and observed fundamental frequencies of this molecule, both for O^{14}NF_3 and for O^{15}NF_3 [654].

The potential energy constants of ONF_3 were evaluated on the basis of the general valence force field theory [655]. The mean-square amplitudes of vibration, the generalized mean-square amplitudes of vibration, Coriolis coupling constants, shrinkage constants, and rotation distortion constants of this molecule were also computed.

The oxygen, nitrogen, and fluorine core-binding energies of ONF_3 have been re-determined. The data indicated strong hyperconjugation, with N—O π -bonding and weak N—F σ -bonding [656]. The core and valence ionization potentials together indicated that the highest occupied molecular orbital (HOMO) of ONF_3 (derived mainly from the O p π orbitals) is weakly anti-bonding. This result was consistent with other data if it was assumed that the latter orbital has considerable fluorine lone-pair character and that the orbital derived mainly from the N—F σ orbitals (at lower energy) has considerable N—O π character.

To avoid exceeding eight valence electrons on nitrogen and to satisfy the high electronegativity of fluorine, the NF_3O molecule is best described as an $\text{F}_2\text{NO}^+\text{F}^-$ type structure in which the negative charge is evenly distributed over all three fluorine ligands. This assumption is supported by the unusually long (1.432 Å) and polar N—F bonds observed for NF_3O [657].

6.4.3 Chemical Properties of Trifluoramine Oxide

Trifluoramine oxide is a strong oxidizing agent toward many organic and inorganic materials but is resistant to hydrolysis, even by strong aqueous bases. The latter property is useful in purification, since common impurities (SiF_4 , NO_2 , NOF , NO_2F) are easily removed by scrubbing with strong aqueous KOH solution without significant loss of F_3NO . Carefully purified F_3NO is stable in glass and most metals at 298 K (25 °C).

6.4.3.1 Thermal Decomposition of Trifluoramine Oxide

Trifluoramine oxide gas may be heated to 573 K (300 °C) (atmospheric pressure) for short periods in nickel or Monel without change, but prolonged heating (longer than 1–2 h) caused increasing degradation to nitrosyl fluoride and secondary products (NO_2 , NO_2F , NO). It never decomposed to NF_3 and O_2 .

At temperatures above 523 K (250 °C), F_3NO is known to form an equilibrium with FNO and F_2 that, in the presence of SbF_5 , is continuously shifted to the FNO and F_2 side by the formation of the stable NOSbF_6 and NF_4SbF_6 salts.

6.4.3.2 Photolysis of Trifluoramine Oxide

Gases passing through the inlet of a mass spectrometer are usually ionized by electron bombardment, but they can also be ionized by UV radiation. If the wavelength of the UV radiation is varied, coming from the long-wavelength end of the spectrum until first ionization is detected, this photolysis/mass spectrometry method can be used to determine the bond strengths of the bonds being broken. Photoionization yield curves for the ONF_3^+ , ONF_2^+ , and NO^+ ions of NF_3O were measured from the threshold to 600 Å [227]. The ionization energies were used to calculate heats of formation of the ions, ionization energies of radicals, and bond dissociation energies. The heat of formation of ONF_3 was $-3.02\text{ eV} = -69.6\text{ kcal/mol} = -291\text{ kJ/mol}$, and the dissociation energy $D(\text{O}-\text{NF}_3)$ was 4.3 eV and $D(\text{ONF}_2-\text{F})$ was 1.9 eV.

After about 60 min of exposure of trifluoramine oxide in an argon matrix at 8 K to UV radiation of wavelengths 240–400 nm, the resultant F_3NO spectrum was essentially unchanged [658]. However, after a similar period of exposure (65 min) to photolytic UV radiation of wavelengths 220–900 nm, the IR features of NOF began to appear.

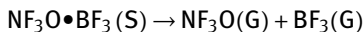
Photolysis of solid F_3NO at 77 K (-196°C) produced the F_2NO radical, which was identified by its nine-line ESR spectrum consisting of a fluorine split 1:2:1 triplet ($a\text{F} = 143.0\text{ G}$), each component of which was further split by ^{14}N into 1:1:1 triplets ($a\text{N} = 94.5\text{ G}$), with $g = 2.0093$ [659]. The data were best interpreted in terms of a pyramidal structure for F_2NO .

6.4.3.3 Reactions of Trifluoramine Oxide

Reactions of Trifluoramine Oxide with Inorganic Substances

Trifluoramine oxide forms stable 1:1 complexes with the Lewis acids AsF_5 and SbF_5 . These complexes are ionic $[\text{F}_2\text{NO}^+][\text{MF}_6^-]$ because the ^{19}F NMR spectrum of each in HF solution showed a 4:5:4 triplet N–F resonance at $\delta_{\text{FCCl}_3} = -331 \pm 3\text{ ppm}$ along with the high-field resonance of the corresponding MF anions.

Trifluoramine Oxide can form white crystalline 1:1 adducts with the Lewis acids BF_3 , AsF_5 , and SbF_5 [660]. In addition to the 1:1 compound, BF_3 can form at 147 K (-126°C) a 2:1 adduct with NF_3O . The thermal stability of these complexes decreased in the order of $\text{NF}_3\text{O}\cdot\text{SbF}_5 > \text{NF}_3\text{O}\cdot\text{AsF}_5 > \text{NF}_3\text{O}\cdot\text{BF}_3 > \text{NF}_3\text{O}\cdot 2\text{BF}_3$. The dissociation pressure–temperature relation has been measured, and thermodynamic data were calculated for the process

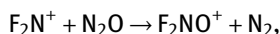


Hydrolysis of $\text{NF}_3\text{O}\cdot\text{AsF}_5$ resulted in the formation of $\text{NO}_2^+\text{AsF}_6^-$. IR and Raman measurements showed that $\text{NF}_3\text{O}\cdot\text{SbF}_5$, $\text{NF}_3\text{O}\cdot\text{AsF}_5$, $\text{NF}_3\text{O}\cdot\text{BF}_3$, and $\text{NF}_3\text{O}\cdot 2\text{BF}_3$ have the ionic structures $[\text{NF}_2\text{O}^+][\text{SbF}_6^-]$, $[\text{NF}_2\text{O}^+][\text{AsF}_6^-]$, $[\text{NF}_2\text{O}^+][\text{BF}_4^-]$, and $[\text{NF}_2\text{O}^+][\text{B}_2\text{F}_7^-]$, respectively. The $[\text{NF}_2\text{O}^+]$ cation (point group C_{2v}) has a structure similar to that of the isoelectronic CF_2O [661].

Trifluoramine oxide oxidized N_2F_4 , N_2O_4 , Cl_2 , or SF_4 to NF_3 , NO_2F , ClF , or SF_6 , respectively, the F_3NO being reduced to NOF in each case [662]. These and other reaction studies indicated that oxidations by F_3NO involve primarily fluorination rather than oxygenation. Trifluoramine oxide was not readily hydrolyzed by water or aqueous base but was attacked by sulfuric acid.

Trifluoramine oxide was found to react rapidly with nitric oxide to give nitrosyl fluoride (FNO) [663]. A free-radical reaction involving the known difluoronitryl (F_2NO) radical was proposed as a plausible mechanism.

Gaseous F_2NO^+ cations have been obtained from the ionization of a $\text{F}_2\text{N}^+/\text{N}_2\text{O}$ mixture under typical chemical ionization conditions [664]. The F_2NO^+ cations originate from the ion-molecule reaction



the occurrence of which has been ascertained by FTIR experiments.

Reactions of Trifluoramine Oxide with Organic Substances

Trifluoramine oxide reacts readily with a variety of amines to form the corresponding N-fluoro and N-nitroso derivatives in good yields [665]. A number of metals, including Ga, Sn, and Sb, are rapidly converted to GaF_3 , SnF_4 , or SbF_5 .

Trifluoramine oxide enabled the selective fluorination of haloolefins [666] and polyfluoroalkyl ethers [667]. NF_3O -Lewis acid complexes were studied by NMR spectroscopy [668]. Reactions of ONF_3 with some perfluoroalkenes result in compounds such as $(\text{CF}_3)_2\text{CFONF}_2$, $\text{F}_2\text{C}(\text{ONF}_2)_2$, and $\text{FOCF}_2\text{ONF}_2$. The compound $\text{FCO}(\text{ONF}_2)$ was synthesized reproducibly in good yields by the reaction of $(\text{FCOO})_2$, N_2F_4 , and small amounts of BF_3 [669, 670]. The compound $\text{F}_2\text{C}(\text{ONF}_2)_2$ had a boiling point of 264 K (-9°C), the vapor pressure described by

$$\log p \text{ (mm Hg)} = 8.075 - \frac{1374}{T} \text{ (K)},$$

and the density equation

$$d = 2.01 - 1.52 \times 10^{-3} T$$

The compound $\text{F}_2\text{COF}(\text{ONF}_2)$ had an estimated boiling point of 244 K (-29°C).

6.4.4 Toxic Properties of Trifluoramine Oxide

Trifluoramine oxide is very toxic. Experiments with albino rats showed that the LD50 concentration for 10-min exposure was between 200 and 500 ppm.

A specially built animal-exposure chamber was used for inhalation-toxicity studies with trifluoramine oxide [671]. The gas was introduced into the chamber through a calibrated micrometer valve. Specified ONF_3 concentrations were reached within

5 min after closure of the chamber and were monitored by a continuous IR scanning technique. The concentrations were stable and reproducible between 10 and 100 ppm.

Acute inhalation and intraperitoneal toxicities of ONF_3 were determined in rats and mice [672]. The LC_{50} values after exposing male rats or mice for 4 h (deaths within 7 days) were 24.2 and 17.5 ppm, respectively. The LC_{50} values after exposing male rats for 60, 30, or 15 min were between 87 and 104 ppm, between 119 and 149 ppm, and between 202 and 240 ppm, respectively. The intraperitoneal LD_{50} values for male rats or mice (deaths within 7 days) were 51.6 and 32.1 mg/kg, respectively. ONF_3 produced strong irritations resulting in pulmonary edema and hemorrhage after inhalation, as well as local denatured changes and accumulation of clear exudate after intraperitoneal injection. ONF_3 was quickly absorbed by rats after intraperitoneal injection. Fluoride increased quickly in the blood and concentrated in various tissues, especially thyroid, bone, and teeth. Most of the fluoride was excreted in urine, and a considerable amount was also recovered in feces.

The adverse effects of NF_3O on lower organisms have been examined [673]. The gas caused minimum damage to plants when they were exposed for 30 min to concentrations as low as 5 ppm. Effects on goldfish maintained in aquaria under 1% NF_3O for 30 min were negligible; salmon were moderately sensitive. Microorganisms in soil were only slightly decreased in numbers by 1 h of exposure, which was done by continuously tumbling soil particles through 1% NF_3O . Potentially useful decontamination reactions were studied. Interhalogens and N_2F_4 can probably be removed from the atmosphere by a mist of aqueous sodium bicarbonate solution. No reagent portable enough and sufficiently effective to remove OF_2 and NF_3O gas from the atmosphere was found. NF_3 is virtually non-reactive.

6.4.5 Applications of Trifluoramine Oxide

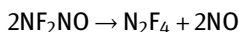
Although much of the synthesis work on nitrogen fluorides and nitrogen oxygen fluorides has been funded by U.S. government agencies interested in their use as rocket propellants, no rocket engine tests using trifluoramine as the oxidizer have yet been reported.

Other applications have been discussed, for instance as a replacement for nitrogen trifluoride in the cleaning of CVD equipment in the production of semiconductors. Nitrosyl fluoride FNO and trifluoramine oxide F_3NO were evaluated as candidates for new CVD chamber cleaning gases [674]. NF_3 and C_2F_6 , which have been used up to this time, were measured as the reference. FNO is highly susceptible to hydrolysis. F_3NO is expected to decompose more easily than NF_3 in the atmosphere because its N—F bond has been weakened by the introduction of an N=O bond into the molecule. Hence, the contribution to global warming of these compounds is expected to be small. Performance of these gases was evaluated by measuring their etch rates and their exhaust gases. The results showed that the etch rate of F_3NO was virtually the same as that of NF_3 , whereas the etch rate of FNO was about half that of NF_3 .

6.5 Nitrosodifluoroamine

The purple color of condensed tetrafluorohydrazine is often due to trace amounts of nitrosodifluoroamine (F_2NNO). It was estimated that as little as 0.1% NF_2NO in liquid N_2F_4 will give a pronounced purple color to the solution. When a mixture of tetrafluorohydrazine and nitric oxide was passed through a coil at elevated temperature (573 K [300 °C]) and then allowed to impinge upon a Pyrex cold finger at liquid nitrogen temperature, a dark purple deposit was formed [675].

In order to get maximum conversion of N_2F_4 into NF_2NO , it was necessary to use an excess of NO. If a sample of prepared NF_2NO is allowed to warm up to room temperature, the gases produced have the following composition (as determined by mass spectrometry): 65.0% NO, 32.4% N_2F_4 , and 1.8% N_2O . This is the composition that one would expect if NF_2NO decomposed according to the equation



This easy dissociation is in reversal of its formation.

Thermally unstable nitrosodifluoroamine can be synthesized from pyrolyzed N_2F_4 and an excess of NO in a cold trap that forms the inlet to a mass spectrometer, with analysis by mass spectrometry immediately after its formation [676]. Operating at low temperatures will also allow one to examine the sample for dimer association in the vapor phase. The appearance potential of NF_2^+ from NF_2NO was 12.12 eV.

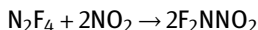
Both *ab initio* methods and DFT methods have been applied to model geometries of F_2NNO , F_2NNO_2 , and their building components (NF_2 , NO, and NO_2) [677]. The geometries and energies of the structures were compared to experimental values when available.

The structure and energetics of several isomers of the nitrosamines have been investigated using quantum chemical calculations [678]. A comparison of the structure and stabilities of the H_2NNO and F_2NNO species resulted in the observation of both species possessing the same lowest energy isomer, i.e., the isomer with F_2NNO connectivity with C_1 symmetry.

Nitrous oxide, N_2O , was observed to react with F_2 under UV irradiation at 77 K (−196 °C) to initially form $\text{F}_2\text{N}_2\text{O}$, which, in accordance with earlier reports from the literature, decomposed above 133 K (−140 °C) to form N_2F_4 and NO [679]. A reaction mechanism for the formation and decomposition of F_2NNO from N_2O and F_2 and from N_2F_4 and NO has been suggested using valence bond theory considerations. The structure of F_2NNO was fully optimized at the electron-correlated level of theory and was shown to possess C_1 symmetry. A frequency analysis clearly showed the C_1 structure to represent a true energy minimum, whereas the earlier proposed planar C_s structure was shown to represent a first-order transition state. See also [18].

6.6 Nitrodifluoroamine

The highly unstable nitrodifluoroamine F_2NNO_2 is formed in the reaction of dissociated N_2F_4 with NO_2 at 583 K and rapid quenching at 77 K:



Nitrodifluoroamine O_2NNF_2 was prepared by passing N_2F_4 through a capillary furnace at 583 K (310 °C), mixing dissociated N_2F_4 ($\bullet NF_2$) with NO_2 at the capillary exit, and immediately quenching the product to 77 K (−196 °C) [680]. From mass spectral data, the appearance potentials for ONF, NO_2F , NO_3F , ONF_3 , $ONNF_2$, and O_2NNF_2 were determined, from which some thermodynamic quantities could be derived. The heats of formation of ONF, NO_2F , and $ONNF_2$ were lower than earlier values reported in the literature, suggesting possible excess energy in the ionization processes. The derived heats of formation of $ONNF_2$ and O_2NNF_2 gave N–N dissociation energies of $D(ON–NF_2) = 0.82$ eV and $D(O_2N–NF_2) = 0.71$ eV, respectively.

6.7 Fluorodinitroamine

NF_3 and $N(NO_2)_3$ are known compounds, whereas the mixed fluoronitroamine $FN(NO_2)_2$ had been unknown until 2014. Fluorodinitroamine, $FN(NO_2)_2$, was prepared by the fluorination of the dinitramide anion using NF_4^+ salts as the preferred fluorinating agent and was characterized by multi-nuclear NMR and Raman spectroscopy [681, 682]. Numerous experimental conditions for the synthesis of $FN(NO_2)_2$ have been investigated, including the use of $KN(NO_2)_2$ or $CsN(NO_2)_2$ as starting materials and NF_4SbF_6 , NF_4BF_4 , F_2 , or $FOSO_2F$ as fluorinating agents. The preferred combinations were $KN(NO_2)_2$ and NF_4SbF_6 in either SO_2 at 209 K (−64 °C) or CH_3CN at 243 K (−30 °C). $FN(NO_2)_2$ is a colorless solid at low temperatures and melts at about 179 K (−94 °C) to a colorless liquid. It is a thermally unstable, highly energetic material that decomposed above 253 K (−20 °C) to N_2O_4 , *trans*- N_2F_2 , N_2O , and FNO_2 . The ^{19}F NMR spectrum showed a single, somewhat broadened resonance at 53 ppm, which was in good agreement with those previously observed for the similar compounds F_2NNF_2 (60.4 ppm), $FN=C(CN)(CH_3)$ (60 ppm), and $FN=C(CF_3)_2$ (48.3 ppm).

7 Nitrogen Chloride Fluorides

Nitrogen trichloride is notoriously unstable and would not be considered as a rocket propellant. Nitrogen trifluoride is stable and has been considered as a rocket propellant. Intermediate compounds exist in the form of nitrogen dichloride fluoride and nitrogen chloride difluoride, which exhibit intermediate stability and are mostly of interest as intermediates in the synthesis of other fluorine compounds. Nobody would want to use them as rocket propellants. Chlorodifluoroamine (chlorodifluoroamine, nitrogen chloride difluoride, ClNF_2) is a gas that can be used as an intermediate in the synthesis of other difluoroamino compounds such as tetrafluorohydrazine.

7.1 Preparation of Chlorodifluoroamine

Chlorodifluoroamine, ClNF_2 , CAS RN [13637-87-1], has been prepared by reaction of difluoroamine with boron trichloride, phosgene, or hydrogen chloride [683]. It can also be obtained by treating a mixture of sodium azide and sodium chloride with elemental fluorine. Ammonia in the form of the simple salts NH_4F and NH_4HF_2 reacts under certain conditions with ClF_3 to yield chlorodifluoroamine, NF_2Cl . The reaction of difluoroamine with hydrogen chloride produced chlorodifluoroamine [684, 685]:



The Lawton patent also contains an IR spectrum of this compound.

The reaction of difluoroamine with chlorine gives chlorodifluoroamine [686]. The difluoroamine precursor can be prepared by hydrolysis of difluorourea or perfluorourea [381, 397, 399, 687]. The difluoroamine has a melting point of 157 K (-116°C), a boiling point of 249.5 K (-23.6°C), and a density of

$$\rho = 1.424 - 0.00202t$$

where ρ is the density in g/cm^3 and t is the temperature in degrees Celsius.

A more convenient synthesis is the reaction of difluoroamine with *tert*-butyl hypochlorite [688]. See also [689].

The chlorofluoroamines NFCl_2 and NF_2Cl were prepared by fluorination of an $\text{NH}_4\text{Cl}/\text{NaCl}$ mixture and characterized by vibrational spectroscopy [690]. For NF_2Cl , two fundamental vibrations had to be reassigned.

7.2 Physical Properties of Chlorodifluoroamine

Chlorodifluoroamine ClNF_2 is readily identified by three intense absorptions in its IR spectrum at 930, 854, and 697 cm^{-1} , corresponding to symmetric and asymmetric N—F stretching and N—Cl stretching, respectively [691].

7.3 Chemical Properties of Chlorodifluoroamine

The reaction of chlorodifluoroamine with mercury produces tetrafluorohydrazine. The reversal of this reaction is the reaction of tetrafluorohydrazine with chlorine, which results only in an equilibrium mixture of the two reactants and the product [692].

The photolysis of chlorodifluoroamine results in the formation of difluoroamino free radicals similar to those formed by photolysis of N_2F_4 [693, 694].

8 Fluoroamine and Difluoroamine

Fluoroamine and difluoroamine are too unstable to be used as rocket propellants, but they can serve as intermediates in the synthesis of more stable fluorides such as tetrafluorohydrazine.

8.1 Fluoroamine

Fluoroamine (monofluoroamine, fluoramine, FNH_2 , CAS RN [15861-05-9]) can be synthesized by vaporizing the adduct $NH_2F \cdot 2HF = NH_3F^+ HF_2^-$ in a dynamic vacuum. The reaction gas is passed through activated, powdered KF to absorb HF and is collected at 76 K [20]:



Above 173 K, fluoroamine decomposes:



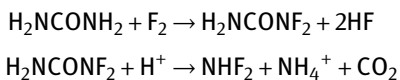
As a weak base, fluoroamine reacts with strong acids, e.g., H_2F_2 , HSO_3F , $HClO_4$, or H_2SO_4 , forming fluorammonium salts $NH_3F^+ X^-$.

8.2 Difluoroamine

Difluoroamine (difluoramine, fluorimide, F_2NH , CAS RN [10405-27-3]) is extremely unstable and requires very careful handling because it often explodes spontaneously, especially on freezing or melting. A summary of the chemistry of difluoroamine is published in [695].

8.2.1 Preparation of Difluoroamine

Difluoroamine can be obtained by the hydrolysis of *N,N*-difluorourea with concentrated sulfuric acid [696]:



8.2.2 Physical Properties of Difluoroamine

Difluoroamine has a melting point of 156.6 K and a boiling point of 249.4 K. The boiling point is considerably higher than the boiling point of NF_3 (144.2 K) due to hydrogen bonding in the liquid, forming molecular clusters. *Ab initio* calculations have been performed on difluoroamine clusters consisting of up to four molecules [697]. The dimer, trimer, and tetramer were all found to exhibit two minima.

8.2.3 Chemical Properties of Difluoroamine

One of the primary properties of ammonia is that it is readily protonated to form ammonium ions. The question was whether substitution of one or two hydrogens in ammonia will change its basicity and the mobility of the remaining hydrogen in ion-exchange reactions. Isotope exchange is one method to determine the rates of protonation and deprotonation. It is known that increasing the acidity will accelerate the proton (deuteron) exchange in NH_3/ND_3 . Similar tests have been conducted with HNF_2 in D_2O [698, 699]. The exchange of hydrogen between HNF_2 and D_2O was first order with respect to HNF_2 and zero order with respect to D_2O , with an activation energy of $18.8 \text{ kJ/mol} = 4.5 \text{ kcal/mol}$.

Electrolytic reduction of HNF_2 in a four-electron process leads to ammonia. Attempts were made to protonate HNF_2 or F_3CNF_2 to see whether ammonium-type cations such as H_2NF_2^+ or $\text{F}_3\text{CNHF}_2^+$ were possible [700, 701]. Under a variety of protonation conditions, no evidence of salt formation could be found.

In another attempt to protonate HNF_2 , successive small increments of HCl were added to HNF_2 in a cold bath adjusted to 161, 146, and 135 K (−112, −127, and −138°C) [702, 703]. The two compounds were miscible over the entire range of compositions and temperatures, and no adduct formation could be detected. Using $\text{Al}(\text{CH}_3)_3$ as the Lewis acid resulted in explosions and/or methane formation.

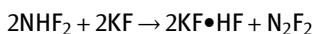
IR and Raman spectra of HNF_2 and DNF_2 in the liquid and solid phases showed that the compounds are associated through hydrogen bridges between the nitrogen atoms [704]. Raman spectra of the KF , RbF , and CsF adducts and IR spectra of the RbF adduct of difluoroamine were interpreted in terms of strongly hydrogen-bridged anions [705]. Potassium, rubidium, and cesium fluoride crystals form complexes when HNF_2 is condensed onto them. When the potassium or rubidium complexes were allowed to warm to room temperature, they reacted further and formed *cis*- and *trans*-difluorodiazene and the alkali metal bifluorides. The cesium complex exploded before

reaching room temperature. The reaction of $\text{KF} \cdot \text{HNF}_2$ with OF_2 resulted in the formation of N_2F_4 .

Difluoramine is a weak base that can form adducts with Lewis acids (BF_3 , BCl_3 , PF_5 , SO_2) that are formed at 195 K and decompose well below ambient temperature. NHF_2 reacts with AsF_5 in anhydrous HF below 195 K to $\text{NH}_2\text{F}_2^+ \text{AsF}_6^-$. Otherwise, difluoramine reacts as an acid. The difluoroamide anion often reacts to form *cis/trans* N_2F_2 in the absence of other reaction partners. Ferric ion Fe^{3+} oxidizes NF_2^- to dinitrogen tetrafluoride N_2F_4 .

8.2.3.1 Decomposition of Difluoroamine

Anhydrous difluoroamine decomposes thermally (in the presence of KF as HF absorber) to dinitrogen difluoride



9 Other Nitrogen–Oxygen–Fluorine Compounds

Another stable polynitrogen ion, the second known example of a stable nitrogen fluoride oxide ion, $[\text{N}_3\text{NFO}]^+$, was prepared as its $[\text{SbF}_6]^-$ salt and characterized by multi-nuclear NMR and vibrational spectroscopy and electronic-structure calculations [706]. The cation is planar and exists as two stereoisomers.

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Nitrogen Oxides

Coverage of nitrogen oxides had to be spread out over seven chapters because a single chapter on the topic would have been very large and would have made it more difficult for readers to find information on a specific compound. In addition, arranging 30 chapters among 5 subvolumes in such a way that each subvolume was about the same size represented a formidable challenge. A book with smaller chapters made our task easier.

The other six chapters in this series are titled “Nitrous Oxide,” “Nitric Oxide,” “Dinitrogen Trioxide,” “Nitrogen Dioxide,” “Dinitrogen Tetroxide,” and “Dinitrogen Pentoxide.”

Nitrogen commonly forms several different oxides with oxygen, depending on the state of oxidation of the central atom, nitrogen. The state of oxidation of nitrogen can be +1, +2, +3, +4, +5, or +6. The correct names of the six oxides are nitrous oxide, N_2O , nitric oxide, NO , dinitrogen trioxide, N_2O_3 , nitrogen dioxide, NO_2 , dinitrogen tetroxide, N_2O_4 , dinitrogen pentoxide, N_2O_5 , and nitrogen trioxide, NO_3 . Nitrogen dioxide, NO_2 , is used mostly in its dimeric form, dinitrogen tetroxide, N_2O_4 , which can be stored as a liquid at room temperature. The state of oxidation of nitrogen in dinitrogen tetroxide is the same as that in nitrogen dioxide. Because the valency of nitrogen in covalent bonds with oxygen is a maximum of four, the structure of dinitrogen pentoxide must be formulated with semipolar bonds, similar to those observed in nitric acid. Nitrogen trioxide, NO_3 , and its dimer N_2O_6 contain peroxide —O—O— linkages, but these compounds are unstable and occur only briefly as intermediates in reactions of other nitrogen oxides.

Nitrogen forms at least six covalently bound oxides, N_2O , NO , N_2O_3 , NO_2 , N_2O_5 , and NO_3 , which are all thermodynamically unstable with regard to their tendency to decompose to dinitrogen and dioxygen. Two of these oxides dimerize by way of $\pi^*-\pi^*$ interactions. Although all nitrogen oxides (in the gas phase) have positive enthalpies of formation, they still are not intrinsically unstable, with the exception of the paramagnetic radical $\bullet\text{NO}_3$, which has not yet been isolated as a pure substance.

As far as rocket propellants are concerned, the first two oxides in this family of nitrogen oxides, nitric oxide and nitrous oxide, have not found the same widespread application as dinitrogen tetroxide and its mixtures with dinitrogen trioxide or nitric acid. The last two oxides in this series, N_2O_5 and NO_3 , are thermally unstable and not suitable as rocket propellants.

During the past 15 years, nitrous oxide, N_2O , has found applications as an oxidizer in hybrid rocket engines, and this use is increasing. It can also be used as a monopropellant.

Oxygen is the third most abundant element in the Universe after hydrogen and helium. Wherever it is available in the presence of nitrogen and exposed to cosmic ra-

diation, one must assume that nitrogen oxides may form and condense in colder parts of the system. Therefore, nitrogen oxides are expected to be present in the solid phase in giant gas planets and “icy” grain mantles of comets and interplanetary particles. Being able to find condensed nitrogen oxides or nitric acid on any extraterrestrial body that might be a destination for future space travel would be a great bonus to In-Situ Resource Utilization (ISRU). The presence of perchlorate in the ice and soil on Mars has been a big surprise, and the occurrence of nitrates falls in the same category.

1 Nomenclature of Nitrogen Oxides

Dinitrogen tetroxide, N_2O_4 , often erroneously or negligently also called nitrogen tetroxide or nitrogen peroxide, and its mixtures with dinitrogen trioxide or nitric acid have found widespread applications as storable and hypergolic oxidizers and occupy the main portion of this chapter. Nitrogen tetroxide would be NO_4 , but this compound does not exist. Another erroneous designation for N_2O_4 is *nitrogen peroxide*, which was derived from the French name for the compound, *peroxyde d'azote*, but translated into English incorrectly. A common abbreviation for N_2O_4 is NTO, which is short for **d**initrogen **t**etroxide. This very popular abbreviation may partially be responsible for the frequently used misleading name *nitrogen tetroxide*. Nobody has proposed thus far to correct the situation by using the abbreviation DNTO for **d**initrogen **t**etroxide. It would be cumbersome to have to add the extra letter D. It would be easier to keep in mind that if the abbreviation NTO is used in this book or in any other rocket propellant literature, this actually stands for **d**initrogen **t**etroxide and the D was dropped as a matter of convenience.

Because the other nitrogen tetroxides, NO_4 and N_3O_4 , do not exist as neutral molecules or are only short-lived, there is very little chance that the name *nitrogen tetroxide* used for N_2O_4 will get confused with other nitrogen tetroxides. NO_4 exists in the form of the short-lived peroxyxynitrate ion NO_4^- , which plays an important role in atmospheric pollution (smog) chemistry. N_3O_4 exists in the form of dinitramide ion N_3O_4^- , which is relatively stable and is present in ammonium dinitramide (ADN), a new rocket propellant ingredient.

There is only a slight possibility of confusion because the common abbreviation (acronym) for 3-**n**itro-1,2,4-**t**riazol-5-**o**ne, a solid energetic material widely used as explosive and propellant additive, is also NTO. However, one can usually guess from the context in which the abbreviation NTO is used whether the author means the liquid oxidizer NTO or the solid explosive NTO.

Dinitrogen pentoxide, N_2O_5 , and nitrogen trioxide, NO_3 , are unstable and unsuitable as rocket propellants. Dinitrogen pentoxide is an active nitrating agent for the synthesis of organic nitro compounds used as energetic materials.

2 Physical Properties of Nitrogen Oxides

The densities and molecular volumina of nitrogen oxides in the frozen state were measured at low temperatures [1]. Table 1 gives a comparison and summary of the most important physical properties of nitrogen oxides.

Table 1: Comparison and summary of physical properties of nitrogen oxides.

Compound name	Chemical formula	Melting point		Boiling point		Oxygen content	Molecular mass g/mol
		K	°C	K	°C	Mass-% O	
Nitrous oxide	N ₂ O	170.7	−102.4	183.6	−89.5	36.35	44.016
Nitric oxide	NO	110	−163	121.3	−151.8	53.32	30.008
Dinitrogen trioxide	N ₂ O ₃	171	−102	—	—	63.14	76.016
Dinitrogen tetroxide (nitrogen dioxide)	N ₂ O ₄ (⇌2NO ₂)	261.9	−11.2	294.3	+21.15	69.55	92.016
Dinitrogen pentoxide	N ₂ O ₅	—	—	Sublimes at 307.1	Sublimes at +34 °C	74.06	108.016
Nitrogen trioxide	NO ₃ (⇌ 1/2 N ₂ O ₆)	131 (dec.)	−142 (dec.)	—	—	77.41	62.008

2.1 Optical Properties and Spectra of Nitrogen Oxides

The spectral properties of nitrogen oxides provide information about the molecular structure of the molecules and excited states they go through as they decompose. Spectra are also used to identify short-lived intermediates of decomposition reactions. Spectroscopy is the main tool in the search for oxides with higher oxidation states of nitrogen or nitrogen oxides formed in complex ring structures that might be useful as more energetic oxidizers in rockets. Most of the spectroscopic work on nitrogen oxides found in the literature deals with the mechanisms of formation, destruction, and identification of nitrogen oxides in the atmosphere, where they are notorious as atmospheric pollutants but also serves a vital mechanism for abiotic nitrogen fixation that provides much needed nitrogen fertilizer nutrients for all growing plants.

2.2 Infrared Absorption Spectra of Nitrogen Oxides

In what follows there are several sections describing the IR spectra of individual nitrogen oxides. Here we provide links to some overview studies that investigate more than one nitrogen oxide at a time, dealing with several as a group and comparing them. The same papers may be referenced again in later sections on specific nitrogen oxides.

A nice summary of IR and Raman spectra of all nitrogen oxides, including their ions, is contained in [2]. IR studies have been made of several oxides of nitrogen trapped at liquid-helium temperatures in matrices of Ar, N₂, O₂, CO₂, H₂, or N₂O [3]. NO was found as the monomer and two forms of dimer, *cis* and *trans*. The *cis* is more stable than the *trans* isomer. NO₂ was found as the monomer, the known stable dimer of planar structure, and two new dimers. One of these has the ONO–NO₂ structure, and the other may be the twisted V_d form of the stable dimer. N₂O₃ was found in its stable form ON–NO₂ and in a second form whose spectrum was consistent with the structure ONONO. Observations on covalent N₂O₅ were also reported.

2.3 Thermodynamic Properties of Nitrogen Oxides

Exact knowledge of the thermodynamic properties of nitrogen oxides is required to calculate theoretical rocket performance and evaluate reactions among the nitrous oxides themselves, including dissociations and (re)combination reactions.

The ideal gas chemical thermodynamic properties for NO, NO₂, N₂O₃, and N₂O₄ for the temperature range 50 to 5000 K were evaluated by a statistical thermodynamic method using the most recent molecular parameters [4]. In the calculations for NO and NO₂, the effects of anharmonicity and vibration-rotation interaction were included. The contributions due to centrifugal distortion were also included for NO₂. For evaluation of the thermodynamic properties for N₂O₃ and N₂O₄ molecules, the rigid-rotor and harmonic-oscillator models were adopted. A free internal rotation was assumed for N₂O₃ and an internal rotation barrier height (V₂) of 6.61 kJ/mol (1.58 kcal/mol) was assumed for N₂O₄. The thermodynamic properties due to hindered internal rotation were calculated using a partition function formed by summation of internal rotation energy levels. The thermodynamic properties for two equilibrium mixtures, NO₂ ⇌ N₂O₄ and N₂O₃/NO/NO₂/N₂O₄, were also calculated. The effects of temperature and pressure on heat capacities and compositions of these two mixtures were illustrated graphically, and the calculated heat capacities and equilibrium constants were in good agreement with available experimental values.

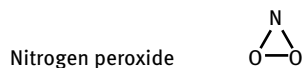
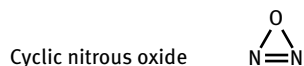
2.4 Molecular Structure of Less Common Nitrogen Oxides

The various chapters of this book contain several sections describing the molecular structure of individual nitrogen oxides. Here we summarize some overview studies that investigate more than one nitrogen oxide at a time, dealing with several as a group. We also discuss some of the less common nitrogen oxides, some of which are only hypothetical and exist only on paper (or on screen).

The nitrogen oxides N_2O_2 , N_2O_3 , and N_2O_4 have many peculiar features: very long, weak N—N bonds, 2.18, 1.864, and 1.782 Å, with low heats of dissociation 11.3, 39.7, and 53.1 kJ/mol (2.7, 9.5, and 12.7 kcal/mol); a typical N—N single bond length is 1.47 Å, for instance, in hydrazine with a heat of dissociation of 19.7 kJ/mol (4.71 kcal/mol). The molecules are planar, although the O—O repulsions are at a maximum for this configuration. The barrier to internal rotation about the N—N axis is higher than would be expected for such long bonds, being 2.9 kcal/mol for N_2O_4 . The dinitrogen oxides are diamagnetic, whereas the building units, NO_2 and NO , are paramagnetic. The $\angle ONO$ bond angles in N_2O_3 and N_2O_4 are unusually large, being 129.8 and 135.4°. The nitroso $\angle NNO$ angles in N_2O_2 , 101.3°, and N_2O_3 , 105.1°, are smaller than in other NO compounds. N_2O_2 , N_2O_3 , and N_2O_4 have only nitrogen-nitrogen σ bonds weakened by oxygen lone-pair delocalization and no N—N π bonding.

One can speculate about the existence of nitrogen oxides that would promise higher performance as rocket propellants, but they have not yet been discovered, and if their existence can be proven, they exist only as short-lived intermediates during the formation or decomposition of other nitrogen oxides or they have to be trapped in a matrix of frozen inert gases. In most instances they can only be isolated and analyzed in a frozen matrix at very low temperatures. It would be possible to use them as cryogenic solid rocket propellants. Examples of this speculative group of nitrogen oxides are as follows:

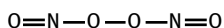
Oxygen azide $N \equiv N = N - O - N = N \equiv N$



Equilibrium geometries, bond dissociation energies, dipole moments, harmonic vibrational frequencies, and IR intensities were calculated for a set of 10 neutral nitrogen oxides (NO , NO_2 , NO_3 , N_2O , *sym*- N_2O_2 , *asym*- N_2O_3 , *sym*- N_2O_3 , *sym*- N_2O_4 , *asym*- N_2O_4 , and N_2O_5) by applying one local and two gradient-corrected non-local functionals in a Gaussian-type-orbital density functional theory method [5]. Comparison with available experimental data showed that, except for the bond dissociation energies,

the local functional gave very accurate molecular properties. Non-local functionals considerably improved the bond dissociation energies, but the results still overestimated the experimental values by about 10 kcal/mol on average. For the other properties, the results obtained with non-local functionals were not necessarily superior to those calculated with the local functional. The properties of two molecules (*sym*-N₂O₃ and *asym*-N₂O₄) were predicted for the first time, and several reassignments were proposed for absorption bands in the vibrational spectra of dinitrogen oxides.

The simple molecule N₂O₄ might exist not only with N—N linkages, but also with O—O linkages. One of the speculative possible structures is



CAS RN [172300-39-9]

Nitroperoxious acid, OO-nitroso ester

Dinitroso peroxide

but it has not been identified as being coexistent with O₂N—NO₂. ONOONO is a short-lived red substance produced by autoxidation of NO with O₂ at 113 K in inert solvents. The red compound was diamagnetic and absorbed light maximally at 500 nm. The ONOONO intermediate was unstable above the melting point of 2-methylbutane, which was used as the matrix, and rapidly converted to O₂NNO₂. This peroxide is related to peroxyntitric acid, HOONO₂, and peroxyntitrous acid, HOONO. Its structure has been calculated using molecular orbital theory.

Six of the nine fundamental vibrational modes for *cis*, *cis*-HOONO, were assigned definitively and one tentatively to the IR absorption spectra of matrix-isolated *cis*, *cis*-peroxyntitrous acid (HOONO), and its deuterated isotopomer DOONO in Ar [6]. Results from coupled-cluster, *ab initio* anharmonic force field calculations helped to confirm some of the assignments.

The rotational spectrum of *cis-cis* HOONO was studied over a broad range of frequencies, 13–840 GHz, using pulsed beam Fourier transform microwave spectroscopy and submillimeter spectroscopy [7]. The inertial defects of HOONO and DOONO were consistent with a planar equilibrium structure with significant out-of-plane H atom torsional motion.

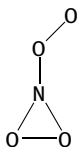
ONOO• is an important intermediate in the autoxidation of nitrogen monoxide by dioxygen. A red isomer of N₂O₄, ONOONO, formed in a matrix at 113 K from nitrogen monoxide and dioxygen, was converted to O₂NNO₂ upon warming. Two intermediates in the autoxidation of NO have been identified: **(1)** ONOO•, which was detected and identified by electron paramagnetic resonance (EPR) spectroscopy at 295 K and atmospheric pressure in the gas phase, and **(2)** ONOONO, a red substance produced at 113 K in a matrix [8]. The rate constant for formation in aqueous solution was higher than that in the gas phase, and, therefore, the half-life of ONOO• is longer in solution.

Pure *sym*-N₂O₄ isolated in solid Ne was obtained by passing cold neon gas over solid N₂O₄ at 158 K (–115 °C) and quenching the resulting gaseous mixture at 6.3 K [9]. Filtered UV irradiation (260–400 nm) converted *sym*-N₂O₄ into *trans*-ONONO₂, a weakly interacting (NO₂)₂ radical pair, and traces of the *cis*-N₂O₂•O₂ complex. Besides the weakly bound ON•O₂ complex, *cis*-N₂O₂•O₂ was also obtained by codeposition of NO and O₂ in solid Ne at 6.3 K, and both complexes were characterized by their matrix IR spectra. The IR spectra of *sym*-N₂O₄ and of *trans*-ONONO₂ in solid Ne were recorded. IR fundamentals of *trans*-ONONO₂ were assigned based on experimental ¹⁶O/¹⁸O isotopic shifts and guided by Density Functional Theory (DFT) calculations. Dinitroso peroxide, ONOONO, a proposed intermediate in the IR photoinduced rearrangement of *cis*-N₂O₂•O₂ to the various N₂O₄ species, was not detected. Its absence in the photolysis products indicated a low barrier (≤10 kJ/mol) for its exothermic O–O bond homolysis into a (NO₂)₂ radical pair.

It has been common practice in the rocket propulsion community to call N₂O₄ *nitrogen tetroxide*, omitting the prefix *di*-, which is chemically incorrect because *nitrogen tetroxide* would refer to the non-existent NO₄. Speculation has it that NO₄, if it existed, could have one of the following molecular structures, most of which have been characterized by computational chemistry, but none of them proved to be stable enough for use as a rocket propellant:

NO₄

1,2,4,5-Tetraoxa-3-azoniaspiro[2.2]pentane
CAS RN [204273-63-2]

NO₄

Dioxaziridinyldioxy
CAS RN [193016-83-0]

NO₄

Tetroxazolidinyl
CAS RN [193016-71-6]

NO_4 exists in the form of the peroxyxynitrate ion NO_4^- (CAS RN [125239-87-4]), whose parent, peroxyxynitric acid, plays an important role in atmospheric air pollution (smog) chemistry. Organic peroxyxynitrates are thermally unstable intermediates (at ambient temperatures) in the atmospheric degradation of hydrocarbons.

2.4.1 Computational Chemistry of Nitrogen Oxides

In many cases, properties of nitrogen oxides that have not yet been identified as existing in the laboratory but have been envisioned by theoretical chemists have been calculated by computational chemistry. This includes nitrogen oxides that exist as short-lived intermediates in the reactions between nitrogen and oxygen or among other nitrogen oxides, and nitrogen oxides of higher states of oxidation of nitrogen that were speculated to make good oxidizers (better than N_2O_4) in rocket propellants.

Self-consistent molecular orbital (MO) bond orders for a number of the simpler nitrogen-oxygen compounds were calculated and attempts made to correlate bond lengths and force constants with bond orders for these molecules [10].

Ab initio computational methods were used to obtain $\Delta_r H^\circ$, $\Delta_r G^\circ$, and $\Delta_r S^\circ$ for the reactions

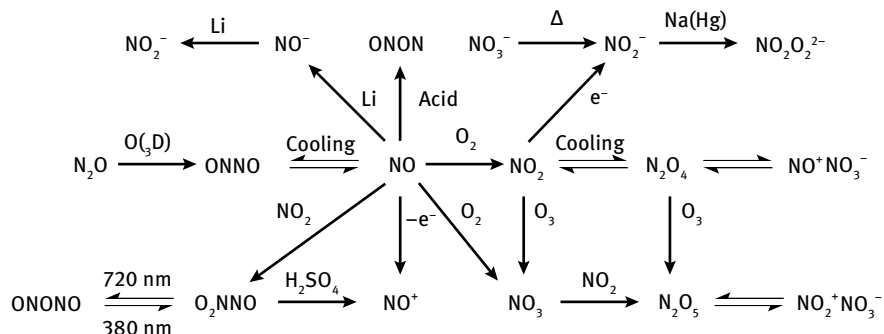


at 298 K [11]. The standard entropies were compared with values cited in the NIST/JANAF tables. With the exception of reaction I, in which the dimer is weakly bound, and reaction V, for which thermodynamic data appear to be lacking, the calculated standard thermodynamic functions of reaction were in good agreement with literature values obtained both from statistical mechanical and various equilibrium methods. The potential surface for the dissociation of N_2O_4 was explored using multi-reference methods. No evidence of a barrier to dissociation was found.

2.5 Chemical Reactions of Nitrogen Oxides

All nitrogen oxides are quite reactive and undergo a multitude of reaction types with other chemicals. A good summary of reactions of nitrogen oxides was published in 1972 [12].

The following schematic illustrates the many interconversion reactions taking place among the several nitrogen oxides [2]:



Laane, J., and J. R. Ohlsen, Characterization of nitrogen oxides

2.6 Summary Literature on Nitrogen Oxides

Since nitrogen oxides have been known for a long time, and because they occupy an important place among industrial chemicals and atmospheric pollutants, a large body of literature exists on the chemistry of nitrogen oxides, but only a fraction of that deals with nitrogen oxides as rocket propellants. We try to fill this gap. Here we give a list of summary and review publications on nitrogen oxides. Most of these deal mainly with dinitrogen tetroxide, but others are covered as well. Most chemical handbooks and encyclopedias have chapters on nitrogen oxides, such as Kirk-Othmer, Ullmann's, or Fedoroff. Other surveys are available in the periodical and report literature [13]. Entire conferences have been devoted to dinitrogen tetroxide and red fuming nitric acid (RFNA).

3 Nitric Oxide

The information on nitric oxide, NO, is in a separate chapter, “Nitric Oxide,” in *Encyclopedia of Oxidizers*.

4 Dinitrogen Trioxide

The information on dinitrogen trioxide, N₂O₃, is in a separate chapter, “Dinitrogen Trioxide,” in *Encyclopedia of Oxidizers*.

5 Nitrogen Dioxide

The information on nitrogen dioxide, NO_2 , is in a separate chapter, “Nitrogen Dioxide,” in *Encyclopedia of Oxidizers*.

6 Dinitrogen Tetroxide

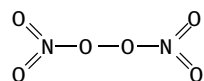
The information on dinitrogen tetroxide, N_2O_4 , is in a separate chapter, “Dinitrogen Tetroxide,” in *Encyclopedia of Oxidizers*.

7 Dinitrogen Pentoxide

The information on dinitrogen pentoxide, N_2O_5 , is in a separate chapter, “Dinitrogen Pentoxide,” in *Encyclopedia of Oxidizers*.

8 Nitrogen Trioxide

The chemistry of nitrogen trioxide has not received much attention from researchers. For quite some time, chemists were not even sure whether this compound existed in its monomeric form, NO_3 , or whether it always occurred in a dimeric form N_2O_6 :



It is known to exist as a free radical, $\bullet\text{NO}_3$. Nitrogen trioxide is said to be formed by the reaction of dinitrogen pentoxide and ozone or by electric discharges in oxygen-nitrogen mixtures. Nitrogen trioxide forms colorless crystals that readily decompose into dinitrogen pentoxide and oxygen. So far, it has not been possible to make solid or liquid nitrogen trioxide in the pure state because it is difficult to separate from ozone. It has been suspected that nitrogen trioxide exists only in equilibrium mixtures with dinitrogen pentoxide and ozone. It has also been suspected that it is a short-lived intermediate during the combustion of rocket propellants where it was observed by mass spectrometry [14].

9 Other Nitrogen-Oxygen Compounds

With a little imagination and trying to build ring, polycyclic, or even caged structures patterned after known hydrocarbon or heterocyclic structures, one can imagine other exotic nitrogen oxides that might turn out to be rocket propellant oxidizers potentially

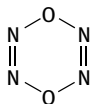
better than dinitrogen tetroxide. Speculation about the existence of higher oxides of nitrogen (higher than N^{+5}) started early [15]. Before actually attempting to synthesize them in the lab, computational chemistry nowadays has enabled theoretical (theoretician) propellant chemists to predict the thermal stability and enthalpy of formation of many of those postulated N_xO_y compounds. Consequently, there are quite a few publications in the literature dealing with purely speculative, imaginative molecules in which many nitrogen and oxygen atoms are linked to form a molecule with a high energy and high oxygen content. Several of these speculative nitrogen oxides were already discussed in the introductory section to nitrogen oxides in the chapter on nitrogen oxides.

Previous studies of open-chain metastable polymers of the nitrogen oxides were extended to polycyclic $(ONNO)_x$ compounds [16]. SCF MO AM1 calculations indicated that such polymers would be comparable in thermodynamic and kinetic stability to the open-chain isomers. Results for the parent molecule, a cyclic dimer of N_2O , and for oligomers ≤ 7 rings in length, and a comparison of neat oligomers and oligomers in which the terminal *cis* azo groups are hydrogenated showed that the favored conformer would be a series of boats. Activation enthalpies for homolytic cleavage of N—N and N—O bonds in three model compounds were on the order of 42–83 kJ/mol (10–20 kcal/mol). Realization of the polymer would be expected to require extreme pressures, in which case the existence of the known *cis*-ONNO in the solid state would probably result in the formation of polycyclic material by the concerted polymerization of the dimer rather than by way of fusion of two open-chain $(NONO)_x$ molecules.

Planar N_x systems, such as $\text{cyclo-}N_5^-$ and N_5^+ , tend to be more stable than nonplanar systems, such as the neutral $\text{cyclo-}N_6$. It has been proposed that the key to stabilization is the separation of the σ and π electron systems [17]. In both $\text{cyclo-}N_5^-$ and N_5^+ , a six- π -electron system is created upon either adding to or removing from the $\text{cyclo-}N_5$ radical one electron. It was speculated that judicious addition of oxygen atoms to polynitrogen ring compounds such as $\text{cyclo-}N_4$ and $\text{cyclo-}N_6$ can increase their thermodynamic and kinetic stabilities, accompanied by only a small loss in their efficiency as high energy density materials, actually improving their utility as oxidizers. The properties of some of these compounds were calculated and compared with the parent all-nitrogen compounds. Coordination of one or more oxygen atoms to the ring leads to effective separation of the σ and π electron systems helping to stabilize the systems. The exocyclic N—O bonds can assume a single- or double-bond character, depending on the ring system.

Some of the nitrogen-oxygen compounds discussed here are closely related to the polynitrogens. The long sought after N_6 hexaazo-benzene ring that is isoelectronic with benzene can be stabilized by adding coordinate-covalent bonds from oxygen. Optimized structures, normal IR harmonic frequencies, heats of formation, and activation energies for unimolecular dissociation were calculated for the N_4O , N_4O_2 , N_6O , N_6O_2 , and N_6O_3 systems with oxygen atoms in the ring or attached to the ring [18]. By increasing the number of oxygen atoms adjacent to the ring, a nitrogen ring with

alternating positive and negative atomic charges can be created. In fact, the N_4O_2 , dioxatetrazine,



and N_6O_3 systems have completely planar structures and computed heats of formation of 523 and 647 kJ/mol (125.0 and 154.7 kcal/mol), respectively. Furthermore, these systems appear kinetically stable with barriers to unimolecular dissociation of 187 and 261 kJ/mol (44.8 and 62.4 kcal/mol), respectively. A boat-shaped conformation (C_{2v} structure) was determined to be a minimum equilibrium structure [19].

Various all-nitrogen molecules have been examined as candidates for high-energy-density materials (HEDMs) because of the energy release that would accompany the dissociation of such a molecule down to N_2 molecules. Numerous N_x molecules have been shown to dissociate too easily to be viable HEDMs, including small N_x all-nitrogen cages. One possible solution to the instability of small N_x cages is oxygen insertion into the N—N bonds. Conversion of N—N bonds into N—O—N bonding groups would relieve much of the ring strain in small N_x cages, thereby stabilizing the molecule and possibly making the N_xO_y molecule a good HEDM. If octaazacubane, N_8 , could be stabilized by attaching oxygen atoms or by changing N—N bonds to N—O—N bridges, that would be a very high energy high-density material. Several cage isomers of N_8O_4 were examined by theoretical calculations to evaluate their suitability as potential HEDMs [20]. Calculations are carried out with Hartree-Fock theory and Møller-Plesset perturbation theory (MP3 and MP4) to obtain the energy released if the molecule decomposes.

A purely speculative compound that has never been synthesized but would make a good rocket propellant is 1,3,5-trioxa-2,4,6-triazine $H_3N_3O_3$. The enthalpies of formation of the gas-phase species were computed according to the atomization energy method and gave $\Delta H_f^\circ(G) = +100.6$ kcal/mol [21]. The enthalpy of sublimation for $H_3N_3O_3$ was estimated as 74 kJ/mol = 17.7 kcal/mol according to Trouton's rule. With the estimated sublimation enthalpy, the enthalpy of formation for solid 1,3,5-trioxa-2,4,6-triazine was calculated to be $\Delta H_f^\circ(S) = +347$ kJ/mol = +82.9 kcal/mol. The density of $H_3N_3O_3$ was calculated to be $\rho = 1.60$ g/cm³ from the molecular volume.

9.1 Trinitroamide N_4O_6

Trinitroamide, trinitramide, N_4O_6 , $N(NO_2)_3$, trinitramine, trinitroamine, constitutes a possible energetic green oxidizer that could be suitable for future high-perfor-

mance rocket propellants. The structure of the molecule has jokingly been called a “propeller” molecule (Figure 1).

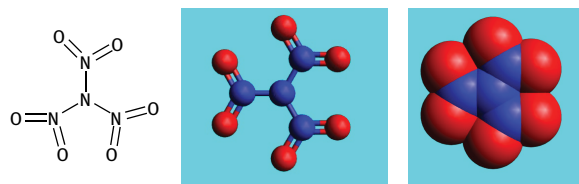


Figure 1: Molecular structure of trinitroamide.

Only a few speculative, theoretical works had predicted this nitrogen oxide until its existence was confirmed experimentally. The heat of formation ΔH_f° (gas) of trinitroamide had been estimated at between +159 and +297 kJ/mol (+38 and +71 kcal/mol), and the N–N bond dissociation energy had been estimated to be 83.7–113 kJ/mol (20–27 kcal/mol) [22].

Ab initio calculations predicted a stable C_3 structure for trinitroamide with N–N bond lengths of 1.545 Å and an enthalpy of formation of +247 kJ/mol (+59 kcal/mol) [23]. Thermal decomposition of trinitroamide most likely would occur via N–N bond cleavage, which would require about 109 kJ/mol (26 kcal/mol).

Results of *ab initio* calculations of the structures and energies of the mono-, di-, and trinitrosamides were compared to mono-, di-, and trinitroamides [24]. Accurate standard heats of formation of this series of nitroamides and nitrosamides were calculated using isodesmic reactions and high-level theories. The nitrosamides were predicted to have heats of formation at 0 K that were 83–166 kJ/mol (20–40 kcal/mol) higher than the analogous nitroamides. The N–N bond strengths were comparable whether a NO or NO₂ group was bonded to the central nitrogen atom. The data suggested that converting the nitro groups to nitroso groups might result in compounds with lower molecular weights, shorter N–N bond lengths, and higher energy content, at the expense of lower oxygen balance. It was suggested that nitrosamides are potentially useful high-energy materials. Using the same computational method, the revised ΔH_f° for NH₂NO₂ was predicted to be 3.8 kcal/mol at 0 K, in close agreement with previous theory, but very different from experiment. Predicted values for ΔH_f° were 142 and 297 kJ/mol (34 and 71 kcal/mol) for di- and trinitramide, respectively, and 92, 272, and 469 kJ/mol (22, 65, and 112 kcal/mol) for mono-, di- and trinitrosamide, respectively. Nitrosamides have bond strengths comparable to those of the nitramides.

The largest nitrogen oxide to date, trinitroamide, has been prepared following extensive quantum chemical studies in which its kinetic stability and several physical properties were estimated. Trinitroamide was finally detected using IR and nuclear

magnetic resonance (NMR) spectroscopy [25]. The compound is highly energetic and shows promise for cryogenic propulsion and as a reagent in HEDM research.

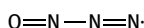
9.2 Nitrogen Tetroxide Cation NO_4^+

The structure and energy of the bicyclic nitrogen tetroxide cation, $\text{D}_{2d}\text{NO}_4^+$, and its C_{2v} transition state for dissociation into NO_2^+ and O_2 have been studied theoretically by the coupled-cluster and similarity-transformed equation-of-motion coupled-cluster methods [26, 27]. The computed energy of decomposition was 573 kJ/mol (137 kcal/mol). The gas-phase heat of formation was predicted to be +1548 kJ/mol (+370 kcal/mol). Nevertheless, its low dissociation barrier (50–71 kJ/mol = 12–17 kcal/mol) and high vertical electron affinity (8.4 eV) indicated that NO_4^+ will have a low stability, which will complicate its experimental observation.



9.3 Azido Oxide N_3O

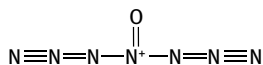
The short-lived nitrogen-rich azido oxide N_3O has been detected in the gas phase by mass spectrometric experiments [28, 29]. The radical has been assigned a minimum lifetime of 0.7 μs , and an open-chain NNNO structure in the quartet state. N_3O^+ ions prepared in the source of a mass spectrometer under low-pressure conditions were submitted to neutralization by collisional electron transfer, leading to the observation of the novel neutral N_3O oxide:



In support of these experiments, the structures and energies of the N_3O^+ precursor ion and the N_3O radical have been calculated by *ab initio* methods. These compounds are too unstable to be used as rocket propellants.

9.4 Heptanitrogen Oxide Cation N_7O^+

The reaction of $\text{NOF}_2^+\text{SbF}_6^-$ with an equimolar amount of HN_3 in anhydrous HF at 228 K (−45 °C) produced $\text{N}_3\text{NOF}^+\text{SbF}_6^-$. When an excess of HN_3 was used, a new compound, $\text{N}_7\text{O}^+\text{SbF}_6^-$, was formed [30]:



However, this compound could not be isolated as a solid and rapidly decomposed in a quantitative manner with N_2O evolution to $\text{N}_5^+\text{SbF}_6^-$. This reaction represents a novel and more convenient synthesis for $\text{N}_5^+\text{SbF}_6^-$ because $\text{NOF}_2^+\text{SbF}_6^-$ is more readily accessible than $\text{N}_2\text{F}^+\text{SbF}_6^-$ and the N_5^+ can be labeled in all five positions with ^{15}N by the simple use of terminally singly labeled N_3^- . The formation of the N_7O^+ cation was established by isotopic labeling experiments and theoretical calculations. It was shown that the addition of a second azido ligand to the same central atom allows for an attack of the negatively charged N_α atom of one ligand by the positively charged N_γ atom of the second ligand, thereby greatly lowering the activation energy barrier toward decomposition and explaining why geminal diazides are much less stable than either monoazides or vicinal diazides.

9.5 Nitrosyl Azide NON_3

Nitrosyl azide, nitroso azide, N_4O , NON_3 , is a compound in the group of covalent (as opposed to ionic) azides. The characterization and usage of the covalent non-metal azides have obviously been hampered by their thermodynamic and kinetic instability. NON_3 , HN_3 , and all of the halogen azides are very hazardous. Especially dangerous are the pure halogen azides in the condensed phase. Violent explosions can also occur in the gaseous state upon sudden variations of the pressure.

It was found through a combined quantum chemical and experimentally observed study of gas-phase IR decomposition products that *trans-trans*- N_4O decomposed via rotation into the *cis-cis* isomer and cyclic N_4O to yield $\text{N}_2\text{O}(\text{C}_{\infty\text{v}})$ and N_2 . The unimolecular decomposition of nitrosyl azide (tetranitrogen monoxide), N_4O , was modeled by computer programs at the electron-correlated, spin-restricted RMP2 level [31–34]. It was demonstrated that the experimentally established *trans-trans*- N_4O (C_s) may either interconvert into *cis-cis*- N_4O , which upon decomposition forms cyclic $\text{N}_4\text{O}(\text{C}_{2\text{v}})$ as an intermediate species to finally give $\text{N}_2\text{O}(\text{C}_{\infty\text{v}})$ and N_2 , or *trans-trans*- N_4O may directly dissociate into cyclic $\text{N}_2\text{O}(\text{C}_{2\text{v}})$ and N_2 . All structures determined were rationalized by energy hypersurface calculations.

Motivated by the isolation and spectroscopic characterization of nitrosyl azide (N_4O), several *ab initio* investigations and valence-bond calculations of the originally reported structure, as well as various hypothetical structural isomers on the potential energy hypersurface, were undertaken [35]. Speculation was also extended to the mode of decomposition of nitryl azide, N_3NO_2 . Geometries and harmonic vibrational frequencies were predicted for the *trans*-chain isomer along with the 6- π electron po-

tentially aromatic ring structure with various levels of theory giving estimates for bond lengths and bond angles for the *trans*-chain and ring isomers. While the ring isomer was predicted to be the most stable structure on the hypersurface, the barrier to dissociation was very low, between 1 and 2 kcal/mol, making isolation theoretically possible but experimentally difficult. This small barrier also detracts from the attractiveness of the N_4O ring structure as a High Energy Density Material (HEDM). The *trans*-chain isomer, however, was found to lie in an energy valley with higher sides, consistent with previous experimental observations. High-level *ab initio* techniques have been used to aid experimentalists in discovering and characterizing new energetic molecules [36]. Methods used ranged from the self-consistent field approximation through DFT to coupled clusters with inclusion of single and double excitations. Characterization of minima and transition states between minima of nitrosyl azide surface revealed that the ring isomer is a poor high-energy-density candidate due to a low barrier to dissociation.

The formation of a new binary isomer of N_2O through the reaction of NS^+ salts with the azide anion was deemed highly unlikely. Therefore, the ongoing quest for cyclic N_2O continued due to the observation of *trans-cis* isomerization of the N_4O moiety [37].

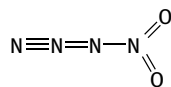
Lucien may have obtained some nitrosyl azide, but in those early days he lacked the instrumentation to unambiguously identify it as a new compound and concluded only from the composition of the decomposition products (N_2O and N_2) that at one point he may have had nitrosyl azide in pure form [38].

Reaction products of the reaction of activated, anhydrous sodium azide with nitrosyl chloride were sublimed under vacuum at low temperature and gave a pale yellow condensate of N_4O [39].

The conformational and structural stability of nitrosyl azide $NNN-N=O$ and nitryl azide $NNN-NO_2$ were investigated by DFT and *ab initio* MP2 calculations [40]. Nitrosyl azide was predicted to exist predominantly in the planar *trans* (the angled NNN and $N=O$ groups are *trans* to each other) structure with a high *trans-cis* rotational barrier of about 46 kJ/mol (11 kcal/mol) as a result of pronounced conjugation between the azide group and the $N=O$ bond. The vibrational frequencies were calculated and the IR and Raman spectra plotted. Complete vibrational assignments were made on the basis of normal coordinate calculations for the stable conformers. For nitrosyl azide, the calculated wave numbers were compared to experimental values obtained from earlier reported Raman spectra of the molecule.

9.6 Nitryl Azide NO_2N_3

In addition to the well-characterized dimer of nitrous oxide (N_2O)₂, an isomeric nitrogen oxide with the gross formula N_4O_2 exists (at least on paper) as nitryl azide (nitroxyl azide, nitronium azide, nitro azide, NO_2N_3) CAS RN [40006-84-6]:



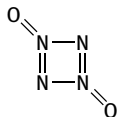
Azide salts, such as the alkali metal salts, react with nitronium salts to form nitryl azide, NO_2N_3 , whose existence was supported by IR and mass spectral data [41], but that observation could not be confirmed subsequently. Nitryl azide was supposed to be relatively stable at temperatures below 263 K (-10°C), but above 273 K (0°C) it decomposed quantitatively to N_2O . The formation of N_2O from N_4O_2 was at one time said to proceed via oxatetrazole-2-oxide as an intermediate.

The reaction behavior of NaN_3 , AgN_3 , and Me_3SiN_3 toward FNO_2 , ClNO_2 , NO_2SbF_6 , and NO_2BF_4 was investigated in search of nitryl azide and similar energetic nitrogen-oxygen compounds [42]. At 243 K (-30°C) or below in a solvent-free system, sodium azide did not react with ClNO_2 , NO_2BF_4 , or NO_2SbF_6 . Below 243 K (-30°C) silver azide did not react with neat ClNO_2 . Pure chlorine azide was isolated by fractional condensation and identified by its low-temperature Raman spectrum (liquid state). Treatment of FNO_2 with NaN_3 at temperatures as low as 195 K (-78°) always ended in an explosion, which was probably due to the formation of FN_3 as one of the reaction products. The reaction of NO_2SbF_6 with NaN_3 in liquid CO_2 ($-55 \leq T \leq -35^\circ\text{C}$) as the solvent afforded a new azide species that was stable at low temperatures in solution only and was investigated by means of low-temperature Raman spectroscopy. The vibrational data gave strong evidence for the presence of a tetranitrogen dioxide, N_4O_2 , which can be regarded as nitryl azide (NO_2N_3). The structure and vibrational frequencies of N_4O_2 were computed by an *ab initio* method.

Five N_4O_2 isomers and their possible decomposition pathways were investigated with Møller-Plesset perturbation theory (MP2) and DFT [43]. The most stable isomer was predicted to be the open-chain C_{2v} structure, which has not been reported previously. For all five N_4O_2 isomers, dissociation energies and eight transition states were studied. The open-chain isomer and the planar (C_{2h}) isomer could be potential candidates for HEDMs owing to their large dissociation energy and moderate dissociation barrier.

Gaseous nitryl azide N_4O_2 can be generated by the heterogeneous reaction of gaseous ClNO_2 with freshly precipitated AgN_3 at 223 K (-50°C) [44]. The geometric and electronic structure of the molecule in the gas phase has been characterized by *in situ* photoelectron spectroscopy (PES) and quantum chemical calculations. The experimental first vertical ionization energy of N_4O_2 is 11.39 eV, corresponding to the ionization of an electron on the highest occupied molecular orbital. An apparent vibrational spacing of $1600 \pm 60 \text{ cm}^{-1}$ on the second band at 12.52 eV further confirmed the preference of an energetically stable linear chain structure in the gas phase. Both calculations and spectroscopic results suggested that the molecule adopts a *trans*-planar chain structure, and a five-membered ring decomposition pathway is more favorable.

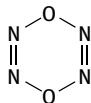
In addition to the nitryl azide configuration, the nitrogen oxides with a gross formula N_4O_2 could also exist in the form of a tetrazetane dioxide:



CAS RN [119708-60-0]
Tetrazetane-1,3-dioxide

A method for stabilizing polyheteroatomic rings containing only N atoms was proposed via introduction of acceptors for the unshared electron pair on the heteroatom, especially atoms of O, thus giving N-oxides. The stability of tetrazete-1,3-dioxide has been calculated by a Modified Neglect of Diatomic Overlap (MNDO) method [45].

In fact, the N_4O_2 system has a completely planar structure and computed heat of formation of 523 kJ/mol (125.0 kcal/mol). Furthermore, the system appears to be kinetically stable with a barrier to unimolecular dissociation of 187 kJ/mol (44.8 kcal/mol), respectively [18]:



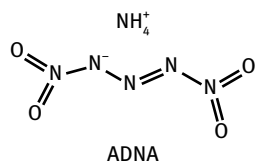
CAS RN [140928-94-5]
1,4-Dioxo-2,3,5,6-tetrazine

Valence bond representations for the decomposition reactions of N_3NO and N_3NO_2 based on standard Lewis and increased-valence structures showed that the electronic reorganizations that are associated with the use of these two types of structures involved electron-pair delocalizations and one-electron delocalizations, respectively, which afforded polar and non-polar representations for the decompositions [32].

The conformational and structural stability of nitryl azide $NNN-NO_2$ and nitrosyl azide $NNN-NO$ were investigated by DFT and *ab initio* calculations [40]. The $-NO_2$ rotational barrier in nitryl azide was predicted from the symmetrical potential function to be about 29.3 kJ/mol (7 kcal/mol). The vibrational frequencies were calculated and the predicted IR and Raman spectra of the *cis-trans* mixture were plotted. Complete vibrational assignments were made on the basis of normal coordinate calculations for the stable conformers of both nitrosyl azide and nitryl azide.

9.7 Dinitramidoamine Anion N_5O_4^-

A new nitrogen-oxygen anion, similar to dinitramide, has been postulated and a synthesis attempted. The properties of the ammonium salt of 1,3-dinitrotriazene, dinitramidoamine, di(nitramido)amine, 1,1,5,5-tetraoxoazapentene(2) have been predicted based on its similarity with ADN, and it was hoped that this would be an environmentally friendly, non-toxic replacement for AP. This as yet unobtainable new salt is also known under its acronym, ADNA. The difference between the new salt and ADN would be only two additional nitrogen atoms inserted between the two nitro groups. The structure of ADNA was expected to be



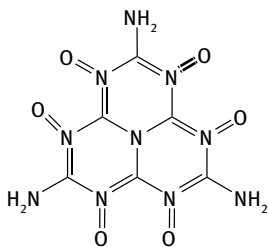
The density was predicted to be 1.76 g/cm^3 , and the enthalpy of formation was predicted to be $+180 \text{ kJ/mol}$ ($+43 \text{ kcal/mol}$). Synthesis efforts with nitrourethane as an intermediate have not yet been successful [46]. It seems highly premature to start worrying about the possible environmental impacts of a chemical that is so unstable that it cannot even be obtained in milligram quantities in the laboratory. The computational methods used for predicting toxicity and environmental impact look very nice but in reality are useless [47, 48].

9.8 Polyazine N-oxides

After most attempts to calculate the predicted heats of formation and stability of polynitrogens had failed to reveal the hoped-for relatively stable HEDM, it was noted that adding oxygen to all-nitrogen compounds would actually stabilize them and at the same time make them more useful as oxidizers in rocket propellants.

The $\text{N}^+ \rightarrow \text{O}^-$ semipolar bond linkages in polyazine nitrogen oxides, if appropriately located, may diminish the destabilization associated with nitrogen catenation. Forty nitrogen oxides of isomeric diazines, triazines, and tetrazines have been computationally characterized in terms of their geometries, relative energies, and (for a representative selection) electrostatic potentials [49]. The presence of $\text{N}^+ \rightarrow \text{O}^-$ linkages does partially counteract the destabilizing effects of nitrogen catenation, although the isomers with complete catenation remain the least stable. The stabilizing influence of $\text{N}^+ \rightarrow \text{O}^-$ groups, and the accompanying changes in bond lengths, can be understood in terms of resonance charge delocalization to the polyazine rings. The

N(O)—N(O) bonds between nitrogens that both bear oxygens tend to be relatively weak. The electrostatic potentials above the polyazine rings become increasingly positive because there are more nitrogens and oxygens; eventually they are positive above all of the carbons and nitrogens and possibly even the oxygens, with negative regions only on the peripheries of the molecules. However, the nitrogens that bear oxygens always have more positive potentials than those that do not. The predicted crystal densities of three tricyclic polyazine nitrogen oxides (one structure shown as an example, but the N=O bonds should be shown as semipolar $\text{N}^+ \rightarrow \text{O}^-$ bonds)



range from 1.96 to 2.03 g/cm³ [50]. The calculated solid-phase enthalpies of formation were between 135 and 314 kcal/mol. The computed detonation velocities and detonation pressures were similar to HMX for two of the compounds and significantly greater for the third, exceeding even CL-20. All three compounds were expected to be less impact sensitive than both HMX and CL-20.

9.9 Nitrohydrazine and Dinitrohydrazines

Nitrohydrazine and dinitrohydrazines have not yet been synthesized and at this time remain purely speculative. Combining the energy of the N—N bonds in hydrazines with the oxidative power of nitro groups should make a good oxidizer. As part of a series of investigations into unusual molecules of potential application to high-energy materials, a series of calculations to determine the optimized structures, geometric parameters, and vibrational frequencies and predict fundamental thermodynamic properties of nitrohydrazine and two dinitrohydrazine isomers was performed [51].

10 Other Nitrogen-Oxygen-Halogen Compounds

Many oxidizers are built around the nitrogen atom as the central atom. Nitrogen is capable of forming strong bonds, single, double, and semipolar bonds with oxygen. Nitrogen also forms bonds, not always stable bonds, and often labile bonds with halo-

gens. Several NO_xX compounds with $x = 1, 2$, or 3 and $X = \text{F}$ were already discussed in *Encyclopedia of Oxidizers*, in the chapter “Nitrogen Fluorides.”

Perchlorates are the most widely used solid propellant oxidizers in rocket propellants. So one would want to combine the perchlorate or chlorate group with nitrogen as the central atom. A good oxidizer, if it can be prepared and stabilized, would be $\text{N}(\text{ClO}_4)_3$.

10.1 Nitrosyl and Nitryl Compounds

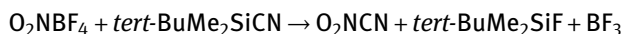
Some nitrosonium and nitronium compounds, e.g., the fluorides and chlorides, are liquids and have more covalent bond character. Some of them were already discussed in *Encyclopedia of Oxidizers*, in the chapter “Nitrogen Fluorides.” Nitrosonium and nitronium compounds have more saline character and are solids at room temperature. That is one reason why some chemists suggest that the words *nitryl* and *nitronium* should designate two different forms of NO_2 : a covalent bond bound form and an ionized salt form. The same holds for nitrosyl and nitrosonium.

10.2 Nitrosonium and Nitronium Compounds

In organizing the vast amount of information on rocket propellant oxidizers, a decision had to be made as to whether nitrosonium and nitronium oxidizer salts should be discussed under nitrogen oxides, from which the cation is derived, or under various chapters for anions like perchlorate and tetrafluoroborate. A similar decision had to be made for the oxonium salts. It was decided to give the cations priority over the anions for the simple reason that we are used to listing the cation part of salts first and the anion part last. But then this chapter on nitrogen oxides had grown to a point where it needed to be subdivided. For this reason detailed discussion of nitrosonium and nitronium perchlorate oxidizer salts was moved to the end of the chapter “Perchlorate Salts” in the discussion on perchlorates. These compounds did not deserve a separate chapter for themselves.

10.2.1 Nitryl Cyanide

Cyanide is a pseudohalogen. Thus, it should be able to form analogs to nitrosyl chloride or nitryl chloride in which the halogen is replaced by a pseudohalogen. The elusive nitryl cyanide, O_2NCN , has been synthesized and characterized by the reaction [52, 53]



It was prepared in good yield, characterized by NMR and vibrational spectroscopy, and studied by theoretical calculations. Nitryl cyanide was separated from unwanted byproducts by fractionated condensation and condensed at 161 K (−112°C). NCNO₂ is colorless in the solid state and in the gas phase. It melts to a colorless liquid at 188 K (−85°C). Small amounts of nitrogen oxides may give it a pale yellow or bluish color. A density of 1.24 g/cm³ was measured for the liquid at 194 K (−79°C). The vapor pressure of NCNO₂ was measured between 169 and 273 K (−96 and 0°C), giving an extrapolated boiling point of 280 K (+7°C) and an enthalpy of evaporation of 28.4 kJ/mol (6.8 kcal/mol). The enthalpy of formation of liquid NCNO₂ was predicted to be +184 kJ/mol (+43.9 kcal/mol). The question was how stable it would be. Pure NCNO₂ is stable at room temperature. Heating for 1 h to 323 or 373 K (50 or 100°C) resulted in only slight decomposition, with most of the NCNO₂ being recovered unchanged, and heating to 413 K (140°C) for several hours was required to achieve complete decomposition. Homolytic bond dissociation into NO₂ and CN free radicals was predicted to correspond to an enthalpy change of 259 kJ/mol (62 kcal/mol). It is assumed that the bond between the NO₂ and the CN part of the molecule is more a covalent bond than that in a saline ionic compound. Nitryl cyanide holds promise as a HEDM and might also prove useful as a HEDM building block.

10.2.2 Nitronium and Nitrosonium Oxalates

In the search for more energetic chlorine-free oxidizers, the enthalpies of formation of the four theoretical compounds bis(nitrosonium) oxalate, bis(nitronium) oxalate, and their covalent ester isomers in the solid state were predicted by computational chemistry (Table 2) [54, 55]. This was done as an example of how computational chemistry can be used as a precursor to actual laboratory work in the search for more energetic and environmentally benign rocket propellants. The predicted specific impulse of mixtures of nitronium oxalate with aluminum was comparable to that of AP/Al mixtures.

Table 2: Predicted enthalpy of formation of nitronium and nitrosonium oxalates.

Compound	Gross formula	Theoretical enthalpy of formation, kcal/mol	Oxygen balance, %
[NO ₂ ⁺] ₂ [COO [−]] ₂	C ₂ N ₂ O ₈	−86.6	+35.5
[NO ⁺] ₂ [COO [−]] ₂	C ₂ N ₂ O ₆	−107.0 ^a	+21.6
O ₂ N—O—CO—CO—O—NO ₂	C ₂ N ₂ O ₈	−113.5 ^a	+35.5
ON—O—CO—CO—O—NO	C ₂ N ₂ O ₆	−96.5	+21.6

Data source: [55]

^aCompounds with the more negative enthalpy of formation were predicted to be the more stable ones.

These compounds would have a very positive oxygen balance, but they have not yet been synthesized. Comparing the ionic versus the covalent isomers, those with the more negative enthalpy of formation were predicted to be the more stable ones.

10.2.3 Nitrosonium Tetrafluorochlorate

Another potential oxidizer and intermediate in the synthesis of other nitrosonium salts is nitrosonium tetrafluorochlorate, $\text{NO}^+\text{ClF}_4^-$ [56]. This is similar to nitrosonium perchlorate, except the oxygens in the anion were replaced by fluorine. It can be prepared by the reaction of nitrosyl fluoride and chlorine trifluoride at temperatures below 273 K. The compound is a white, crystalline solid and a powerful oxidizer. It ignites hypergolically with many organic fuels. The enthalpy of formation was estimated as $\Delta H_f^{298} = -287 \text{ kJ/mol}$ (-68.6 kcal/mol). Attempts to prepare nitronium tetrafluorochlorate were unsuccessful.

10.3 Other Nitrogen-Oxygen-Halogen Compounds

New covalent inorganic perchlorates were prepared from chlorine perchlorate. The compound $\text{I}(\text{ClO}_4)_3$ was partially characterized and nitrogen triperchlorate $\text{N}(\text{ClO}_4)_3$ deduced as a short-lived primary reaction product. The one-valent iodine(I) perchlorate could not be prepared, but a complex perchlorate of iodine(III), $\text{CsI}(\text{ClO}_4)_4$, was indeed synthesized [57].

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Nitromethanes

The topic of nitro compounds had to be distributed over 4 chapters because it would have been a very large chapter that would have made it more difficult for readers to find information on a specific compound and it would have been difficult to arrange 30 chapters among 5 subvolumes so that each subvolume is about the same size. That spacial arrangement was made easier by dealing with smaller chapters.

This chapter is part of the group of three chapters on nitroaliphatic compounds. The topic of nitroaliphatic compounds had to be subdivided into an introduction, the chapter entitled “Nitro Compounds“, the “Nitromethanes“ chapter at hand which covers nitroaliphatic compounds with only one carbon atom, and a chapter on “Nitroaliphatic Compounds“ which contains information on nitroaliphatic compounds with more than one carbon atom.

1 Nitroaliphatic Compounds (Nitroalkanes)

Nitroaliphatic compounds (also called nitroalkanes or nitroparaffins) are produced from alkanes or alkenes and nitric acid or dinitrogen tetroxide (a potentially explosive mixture) which is a very hazardous operation [1]. They are widely used as intermediates in the chemical process industry [2, 3] and as solvents for nitro lacquers.

Supplement 1 to *Tetrahedron* volume 19 (Jun 1963) contains a series of publications on nitroparaffins. The following year another supplement to *Tetrahedron* collected papers presented at an international conference on nitro paraffins in 1963 [4].

This introductory chapter summarizes properties of nitroalkanes as a family group. Individual nitroalkanes are discussed in dedicated sections further down. If we did not discuss the common properties of nitroalkanes as a group as we do it here, some of the typical properties of nitroalkanes which are shared by all nitroalkanes would have to be discussed where they are first encountered under nitromethane, the lowest and most frequently used member of the group, or in later sections. As an introduction, this chapter gives summary tables that make it easier to compare properties of different homologous nitroalkanes that only differ by a CH_2 group or are structural isomers.

The development of energetic compounds continues unabated into the current century, and before chemists can synthesize more energetic materials they need to understand the chemistry of simple nitro compounds. It is with this fundamental need in mind that we have assembled here a fairly thorough collection of references relating to making nitro compounds and using them safely.

Aliphatic nitroalkanes can be subdivided into six groups depending on their molecular structure:

Primary nitroalkanes	RCH_2NO_2
Secondary nitroalkanes	$\text{R}'\text{R}''\text{CHNO}_2$
Tertiary nitroalkanes	$\text{R}'\text{R}''\text{R}'''\text{CNO}_2$
Geminal dinitroalkanes	
Terminal gem-dinitroalkanes	$\text{RCH}(\text{NO}_2)_2$
Internal gem-dinitroalkanes	$\text{R}'\text{C}(\text{NO}_2)_2\text{R}''$
Vicinal dinitroalkanes	$\text{R}'\text{CH}(\text{NO}_2)\text{CH}(\text{NO}_2)\text{R}''$
Trinitromethylalkanes	$\text{R}'\text{R}''\text{CHC}(\text{NO}_2)_3$

1.1 Production of Mononitroalkanes

Nitroalkanes can be prepared by direct nitration of aliphatic or alicyclic hydrocarbons with either nitric acid or nitrogen dioxide or dinitrogen pentoxide in the vapor phase at elevated temperatures but this is a very hazardous operation since one is essentially feeding rocket propellants into a reactor just short of ignition or explosion conditions. Dilution with inert gases helps to prevent a disaster. These free radical reactions typically do not give one specific product but result in mixtures of nitro compounds with varying stages of nitration and nitro groups attached to different carbon atoms in the molecule [5]. These product mixtures then have to be separated by fractionated distillation or extraction. In $\text{C}_{>2}$ hydrocarbons, tertiary carbons are nitrated most readily, followed by secondary and primary carbon atoms in that order, which are less reactive. At the higher temperatures, hydrocarbon chains are often broken and nitroalkanes with less carbons than the starting alkane are formed along with the intended product. For instance, nitration of propane results in a mixture of 2-nitropropane, 1-nitropropane, 2,2-nitropropane (a trace), nitroethane, and nitromethane. A good summary is the book *Synthetic Routes to C-Nitro Functionality* [6]. See also [7–9].

The hydrogens adjacent to nitro groups, in particular those adjacent to two or three nitro groups are quite acidic. These compounds can act as acids and form salts with strong bases. Many of these solid salts can be used as ingredients in solid propellants.

Because some nitroalkanes are used as solvents and as intermediates in organic synthesis, the physical properties of nitroalkanes are well characterized and the data are fairly accurate. Several summaries of the physical and chemical properties of nitroalkanes have been published as summarized in Table 1.

Table 1: Summary of publications on physical and chemical properties of nitroalkanes.

Topic	Author	Year	Pages	References
Aliphatic nitro compounds	Levy and Rose	1947	37	[10]
Nitroparaffins	Toops	1956	3	[11]
Nitration of hydrocarbons	Topchiev	1959	329	[12]
Nitration methods and mechanisms	Olah, Malhotra, and Narang	1989	330 + xii	[13]
Nitrocarbons	Nielsen	1995	190 + x	[14]
The nitro group in organic chemistry	Ono	2001	392	[15]

1.2 Physical Properties of Mononitroalkanes

Table 2 is a summary of physical properties of mononitroalkanes.

Table 2: Physical properties of nitroalkanes.

Compound	Density at 298 K = 25 °C	Refractive index n_D^{20}	Approximate melting point		Absolute viscosity at 298 K = 25 °C
	g/cm ³		K	°C	centiPoise
Nitromethane	1.1286	1.3818	244	−29	0.632
Nitroethane	1.0413	1.3917		—	0.661
1-Nitropropane	0.9934	1.4018		—	0.798
2-Nitropropane	0.9821	1.3944	180	−93	0.750
1-Nitrobutane	0.9688	1.4108		—	0.931
2-Nitrobutane	0.9609	1.4044	141	−132	0.878
1,1-Dinitropropane	1.2610	1.4339	231	−42	2.535
2,2-Dinitropropane	1.30	—	326	53	—
1,3-Dinitropropane	1.354	1.4654	253	−20	—
Trinitromethane	1.615	1.4454	298	25	—

Data source: [16]

1.2.1 Freezing Points of Mononitroalkanes

The freezing points of mononitroalkanes are listed in Table 3. A method has been developed to predict melting/freezing points of nitroaliphatic compounds from the molecular mass and molecular structure [17]. The list of examples comparing predicted freezing/melting points to measured data included 13 nitroaliphatic compounds. The average deviation of predicted temperature from measured temperatures was 5.4%. See also reference [18]. These methods are based on the elemental composition of energetic compounds and the contributions of some specific polar groups/structural moieties as additive and non-additive functions, respectively.

Table 3: Freezing points of mononitroalkanes.

Compound	Freezing point	
	K	°C
Nitromethane	244.60	−28.55
Nitroethane	183.63	−89.52
1-Nitropropane	169.16	−103.99
2-Nitropropane	181.83	−91.32
1-Nitrobutane	191.82	−81.33
2-Nitrobutane	Glass formation	
1-Nitro-2-methylpropane	196.30	−76.85
2-Nitro-2-methylpropane	246.92	−26.23

Data source: [11]

1.2.2 Boiling Points of Mononitroalkanes

The boiling points and other physical properties of mononitroalkanes are listed in Table 4. A similar list of boiling points of mononitroalkanes is given in Table 5.

1.2.3 Densities of Mononitroalkanes

The densities of nitroalkanes as a function of temperature can be calculated from the equation

$$\rho = c - dt$$

where ρ is the density in g/cm^3 , t is the temperature in $^{\circ}\text{C}$ and c and d are the constants listed in Table 6. Another source gives a list of densities and temperature coefficients of a series of mononitroalkanes as shown in Table 7.

Table 4: Physical properties of mononitroalkanes.

Compound	Density, g/cm^3	Viscosity, cPs	Boiling point T_b , K	Surface tension, dyn/cm	Parachor	Critical temperature T_c , K	T_b/T_c
Nitromethane	1.13118	1.37872	375.0	36.78	132.7	622.7	0.60
Nitroethane	1.03819	1.39015	387.9	31.31	171.0	661.8	0.59
1-Nitropropane	0.99569	1.39901	404.6	29.28	208.1	675.2	0.60
2-Nitropropane	0.98410	1.39206	393.1	28.07	208.3	617.9	0.64
1-Nitrobutane	0.96770	1.40852	426.7	29.20	247.6	668.5	0.64
2-Nitrobutane	0.96047	1.40222	413.1	28.65	248.3	623.7	0.66

Data source: [19]

Note: Properties at 298 K unless otherwise stated

Note: 1 dyn = 10^{-5} N

Table 5: Calculated boiling points of mononitroalkanes.

Compound	Boiling point at 760 mm Hg		Pressure coefficient, °/mm Hg
	K	°C	
Nitromethane	171.95	101.2	0.0427
Nitroethane	159.08	114.07	0.0445
1-Nitropropane	141.97	131.18	0.0467
2-Nitropropane	152.90	120.25	0.046
1-Nitrobutane	120.38	152.77	0.049
2-Nitrobutane	133.65	139.5	0.0485
1-Nitro-2-methylpropane	131.43	141.72	0.0482
2-Nitro-2-methylpropane	145.99	127.16	0.0473

Data source: [11]

Table 6: Constants for surface tension and density of aliphatic nitroparaffins from 298 to 333 K (25–60 °C).

Compound	Surface tension		Density	
	a	b	c	d
Nitromethane	39.25	0.1387	1.16576	0.001383
Nitroethane	34.03	0.1090	1.06823	0.001202
1-Nitropropane	31.74	0.0985	1.02300	0.001093
2-Nitropropane	30.78	0.1084	1.01208	0.001119
1-Nitrobutane	31.65	0.0979	0.99170	0.000960
2-Nitrobutane	31.32	0.1067	0.98455	0.000963

Data source: [19]

Table 7: Densities and temperature coefficients of mononitroalkanes.

Compound	Temperature, °C			Temperature coefficient
	20.0	25.0	30.0	
	Density, g/cm ³			d _{density} /dT
Nitromethane	1.13816	1.13128	1.12439	0.001377
Nitroethane	1.05057	1.04464	1.03870	0.001187
1-Nitropropane	1.00144	0.99609	0.99073	0.001071
2-Nitropropane	0.98839	0.98290	0.97740	0.001099
1-Nitrobutane	0.97344	0.96848	0.96352	0.000992
2-Nitrobutane	0.96535	0.96036	0.95536	0.000999
1-Nitro-2-methyl-propane	0.96349	0.95848	0.95347	0.001002
2-Nitro-2-methyl-propane	Solid	Solid	0.95028	0.001128

Data source: [11]

For some applications of nitroalkanes, such as in explosives, the density is an important performance parameter. Densities of nitroalkanes can be determined experimentally or can be predicted theoretically. One of the first predictive methods was based on the group additivity method [20], comparing predictions for 173 energetic compounds with experimental results.

Correlations to predict crystal density based on two different models were introduced for 82 different energetic compounds including 13 nitroaliphatic compounds whose molecules contained functional groups common to CHNO explosives [21–23]. Additional work expanded the list of energetic materials to 172 compounds [24]. Root mean square (rms) deviations for acyclic and cyclic nitramines were worse than for nitrate esters and nitroaliphatic explosives. This method is a simple procedure for calculating crystal density of energetic compounds and gave good results as compared to group additivity methods for estimating the density of organic explosives. The predictions are less accurate for liquid nitroalkanes.

1.2.4 Vapor Pressures of Nitroalkanes

Table 8 is a summary of vapor pressure data for nitroalkanes.

Table 8: Vapor pressures of nitroalkanes.

Temperature, °C	Vapor pressure, mm Hg							
	Nitro-methane	Nitro-ethane	1-Nitro-propane	2-Nitro-propane	1-Nitro-butane	2-Nitro-butane	1,1-Dinitro-propane	2,2-Dinitro-propane
10	16.12	8.52	3.96	7.05	1.23	2.79		
20	27.89	15.65	7.52	12.99	2.50	5.48		
25	36.26	20.89	10.00	17.27	3.50	7.46		
30	46.67	21.41	13.48	22.65	4.82	10.01		
40	73.21	46.20	23.24	38.11	5.85	17.29		
50	117.1	74.55	38.41	61.32	15.49	28.63	1.62	
60	178.2	113.2	61.17	95.22	26.00	46.18	3.27	
70	262.7	173.9	94.32	143.6	42.08	71.67	6.37	10.78
80	377.7	254.2	140.9	211.0	65.58	108.2	11.10	17.82
90	630.2	361.1	204.5	299.1	99.50	158.8	18.75	28.40
100	730.4	499.4	280.5	416.4	145.8	228.1	30.50	42.80
110		678.6	401.2	564.2	207.1	318.8	48.88	64.57
120			545.1		292.5	436.5		94.35
130			728.2		399.4	584.1		135.8
140					533.8	760.0		178.5
150					696.0			259.5
160								360.8
170								491.5
180								659.0

Data source: [16]

The constants for the Antoine equation for the calculation of the vapor pressures of eight different mononitroalkanes are given in reference [11].

1.2.5 Viscosities of Mononitroalkanes

Viscosities of mononitroalkanes are listed in Tables 2 and 4 above.

1.2.6 Surface Tensions of Mononitroalkanes

The surface tensions of nitroalkanes as a function of temperature can be calculated from the equation

$$\gamma = a - bt$$

where γ is the surface tension in dyn/cm, t is the temperature in °C, and a and b are the constants listed in Table 6 above. Surface tensions at 298 K are listed in Table 4 above.

1.2.7 Refractive Indices of Mononitroalkanes

Refractive indices of mononitroalkanes were already contained in Table 2 above. Additional data for refractive indices of eight different mononitroalkanes at three different temperatures are available in reference [11].

1.2.8 Spectra of Mononitroalkanes

An analysis of the dependence of the frequencies of the valence vibration on the position of the $-\text{NO}_2$ group and the structure of the substituent was conducted in a series of nitro compounds [25, 26]. The inductive and steric effects, as well as the effect of conjugation, influence the position of the band of the anti-symmetric valence vibration of the $-\text{NO}_2$ group. A linear dependence of the band of the anti-symmetric valence vibration on the induction constant of the substituent was found. The position of the band of the symmetrical vibration of the $-\text{NO}_2$ group is determined chiefly by the steric hindrances of the substituent.

Spectra of nitroalkanes are useful to identify internal structures of the molecules and to calculate thermodynamic properties. Specifically, rotation around the C—N axis contributes to the spectra and the stability of the molecule. Internal rotation in n -mononitroalkanes of the type $\text{CH}_3(\text{CH}_2)_n\text{NO}_2$, $n \leq 7$ was computed by density functional theory methods [27]. Conformations and 36 potential functions for all rotations were found. It was shown that as the hydrocarbon chain became longer, the potential functions that describe particular molecular fragments changed only negligibly beginning from a certain n .

Harmonic oscillator approximations are often used to calculate the partition function for low frequency modes that represent hindered internal rotation. Using harmonic oscillator approximations may lead to significant errors when internal rotation

of functional groups in molecules involves hindered or free rotation. Anharmonic oscillator approximation methods should be used for the proper reproduction of the energies of excited vibrational states, especially at high temperatures. A theoretical study using anharmonic oscillator approximation and explicit treatment of internal rotation was performed to explain the effect of internal rotation and anharmonic oscillator approximation on thermodynamic parameters of nitroethane and 1-nitropropane and 2-nitropropane [28].

1.2.9 Thermodynamic Properties of Nitroalkanes

Nitroalkanes are of interest either as rocket propellants by themselves or as models for other, more complex nitro compounds. Having accurate thermodynamic properties is important for predicting performance as a rocket propellant.

1.2.9.1 Summaries of Thermodynamic Properties of Nitroalkanes

Thermodynamic properties of selected nitroalkanes are listed in the individual sections below, starting with nitromethane and ending with more complex nitroalkanes that also contain other substituents in addition to hydrogen. There are several summaries of thermodynamic properties of nitroalkanes which can be consulted if additional data are needed.

1.2.9.2 Experimental Determination of Thermodynamic Properties of Nitroalkanes

The heats of combustion of six mononitroalkanes and four polynitroalkanes, including three sets of isomers, were determined experimentally in a combustion bomb calorimeter [16]. Because qualitative analyses of products of combustion gave no indications of the presence of oxides of nitrogen or nitric acid in the gaseous products of combustion, the products of combustion in all experiments were assumed to be gaseous carbon dioxide, gaseous nitrogen, and liquid water. Standard enthalpies of formation were calculated from the experimental energies of combustion as summarized in Table 9.

If one converts the heat of combustion of Table 9 from kcal/mol to kcal/kg as shown in Table 10, the effect of elongating the hydrocarbon chain on the heat of formation can be studied more easily.

If one correlates these data with the oxygen balance, the heats of combustion of nitroparaffins can be shown to follow a linear function of the oxygen balances of the molecules (Figure 1), and an equation was derived that relates these two variables with an average error of estimate of about 2% of the experimental values. An equation of the form:

$$\Delta E_{\text{comb}} = (26.418)(\text{oxygen balance}) - 1792.3$$

Table 9: Heat of combustion and enthalpy of formation of nitroalkanes.

Compound	Standard State	Heat of combustion $-\Delta E^\circ$		Enthalpy of formation ΔH_f		Molecular mass		Oxygen balance	
		kJ/mol at 298 K	kcal/mol at 25 °C	kJ/mol at 298 K	kcal/mol at 25 °C	g/mol	%		
Nitromethane	Liquid	735 ± 0.8	175.70 ± 0.18	-89 ± 0.8	-21.28 ± 0.18	61.04002		-39.3	
Nitroethane	Liquid	1362 ± 1.3	325.57 ± 0.30	-140 ± 1.3	-33.48 ± 0.31	75.0666		-95.9	
1-Nitropropane	Liquid	2013 ± 2.6	481.07 ± 0.61	-168 ± 2.6	-40.05 ± 0.61	89.09318		-134.7	
2-Nitropropane	Liquid	1997 ± 0.7	477.34 ± 0.17	-183 ± 0.7	-43.78 ± 0.17	89.09318		-134.7	
1-Nitrobutane	Liquid	2666 ± 1.3	637.16 ± 0.32	-193 ± 1.3	-46.03 ± 0.32	103.11976		-162.9	
2-Nitrobutane	Liquid	2651 ± 1.5	633.58 ± 0.36	-208 ± 1.5	-49.61 ± 0.36	103.11976		-162.9	
1,1-Dinitropropane	Liquid	1871 ± 1.4	447.22 ± 0.33	-171 ± 1.4	-40.78 ± 0.34	134.09074		-59.7	
1,3-Dinitropropane	Liquid	1818 ± 1.4	434.48 ± 0.33	-224 ± 1.4	-53.51 ± 0.33	134.09074		-59.7	
2,2-Dinitropropane	Solid	1854 ± 2.7	443.12 ± 0.64	-188 ± 2.7	-44.87 ± 0.64	134.09074		-59.7	
Trinitromethane	Liquid	469	112.10	+78	+18.63	151.03514		+37.1	

Data source: [16]

Table 10: Correlation of heat of combustion and oxygen balance of nitroalkanes.

Compound number	Compound name	Oxygen balance, %	Heat of combustion, kcal/kg
1	Nitromethane	-39.3	2881
2	Nitroethane	-95.8	4340
3	1-Nitropropane	-134.6	5403
4	2-Nitropropane	-134.6	5361
5	1-Nitrobutane	-163.0	6182
6	2-Nitrobutane	-163.0	6147
7	1,1-Dinitropropane	-59.6	3338
8	1,3-Dinitropropane	-59.6	3243
9	2,2-Dinitropropane	-59.6	3308
10	2,3-Dimethyl-2,3-dinitrobutane	-127.1	5110
11	2,2-Dimethyl-1,3-dinitropropane	-108.5	4606
12	Trinitromethane	+37.1	746
13	1,1,1-Trinitroethane	+4.9	1777
14	2-Methyl-2,3,3-trinitrobutane	-65.6	3381
15	2-Methyl-2,3,3-trinitropentane	-83.2	3944
16	Tetranitromethane	+49.0	543
17	2,2,3,3-Tetranitrobutane	-20.2	2460

Data source: [16]

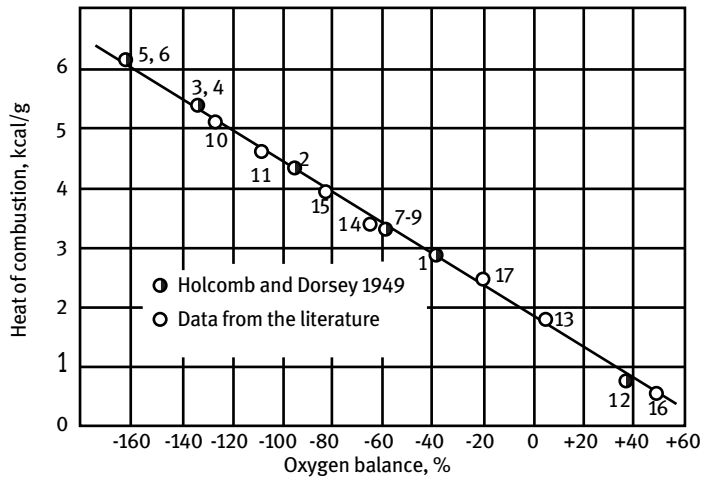


Figure 1: Correlation between heat of combustion and oxygen balance of nitroalkanes (reprinted and modified from [16], with permission from © 1949 American Chemical Society; permission conveyed through RightsLink.)

was derived where ΔE_{comb} is expressed in kilocalories per kilogram. The numbers adjacent to the data points in Figure 1 are the numbers of the compounds listed in Table 10.

The standard molar enthalpies of vaporization or sublimation of 1-nitropentane and nitrocyclohexane were derived from vapor pressure measurements, and the standard enthalpies of formation of nitrocyclohexane were measured using combustion calorimetry [29]. The results were then compared to predictions based on additivity rules.

1.2.9.3 Computational Methods for Prediction of Thermodynamic Properties of Mononitroalkanes and Polynitroalkanes

Prediction of Enthalpies of Formation

Thermodynamic properties of simple nitroalkanes and difluoroamino alkanes can be predicted based on quantum-mechanical calculations. The heats of formation of a series of polyatomic molecules containing $-\text{NO}_2$ and/or $-\text{NF}_2$ groups have been determined using the isodesmic procedure of Pople et al. [30–32]. An excellent correlation between the semiempirical heats of formation and the corresponding available experimental data was observed. It was found that $-\text{NO}_2$ and $-\text{NF}_2$ groups have large and comparable destabilizing effects when it comes to evaluate the thermal stability of the molecules.

The well-known simple Benson method predicts the heats of formation of gaseous compounds by adding the contributions by individual bonds. Expanding on this method, a similar additive method was developed for estimating the gaseous heats of formation of energetic molecules containing $-\text{NO}_2$ and/or $-\text{NF}_2$ groups and its accuracy was checked against measured values taken from previously published sources [33].

The ideal gas (**not** condensed phase!) thermodynamic properties of 29 nitro and nitrate compounds, high explosives such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX, cyclotrimethylenetrinitramine), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX, octogen), pentaerythritol trinitrate (PETN), normal propyl nitrate (NPN), and glycerol trinitrate (GTN) and propellants were predicted from spectroscopic data and compared to calorimetric results reported in the literature [34, 35]. The fundamental vibrations, the bond lengths, and the moments of inertia of all the molecules were calculated using semi-empirical methods. The resulting thermodynamic properties were represented in a polynomial form, ready for use in rocket propulsion I_{sp} calculations. The format used was the OLD NASA CEC polynomial format and consisted of two sets of polynomial coefficients for each species [36]. The first set of seven coefficients represented the properties above 1000 K, and the second from 200 to 1000 K. Both polynomials gave the same values at 1000 K for the properties. The 15th (last) coefficient represented the enthalpy of formation $\Delta H_f(298)/R$. The results are summarized in Table 11.

Table 11: Ideal gas thermodynamic properties of nitro and nitrate compounds.

Gaseous (vapor) compound name	Formula	ΔH_f^{298} kJ/mol	S^{298} JK ⁻¹ mol ⁻¹	C_p^{300} JK ⁻¹ mol ⁻¹
Nitromethane	CH ₃ NO ₂	-80.75	282.86	55.77
Nitromethyl free radical	•CH ₂ NO ₂	152.47	288.22	59.08
Nitromethane	CD ₃ NO ₂	-61.79	291.67	63.45
Nitromethane	CD ₂ HNO ₂	-57.72	289.26	61.07
Nitromethane	CDH ₂ NO ₂	-52.53	286.94	59.23
Dinitromethane	CH ₂ (NO ₂) ₂	-61.51	358.10	86.71
Trinitromethane	CH(NO ₂) ₃	-13.39	435.57	134.59
Tetranitromethane	C(NO ₂) ₄	82.38	503.72	176.73
Nitroethylene	H ₂ C=CHNO ₂	33.28	300.50	74.01
Dinitroethylene	C ₂ H ₂ (NO ₂) ₂	59.41	359.19	110.91
Nitroethane	C ₂ H ₅ NO ₂	-103.78	320.51	79.38
Nitropropene	CH ₃ CH=CHNO ₂	9.99	330.00	94.01
Nitrocyclopropane	C ₃ H ₅ NO ₂	17.57	317.04	91.01
Nitroazetidine	C ₃ H ₆ N—NO ₂	114.12	328.95	101.21
1,3,3-trinitroazetidine	C ₃ H ₄ N(NO ₂) ₃	128.45	357.32	135.97
RDX hexogen	C ₃ H ₆ N ₆ O ₆	192.00	482.44	231.26
Nitropropane	C ₃ H ₇ NO ₂	-124.27	350.05	104.61
HMX octogen	C ₄ H ₈ (N—NO ₂) ₄	187.86	568.83	276.66
Nitrobutane	C ₄ H ₉ NO ₂	-143.93	369.87	155.74
<i>n</i> -Nitropentane	C ₅ H ₁₁ NO ₂	-164.43	390.91	137.89
<i>n</i> -Nitrohexane	C ₆ H ₁₃ NO ₂	-185.35		

Data source: [35]

The established modes of interaction of nitro groups in nitro derivatives of methane in condensed and gaseous states along with data on the kinetics of their thermal decomposition provided a set of energies of dissociation of C—NO₂ bonds based on enthalpies of formation from research and literature data [37, 38]. These values enabled one to determine the enthalpies of formation of nitromethyl radicals and energy of dissociation of C—H bonds. The energies of dissociation of C—H bonds do not depend on quantity of nitro groups connected to atoms of carbon, as in the halogen derivatives of methane. The enthalpies of formation of radicals •CH₂NO₂, •CH(NO₂)₂, •C(NO₂)₃, ••CHNO₂, ••C(NO₂)₂, and •••CNO₂, and the energies of dissociation of —NO₂ groups from radicals of the nitro derivatives of methane were then calculated.

Thermodynamic properties, enthalpy (ΔH_f) and Gibbs energy (ΔG_f) of 21 energetic nitro compounds were predicted by computational methods [39]. The enthalpy and the Gibbs energy of formation obtained exceeded those reported in the literature. The calibrated least-squares parameters and parametric equations were used to predict ΔH_f and ΔG_f for five newly developed energetic nitro compounds for further applications.

The heats of formation of CH_3NO_2 and $\text{CH}_2=\text{CHNO}_2$, as well as anions derived from some of the molecules, have been calculated using *ab initio* molecular orbital theory [40].

The standard enthalpies of formation at 298 K and heat capacities and entropies in the temperature range of 300–5000 K for a range of nitro compounds were computed by means of a density functional theory in quantum chemistry [41].

Heats of formation of condensed phase nitroalkanes, nitrate esters, and nitramines can be interpolated from a collection of measured heats of combustion of different energetic materials based on elemental composition and various structural and functional group parameters of CHNO energetic compounds [42]. This method can provide predictions for energetic compounds compared to the calculated outputs of the best empirical and complex quantum mechanical methods [43].

The heats of formation of nitro compounds can be calculated by a semi-empirical molecular orbital (MO) method, although in the case of polynitro compounds, differences between observed and calculated values become slightly larger. By combining heats of vaporization and sublimation obtained by the additivity rule with ΔH_f° in gas phase obtained by other methods, ΔH_f° in condensed phase could be estimated with sufficient accuracy [44, 45].

The C– NO_2 bond dissociation energies and the heats of formation of nitromethane and polynitromethanes (dinitromethane, trinitromethane, and tetranitromethane) in gas phase at 298.15 K were calculated theoretically using density functional theory and other methods in combination with different basis sets [46]. It was found that the accuracy of C– NO_2 bond dissociation energies can be improved by switching to different functionals. As the number of NO_2 groups on the same C atom increases, one functional performed better than the other functional. All four functionals yielded satisfactory predictions for the enthalpy of formation in the gas phase with deviations of <2 kcal/mol from experimental ones for $\text{CH}_2(\text{NO}_2)_2$ and $\text{CH}(\text{NO}_2)_3$. For the $\text{C}(\text{NO}_2)_4$ molecule, a different basis set augmented with polarization functions and diffusion functions was required to yield a good result.

The gas phase enthalpies of formation of mononitromethane, dinitromethane, trinitromethane, and tetranitromethane and nitroethane, as well as of their nitrite and *aci*-form isomers, and the enthalpies of the C–N bond dissociation and isomerization of these nitroalkanes were calculated using different multi-level and density functional theory (DFT) based methods [47]. The calculated values of the formation and reaction enthalpies were compared with experimental data wherever these data were available. It was found that only the G3 procedure gave accurate (within 1 kcal/mol) results for the formation enthalpy of nitroalkanes, their isomers and radical products. The G3 procedure and two new hybrid meta-DFT methods proposed by Truhlar's group [48] showed good results for the reaction enthalpies of the nitromethane isomerization and the C–N bond dissociation. The results can be used to analyze thermodynamics of the dissociation and isomerization reactions of the polynitro-substituted methanes.

The gas-phase enthalpies of formation of 57 aliphatic nitro compounds and nitramines (mononitro and polynitro compounds including cyclic compounds and well-known explosives such as hexogen, octogen, and CL-20) were calculated using the Gaussian-4 (G4) theory applied to atomization and isodesmic reaction energies [49]. It turned out that the $\Delta H_f^{298}(\text{G})$ values calculated from the atomization reactions were underestimated by an average of 10 kJ/mol, and they could not be used for the assessment of inaccuracies in the experimental enthalpies of formation. Much better agreement between theory and experiment was obtained using the isodesmic reaction procedure. Several isodesmic reactions were investigated for each compound. High accuracy of most experimental data was confirmed by the agreement with theoretical results. The differences between the calculated and the experimental enthalpies of formation in the range from 8 to 53 kJ/mol were attributed to possible errors in the experimental values for 17 compounds. The theoretical $\Delta H_f^{298}(\text{G})$ values were recommended for these compounds as being more reliable than the experimental values. A reference data set of internally consistent gas-phase enthalpies of formation of nitro compounds and nitramines was provided. Both experimental and calculated values were included in this data set. In addition, the enthalpies of sublimation or vaporization were evaluated for some compounds by taking into account the literature data on the condensed phase enthalpies of formation and the $\Delta H_f^{298}(\text{G})$ values recommended in this work. Thus, a set of self-consistent values of the enthalpy of formation in both condensed and gaseous phases and the enthalpy of sublimation or vaporization could be obtained for most of nitro compounds studied.

While most theoretical computations give only the predicted gas phase enthalpies of formation of nitro compounds, a different methodology will give the enthalpies of formation even in the condensed state. An additive method for predicting the standard heats of formation at 298 K of aliphatic and alicyclic polynitro-compounds in the condensed state consists of three steps: **(1)** the evaluation of the enthalpy of formation in the gaseous state, **(2)** the estimation of the enthalpy of vaporization for a liquid or enthalpy of sublimation for a solid and **(3)** the calculation of interaction terms, mainly between NO_2 groups [50, 51]. The uncertainties of predicted values turned out to be within only a few kcal/mol. As an example of application for the enthalpies of formation, it was shown that the theoretical specific impulse of high-energy solid propellants could be calculated with a relative uncertainty of less than 1%.

Prediction of Heat of Combustion

A method for estimating the gross and net heats of combustion of nitroaliphatic compounds and nitrate esters was based on elemental compositions as well as the presence of some specific polar groups and molecular fragments [52]. The method can be used for organic compounds with at least one nitro, nitramine or nitrate functional groups. The predicted results showed that this method gives reliable predictions of

heats of combustion with respect to the group additivity method and computed values based on atom-type electrotopological state indices.

1.2.9.4 Heat of Evaporation of Mononitroalkanes

Table 12 is a summary of the latent heats of evaporation of nitroalkanes.

Table 12: Latent heats of evaporation of nitroalkanes.

Compound	Latent heat of evaporation at 298 K = 25 °C	
	kJ/mol	kcal/mol
Nitromethane	38.0 ± 0.4	9.09 ± 0.09
Nitroethane	41.6 ± 0.4	9.94 ± 0.10
1-Nitropropane	43.4 ± 0.4	10.37 ± 0.10
2-Nitropropane	41.3 ± 0.4	9.88 ± 0.10
1-Nitrobutane	48.6 ± 0.5	11.61 ± 0.12
2-Nitrobutane	43.8 ± 0.4	10.48 ± 0.10
1,1-Dinitropropane	62.5 ± 0.6	14.93 ± 0.15

Data source: [16]

1.3 Chemical Properties of Mononitroalkanes

The most important chemical reaction of mononitroalkanes is the formation of aci-salts with alkalis. In most cases, the aci-salts are more reactive than the parent acid.

Nitroparaffins can be reacted with formaldehyde to obtain nitro alcohols, which can be further esterified with nitric acid (e.g. in the synthesis of nitroisobutylglycerol trinitrate or nitromethylpropanediol dinitrate).

1.3.1 Thermal Stability and Decomposition of Mononitroalkanes

Nitro compounds are of interest as energetic chemicals in propellants and explosives. As such, it is very important to have a thorough understanding of the decomposition of these compounds, both the unintended decomposition during storage, often at above nominal temperatures in tropical climates, and the intended, carefully controlled decomposition in a rocket chamber. The threshold of autoignition of nitroalkane vapors in the presence and even in the absence of air is an important safety parameter.

Nitro compounds may decompose via two different mechanisms: a molecular mechanism, when a molecule of HNO_2 is detached and the corresponding alkene is formed, and a free radical mechanism, in which the reaction starts with the breaking of the C—N bond. A study of the reactions of the former type is of considerable interest in the light of the general theory of elimination reactions in the gas phase. The radical decomposition of nitroalkanes is characterized by high values of the pre-exponential

factors [53]. The activation energy in this instance equals the energy for breaking the bond. Secondary reactions have little influence on the rate of radical decomposition of *gem*-polynitroalkanes, therefore the study of the kinetics of the decomposition can be an effective method of determining the energy for the breaking of the C–N bond in these compounds.

The contribution of the heterogeneous reaction to the rate of the gas phase decomposition of nitroethane, 1-nitropropane and 2-nitropropane was determined by varying the ratio of the surface to the volume of the reaction vessel [54]. The activation energies of the homogeneous decomposition of these compounds differed from the literature data obtained by different methods.

An analysis of experimental data on the decomposition of aliphatic nitro compounds revealed effects of the structure of the molecule and substituents in the alkyl group on the pre-exponential factor of the reaction rate constants and activation energies [55]. The pre-exponential factor and activation energy of 28 nitroalkane compounds were compared to their molecular structure and substituent effects in the alkyl group. The value of the pre-exponential factor depends on the contribution of three factors, manifested in the formation of the activated complex: liberation of the internal rotation relative to the dissociating C–N bond, a decrease in the frequencies of the deformational vibrations associated with this bond and rotation of the alkyl groups next to the reaction center. Empirical rules were noted: 1) in the series $\text{RCH}_n(\text{NO}_2)_{3-n}$, activation energy does not depend on the length of the alkyl chain R. For $n = 1$, $E = 197\text{--}201 \text{ kJ/mol} = 47\text{--}48 \text{ kcal/mol}$; for $n = 0$, $E = 172\text{--}178 \text{ kJ/mol} = 41\text{--}43 \text{ kcal/mol}$; 2) substituents R, H, and F in the α -position to the nitro group have the same influence on the activation energy; 3) when one NO_2 group is replaced by Cl, the activation energy is reduced by approximately 4 kJ/mol (1 kcal/mol); 4) Br and I reduced the activation energy to a greater degree than Cl.

The thermal decomposition of dilute *n*-nitroalkanes (nitromethane, 1-nitropropane = CAS RN [108-03-2], 2-nitropropane = CAS RN [79-46-9]) vapors (0.005–0.3 vol.-% diluted with air) in shock tubes was followed by recording the IR spectra of these compounds and their decomposition products [56]. A 1st-order rate law was followed and NO_2 was a primary dissociation product. The rate constants could be correlated with the C–N bond dissociation energy.

The pyrolysis of the alkyl radical sources RNO_2 ($\text{R} = \text{C}_1\text{--C}_6$ alkyl) in incident and reflected shock waves was examined at 900–1400 K and 1–30 atm by measuring NO_2 concentration profiles and deriving RNO_2 and $\text{R}^\bullet$ dissociation kinetic data [57]. The reactions behind the shock waves were followed by recording light absorption-time profiles of the decomposing molecules and the produced NO_2 . In addition, there are three earlier, separate publications by the same authors on MeNO_2 [58], EtNO_2 [59] and PrNO_2 [60] that will be discussed in more detail further down in this chapter.

These shock tube tests were similar to those conducted by other investigators later [61]. The thermal decomposition of dilute mixtures (0.2% by volume) of R-NO_2 ($\text{R} = \text{C}_2\text{H}_5$, *i*- C_3H_7 , *tert*- C_4H_9) in argon was investigated in the temperature

range 800–1000 K by a comparative rate method using ethyl bromide and isopropyl bromide as internal standards. Under these experimental conditions, the decomposition proceeded via C–N fission in competition with five-center elimination of HONO. The obtained values of activation energies were then compared with those obtained from thermochemical calculations. Comparisons of the reactions in the pyrolysis of nitro compounds, nitroso compounds and alkyl nitrates were published in [62, 63].

The influence of molecular structure on the rates and mechanisms of the gas-phase reactions of aliphatic nitro compounds and the structures of the transition states in the C–N dissociation and HNO_2 elimination processes were examined [64]. The characteristic features common to the decomposition of C-nitro compounds in the condensed phase are described, based on the C–N bond dissociation energy and the influence on the latter exerted by electronic, steric, and conformational effects. A bibliography included 86 references.

A relationship has been derived between the activation energies E_a of low-temperature non-autocatalyzed thermolysis of nitroparaffins and their oxygen balances [65]. An analogous relationship has also been found for pre-exponents of $\log A$. A direct relationship existing between E_a values and the impact sensitivity of the nitro compounds in a condensed state was confirmed by the first relationship. From these two relationships, the molecular structural dependences of the thermal reactivity of nitroparaffins in both gaseous and liquid states can be correlated. For the thermolysis of mononitromethane in the liquid state, a primary homolytic pseudo-monomolecular fragmentation decomposition mechanism was proposed.

Structure-property correlation equations for the activation energies of thermal decomposition of nitro compounds in the gas phase can be obtained based on structural descriptors [66]. Correlation equations were constructed using a computing program based on data for 90 nitro compounds belonging to various chemical classes.

Geometric molecular structure parameters of nitro and fluoronitro derivatives of nitromethane, nitroethane, 1-nitropropane, and 1-nitrobutane (for which experimental data on kinetics of radical gas-phase decomposition were available) have been determined by a computational method [67, 68]. Correlations between changes in logarithms of the activation energy and those in the lengths of C–N – and C–H-bonds as well as in the ionization potentials have been found. The major changes in the C–N- and C–H bonds occurred when bulky atoms and groups (NO_2 , Cl, Br, and I) were introduced into the molecules. An equation was derived which allowed one to perform a high-accuracy determination of the activation energy for radical gas-phase decomposition of nitroalkanes using the coefficients of steric interactions in the molecules calculated by methods of molecular mechanics. In attempting to explain the abnormally low thermal stability of dinitromethane, a mechanism was suggested that included the elimination of water from the aci-form of dinitromethane.

A theoretical study of the formation and destruction of the aci-forms of nitromethane and dinitromethane based on a quantum chemical study of the dehydration mechanism of CH_3NO_2 and $\text{CH}_2(\text{NO}_2)_2$ molecules has shown that a water

molecule eliminates from the respective *aci*-forms, formation of the latter being the rate-limiting step of the whole process [69].

Data from experimental and theoretical studies of thermal decomposition of C-nitro and N-nitro compounds of aliphatic, alicyclic, aromatic and heteroaromatic compounds, which formed the basis for the development of an *ab initio* approach to the prediction of the mechanisms of thermolysis of energetic compounds, were used to develop relationships between the structures and thermolysis mechanisms of nitro compounds [70]. Using the Recombination Reaction Network strategy and Computer Assisted Structure Building software, full reaction mechanisms for the thermal destruction of nitro compounds at different thermal decomposition levels (including extensive ones) could be simulated and the full set of possible mechanisms of thermal decomposition of 38 chemically different nitro compounds was presented.

A relationship has been derived to predict the activation energies (E_a) of low-temperature non-autocatalyzed thermolysis of nitroparaffins through suitable combination of elemental composition [71]. This correlation of E_a was based on experimental data using the isothermal monomethric method, which is useful method to examine the kinetics of thermolysis of energetic materials in vacuum. This method used the optimized numbers of carbon, hydrogen and oxygen divided by the molecular weight of nitroparaffins to obtain a reliable correlation. This correlation is a general relationship because it can be applied for various nitroparaffins as compared to previous methods which used oxygen balance for some specific groups of compounds. A similar predictive method can be used to predict the autodetonation temperature of nitro compounds [72]. The pyrolysis of nitroalkanes and nitroarenes is described in [73].

1.3.2 Reactions of Mononitroalkanes

Substitution of hydrogen in the alkyl group in nitroalkanes does not always result in the desired products. The types of products are less predictable than for reactions with halogenoalkanes [74]. The main difference is that many nitro compounds react in the *aci*-form because the hydrogen in the alpha-position is activated by drawing electrons away from it.

Methyl groups are usually electron-donating relative to hydrogen when introduced into molecules, and their consequent acid-weakening properties are well known. Methyl substitution at the α -position of nitroparaffins, however, has quite the opposite effect: for example, in the simple series nitromethane, $pK_a = 10.22$, nitroethane, $pK_a = 8.60$, and 2-nitropropane, $pK_a = 7.74$, a marked increase in acidity accompanies methyl substitution [75]. 2-Nitropropane was the strongest acid from a group of ten $C_{n \geq 2}$ nitroalkanes. Similar data in Table 13 show that the acidity constant of mononitroalkanes decreases (i.e., acidity increases) with increasing length of the alkyl chain. In a typical example, the pK_a values of RCH_2NO_2 decreased in the order $CH_3NO_2 > CH_3CH_2NO_2 > (CH_3)_2CHNO_2$ in water, whereas the rate of proton

abstraction by hydroxide ion decreased in the same order. This phenomenon is sometimes referred to as the “nitroalkane anomaly”. Nitroalkane anomaly does not exist in the gas phase.

Table 13: Acid dissociation constants of mononitroalkanes.

Compound	Formula	pK_a	pK_a
Nitromethane	H_3CNO_2	10.18	10.24
Nitroethane	$H_3CCH_2NO_2$	8.46	8.6
1-Nitropropane	$H_3CCH_2CH_2NO_2$	8.98	—
2-Nitropropane	$(H_3C)_2CHNO_2$	7.67	—

Data sources: W. R. Grace Co. Datasheet, [76]

1.4 Safety Properties of Mononitroalkanes

1.4.1 Drop Weight Impact Sensitivities of Mononitroalkanes

A method for prediction of impact sensitivity of nitroaliphatic compounds was based on some structural parameters of $C_aH_bN_cO_d$ explosives [77]. Three essential parameters would be needed in this scheme which contain $a + b/2 - d$ and the number of nitrogens as well as the number of $R-C(NO_2)_2-CH_2-$ structural parameters attached to oxygen of carboxylate functional groups where R is alkyl groups. The results were compared with experimental data and some empirical correlations. Predicted impact sensitivities for 58 explosives had a root mean square (rms) of deviation from experiment of 27 cm, which was considered good agreement with respect to less accurate values obtained with previous empirical models.

Drop weight impact sensitivities of 58 liquid explosives and melts of high explosives were summarized in [78]. Compounds that were solids at room temperature were heated to just above their melting points. This paper contained data on 4 nitroalkanes, 12 alkyl nitrate esters, 8 azidonitro compounds, 5 fluoronitro compounds and 14 nitramines. The data for individual nitro compounds were extracted from that paper and inserted in the hazard property tables of individual compounds (Table 14). The compound numbers in the first column of the table are the same as those used in Figure 2. The drop weight sensitivity was determined with a mass of 2.5 kg and the 50% heights in cm are listed in Table 14 and shown in Figure 2.

The drop weight sensitivity apparatus used for these tests differed from that used per American Society for Testing and Materials (ASTM) D2540 in that it deliberately subjected the samples to two consecutive impacts (whereas methods used in the US specifically prevent rebound and second impacts). The first impact causes cavitation and release of bubbles which sensitizes the explosive to the second impact. Linear correlations between the impact sensitivity of liquid high explosives and the maximum volumetric heat of explosion were obtained for several groups of

Table 14: Correlation between drop weight impact sensitivities of nitroalkanes, heat of formation, and heat of explosion.

No. Compound	H_{50}	T		ΔH_0		ρ	$Q_{\max}$	$\rho Q_{\max}$
	cm	K	°C	kJ/mol	kcal/mol	g/cm ³	kcal/g	kcal/cm ³
6 (O ₂ N) ₃ CCH ₂ CH ₂ C≡N	29.0	293	20	-50	-12	1.52	1.533	2.33
13 CH ₃ NO ₂	160	293	20	-114	-27.30	1.13	1.62	1.83
21 (NO ₂) ₃ CCH ₂ O(CH ₂) ₃ OCH ₂ C(NO ₂) ₃	9	293	20	-464	-111.1	1.59	1.626	2.59
22 (NO ₂) ₃ CCH ₂ O(CH ₂) ₂ OCH ₂ C(NO ₂) ₃	7.5	308	35	-438	-104.6	1.60	1.647	2.64

Data source: [78]

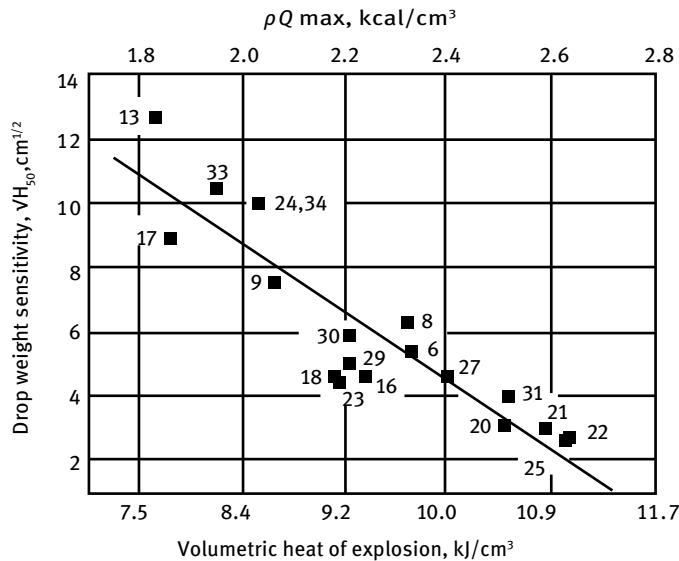


Figure 2: Correlation between the sensitivity of aliphatic nitro compounds not containing azide and nitramine groups and their maximum volumetric heats of explosion (republished and modified from [78], with permission of © 2010 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

compounds, allowing one to predict the sensitivity of hitherto untested liquid high explosives based on physicochemical properties and elemental composition. Similar relationships were derived between drop weight sensitivity and onset of thermal decomposition. For aliphatic nitro compounds not containing azido or nitramino groups the correlation was (Figure 2)

$$H_{50} = [(30.0 \pm 2.8) - (10.6 \pm 1.3)\rho Q_{\max}]^2$$

The C—NO₂ bond dissociation energies of a series of model C-nitro compounds and 26 energetic C-nitro compounds have been calculated using density functional theory methods and compared to the measured drop weight impact sensitivity [79]. A linear relationship could be established. See also reference [80].

1.5 Toxic Properties of Mononitroalkanes

Toxicity properties of all mononitroalkanes are so similar that they can be discussed here together as a group [81]. The main difference between the different mononitroalkanes is their vapor pressure. Sections dealing with toxicity of individual mononitroalkanes are further down in this chapter, followed eventually by similar sections on polynitroalkanes.

Although aliphatic nitro compounds, aliphatic nitrates and aliphatic nitrites have several features in common (nitrogen–oxygen grouping, explosiveness, methemoglobin formation), there are significant differences in their toxic effects. Some of their attributes were summarized in a review paper [82]. The esters of nitric and nitrous acids, where nitrogen is linked to carbon through oxygen, are very similar in their pharmacological effects. Both produce methemoglobinemia and vascular dilatation with hypotension and headache. These effects are transient. None of the series has appreciable irritant properties. Pathological changes occur in animals only after high levels of exposure and are generally non-specific and reversible. Nitro compounds, like nitrates and nitrites, cause methemoglobinemia in animals. Heinz body formation parallels this activity within the series. Although some members are metabolized to nitrate and nitrite, there is no significant effect on blood pressure or respiration. In addition to respiratory tract injury, cellular damage may be observed in the liver and kidneys. Skin absorption is negligible except for the nitroolefins.

Guinea pigs, rabbits, monkeys, and a few rats were exposed to mononitroalkanes by oral administration, skin application, and inhalation [83]. No injury or death followed after any skin application. The weight of the molecule intensified and prolonged the toxic action. The most severe liver damage seen, with fatty infiltration, was caused by nitropropane. Severe central nervous system irritation followed inhalation of nitromethane. Loss of weight and a reduction in erythrocytes and hemoglobin were of uniform occurrence, but within normal limits and recovery was prompt. Lethal concentrations were far below narcotic concentrations, which cannot be used as a warning.

Summaries of toxicity information for nitromethane, nitroethane, 1-nitropropane, 2-nitropropane, trinitromethane and tetranitromethane were compiled in a government report [84]. Oral and inhalation toxicities and the degree of histological damage increase with increasing molecular weight of the compounds. Nitromethane and nitroethane (rat oral LD₅₀ > 1000 mg/kg) are less toxic than 1-nitropropane or 2-nitropropane (500–700 mg/kg), which in turn are less toxic than

tetranitromethane and trinitromethane (~300 mg/kg). The primary effects included histological liver damage and central nervous system depression, both atactic and narcotic changes, regardless of the route of administration or the duration of exposure. Vapor exposures also caused respiratory tract and conjunctival irritation and pulmonary edema. Symptoms of exposure in humans included headache, nausea, damage to the respiratory tract and liver damage. Most of human exposures to nitroparaffins resulting from occupational pursuits have been due to 2-nitropropane. The four higher molecular weight nitroparaffins (1-nitropropane and 2-nitropropane, tetranitromethane, and trinitromethane) additionally have been demonstrated to be methemoglobin poisons in animals. Chronic inhalation exposure to 2-nitropropane has been associated with the development of precancerous lesions in the liver and hepatocellular cancer in rats, and 2-nitropropane was a positive mutagen in the Ames Salmonella assay.

The more severe toxicity of polynitroalkanes such as trinitromethane or tetranitromethane is quite different from that of mononitroalkanes and will be dealt with in a separate section further down in this chapter (Section 5.5 and 6.10).

The Occupational Safety and Health Administration (OSHA) permissible exposure limits (PEL) total weight average (TWA) for nitromethane is 100 ppm and the OSHA PEL TWA for nitroethane is also 100 ppm. These values are quite high (safer) in comparison to nitrobenzene (OSHA PEL TWA = 1 ppm), which shows that the aliphatic nitro compounds are not nearly as toxic as their aromatic counterparts.

Nitromethane, nitroethane, and nitropropane are commonly used as solvents for lacquers, paints, and inks, and a large part of the general population may be exposed to vapors when doing painting. The synthesis of moisture-sensitive nitronium salts like nitronium perchlorate is best done in nitromethane as the solvent.

The hepatotoxic and mutagenic potentials of nitromethane, nitroethane, and 2-nitropropane were assessed biochemically and histopathologically in mice [85]. In male mice, plasma activities of the hepatic enzymes were significantly elevated 48, 72, and 96 h after i.p. administration of 9 mmol/kg 2-nitropropane, but not after administration of nitromethane or nitroethane. In female mice a dose of 6.7 mmol/kg of 2-nitropropane was sufficient to cause hepatotoxicity. The histopathological evaluation supported the biochemical results, and livers of mice that had received 2-nitropropane (9 mmol/kg) showed damage. Mutagenicity was tested in *Salmonella typhimurium* tester strains TA98, TA100, and TA102. Both 2-nitropropane and its anionic form, propane-2-nitronate, were mutagenic but the nitronate was the more powerful mutagen. Neither nitromethane, nitroethane nor their nitronates caused an increase in the number of revertant colonies over those seen in control plates. The results suggested that the primary nitroalkanes are much less hepatotoxic and mutagenic than 2-nitropropane.

1.6 Applications of Nitroalkanes

The list of industrial applications of nitroalkanes is very long, too long to include in this book. We are listing here only a few summaries on uses of nitroalkanes as energetic materials in propellants and explosives. A recent book on liquid explosives contains a chapter on nitro compounds as liquid explosives [86].

2 Nitromethanes

In methane 1–4 hydrogen atoms can be replaced by nitro groups, forming a family of progressively more oxygen-rich organic oxidizers.

2.1 Comparative Evaluation of Physical Properties of Nitromethanes as a Group

Table 15 is a summary of physical properties and acidity constants of nitromethanes. Due to the electrophilic nature of the nitro group, replacing more and more hydrogen atoms in methane by nitro groups causes the remaining hydrogens to become more and more acidic, to the point that trinitromethane is a weak acid and forms salts with many metals and with ammonium or hydrazinium cations; however, the increase in acidity, as measured by pK values in various solvent systems, is not proportional to the number of nitro groups present, a dampening effect being observed upon substitution [87, 88].

2.2 Comparative Evaluation of Chemical Properties of Nitromethanes as a Group

A computational investigation of the nitro, nitrite, and *aci*-form isomers and the isomerization reactions of mononitromethane, dinitromethane, trinitromethane, and tetranitromethane showed that the isomerization displacement of NO₂ by ONO groups was surprisingly thermodynamically favored for dinitromethane, trinitromethane, and tetranitromethane [89]. The molecular stability decreased and the isomerization became easier by increasing the number of nitro groups. The largest attraction among substitutes took place through the central carbon atom in C(ONO)₄ and led to a higher stability than that of the C(NO₂)₄ isomer.

Table 15: Effect of progressive substitution of hydrogen in methane by nitro groups on physical properties.

Compound	Formula	Melting point		Boiling point		Acidity, pK	
		K	°C	K	°C	Niemeyer [87]	Rezende [76]
Methane	CH ₄	90.67	−182.48	111.7	−161.5	—	—
Nitromethane	CH ₃ NO ₂	244.6 ± 0.05	−28.55 ± 0.05	374.1 ± 0.8	101 ± 0.8	10.24	10.24
Dinitromethane	CH ₂ (NO ₂) ₂			Decomposition		3.57	3.63
Trinitromethane	CH(NO ₂) ₃	292	18.9	Decomposition		0.17	0.06
Tetranitromethane	C(NO ₂) ₄	287.05 ± 0.2	13.9 ± 0.2	399.2	126.1	—	—

3 Nitromethane

Nitromethane, mononitromethane, H_3CNO_2 , NM, Chemical Abstracts Service (CAS) RN [75-52-5], is the lowest member of the family of nitro compounds, and one of the most important ones at the same time.

3.1 Production of Nitromethane

The four lower mononitroparaffins (nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane) are produced on a large industrial scale by oxidizing an excess of vapor-phase propane with nitric acid at a temperature range of 643–723 K (370–450 °C) and pressure of 0.8–1.2 MPa (8–12 atmospheres). This reactant combination sounds more like a rocket propellant and indeed explosions can occur during this process. Approximately 40% of the nitric acid is converted to nitroparaffins; the remainder acts as an oxidizing agent to produce unwanted oxygenated by-products and is reduced to nitric oxide. The products are 48.2 mol-% 2-nitropropane, 22.0 mol-% nitromethane, 16.6 mol-% nitroethane, and 13.2 mol-% 1-nitropropane. Industrial grades of nitroethane contain these byproducts as contaminants.

Commercial nitromethane that needs to be purified to determine accurate physical properties can be purified by a sequence of aqueous solution washings of sodium bicarbonate, sodium bisulfite, and sulfuric acid, followed by two fractionated distillations, one at ambient pressure and one at reduced pressure, on long columns with high reflux ratios and discarding the early fractions [90]. It is difficult to separate the azeotrope formed between nitromethane and water to obtain an anhydrous product with better than 99.9 mol-% nitromethane.

3.2 Physical Properties of Nitromethane

The physical properties of nitromethane are well characterized and the data are fairly accurate. Several summaries of the physical and chemical properties of nitromethane have been published as summarized in Table 16.

Very good summaries of literature data including physical properties, thermodynamic properties and kinetics of decomposition were compiled specifically to collect information for the intended utilization of nitromethane as a rocket propellant [93, 99]. Standard textbooks and encyclopedias on explosives contain chapters on nitromethane [100, 101].

Table 16: Physical properties of nitromethane.

Property	S.I. units	Other units	Source	References
Molecular mass	61.040 g/mol	16.38 mol/kg	NIST Chemistry WebBook	[91]
Freezing point	244.6 K	-28.55 °C	Coetzee and Chang	[92]
	244.6 K	-28.55 °C	Makovky and Lenji	[93]
	244.6 K	-28.55 °C	Toops	[11]
	244.77		Jones and Giauque	[94]
Triple point temperature				
Triple point pressure	0.14015 kPa			
Boiling point	374.35 K	101.20 °C	Coetzee and Chang	[92]
	374.35 K	101.2 °C	Toops	[11]
	374.1 ± 0.8	101 ± 0.8 °C	NIST Chem WebBook, Average of 17 values	[91]
Density at 298 K				
Surface tension at 293 K	37.48 mN/cm	1.13124 g/cm ³	Coetzee and Chang	[92]
Refractive index n_D^{20}	1.3818	0.0375 N/m	Coetzee and Chang	[92]
Enthalpy of formation, liquid ΔH_f^{298}	-113.1 kJ/mol	-1852.8 kJ/kg	Holcomb and Dorsey	[16]
	-113.1 kJ/mol	-1852.8 kJ/kg	McCullough et al.	[95]
	-113.1 kJ/mol	-1853.5 kJ/kg	Meyer, Koehler and Homburg	[96]
	-113.1 kJ/mol	-1852.8 kJ/kg	PEPCODED.DAT	[97]
	-113.1 kJ/mol	-1852.8 kJ/kg	Stull, Westrum, and Sinke 1969	[98]
Enthalpy of formation, vapor ΔH_f^{298}	-74.72 kJ/mol	-1224.1 kJ/kg	Stull, Westrum, and Sinke 1969	[98]
Heat of evaporation at normal b.p.	33.97 kJ/mol	556.4 kJ/kg	Stull, Westrum, and Sinke 1969	[98]

3.2.1 Freezing Point, Boiling Point, and Phase Diagrams of Nitromethane and Nitromethane Mixtures

Studying the thermodynamic melting point of crystalline nitromethane by molecular dynamics simulation computations, the melting mechanism of superheated crystalline nitromethane, and the physical properties of crystalline and glassy nitromethane showed that the maximum superheating and glass transition temperatures of nitromethane were 316 and 160 K, respectively, for heating and cooling rates of 8.9×10^9 K/s [102]. Using the hysteresis method and by taking the glass transition temperature as the supercooling temperature, a value of 251 K for the thermodynamic melting point was in excellent agreement with the two-phase result of 255.5 K and measured value of 244.73 K.

The boiling point of the azeotrope formed between nitromethane and water is 356.74 K (83.59°C). The azeotrope distillate contains 76.4 mass-% nitromethane. A phase diagram that includes triple point and critical point was constructed from literature data (Figure 3).

During production of nitroalkanes, often mixtures of nitromethane and nitroethane are obtained that need to be separated by fractionated distillation. In other applications, nitroethane is added to nitromethane on purpose to reduce its sensitivity and the vapor and liquid composition of binary mixtures must be known. In either case, it will be necessary to know the vapor phase diagram of binary mixtures of nitromethane and nitroethane [103].

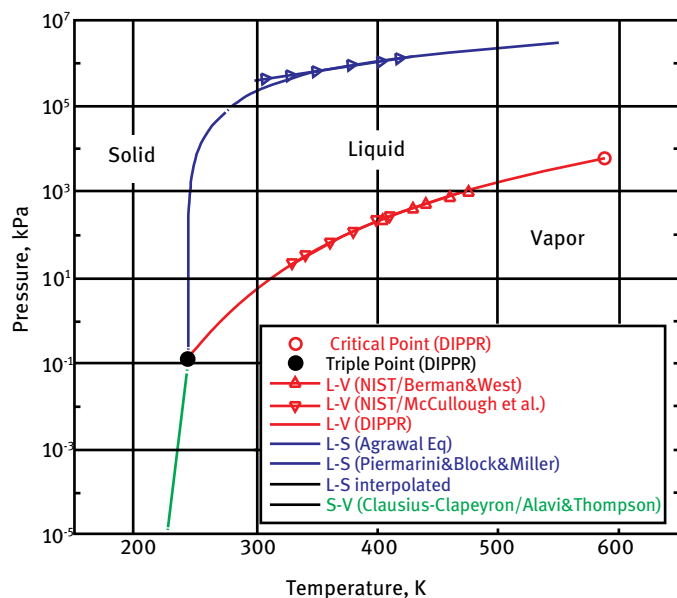


Figure 3: Phase diagram of pure nitromethane (reproduced and modified from [99] with permission from Dr. Eric Boyer 26 April 2021.)

3.2.2 Density of Nitromethane and Nitromethane Mixtures

Density data from different sources, not always very consistent with each other, are collected in Table 17.

Table 17: Density of nitromethane.

Temperature		Density	Source	References
K	°C	g/cm ³		
293	20	1.13749	Thompson, Coleman, and Helm 1954	[90]
298	25	1.13064	Thompson, Coleman, and Helm 1954	[90]
303	30	1.12398	Thompson, Coleman, and Helm 1954	[90]
293	20	1.13816	Toops 1956	[11]
298	25	1.13128	Toops 1956	[11]
303	30	1.12439	Toops 1956	[11]
298	25	1.1385	Meyer, Koehler and Homburg	[96]
298	25	1.1314	Smyth and Walls 1935	[104]
283	10	1.1490	Bellinger et al. 1948a	[105]
298	25	1.1287	Bellinger et al. 1948a	[105]
313	40	1.1080	Bellinger et al. 1948a	[105]
293	20	1.1359	Cantoni and Feldman 1953	[103]

The density of liquid nitromethane between 298 and 473 K (25 and 200 °C) can be calculated from the following equation [106]:

$$\rho = 1.1615 - 1.1952 \times 10^{-3}t - 1.553 \times 10^{-6}t^2$$

where ρ is the density in g/cm³ and t is the temperature in °C.

Density data from several sources have been examined and curve-fitted to result in the equation published by the Design Institute for Physical Properties (DIPPR) database, which is good for the temperature range 245–588 K:

$$\rho = \frac{A}{B[1 + (1 - \frac{T}{C})^D]}$$

where ρ is the density in g/cm³, T is the temperature in kelvin and the constants A through D are A = 1.3793, B = 0.23918, C = 588.15, and D = 0.29030.

A number of studies reported the physical properties of nitromethane and alcohol mixtures including miscibility. Deuteration both in the OH group of alcohol and/or the methyl group of nitromethane increased (widened) the domain of the limited miscibility of nitromethane and alcohol mixtures [107].

When measuring the solubility of nitromethane and water in each other, it appeared that deuteration in the OH group of water increased the region of limited mis-

cibility, while deuteration in the methyl group of nitromethane decreased this region [108]. Excess volumes, densities, and viscosities of binary mixtures of aliphatic alcohols (C_1 – C_4) with nitromethane were measured [109]. Temperature dependence of densities and speeds of sound of nitromethane and butanol isomers were measured in the range 288–308 K [110]. Although no application to propulsion was given as a reason for doing this work, the inclusion of butanol in these studies is interesting since it had previously been shown to act as a desensitizer. The coefficient of thermal expansion of nitromethane between 278 and 313 K (5 and 40 °C) is $1.24 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$ [111].

3.2.3 Compressibility, Velocity of Sound, and Equation of State of Nitromethane

The compressibility of nitromethane is $7.26 \times 10^{-10} \text{ m}^2/\text{N}$ ($7.36 \times 10^{-5} \text{ atm}^{-1}$) [112]. The velocity of sound in liquid nitromethane at 298 K (25 °C) is $1.30 \pm 0.05 \text{ mm}/\mu\text{s}$ [111].

The pressure and temperature effects on the structural properties of denser liquid nitromethane have been examined computationally in terms of some characteristic pair radial distribution functions [113]. With potential functions including the harmonic intramolecular interaction and Lennard-Jones plus columbic intermolecular interactions, classical dynamic simulations were performed for liquid nitromethane. Constant pressure-temperature and constant volume-temperature simulations in the range of pressure from 101 kPa to 24.3 GPa and the range of temperature from 300 to 1300 K. The classical molecular dynamics simulation gave results close to experimental results, but the calculated Hugoniot pressure was too high compared to experimental results. The computed shock temperature was lower than the experimental one. Analysis of the pair correlation functions revealed that the short-range repulsion becomes very important at high density.

A reliable equation of state (EOS) for unreacted liquid nitromethane is needed for computations of detonation velocity and detonation pressure and to predict the behavior of liquid nitromethane under conditions of very high pressure that precede the detonation front. There are several equations of state for nitromethane described in the literature.

One example of an EOS predicts the hot spot size required for propagation of detonations in nitromethane [114]. An early method for developing an EOS for nitromethane was based on extended integration schemes [115]. The energy-pressure-volume EOS was derived from a combination of the known variation of energy with temperature along the atmospheric pressure isobar and the Hugoniot jump relations. The energy-entropy-volume equation was generated by a numerical integration of the coupled differential equations governing the entropy and temperature variation along a Hugoniot curve.

The EOS proposed by Winey et al. [116] was based on a method where the specific heat C_v , the isothermal bulk modulus B_T and the coefficient of thermal pressure $(\partial P/\partial T)_V$ were modeled as functions of temperature and volume using experimental

data. In order to test this EOS, temperature measurements using time-resolved Raman spectroscopy were obtained from nitromethane subjected to stepwise loading. Calculations using the new EOS showed good agreement with the measured temperatures. Comparison with previous EOS models showed that simplifying assumptions, such as holding $(\partial P/\partial T)_V$ or γ_V constant, would lead to significant inaccuracies in temperature predictions for shocked nitromethane.

A perturbation calculational technique was used to predict the thermodynamic properties of nitromethane at high pressures [117]. The intermolecular interaction can be described by a spherically symmetric, exponential-6 potential and an angular dependent, multi-polar contribution. Isothermal compression and the shock Hugoniot for nitromethane can be characterized by the theory. Molecular dynamics calculations, with the intermolecular forces constructed from interatomic interactions, can describe the experimental observations under consideration. There was a considerable difference in the predicted shock temperatures from the two methods.

An EOS for unreacted nitromethane provided accurate temperatures required to support a temperature-dependent reaction rate within a reactive flow model [118]. A quasi-harmonic form was normalized to shock wave data, but with a more rigorous treatment of thermal modes. A reactive flow model that included temperature as well as mechanical state was used to investigate shock initiation in nitromethane. Temperatures predicted by the model for various off-Hugoniot states in reactive configurations showed reasonable agreement with data from experimental measurements.

A new molecular force field for nitromethane obtained by means of Monte Carlo molecular simulations was proposed that lead to a good description of shock properties [119]. Results of calculated properties of shocked nitromethane are in good agreement with experimental shock Hugoniot data, including temperature measurements of second shock Hugoniot.

The Hugoniot curve of inert (non-reactive) nitromethane can be computed using Monte Carlo simulations with a modified version of an adaptative equation of state and intermolecular potential data [120]. Molecular dynamic simulations of nitromethane decomposition have been performed using a reactive potential, allowing the calculation of kinetic rate constants and activation energies.

Another EOS of unreactive shocked liquid nitromethane was not based on extended integration schemes but the complete EOS was computed by microscopic calculations with molecular simulations [121]. Measured shock temperatures and second shock temperatures were accurately reproduced which indicated the quality of the equation.

3.2.4 Critical Point Properties of Nitromethane

Under conditions of the critical point, nitromethane is likely to explode prematurely before any measurements can be taken. The critical point data were derived from other physical properties [122–124]:

$$T_{\text{crit.}} 588 \text{ K} = 315^\circ\text{C}$$

$$P_{\text{crit.}} 6.28 \pm 0.1 \text{ MPa} = 62.2 \pm 1 \text{ atm} = 63.10 \text{ bar}$$

$$\rho_{\text{crit.}} 0.352 \pm 0.004 \text{ g/cm}^3 = 5.77 \text{ mol/L}$$

3.2.5 Vapor Pressure of Nitromethane

The vapor pressures of nitromethane as a function of temperature are listed in Table 18 in comparison to that of nitroethane. The vapor pressure of nitromethane can be calculated from the following equations:

The first equation in the form of an Antoine equation based on 15 data points taken between 328 and 409 K (55 and 136 °C) gives the vapor pressure as follows [95]:

$$\log p_v = 7.28050 - \frac{1446.186}{t + 227.515}$$

where p_v is the vapor pressure in mm Hg and t is the temperature in °C. From another source, an Antoine type equation can give the vapor pressure very accurately [11]:

$$\log p_v = 7.274170 - \frac{1441.610}{t + 226.939}$$

Table 18: Vapor pressure of nitromethane and nitroethane.

Temperature		Vapor pressure	
K	°C	Nitromethane	Nitroethane
		mm Hg	mm Hg
283	10	16.12	8.52
293	20	27.89	15.65
298	25	36.26	20.89
303	30	46.67	27.41
313	40	75.21	46.20
323	50	117.1	74.55
333	60	178.2	113.2
343	70	262.7	173.9
353	80	377.7	254.2
363	90	530.2	361.1
373	100	730.4	499.4
383	110		676.6

Data source: [16]

where p_v is the vapor pressure in mm Hg and t is the temperature in °C. Taking the McCullough et al. [95] data and converting them to Antoine equation parameters for the temperature range 329–409 K results in

$$\log_{10}(P) = 4.40542 - [1446.196/(T - 45.633)]$$

where P is the vapor pressure in bar and T is the temperature in kelvin. The normal boiling point from this equation is 374.35 K (101.19 °C).

Another equation based on measurements between 403 and 473 K (130 and 200 °C) gives the vapor pressure in units of atmospheres [106]:

$$\log p = 10.8210 - 3905.39/(t + 260)$$

where p is the vapor pressure in atm and t is the temperature in °C. Taking the Berman and West [106] data and converting them to Antoine equation parameters for the temperature range 405–476 K results in

$$\log_{10}(P) = 4.11350 - [1229.574/(T - 76.221)]$$

where P is the vapor pressure in bar and T is the temperature in kelvin. The same data were also expressed in the form of a Cox equation:

$$\log p_v = A \left(1 - \frac{374.347}{T} \right)$$

$$\log A = 0.845118 - 6.1497 \times 10^{-4} T + 6.0541 \times 10^{-7} T^2$$

where p_v is the vapor pressure in atm and T is the temperature in kelvin. This latter equation allows some extrapolation beyond the range of measured data.

The vapor density of nitromethane vapor was measured by the Dumas method between 380 and 439.6 K (107 and 166.5 °C) [125]. The measured densities were 1–2% higher than values calculated from the ideal gas law. In spite of its high dipole moment (3.44 D), nitromethane molecules are not significantly associated in the vapor phase.

The DIPPR database offered the following equation which was the result of combining and curve-fitting data from several sources:

$$P = e^{\left(A + \frac{B}{T} + C \ln T + DT^E \right)}$$

where P is the pressure in Pa and T is the temperature in kelvin. The coefficients A, B, C, D, and E are listed in Table 19. See also reference [94].

Table 19: Coefficients for nitromethane vapor pressure correlation.

Temperature, K	A	B	C	D	E
244–588	8.7411 E01	–7.1332 E03	–9.7786	7.9061 E–06	2.0000

Data source: DIPPR

3.2.6 Viscosity of Liquid Nitromethane

The viscosity of liquid nitromethane is listed in Table 20.

Table 20: Viscosity of liquid nitromethane.

Temperature		Absolute viscosity	Data source	Ref.
K	°C	cPs		
288	15	0.694	Makovky and Lenji 1958	[93]
298	25	0.632		
303	30	0.595	Thompson, Coleman, and Helm 1954	[90]
293	20	0.646		
298	25	0.608		
303	30	0.574	Bellinger et al. 1948a	[105]
283	10	0.748		
298	25	0.625		
313	40	0.533		

Nitromethane that has been gelled to reduce the leakage potential, prevent sloshing or to suspend solid particulate additives has a higher viscosity, and its rheological behavior is different from that of ungelled nitromethane [126]. Its viscosity determines the droplet size and combustion rate when sprayed into a combustion chamber [127].

3.2.7 Surface Tension of Nitromethane

Literature data for the surface tension of liquid nitromethane are listed in Table 21.

Table 21: Surface tension of nitromethane.

Temperature		Surface tension		Source	Ref.
K	°C	dyn/cm	N/m		
288	15	37.74	0.0377	Makovky and Lenji 1958	[93]
298	25	36.97	0.0370		
303	30	35.48	0.0355	Thompson, Coleman, and Helm 1954	[90]
293	20	37.5	0.0375		
298	25	36.7	0.0367		
303	30	35.9	0.0359		

Note: $10^5 \text{ dyn} = 1 \text{ N}$; $1 \text{ dyn/cm} = 10^{-5} \text{ N/cm} = 10^{-3} \text{ N/m}$

3.2.8 Thermal Conductivity of Nitromethane

The thermal conductivity of liquid nitromethane is $0.216 \text{ W m}^{-1} \text{ K}^{-1}$ ($5.17 \times 10^{-4} \text{ cal cm}^{-1} \text{ }^{\circ}\text{C}^{-1} \text{ s}^{-1}$) [112].

3.2.9 Optical Properties of Nitromethane

3.2.9.1 Infrared Spectra of Nitromethane

Infrared spectra of nitromethane are useful to verify the purity of nitromethane samples, to detect leaked nitromethane in the air surrounding storage facilities and to track the rate of decomposition of nitromethane in a monopropellant reactor. The IR spectrum of nitromethane vapor is shown in Figure 4.

The gas-phase infrared spectra of nitromethane, the various skeletal modes of vibration, and the vibrations of the methyl group with dipole changes parallel to the carbon-nitrogen have vibration-rotation band contours, which are of the expected type as calculated from the moments of inertia for overall rotation of the molecule [129]. The perpendicular vibrations of the methyl groups all had complex contours, and in a number of cases widely spaced fine structure lines were present. These could only be accounted for in terms of internal rotation degrees of freedom. This was expected because in classical terms the internal rotation frequencies modulate the oscillating vibrational dipole moment of these (and only these) methyl vibrations. In quantum-mechanical terms this leads to additional transitions involving changes in the quantum number for internal rotation. Analyses of the bands in this manner lead to information about the band origins and to reasonable values for the Coriolis coupling constants of the degenerate vibrations.

IR spectroscopic data obtained for binary and ternary liquid mixtures showed that nitromethane may act as proton donor for weak hydrogen bonds with appropriate

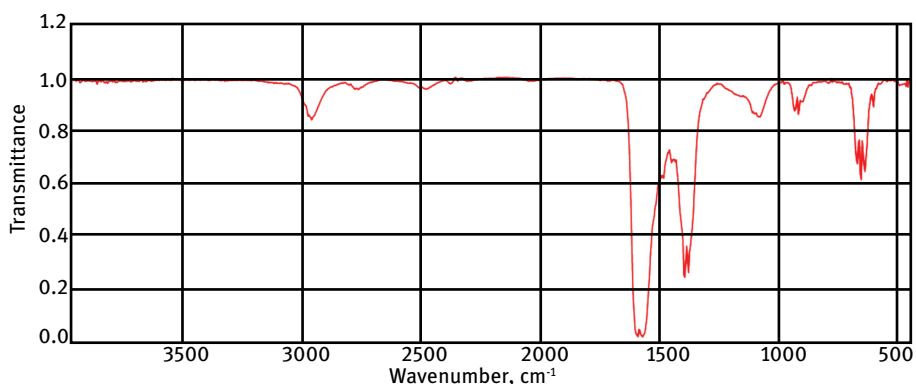


Figure 4: Infrared spectrum of nitromethane vapor (reproduced and modified with permission from [128])

acceptor groups in solvents [130]. At low concentrations of nitromethane in CCl_4 an equilibrium between monomer molecules and predominantly anti-parallel oriented ($\rightleftharpoons$) dimers may be inferred from IR spectroscopic and static dielectric studies. The IR and Raman spectroscopic data provided conclusive evidence for the preservation of a predominantly anti-parallel orientation at high nitromethane concentrations and even in pure liquid nitromethane. Similar observations were made with Raman and nuclear magnetic resonance (NMR) spectra, showing that intermolecular self-association slows the spinning motion of nitromethane in the liquid phase [131].

The infrared spectra of normal and deuterated nitromethane isolated in a nitrogen matrix were recorded from 4000 to 250 cm^{-1} [132]. Peaks have been assigned to monomer and dimer species by varying the concentration of nitromethane in the matrix. The frequencies of the monomer have been used in a normal coordinate analysis and the force constants agreed well with those of the gas phase. The Cartesian displacements of the atoms for each normal mode showed that for the “ NO_2 anti-symmetric vibration” there was considerably more motion of the hydrogen atoms. The results will make it possible to estimate the moments of inertia of the dimer and force constants for the pair necessary for assessing partition functions for dimer formation under all conditions of temperature and pressure.

The vibrational relaxation processes of totally symmetric ν_1 (CH stretching and ν_5 NO_2 bending) motions of liquid nitromethane have been studied as a function of temperature and concentration in CD_3NO_2 and CCl_4 solutions [133]. The experimental vibrational correlation functions of these two modes have shown that relaxation is collision-assisted and suitable for modeling with a stochastic theory.

Answers to the question about the barrier height for the internal rotation of the methyl group around the C—N axis in nitromethane have been sought by many studies, either using experimental procedures or by means of theoretical approaches. From different literature data one can deduce that the potential surface and consequently the barrier height for the internal rotation is dependent essentially on the molecular physical state. In the gas phase, where molecular interactions are almost absent at atmospheric pressure and room temperature, it has been reported that this barrier is nearly non-existent, being ca. 25 J/mol (6 cal/mol) for the light nitromethane, and 21.7 J/mol (5.2 cal/mol) in the case of d_3 -nitromethane. Therefore, the rotation of the methyl group around the C—N single bond is quasi free, and should be associated with a torsional motion at very low frequency [134].

Infrared and Raman spectroscopy has been used to study totally symmetric ν_4 and ν_5 motions of CH_3NO_2 and CD_3NO_2 isotopomers, in order to ascertain the nature of the low-frequency features appearing in these bands. A study of the gaseous phase IR spectra and of the temperature effects, carried out under high-resolution conditions on both liquid and gaseous molecules, showed that these features are connected to the effects of conformational population and not to hot band transitions, as it had been previously reported [135].

The methyl C—H stretching overtone spectra of gaseous nitromethane have been recorded with Fourier transform infrared (FTIR) spectroscopy in the $\Delta\nu_{\text{CH}} = 1$ –4 regions and by intracavity laser photoacoustic spectroscopy in the $\Delta\nu_{\text{CH}} = 5$ and 6 regions [136]. They all exhibited a complex structure with, at $\Delta\nu_{\text{CH}} = 1$ and 2, a characteristic asymmetric top vibration-rotation profile, which vanished as vibrational energy increased. The perpendicular stretching vibrations exhibited a widely spaced fine structure profile resulting from a Coriolis coupling induced by the methyl internal rotation. These excited spectra have been analyzed with a theoretical model, which in the adiabatic approximation, took into account the coupling of the anharmonic C—H stretch vibrations with the quasi-free internal rotation of the methyl group and with isoenergetic combination states involving methyl bending modes. These calculations successfully described the relative intensity and frequency of each peak within a given overtone.

Non-equilibrium molecular dynamic simulations were used to study vibrational energy relaxation in liquid nitromethane after excitation of the C—H stretching vibrations [137]. The simulated liquid was assumed to consist of a mixture of excited and unexcited molecules, where the unexcited molecules were used to monitor excitation of the bath upon vibrational relaxation of the excited molecules. The results were in qualitative agreement with experimental measurements in liquid nitromethane after mid-IR excitation in the C—H stretching region. The simulation results indicated that the excited C—H stretching vibrations deposit energy predominantly into the remaining vibrations in the molecules. These vibrations relax at different rates, resulting in a multi-stage vibrational cooling process for nitromethane, in agreement with experimental results.

The effects of pressure on the vibrational spectra of crystalline nitromethane have been studied by computing normal mode frequencies, eigenvectors, and classical power spectra at several hydrostatic pressures between 0 and 27.3 GPa [138]. The purpose of the study was to determine the limits within which the force field, and classical mechanics more generally, accurately represented the pressure effects observed experimentally. The results exhibited good agreement between the calculated normal mode frequencies (and especially their pressure-dependent shifts) and those obtained in experimental and theoretical studies. Comparisons of the pressure dependencies near room temperature to experimental pressure-dependent IR spectra for particular vibrational modes yielded, in the case of the C—N stretch, a CH_3 deformation and the NO_2 asymmetric stretch.

3.2.9.2 Raman Spectra of Nitromethane

The frequency shifts of the C—N stretching mode of shock-compressed nitromethane have been measured using coherent anti-Stokes Raman scattering [139]. Shock pressures up to 11 GPa were achieved using a two-stage light gas gun. The frequency shifted Raman signal was generated using single-pulse Nd:YAG and broadband type lasers.

Raman and coherent anti-Stokes Raman spectroscopy and transient optical Kerr effect measurements were performed to study rotational and vibrational relaxations in the totally symmetric ν_4 mode in CH_3NO_2 [140].

Time-resolved Raman spectra of liquid nitromethane shocked to 140 kbar peak pressure showed that the C—N stretch (917 cm^{-1}), CH_3 stretch (2968 cm^{-1}), and the NO_2 stretch/ CH_3 bend ($1400/1377\text{ cm}^{-1}$) vibrations would all harden when peak pressure was obtained [141]. Upon unloading from 140 kbar, the C—N stretch vibration reverted back without any signs of irreversible change. The CH_3 stretching mode exhibited the largest increase with peak pressure. The observed frequency hardening and band broadening indicated strong intermolecular interactions at these shock pressures. When shocked by stepwise loading to 14.2 GPa, changes in the nitromethane vibrational modes and the spectral background were characteristic of the onset of reaction [142].

Polarization-sensitive coherent anti-Stokes Raman scattering spectroscopy was applied for detailed analyses of vibrational resonances of neat liquid nitromethane in the spectral range $900\text{--}1500\text{ cm}^{-1}$ [143], and showed that the main totally symmetric band ν_4 at 917 cm^{-1} and its observed asymmetry on the lower wave number side (previously assigned to hot bands) are in fact two different bands. Raman spectra indicated that at pressures above 4 GPa, the methyl group in nitromethane is locked and rotated about 45 from its position at lower pressures [144].

The phase transitions and the decomposition limits of nitromethane have been examined by Raman scattering in the pressure and temperature range of $0\text{--}25\text{ GPa}$ and $293\text{--}423\text{ K}$ and by analysis of the evolution of different Raman modes [145, 146]. Three new solid phases of nitromethane called III, IV, V have been detected [147]. A first chemical transformation was observed by the disappearance of nitromethane Raman modes and by the irreversible formation of a transparent solid called compound I. A second chemical transformation at higher temperature than the first one, was observed by the sudden darkening of the sample. A comparison of the Raman spectrum of nitromethane- h_3 with new high pressure Raman spectroscopic results for isotope-labeled nitromethane- d_3 and nitroethane allowed one to characterize the physico-chemical behavior of these three compounds in relation to their detonation properties [148].

A detailed Raman spectroscopic study of nitromethane in the temperature interval from room temperature to 15 K showed that the crystal structure was stable from 15 to 242 K [149]. In the interval $243\text{--}244\text{ K}$ a new phase was observed before the transition into the liquid state took place. These observations were supported by differential scanning calorimetry (DSC) measurements which indicated the existence of an intermediate phase between the stable crystal form and the liquid phase. The activation energy for the internal rotation of the methyl group was $25 \pm 1\text{ meV}$, which was in good agreement with the energy difference between the ground energy level and the barrier ridge as determined by previous neutron and Raman scattering experiments.

Anti-Stokes Raman scattering was used to monitor vibrational energy redistribution in the ambient temperature normal nitromethane and perdeuterated nitromethane after ultrafast IR excitation of either the symmetric or asymmetric C–H- or C–D-stretch transitions [150]. The instantaneous populations of most of the 15 nitromethane vibrations were determined, and a global fitting procedure with a master equation was used to fit all the data. The pump IR pulses excited not only C–H and C–D stretches but also certain combinations of bending and nitro stretching fundamentals. The coupled vibrations that comprise the initial state were revealed via the instantaneous rise of the anti-Stokes transients associated with each vibrational fundamental.

3.2.9.3 Ultraviolet Spectra of Nitromethane

The UV spectrum of nitromethane is shown in Figure 5. The UV absorption spectrum of nitromethane was measured under various conditions [151]. Besides the weak band at 270 m μ , a strong band, which may be regarded as due to the longest wavelength $\pi \rightarrow \pi^*$ transition band, was observed at 198 m μ in the gaseous state. When the absorption spectrum of nitromethane was measured in aqueous solutions with several different pH values, a strong band was observed at 233 m μ . From the fact that the pK_a value evaluated on the basis of the pH dependence of the absorption intensity was equal to that obtained electrometrically, it was concluded that the 233 m μ band is to be ascribed to the nitromethyl anion ($^-\text{CH}_2\text{—NO}_2$). The π -electron structure of the anion was studied theoretically by taking into account configuration interactions in terms of the ground state, charge transfer, and locally excited configurations. It was shown that the 233 m μ band of the anion may be interpreted as an intramolecular charge-transfer absorption involving a large electron transfer from $^-\text{CH}_2$ toward NO_2 .

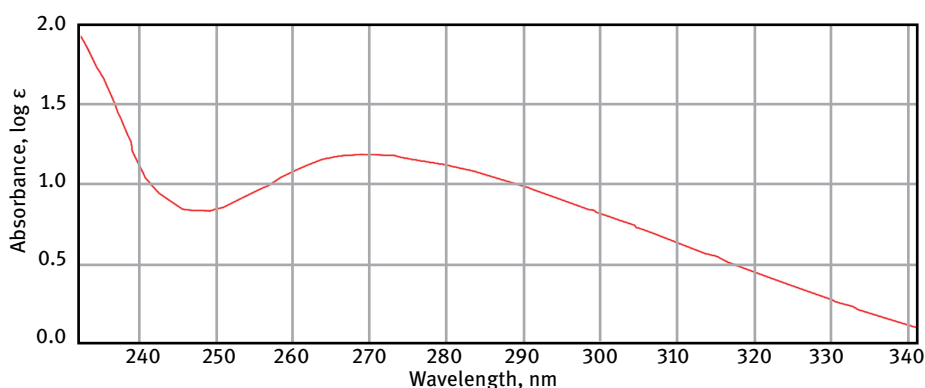


Figure 5: UV spectrum of nitromethane (reproduced and modified with permission from [91], Grammaticakis 1950, retrieved 7 June 2021)

The electron structures, electron spectra, and the self-consistent molecular orbitals and energies of the π -electron system have been calculated by a semiempirical method [152]; however, for the non-bonding σ -electron system Hückel-type molecular orbitals were used. The non-bonding 2p oxygen orbitals of nitromethane were very slightly modified by mixing with the σ -electron system. The calculated transition energies of nitromethane were in reasonable agreement with experimental results.

Polarized emission spectra from photodissociating nitromethane excited at 200 and 218 nm showed a strong progression in the —NO_2 symmetric stretch and at 200 nm a weak progression in the —NO_2 symmetric stretch in combination with one quantum in the C—N stretch [153]. The analysis of the photon angular distribution measurements and consideration of the absorption spectrum indicated that the time scale of the dissociation was too fast for molecular rotation to contribute significantly to the observed reduction in anisotropy. The analysis suggested a reassignment of the minor dissociation channel, first evidenced in photofragment velocity analysis experiments, which detected a pathway producing slow CH_3 fragments, to the near threshold dissociation channel leading to $\text{CH}_3 + \text{NO}_2$.

Time-resolved UV-visible absorption spectroscopy was used to examine the chemical decomposition in neat liquid nitromethane subjected to stepwise shock loading to 19 GPa [154, 155]. Up to a peak pressure (temperature) of 13.8 GPa (854 K), no sign of chemical reaction was observed in the $n\pi^*$ absorption band centered at 270 nm.

3.2.9.4 Microwave Spectra of Nitromethane

The microwave spectra of nitromethane and five isotopic species have been measured to determine the molecular structure [156]. Ground-state moments of inertia for the $m = 0$ internal rotation state gave the following structure: C—N = 1.489 Å, N—O = 1.224 Å, $\angle \text{ONO} = 125.3^\circ$, and $\angle \text{NCH} = 107.2^\circ$. Nuclear spin weightings for various $|K - m|$ states, derived using non-rigid group theory, have been confirmed by relative intensity measurements in the microwave spectra. The structure and bonding of nitromethane was compared to that of some related molecules. The structure of the nitro group in nitromethane was shown to fit a series of NO_2 compounds where the parameters varied according to the electronegativity of the attached R grouping.

The $J = 1$ to $J = 2$ and $J = 2$ to $J = 3$ transitions for CH_3NO_2 and CD_3NO_2 have been assigned for several internal rotational states [157]. The best values of the rotational constants B and C were found to be 10542.7 and 5876.7 Mc/s for CH_3NO_2 and 8697.1 and 5254.3 Mc/s for CD_3NO_2 . The rotational constant for the NO_2 group about the symmetry axis is 13277.5 Mc/s. The dipole moment of CH_3NO_2 is 3.46 ± 0.02 Debye units. Other sources report 3.44 D. See also [158–160].

3.2.9.5 Index of Refraction of Nitromethane

The index of refraction of nitromethane at different temperatures is listed in Table 22.

Table 22: Index of refraction n_D of nitromethane.

Temperature		Index of refraction n_D	References
K	°C		
293	20	1.38188	[11]
293	20	1.38197	[90]
298	25	1.37963	[90]
298	25	1.3818	[16]
298	25	1.37964	[11]
303	30	1.37738	[11]
298	25	1.37970	[104]
293	20	1.3821	[103]

Additional data on the index of refraction of nitromethane at three different temperatures and seven different wavelengths are listed in Table 23.

Table 23: Index of refraction of purified nitromethane at different wavelengths.

Temperature		Wavelength, Å						
K	°C	6678.1	6562.8	5892.6	5460.7	5015.7	4861.3	4158.3
		He _r	H _c	Na _D	Hg _e	He _v	H _F	Hg _g
293	20	1.37900	1.37944	1.38197	1.38416	1.38705	1.38828	1.39354
298	25	1.37669	1.37713	1.37963	1.38179	1.38468	1.38588	1.39115
303	30	1.37442	1.37479	1.37730	1.37948	1.38232	1.38345	1.38874

Data source: [90]

The index of refraction of shock-compressed liquid nitromethane has been determined from 7.5 to 9.5 GPa under the condition of 1-dimensional compression in the liquid [161]. Diagnostic information obtained by means of streak camera photography and velocity interferometry was compared with previously obtained EOS information in order to evaluate the refractive index of the shocked liquid prior to the onset of chemical decomposition.

3.2.10 Electrical Properties of Nitromethane

The dipole moment of liquid CH_3NO_2 is 3.46 ± 0.02 Debye units [157]. Other sources [92] reported a dipole moment of 3.56 D. Other sources gave a dipole moment of 3.17 D.

The relative permittivity (dielectric constant), ϵ/ϵ_0 is 35.94 [92]. These numbers can be compared to the dielectric constants for higher nitroalkanes, 3.19 D for nitroethane, 3.4 D for 2-nitropropane and 3.29 D for 1-nitrobutane.

The values of the dielectric constants of dilute solutions of nitromethane in heptane were used to calculate the dipole moments of the solute molecules, but the values thus calculated were considerably lower than those previously obtained in the gaseous state [104]. Measurements of the dielectric constant of pure liquid and solid nitromethane failed to show the existence of molecular rotation in the solid state. At 70 kHz and 183–244 K (–90 to –29 °C) (just below the melting point, 244.5 K = –28.6 °C), the dielectric constant of solid nitromethane increased from 3.39 to 3.93. The dielectric constant of liquid nitromethane between 246.4 and 300.5 K (–26.7 and +27.4 °C) decreased from 44.46 to 34.48. The dipole moment of nitromethane vapor at 298 K was 3.28 D (calculated) or 3.42 D (observed).

The electrical conductivity of dry nitromethane is $6.56 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$. Resistivity, relative static dielectric permeability, and electrical polarization relaxation time were measured for nitromethane that was compressed by a shock wave to pressures between 0.79 and 8.69 GPa [162]. Over this pressure range, the delay time for initiation of detonation exceeded 1 μs , which was sufficient time to measure properties of the unreacted material. The viscosity of nitromethane at high dynamic pressures was computed from other data.

3.2.11 Magnetic Properties of Nitromethane

Chemical shifts of protons in nitroalkanes at 60 MHz are affected by the inductive effect of the nitro group and the diamagnetic anisotropy of the C–C bond in nitroalkanes with $C_{n>1}$ [163]. The inductive effect was shown to extend as far as the fourth carbon atom in an *n*-alkyl chain. The ^1H chemical shifts in the series CH_4 , CH_3NO_2 , $\text{CH}_2(\text{NO}_2)_2$, $\text{CH}(\text{NO}_2)_3$ decreased in the order 9.767, 5.72, 3.90, 2.48 ppm. NMR studies of the deuteron and proton relaxation rates of liquid nitromethane at various temperatures indicated that the spin-rotation interaction contribution and the spin-rotation relaxation times provided evidence for large spin-rotation effects due to the internal rotation of the methyl group [164, 165].

3.2.12 Thermodynamic Properties of Nitromethane

Because nitromethane has been used as a model substance for study of other explosives containing nitro groups, its thermodynamic properties have been thoroughly investigated both experimentally and theoretically/computationally, not always with full agreement between the different sets of data.

Most of the thermodynamic data for nitromethane are for the compound in the liquid state at room temperature and sea level atmospheric pressure; however, in the detonation shock front, nitromethane is highly compressed and its thermodynamic properties are different from those at normal pressure.

A method was suggested for calculating thermodynamic parameters of shock-compressed nitromethane, for which isentropic curves cannot be constructed due to the lack of appropriate initial data for entropy [166]. The method was based on the fact that in the space where dependences of the wave velocity, pressure, and internal energy on mass velocity are determined for each space point within a known set of initial thermodynamic quantities by shock-wave experiments without breaks and fractures, all the thermodynamic parameters of state can be uniquely determined without any additional information. The Grüneisen parameter and velocity of sound were calculated by differentiating a family of shock adiabats obtained for different initial temperatures.

3.2.12.1 Heat Capacity of Nitromethane

Heat capacity data for liquid nitromethane are listed in Table 24. The specific heat of nitromethane was determined using an adiabatic technique in a glass calorimeter at temperatures near 311, 344, and 372 K (100, 160, and 210 °F) [167]. The heat capacity of saturated liquid nitromethane (under its own vapor pressure) in the temperature range from 308–473 K (35–200 °C) can be expressed by the equation

$$C_p = 104.4 + 6.381 \times 10^{-2}t + 3.175 \times 10^{-6}t^2 - 8.131 \times 10^{-7}t^3 + 4.073 \times 10^{-9}t^4$$

where C_p is the heat capacity in $\text{J mol}^{-1} \text{K}^{-1}$ and t is the temperature in °C [168]. The same data for liquid nitromethane for a temperature range from 244 to 473 K (–29 to +200 °C) can be expressed by a simpler second-order polynomial with a 3% error probability:

$$C_p = 1.1627 \times 10^5 - 135.3T + 0.345T^2$$

Table 24: Heat capacity of nitromethane.

Physical state	Temperature		Heat capacity				Source	References
	K	°C	$\text{J g}^{-1} \text{K}^{-1}$	$\text{cal g}^{-1} \text{°C}^{-1}$	$\text{J mol}^{-1} \text{K}^{-1}$	$\text{cal mol}^{-1} \text{°C}^{-1}$		
Liquid	290.15	17	1.7238	0.412			Armstrong 1960	[169]
Liquid	294.25	21.1	1.7071	0.408				
Liquid	317.65	44.5	1.6652	0.398			Jones and Giauque 1947	[94]
Liquid	298.15	25	1.736	0.415	105.98	25.33		
Liquid	308	35	1.740	0.416	106.22	25.39	Berman and West	[168]
Vapor	298.15	25	0.939	0.224	57.32	13.70	McCullough et al. 1954	[95]

$$M = 61.040 \text{ g/mol} = 16.3827 \text{ mol/kg}$$

where C_p is the heat capacity in $\text{J mol}^{-1} \text{K}^{-1}$ and T is the temperature in kelvin. The vapor heat capacity of nitromethane in the range 363–523 K (90–250 °C) can be calculated from the following equation [95]:

$$C_p = 2.352 + 4.2882 \times 10^{-2}T - 1.694 \times 10^{-4}T^2$$

where C_p is the molar heat capacity in $\text{cal K}^{-1} \text{mol}^{-1}$ and T is the temperature in kelvin.

The constant volume heat capacity c_v along a locus of Chapman-Jouguet (CJ) states of nitromethane was calculated from varied initial densities ρ_0 , but only provisional values of c_v were obtained [170]. Acquisition of ρ_0 is accomplished by changing the initial temperature, but this also changes the initial internal energy E_0 and creates some problems. An equation for c_v was developed which contained the experimental T_{CJ} , assumed to be constant over the rather narrow range of ρ_0 of the other input data, and $\gamma = c_p/c_v$.

3.2.12.2 Enthalpy of Formation of Nitromethane

A comparison of data for the enthalpy of formation of nitromethane has already been included in Table 9 above.

Experimental Determination of the Enthalpy of Formation of Nitromethane

A new internally consistent experimental data set of $\Delta H_f^{298}(\text{G})$ values for nitromethane and nitrobenzene was compared with the results of one of the most accurate first-principles G4 computation method applied to both atomization and isodesmic reactions. It was shown that the atomization reaction procedure underestimated the values by 6.6 kJ/mol for nitromethane.

The heat of formation of liquid nitromethane calculated from the heat of combustion was derived as $-113 \pm 0.4 \text{ kJ/mol}$ (-26.9 kcal/mol), but this value may not be very accurate [171].

Table 25 gives a summary of enthalpy of formation data for nitromethane. The table shows a surprisingly wide scatter of data. The NASA chemical equilibrium with applications (CEA) [36] and the PROPEP [97] ingredient data lists used -113.1 kJ/mol , and this is assumed to be the most reliable number.

Computation of the Enthalpy of Formation of Nitromethane

The enthalpy and entropy of nitromethane were calculated based on the theorem of corresponding states and presented in the form of temperature-enthalpy and temperature-entropy diagrams [174].

Table 25: Enthalpy of formation of nitromethane.

Physical state				References	
Liquid		Vapor			
kJ/mol	kcal/mol	kJ/mol	kcal/mol		
−92.9	−22.2 ± 0.3	−54.8	−13.1	Cass et al. 1958	[172]
−113 ± 0.4	−27.0 ± 0.1			Lebedeva and Ryadnenko 1973	[171]
		−81 ± 1	−19.4	Knobel et al.	[173]
−113.1 ± 0.63	−27.03 ± 0.15			NIST Chemistry WebBook	[91]
−89.04 ± 0.75	−21.3 ± 3.1			Holcomb and Dorsey	[16]
−113.1	−443 cal/g = −27.04 kcal/mol			PEPCODED.DAF	[97]
Molecular mass: 61.040 g/mol					

Molecular mass: 61.040 g/mol

Two experimental values (-80.7 ± 1.2 and -74.5 ± 0.4 kJ/mol = -19.3 ± 0.3 and -17.8 ± 0.1 kcal/mol) for the gas phase heat of formation $(\Delta H)_f^{298}$ of nitromethane vapor have been reported in the literature. Although these values differ by only 1.5 kcal/mol, substantially greater differences in results occur when these differing values were used to calculate other thermodynamic properties. This was especially evident when these two values for the $(\Delta H)_f^{298}$ of nitromethane were used to extrapolate to thermodynamic properties of polynitro compounds. For example, when density functional theory (DFT) was coupled with the use of isodesmic reactions, the $(\Delta H)_f^{298}$ of octanitrocubane turned out to be 672 or 722 kJ/mol (160.6 or 172.6 kcal/mol), depending on which value was used. This discrepancy was examined using several computational models and several levels of theory [175]. The results coupled with a comprehensive review of the literature supported the lower (-80.7 ± 1.2 kJ/mol = -19.3 ± 0.3 kcal/mol) experimental value.

Enthalpies of formation of gaseous nitromethane and nitrobenzene were calculated by Gaussian-4 method with the use of isogyric and isodesmic reactions [176]. Of the two widely used experimental values for nitromethane (-74.5 and -81.0 kJ/mol), the calculations provided strong support for the first one being the more accurate one.

3.2.12.3 Heat of Fusion of Nitromethane

The enthalpy of fusion of nitromethane at 244.77 K is 9.703 kJ/mol and the entropy of fusion at 244.77 K is 39.64 J mol⁻¹ K⁻¹ [94].

3.2.12.4 Heat of Evaporation of Nitromethane

Data for the heat of evaporation of nitromethane at its normal boiling point are summarized in Table 26.

Table 26: Heat of evaporation of nitromethane.

Heat of evaporation		Temperature	Year	Author	References
kJ/mol	kcal/mol	K			
38.37	9.171	298.15	1958	Makovky and Lenji	[93]
38.37	9.171	298.15	1954	McCullough et al.	[95]
38.5	9.22			Meyer, Koehler and Homburg	[96]
38.27	9.15		1986	Coetzee and Chang	[92]
33.99	8.12	374.4	1985	Majer and Svoboda	[177]
38.271	9.15	298.15	1947	Jones and Giauque	[94]
38.03 ± 0.38	9.09 ± 0.09	298.15	1949	Holcomb and Dorsey	[16]
Entropy of evaporation					
J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹				
128.36	30.68	298.15	1947	Jones and Giauque	[94]

The heat of evaporation in the temperature range 318–374 K can be calculated from [95]:

$$\Delta H_{\text{vap}} = 11730 - 4.9977T - 1.2400 \times 10^{-2}T^2$$

where ΔH_{vap} is the heat of evaporation in cal/mol and T is the temperature in kelvin.

In a different format, the enthalpy of evaporation at saturation pressure as a function of temperature can be calculated from

$$\Delta H_{\text{vap}} = 53.33 \exp(-0.2732T_r)(1 - T_r)^{0.2732}$$

where ΔH_{vap} is the enthalpy of evaporation in kJ/mol, T_r is the reduced temperature $T_r = T/T_c$ and T_c is the critical temperature, 588 K. See also reference [94].

3.2.12.5 Heat of Combustion of Nitromethane

It is known that the combustion is an exothermic process and sometimes heats of combustion are listed as negative numbers to stay in compliance with thermodynamic nomenclature conventions; however, for the sake of simplicity, we are not carrying along the minus signs. Until 1971, the data on the heat of combustion of liquid nitromethane were somewhat contradictory, ranging anywhere from ΔH_{comb} 718 to 709 to 710 kJ/mol (171.7 to 169.4 or 169.8 kcal/mol). These data differed from the results of more recent investigations. Other literature references reported the heat of combustion of nitromethane as 733 ± 0.7 kJ/mol, 730 ± 1.2 kJ/mol or 709 ± 0.6 kJ/mol (175.25 ± 0.18 kcal/mol, 174.4 ± 0.3 kcal/mol or 169.5 ± 0.15 kcal/mol). The heats of combustion of nitromethane and also of dinitromethane were therefore measured more accurately [173]. A sample of nitromethane was purified by drying and fractional distillation and the purity of the sample was estimated at 99.9%.

The heat of combustion of nitromethane was then re-examined and found to be $702.9 \pm 1.2 \text{ kJ/mol}$ ($168.0 \pm 0.3 \text{ kcal/mol}$). The heat of formation of nitromethane in the gas phase is therefore $\Delta H_f^{298} = +80.7 \pm 1.2 \text{ kJ/mol} = +19.3 \pm 0.3 \text{ kcal/mol}$. The enthalpies of combustion of highly pure nitromethane and nitrobenzene have been measured with precise combustion calorimetry and enthalpies of vaporization for both compounds were collected from the literature and evaluated, then compared to results from molecular orbital quantum chemical calculations [178]. Heat of combustion data for nitromethane from different sources are summarized in Table 27.

Table 27: Heat of combustion of nitromethane.

Heat of combustion, ΔU				Data source	References
kJ/mol	kcal/mol	kJ/kg	kcal/kg		
708.8	169.4	11610	2775	Makovky and Lenji 1958; at 293 K	[93]
733.25 ± 0.75	175.25 ± 0.18	12013 ± 12	2871	Holcomb and Dorsey 1949	[16]
709.15 ± 0.59	169.49 ± 2.5	11617 ± 9.7	2776 ± 2.3	Cox and Pilcher 1970	[179]
729.7 ± 1.2	174.4 ± 0.3	11954 ± 21	2857 ± 5	Cass et al. 1958	[172]
703 ± 1	168 ± 0.2	11517 ± 16	2753 ± 3.8	Knobel, Miroshnichenko, and Lebedev 1971	[173]
709.6 ± 0.4	169.6 ± 0.1	11625 ± 6.6	2778 ± 1.6	Lebedeva and Ryadenko 1973	[171]

$$M = 61.040 \text{ g/mol} = 16.38 \text{ mol/kg}$$

Heats of combustion are listed here as positive numbers, although everybody realizes that this is an exothermic process and the numbers should be negative by thermodynamic conventions. When determined calorimetrically under constant volume in a combustion bomb, the energy released is designated as energy, not enthalpy. The enthalpy of combustion is calculated by the equation

$$-\Delta H_c = -\Delta E_c - w - \Delta n(RT)$$

where ΔE_c is the energy of combustion as determined in the calorimeter, w is the Washburn correction, Δn is the change of the number of mols in the reaction, R is the gas constant and T is the absolute temperature. This correction reduces bomb calorimetric data from bomb conditions to conditions in which the reactants and products are in their standard states at atmospheric pressure. ΔH_c and ΔE_c differ only by a few percent. When reading literature data on heat of combustion, it is not always clear if this correction has been applied or not.

Table 9 in chapter “Nitroaliphatic Compounds” of *Encyclopedia of Oxidizers* contains heat of combustion data on ten nitroalkanes based on data from Holcomb and Dorsey [16]. See also [94, 180].

3.2.13 Solubility of Nitromethane

3.2.13.1 Solubility of Nitromethane in Water

Nitromethane is only sparingly soluble in water. For most applications, one will want to use nitromethane as dry and water-free as possible; however, there are a few applications where the dissolved water will help, for instance in lowering the flame temperature of nitromethane in a gas (steam) generator. Based on IR measurements, nitromethane may form a hydrate adduct with water. Nitromethane forms an azeotrope with water. At 293 K, 2.2 mL of water will dissolve in 100 mL of nitromethane. The solubility of nitromethane in water increases with temperature (Table 28).

Table 28: Solubility of nitromethane in water.

Temperature		Solubility, mass-% nitromethane in water
K	°C	
268	−5	8.065
291	18	10.53
310	37	12.55
321.65	48.5	14.48
330	57	16.08
341.65	68.5	18.97
348.65	75.5	21.54
349.65	76.5	22.33
358.65	85.5	25.92
367	94	32.02
372.65	99.5	39.19
375	102	45.2
376.75	103.6 (critical temperature of saturation)	59.6

Data source: [181]

Henry's Law constants for solubility of nitromethane in water at 298.15 K given in the literature vary anywhere between 35 and 45 mol kg^{−1} bar^{−1} [91]. At 293 K = 20 °C, 9.5 mL of nitromethane will dissolve in 100 mL of water.

3.2.13.2 Solubility of Water in Nitromethane

At 293 K = 20 °C, 2.2 mL of water will dissolve in 100 mL of nitromethane. In other units of measurement, the water content in saturated nitromethane is 1.8 mass-% at 293 K, 2.1 mass-% at 298 K, and 7.6% at 343 K.

3.2.14 Molecular Structure of Nitromethane

When looking at the molecular structure of nitromethane (Figure 6), one must remember that it is an isomer of methyl nitrite, which is much less stable than nitromethane. Electron diffraction studies lead to the following structure for nitromethane [182].

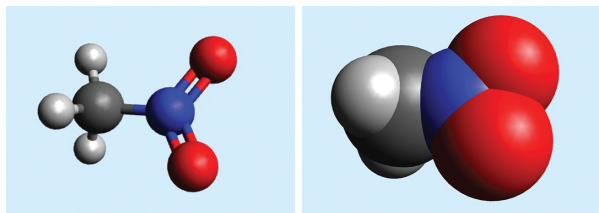


Figure 6: Molecular structure of nitromethane.

The molecular structure of nitromethane is characterized by the partially impeded rotation of the NO_2 and CH_3 groups around the axis of the C—N bond. Sometimes studies of the molecular structure and spectra of nitromethane are combined with an examination of nitrobenzene, both molecules sharing a C—N bond, but with different degrees of impedance of the free rotation. For the three highest occupied orbitals and the lowest unoccupied one, electron density is concentrated at the NO_2 end of the molecule.

The crystal structure of solid nitromethane is orthorhombic, space group $P 2_1 2_1 2_1$ with cell parameters of $a = 5.1832 \text{ \AA}$, $b = 6.2357 \text{ \AA}$, $c = 8.5181 \text{ \AA}$ at $T = 4.2 \text{ K}$, and $Z = 4$. Two models were used to describe the thermal motion of the methyl group, one with anisotropic temperature factors for the hydrogen atoms constrained to correspond to a threefold rotation around the C—N bond, and the other treating the group as a rigid body, with a torsional oscillation about the C—N bond axis [183].

Many investigations of nitromethane in any of the three physical states have concentrated on the internal rotation of the two molecule halves around the C—N bond and the steric hindrance to free rotation. Intramolecular hydrogen bonding forces are exerted between the oxygen on the nitro group and the hydrogen on the methyl group. The thawing of the rotation adds another degree of freedom to the possible modes of fundamental vibrations. The internal rotation has been studied by IR, microwave, and neutron scattering spectrometry.

The torsional transitions and tunneling splitting of solid nitromethane NO_2CH_3 and NO_2CD_3 were measured by inelastic neutron scattering and analyzed as functions of pressure and temperature [184]. Contrary to all previously observed pressure dependence of hindered rotors, the ground state splitting increased with pressure while the torsional frequencies decreased [185]. The barrier of rotation in solid nitromethane is very small: 25 kJ/mol (6 kcal/mol). Quasi-elastic scattering spectra have been obtained for several values of momentum transfer at 5 temperatures between 50 and 150 K. The

spectra were shown to be consistent with jumps of 120° about an axis coincident with the C—N bond. The temperature dependence of the residence time indicated a barrier of only 979 J/mol (234 cal/mol). An inelastic neutron spectrum obtained at 4.2 K suggested a tunnel splitting of the torsional ground state of 0.045 ± 0.005 meV, which was consistent with the derived activation energy [186, 187].

In the example of polynitroalkanes it was shown by computation that fluorine substitution for the hydrogen atoms practically did not affect the value of the dissociation energy of C—N bond, but chlorine (and also bromine or iodine) atoms caused a considerable decrease in the activation energy of the radical gas phase decomposition and C—N bond length, which was even larger than that in the case of introduction of an additional nitro group into the molecule. Consecutive substitution of hydrogen atoms by fluorine atoms in nitromethane leads to monotonous increase in C—N interatomic distance and decrease in $r(\text{NO})$ value [188].

In addition to experimental measurements of various spectra that reveal the molecular structure of nitromethane, numerous computational studies have attempted to interpret the observed spectra and predict physical properties of nitromethane in the vapor, liquid, and solid state from *a priori* assumptions. These calculations were performed not so much for the interest in nitromethane alone, but mostly to develop methods that can be applied to other, more complex and more important nitro compounds. The structure of nitromethane was the easiest to model and would be the starting point to prove the validity of the model by comparing computational to experimental results. In many commercial and military explosives, the stability of the molecule is determined by the lability of the C—NO₂ bond. A better understanding to the effect of adjacent atoms and atom groups on the stability or lability of the C—NO₂ bond will allow chemists to synthesize thermally more stable explosives and rocket propellants.

3.2.14.1 Computational Studies of the Molecular Structure of Liquid Nitromethane

Ab initio and modified neglect of diatomic overlap (MNDO) calculations were performed to study the molecular structure and vibrational frequencies of nitromethane and the nitromethyl radical [189]. For nitromethane, the two rotational conformers were predicted to differ in energy by only 0.01 kcal/mol. Vibrational frequencies of the staggered and eclipsed conformations were compared to experimental frequencies. Similar studies were done for the nitromethyl radical, an intermediate in the nitromethane decomposition.

Molecular dynamic simulations of liquid nitromethane has been carried out in which a density functional procedure was used to compute the properties needed to establish the intermolecular force field [190, 191], also for liquid nitromethane shocked to very high pressures [192]. The intermolecular force field was subsequently updated by further density functional calculations. Because of the high dipole moment and presence of the aci-form, molecules are associated and clustered. The first and second shells of neighbors were found to be at radii of about 6 and 11 Å from a given ni-

tromethane molecule. The O—H partial pair correlation functions indicated the presence of C—H...O hydrogen bonding.

A potential energy function with harmonic intramolecular and Lennard-Jones plus Coulombic intermolecular terms was tested in molecular dynamics simulations of liquid nitromethane [193]. Parameters were adjusted iteratively until satisfactory agreement with density functional pair calculations and experimental data was achieved. The properties computed were the heat of vaporization, dielectric constant, self-diffusion coefficient, density, heat capacity at constant pressure, single molecule and collective dipole moment reorientation times, the vibrational spectrum and the effect of increasing pressure upon the C—N stretching frequency. The results were in reasonable accord with experimental results, the greatest discrepancy being for the dielectric constant.

Nitromethane dimers may form in the vapor phase and in the liquid phase due to “tail-to-end” orientation of two neighboring molecules. Three optimized geometries of nitromethane dimer have been calculated [194]. Dimer binding energies have been corrected for the basis set superposition error and the zero point energy. Computed results indicated that the cyclic structure of $(\text{CH}_3\text{NO}_2)_2$ is the most stable of three optimized geometries, whose corrected binding energy is 17.29 kJ/mol. In the optimized structures of nitromethane dimer, the intermolecular hydrogen bond has not been found. The charge-transfer interaction between CH_3NO_2 subsystems is weak. The correlation interaction energy makes a small contribution to the intermolecular interaction energy of the dimer.

A quantum-chemical study of reactions leading to the formation of *aci*-nitromethane (*aci*-NM) and *aci*-dinitromethane (*aci*-DNM) and their decomposition with elimination of water employed an *ab initio* restricted Hartree-Fock (RHF) method with inclusion of electron correlation, a DFT approach and a semiempirical method [195]. The formation of *aci*-NM and *aci*-DNM was found to be the limiting step of the mechanisms under study. For dinitromethane the barrier to reaction was substantially lower than for nitromethane. The estimates of the heights of the barriers to formation found from DFT calculations (258 kJ/mol for *aci*-NM and 218.5 kJ/mol for *aci*-DNM) were suggested to be the most reliable.

A classical potential consisting of both intramolecular and intermolecular terms that was initially developed for the simulation of crystalline nitromethane has been used to investigate the dynamics of liquid nitromethane at various temperatures and pressures [196]. The validation of the proposed potential model was done for a large number of static and dynamic properties including the heat of vaporization, the variation of density with temperature and pressure, the thermal expansion coefficient, the self-diffusion coefficients, the viscosity coefficient, the dielectric constant, the bulk modulus and the variation of vibrational frequencies with pressure. The analyses performed using constant pressure and temperature and constant volume and temperature molecular dynamics simulations showed that the potential vs. distance method accurately reproduced the structural properties of liquid nitromethane at ambient

pressure in the temperature range 260–374 K as well as the compression effects up to 14.2 GPa.

Simulation and diffraction (X-ray diffraction, XRD and neutron diffraction) studies were compared in an effort to determine the liquid structure of nitromethane [197]. The diffraction methods were performing very well in the determination of intramolecular structure, but they did not give detailed structural information on the intermolecular structure. The good agreement between the diffraction experiments and the results of molecular dynamics simulations encouraged the use of simulations using partial radial distribution functions and orientational correlation functions for a more detailed description of the liquid structure. Liquid nitromethane can be described as a molecular liquid without strong intermolecular interactions such as hydrogen bonding but with detectable orientational correlations resulting in preferential anti-parallel ordering of neighboring molecules.

An integral equation theory for molecular liquids, Reference Interaction Site Model (RISM), was applied to understand the liquid structure of nitromethane [198]. In the theory, liquid structure can be described by a set of paired correlation functions. With the aid of *ab initio* molecular orbital calculations, it was possible to correlate representative peaks with specific configurations of nitromethane molecules.

3.2.14.2 Computational Studies of the Structure of Solid Nitromethane

At room temperature nitromethane is a liquid and much modeling has been done for the liquid, but the interest in the molecular structure of solid nitro compounds as energetic materials is actually higher than that in liquid nitro compounds. Therefore, additional modeling was done on solid nitromethane instead of liquid nitromethane.

Monte Carlo calculations of the crystal lattice parameters of solid nitromethane were performed to obtain sufficient information concerning the intermolecular interactions between molecules of nitromethane in order to produce, via computer simulation, a reliable EOS and other related properties in the condensed phase [199]. The results compared well to experimental investigations of properties of the crystal by neutron spectroscopy at 4.2 K and pressures below 1 GPa ([185, 187, 200]).

The sensitivity of nitromethane crystals to shock initiation shows anisotropy, where the sensitivity is orientation-dependent [201].

The dynamics of a nitromethane crystal as a function of temperature and pressure can be described by a classical potential method [202, 203]. The intramolecular part of the potential would be taken as superposition of bond stretching, bond bending and torsional angle twitching terms. These terms were parameterized on the basis of the geometric and spectroscopic data obtained using *ab initio* molecular orbital calculations performed on an isolated molecule. The analyses performed using constant pressure and temperature molecular dynamic simulations and molecular packing calculations indicated that the proposed potential model is able to accurately reproduce the changes of the structural crystallographic parameters as functions of tem-

perature or pressure. In addition, the calculated bulk modulus of nitromethane was found to be in excellent agreement with the corresponding experimental results. The predicted and experimentally observed 45° change in methyl group orientation in the high-pressure regime relative to the low-temperature configuration agreed with each other. The analysis of the linear expansion coefficients and linear compression data indicated anisotropic behavior for the unit cell edges.

The combined effect of pressure and molecular vacancies on the atomic structure and electronic properties of solid nitromethane, a prototypical energetic material, was theoretically studied using a self-consistent charge density-functional tight-binding method [204]. Changes induced in the band gap of this system by uniform and uniaxial strain of up to 70%, corresponding to static pressure in the range of up to 200 GPa, and the effects of molecular vacancies with densities ranging from 3 to 25% have been considered. A surprising finding was that uniaxial compression of about 25–40 GPa along the *b* lattice vector causes the C–H bond to be highly stretched and leads to proton dissociation. This event also occurs under isotropic compression but only at much higher pressure, being indicative of a detonation chemistry which is preferential to the pressure anisotropy.

The structural, vibrational, and electronic properties of solid nitromethane under hydrostatic pressure of up to 20 GPa have been studied using a density functional theory method [205]. The changes of cell volume, lattice constants, and the molecular geometry of solid nitromethane under hydrostatic loading, and the bulk modulus B_0 were computed, and its pressure derivative B_0' was fitted from the volume-pressure relation. The theoretical results were then compared with available experimental data. The electron band gap of nitromethane changed under high pressure. Based on the optimized crystal structures, the vibrational frequencies for the internal and lattice modes of the nitromethane crystal at ambient and high pressures were computed, and the pressure-induced frequency shifts of these modes were identified.

Structural change of crystalline nitromethane and the formation of hydrogen bonds under high pressure were simulated by molecular dynamic calculations [206]. Under high pressure, the angles between C–N bonds and X, Y, and Z axes have changed. Calculations of pair correlation function $g(r)$ of O and H atoms indicated a new peak near 1.6 Å, which indicates the formation of the hydrogen bonds between O and H atoms. The distribution of the angles of the C–N bonds orientations, the distribution of the dihedral angle of CNOO, and the charge distribution of nitromethane molecules were calculated under various pressure conditions and a comparison was made between low and high pressure structures. Hydrogen bonding has an effect on stability of explosive materials.

The structural and vibrational properties of solid nitromethane were studied using first principles density functional calculations [207]. The ground state properties were calculated using a plane wave pseudopotential code with either the local density approximation, the generalized gradient approximation, or with a correction to

include van der Waals interactions. The calculated equilibrium lattice parameters and volume using a dispersion correction were found to be in reasonable agreement with experimental results. The optical properties of this material, namely the absorptive and dispersive part of the dielectric function, and the refractive index and absorption spectra were calculated and the contribution of different transition peaks of the absorption spectra were analyzed. The static dielectric constant and refractive indices along the three nonequivalent crystallographic axis directions indicated that this material has a considerable optical anisotropy.

3.2.14.3 Changes of the Molecular Structure of Nitromethane under Very High Static Pressure

It is well known that rapid compression of nitromethane in a shock wave will cause it to explode. The question is if there are structural changes in the molecule preceding the detonation that make it more sensitive to decomposition. It was attempted to detect structural changes by slowly subjecting nitromethane to very high static pressure that might lead to ignition.

The structure of single crystals of nitromethane in diamond anvil cells has been studied by XRD at room temperature and pressures of 0.3–6 GPa [208]. The crystal structure was similar to the low temperature, ambient pressure structure. At 3.5 GPa, the methyl group was rotated 45° from the position in the low pressure, low temperature form. Raman spectra taken at pressures up to 11.7 GPa showed that all molecular vibrational frequencies increased with pressure.

In addition to reactions with proton acceptors, the *aci* form of nitromethane may also form under the influence of high pressure. Static high pressure (~2 GPa) produced an increased concentration of the *aci* ion of nitromethane [209]. The presence of the *aci* form was inferred from accelerated hydrogen/deuterium isotope exchange between CH₃NO₂ and CD₃NO₂ induced by pressure. The isotope exchange was followed by Raman spectra measurements and by ¹³C NMR. This observation provided an explanation for the pressure-dependent self-explosive behavior of nitromethane.

The room temperature pressure-induced reaction of nitromethane has been studied by means of infrared spectroscopy in conjunction with *ab initio* molecular dynamic simulations [210]. The evolution of the IR spectrum during the reaction has been monitored at 32.2 and 35.5 GPa performing the measurements in a diamond anvil cell. The simulations allowed the characterization of the onset of the high-pressure reaction, showing that its mechanism had a complex bimolecular character and involved the formation of the *aci* ion of nitromethane. On decompression of the sample, after the reaction, a continuous evolution of the product was observed with a decomposition into smaller molecules. The major reaction product on decompression is *N*-methylformamide, the smallest molecule containing the peptide bond. The high-pressure reaction of crystalline nitromethane under illumination

at 458 nm was also experimentally studied. The reaction threshold pressure was significantly lowered by the electronic excitation through two-photon absorption, and methanol and ammonium carbonate were also formed.

3.2.14.4 Crystal Structure of Solid Nitromethane

The crystal structure of solid nitromethane is orthorhombic, space group $P2_12_12_1$ with cell parameters of $a = 5.1832 \text{ \AA}$, $b = 6.2357 \text{ \AA}$, $c = 8.5181 \text{ \AA}$ at $T = 4.2 \text{ K}$, and $Z = 4$ [183].

It is possible that a detonation front moving through solid nitromethane will liquefy the solid before it detonates. Modeling the melting process gives a better understanding of detonation propagation in solid nitromethane.

Molecular dynamic studies of melting of nitromethane have been carried out using two methods: (1) void-nucleated melting with the gradual heating of the lattice and (2) equilibration of coexisting liquid and solid phases [211]. The results were in near agreement with each other. The values of the melting temperature T_m computed by using the intermolecular interaction potential method were found to be in good agreement with the experimental data at various values of pressure ranging from 1 atm to 30 kbar. A comparison of computed T_m with and without the presence of molecular vibrations revealed that T_m is insensitive to the intramolecular interaction term of the potential energy function, but depends strongly on the intermolecular interactions, particularly the Coulombic term.

It is unlikely that nanoparticles of frozen nitromethane would be used as rocket propellants, but the association of several (many) molecules first into adducts, then into clusters, then into nanoparticles and then into solid massive nitromethane crystals has been modeled mathematically [212]. This is the reverse process of melting. The melting temperatures predicted by the various properties were consistent with one another and showed that the melting temperature increased with particle size, approaching the bulk limit for the largest particle.

Studying the thermodynamic melting point of crystalline nitromethane by molecular dynamic simulation computations, the melting mechanism of superheated crystalline nitromethane, and the physical properties of crystalline and glassy nitromethane showed that the maximum superheating and glass transition temperatures of nitromethane were 316 and 160 K, respectively, for heating and cooling rates of $8.9 \times 10^9 \text{ K/s}$ [102]. Using the hysteresis method and by taking the glass transition temperature as the supercooling temperature, a value of 251 K for the thermodynamic melting point was in excellent agreement with the two-phase result of 255.5 K and measured value of 244.73 K. In the melting process, the nitromethane molecules begin to rotate about their lattice positions in the crystal, followed by translational freedom of the molecules. A nucleation mechanism for the melting was illustrated by the distribution of the local translational order parameter. The thermal expansion coefficient and bulk modulus were predicted to be about two or three times larger in crystalline nitromethane than in glassy nitromethane. The vibrational density of states was almost identical in both phases.

The melting of nitromethane initiated at solid-vacuum interfaces has been investigated using molecular dynamic simulations with a realistic force field [213]. The calculated melting point (251 ± 5 K) was in good agreement with experimental results (244.73 K) and values obtained previously (approximately 255.5 and 266.5 ± 8 K) using other simulation methods. There was a slight dependence of the melting temperature on the orientation of the exposed crystallographic face.

Angle dispersion X-ray diffraction experiments on nitromethane single crystals and powder were performed at room temperature as a function of pressure up to 19.0 and 27.3 GPa, respectively, in a membrane diamond anvil cell [214]. The atomic positions were refined at 1.1, 3.2, 7.6, 11.0, and 15.0 GPa using the single crystal data, while the EOS was extended up to 27.3 GPa, which is close to the nitromethane decomposition threshold pressure at room temperature in static conditions. The crystal structure was found to be orthorhombic, space group $P2_12_12_1$, with four molecules per unit cell, up to the highest pressure. In contrast, the molecular geometry underwent an important change consisting of a gradual blocking of the methyl group libration about the C–N bond axis, starting just above the melting pressure and completed only between 7.6 and 11.0 GPa. Above this pressure, the orientation of the methyl group is quasi-eclipsed with respect to the N–O bonds. This conformation allows the build-up of networks of strong intermolecular $O \cdots H-C$ interactions mainly in the *bc* and *ac* planes, stabilizing the crystal structure.

Molecules subjected to shock waves will, in general, undergo significant intramolecular distortion and exhibit large amplitude orientational and translational displacements relative to the unshocked material. A molecular dynamics study of the response of crystalline nitromethane subjected to supported shock waves propagating normal to (100) crystal face was performed using the non-reactive but vibrationally accurate force field method [215]. Shocks were initiated with assumed impact velocities of $U_p = 0.5, 1.0, 2.0$, and 3.0 km/s in crystals at initial temperatures of $T_0 = 50$ and 200 K. Structural and dynamic properties of the material corresponding to orientation in the lattice, translational symmetry, and mass transport were computed as functions of time. The results provided clear evidence of melting for shocks initiated by impacts of at least $U_p = 2.0$ km/s and provided insights into the evolution of changes at the molecular mode level associated with the onset of the melting instability in shocked crystal.

The reverse of melting, the crystallization of nitromethane from the melt on the (100), (010), (001), and (110) crystal surfaces at 170–220 K has been investigated using constant volume and temperature molecular dynamic simulations with a realistic, fully flexible force-field method [216]. The crystallization process and the nature of the solid-liquid interface have been investigated by computing the molecular orientations, density, and radial distribution functions as functions of time and location in the simulation cell. During crystallization the translational motion of the molecules ceases first, after which molecular rotation ceases as the molecules assume proper orientations in the crystal lattice. The methyl groups are hindered rotors in the liquid;

hindrance to rotation is reduced on crystallization. The width of the solid-liquid interface varies between 6 and 13 Å (about 2–5 molecular layers) depending on which crystal surface is exposed to the melt and which order parameter is used to define the interface.

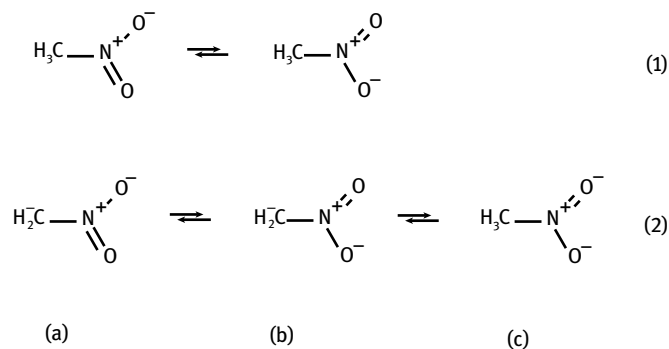
3.3 Chemical Properties of Nitromethane

Nitromethane can be stored at room temperature without decomposition. Its storage stability is very good. It has been observed that nitromethane containers may create negative pressure, possibly by absorption of oxygen from the air in the ullage, but this does not affect the purity of the product.

The oxygen balance of nitromethane is –39.3%. It is quite fuel-rich and any attempt to use it as a monopropellant without additional oxidizer will result in a very sooty exhaust. Attempts to clean up the exhaust by adding oxidizers to the nitromethane may result in detonable mixtures, which would be undesirable for rocket propellants.

3.3.1 Acid-Base Reactions of Nitromethane

Nitromethane is a very weak proton acceptor, as shown by a pK_a value near –12 for its conjugate acid in aqueous sulfuric acid or acetonitrile, $pK_a = -9.5$. By comparison, nitromethane is by no means a very weak proton donor, as shown by its pK_a value of 10.2 in aqueous solution. The cause of this considerable acidity is evident from a consideration of the resonance forms of nitromethane (1) and of its conjugate base (2):



The major resonance stabilization of the anion derives from the tautomeric structure (c). It is also necessary to explicitly consider the effect of tautomerism in the determination of the pK_a values of nitroalkanes.

transition state was calculated to lie 237 kJ/mol (56.7 kcal/mol) above nitromethane (with zero-point energy). The C—N bond dissociation energy was 216 kJ/mol (51.7 kcal/mol).

Tautomerism is competitive with many other processes that occur during detonation [218].

The mechanism of the unimolecular rearrangement between nitromethane and methyl nitrite isomers and the CH_3NO_2 potential energy surface was constructed using different molecular orbital and density functional theory methods including a few lower lying isomeric intermediates [219]. The C—N bond dissociation energy was 251 ± 8 kJ/mol (60 ± 2 kcal/mol) in line with available experimental results. The computations demonstrated that the methyl migration involves a “tight” transition state whose electronic wave function is dominated by the Hartree-Fock configuration. Calculations are thus internally consistent indicating that the energy of the transition state for 1,2- CH_3 shift is at least 25 kJ/mol (6 kcal/mol) above the $\text{CH}_3 + \text{NO}_2$ asymptote, which does not agree with experimental findings.

The low-lying energy pathways for the decomposition/isomerization of nitromethane have been investigated using different molecular orbital methods [220]. The results showed that in addition to the commonly known $\bullet\text{CH}_3 + \bullet\text{NO}_2$ products formed by direct C—N bond breaking and the *trans*- CH_3ONO formed by nitro-nitrite isomerization, nitromethane can also isomerize to *cis*- CH_3ONO via a very loose transition state lying 248 kJ/mol (59.2 kcal/mol) above CH_3NO_2 . Kinetic results indicated that in the energy range of 247 kJ/mol (59 kcal/mol), production of $\text{CH}_3\text{O}\bullet + \bullet\text{NO}$ will be dominant, whereas above the C—N bond-breaking threshold, the formation of $\bullet\text{CH}_3 + \bullet\text{NO}_2$ sharply increases and becomes dominant.

3.3.3 Hypergolic Ignition of Nitromethane

When using nitromethane as a rocket propellant, it would be useful to have a hypergolic reagent that can be injected along with nitromethane for a few seconds to get the reaction started. Sodium-potassium alloy produced an immediate hypergolic reaction with nitromethane and has been used successfully many times in initiating the decomposition of nitromethane in a 220-N (50-lb_f) thrust chamber [221]. Concentrated solutions of lithium, sodium, or potassium in ammonia produced a hypergolic reaction with nitromethane within a few seconds of contact. Chlorine trifluoride can react explosively with nitromethane under certain conditions and was not recommended.

3.3.4 Decomposition Reactions of Nitromethane

Because nitromethane has often been used as a simple model substance for other, more complex nitro compounds, most of them used as explosives rather than rocket propellants, there has been much work done on the thermal decomposition of nitromethane. The controlled thermal decomposition of nitromethane would also be

of interest for gas generators using nitromethane in a thermal bed and those using catalytic beds to facilitate the start-up of the reaction. The catalytic decomposition of nitromethane and practical applications of nitromethane in rocket engines and gas generators will be discussed in *Encyclopedia of Monopropellants*. Here we summarize only academic studies of reaction kinetics that can be safely conducted indoors on a bench top.

3.3.4.1 Slow Thermal Decomposition of Nitromethane

Both the slow and the fast thermal decomposition of nitromethane have been studied in exhaustive detail because nitromethane is a simple molecule, serves as a standard model for more complex nitro compounds used as commercial and military explosives, and can potentially be used as a monopropellant in rockets. Although it is a simple molecule, the decomposition reactions are nevertheless complex and can follow several pathways. In this section we deal only with homogeneous (liquid phase and vapor phase) decomposition of nitromethane. The heterogeneous, catalytic decomposition of nitromethane will be discussed in a later section on the use of nitromethane as a rocket propellant.

Kinetic rates of nitromethane vapor decomposition in a constant volume apparatus were derived from pressure changes at constant temperature for temperatures ranging from 663 to 693 K = 390–420 °C [222]. The times necessary for 25, 50, and 75% of the total pressure increase were measured as intermediate data points.

Above 573 K (300 °C), nitromethane decomposed slowly. Between 573 and 633 K, nitromethane occasionally detonated. Runaway decomposition of 2-mL samples of nitromethane in a stainless steel bomblet started at 684 K (411 °C) [123]. There was only slow decomposition below 673 K (400 °C) indicated by a pressure rise in the bomblet.

The decomposition of nitromethane was studied in a static system. Two procedures for determining the rate of decomposition were considered: the manometric method, and the infrared, *in situ* method. The activation energy of slow thermal decomposition in a first-order reaction was 221.7 kJ/mol (53 kcal/mol) [221]. The reaction rate equation was

$$k_1 = 7.8 \times 10^{15} \exp(-53300/RT)$$

where k_1 was the rate constant in min^{-1} and T was the temperature in kelvin.

Thermal decomposition of nitromethane at different heating rates was measured by DSC [223]. The data from different heating rates were analyzed with the isoconversional Friedman method. The heat of decomposition, exothermic onset temperature, time to reach the maximum rate under the adiabatic condition (TMR_{ad}) and the self-accelerating decomposition temperature (SADT) were derived via the advanced thermokinetic software and an advanced thermokinetic and thermal safety software package. The onset exothermic temperature of nitromethane tended to increase with the decomposition heat decrease while the scanning rate was rising. The time at the initial temperature to reach the maximum rate under adiabatic conditions was 24 h at

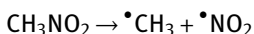
422 K (149 °C). The temperature to reach the maximum rate under adiabatic conditions in a package of nitromethane with an inner radius of 50 cm was 434 K (161 °C).

3.3.4.2 Kinetics of Nitromethane Decomposition

When designing a rocket using nitromethane as the propellant one must know the decomposition kinetics. Decomposition will take place by homogeneous gas (vapor) phase reactions and also as heterogeneous reaction on the walls or on the surface of catalysts. Kinetic studies of homogeneous nitromethane vapor decomposition are usually conducted at low pressures or at low partial pressures with dilution by inert gases to avoid detonations. The thermal homogeneous decomposition of nitromethane was studied by a static method over the temperature range 653–703 K (380–430 °C) at pressures between 26 and 53 kPa (200 and 400 mm Hg) and shown to be a first order reaction with a rate constant of

$$k = 10^{14.6} \exp(-53600/RT) \text{ s}^{-1}$$

The dissociation energy of the C–N bond in nitromethane was estimated to be 222 kJ/mol (53 kcal/mol). The main products were NO, CH₄, CO, and H₂O, with some CO₂ and small quantities of C₂H₆, C₂H₄, and N₂O [224, 225]. The initial step was assumed to be



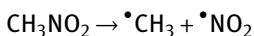
Kinetic tests indicated that the first step of decomposition is the fission of the C–N bond [226].

A study of the thermal decomposition of nitromethane was made by a flow method, with nitrogen as carrier gas, and the progress of the reaction was followed by polarographic analysis of the effluent from the reactor [227]. The decomposition followed a first-order law, and over the range 693–753 K (420–480 °C) the rate could be represented by the equation

$$k = 2.7 \times 10^{13} \exp(-50000/RT) \text{ s}^{-1}.$$

At 693 K (420 °C), *k* was in good agreement with the value obtained by the static method, but at higher temperatures the observed rate was lower than that reported previously. Although the energy of activation is close to that required to break the C–N bond, the high initial yield of formaldehyde obtained in the flow-method experiments suggested that the rate is in part determined by an intramolecular rearrangement.

The thermal decomposition of nitromethane at 628 K (355 °C) was studied in the pressure range from 1.24 to 2.07 MPa (180–300 psia) [228]. The presence of large amounts of hydrogen cyanide in the exhaust suggested a mechanism other than the simple



reaction which occurs at lower pressures. Addition of NO inhibited the rate of CH_3NO_2 decomposition.

In the range 700–1200 K the reaction rate of the reaction $\text{CH}_3\text{NO}_2 \rightarrow \bullet\text{CH}_3 + \text{NO}_2$ is

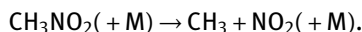
$$k = 2.50 \times 10^{11} \exp(E_a/RT) = 2.50 \times 10^{11} \exp(1.79 \times 10^5/RT)$$

where E_a is the activation energy in J/mol and T is the temperature in kelvin [229]. See also reference [230].

A Variable Encounter Method was used to study the pyrolysis of nitromethane vapor at temperatures from 816 to 1092 K with two reactors of differing geometry having fused silica surfaces [231]. The probability of reaction per collision with the reactor surface was measured. Nitromethane is one of the more efficient energy transfer agents; however, in addition to the size (vibrational eigenstate density) and the polarity of the molecules, the nature of the hot surface also seemed to play a role.

The homogeneous gas-phase decomposition of nitromethane was modeled and subjected to a sensitivity analysis of the main operating parameters (temperature, pressure) [232].

The decomposition of nitromethane was investigated in a shock tube at 990–1600 K, initial concentration of nitromethane in a mix with Ar in the range of 30–10000 ppm, and maximum variation of pressure behind the shock waves by a factor of 240 [233]. The consumption of nitromethane was observed at $\lambda = 230$ nm and the yield of NO_2 radicals was measured at $\lambda = 405$ nm. The elementary rate constants (k_1) of nitromethane decomposition were measured for:



Even in diluted mixes with Ar the process of nitromethane decomposition could be described by exponential dependence only at its initial stages and at high temperatures. The rate constants for low ($k_{1,0}$) and high ($k_{1,\infty}$) pressure limits were:

$$k_{1,0} \approx 10^{17.3} \exp(-42/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

and

$$k_{1,\infty} \approx 10^{16.2} \exp(-59.7/RT) \text{ s}^{-1}.$$

Data for the thermal decomposition of nitromethane vapor over the temperature range from 580 to 700 K at pressures of 0.5 kPa to 4.04 MPa (4 Torr to 40 atm) were critically analyzed [234]. On the basis of published literature data, the rate constants k of nitromethane decomposition at the upper pressure limit were determined and were in good agreement with the results of extrapolation of the high temperature (1000–1400 K) k values [233] to lower temperatures. The reasons why the nitromethane decomposition rate constants differed by two orders of magnitude at low temperatures are up for discussion. A general expression for the nitromethane

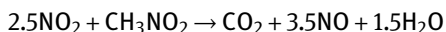
decomposition rate constant at the upper pressure limit over the 580–1400 K temperature range was determined as:

$$k = (1.8 \pm 0.7) \times 10^{16} \exp[(-58.5 \pm 2)/RT] \text{ s}^{-1}$$

These data disproved the hypothesis that a nitro-nitrite rearrangement takes place during the nitromethane decomposition at low temperatures.

3.3.4.3 Effects of Additives on Kinetic Rates of Nitromethane Decomposition

It had been postulated that the formation of nitrogen dioxide is the first step in the thermal decomposition of nitromethane. If this is true, the following reaction maybe important:



In this instance the addition of nitrogen dioxide to nitromethane should result in an increased rate of decomposition. From the results with added nitrogen dioxide it must be concluded that if nitrogen dioxide is formed in the thermal decomposition of nitromethane this reaction cannot be important. Both nitrogen dioxide and nitric oxide, if present in equal amounts, appeared to inhibit the decomposition of nitromethane at 628 K (355 °C) and 1.3–1.5 MPa (190–220 psia) to the same extent [235, 236].

It is possible that the inhibitory action of nitrogen dioxide is actually attributable to nitric oxide. Nitric oxide is known as a free radical scavenger and usually has a noticeable effect on the kinetic rate of reactions that involve free radicals. Adding catalytic agents to nitromethane that are also effective in decomposing NO will enhance the rate at which nitromethane decomposes in a rocket engine [237].

It had been observed that the addition of oxygen to nitromethane in a rocket motor considerably lowered the characteristic length (L^*) and the pressure required for stable operation. Because L^* is related to the time the propellant remains in the combustion chamber, it was assumed that the function of oxygen was to increase the rate of decomposition of nitromethane sufficiently to effect complete decomposition in a shorter time than is otherwise possible. If this explanation is valid, one would expect that under the conditions of the present investigation the addition of 13% oxygen should result in a considerable increase in the percentage of nitromethane decomposed, but experiments showed that the addition of oxygen did not affect the rate of decomposition of nitromethane for 5, 15, and 30 min of reaction time.

A study was made of the decomposition of nitromethane in the presence of various inhibitors (NO, toluene, *cis*-2-butene), and at various ratios of the surface area and volume of the reaction vessel [238]. The decomposition of nitromethane proceeded as a homogeneous monomolecular reaction.

The thermal explosion times of liquid nitromethane were measured at 1, 10, and 50 kbar and between 433 and 653 K (160 and 380 °C) [239]. At constant pressure, the explosion time decreased as the temperature increased. At constant temperature, the explosion time decreased as the pressure increased. For a constant explosion time of

10 s, at 1 kbar the required temperature was 642 K = 369 °C, at 10 kbar it was 600 K = 327 °C and at 50 kbar it was 498 K = 225 °C (Table 29). The increase in decomposition rate with increasing temperature is explainable by Arrhenius type kinetics. At 498 K = 225 °C, an increase by a factor of 5 in pressure caused a decrease by a factor of 50 in explosion time. Similar tests were performed with three dinitropropane isomers in an effort to determine the effect of hydrogen in the α -position on the rates of decomposition and the ease of the C—N bond rupture.

Table 29: Arrhenius constants and time to explosion for liquid nitromethane at high pressures.

Pressure	Pre-exponential factor	Activation energy		Temperature for time to explosion of 10 s	
kbar	s ⁻¹	kJ/mol	kcal/mol	K	°C
1	10 ⁶	83.7	20	642	369
10	10 ^{5.3}	92	22	600	327
50	10 ⁴⁰	531	127	498	225

Data source: [239]

It is well known that the detonability and thermal decomposition of nitromethane are greatly enhanced by the addition of organic amines, forming some of the very sensitive *aci*-salts. The thermal decomposition of nitromethane by itself was compared to the accelerated decomposition of nitromethane activated by addition of diethylamine. Laser-initiated decomposition of single aerosol particles in the source region of a time-of-flight spectrometer, followed by vacuum ultraviolet laser ionization and mass analysis of the reaction products, revealed the identity of species formed in the early stages of condensed-phase decomposition in nitromethane and nitromethane-diethylamine mixtures [240]. In pure nitromethane, the initial stages of decomposition can be characterized by unimolecular processes. At near-threshold energies, the cleavage of the C—N bond to form $\bullet\text{CH}_3$ and $\bullet\text{NO}_2$ dominated the dynamics, and at higher energies evidence of rearrangement to methyl nitrite was found, followed by the formation of $\text{CH}_3\text{O}\bullet$ and $\bullet\text{NO}$. In nitromethane seeded with 0.1% diethylamine, an additional channel was observed which produced ionic intermediates. Detection of protonated diethylamine and the nitromethane *aci*-anion confirmed that an acid-base reaction is involved in this case. Deuterium labeling studies indicated a hydrogen atom transfer reaction between the nitromethane *aci*-anion and neutral nitromethane that produced the weakly bound nitromethane anion, the precursor to $\bullet\text{CH}_3$ and $\text{}^-\text{NO}_2$.

3.3.4.4 Effects of Pressure on Nitromethane Decomposition

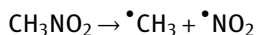
The thermal decomposition of liquid nitromethane was studied at 608 K (335 °C) and in the pressure range from 1.24 to 2.07 MPa (180–300 psia) [228]. Large quantities of nitric

oxide inhibited the rate of disappearance of nitromethane, which was in agreement with a non-chain radical mechanism.

The thermal decomposition of liquid nitromethane has been studied under approximately 4.05 MPa (40 atm) pressure and over the temperature range of 585–613 K (312–340 °C), and shown to be approximately first order with a rate constant given by [241]:

$$k = 10^{13.73} \exp(-49200/RT) \text{ s}^{-1}$$

The main decomposition products were nitric oxide, hydrogen cyanide, carbon dioxide, formaldehyde, and water, with some carbon monoxide and small quantities of methane and nitrous oxide. In addition to this, a solid of the empirical formula $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2$ accumulated as the reaction proceeded. The amount of hydrogen cyanide produced was found to depend on the initial pressure. The initial step in the decomposition was considered to be the same as in the low-pressure range:



The effect of pressure on the rates of decomposition of nitromethane was measured at pressures up to 1.1 GPa [242]. The mechanisms of thermolysis were inferred from kinetic studies and product composition analysis. The rate-controlling step for nitromethane decomposition in toluene at 503 K (230 °C) at low pressures was homolysis of the C–N bond. Beyond 20% conversion, the decomposition was autocatalytic. At high pressure, nitromethane had another reaction path which supplanted homolysis. It was proposed that nitromethane then forms an intermediate by cyclization of its *aci*-form. The high-pressure process was characterized by a first-order rate law without primary kinetic isotope effect, a low activation energy (119.2 kJ/mol = 28.5 kcal/mol), a negative activation volume (–5.5 mL/mol) and formation of products which could not be attributed to radical intermediates. At high conversion, the reaction became autocatalytic as a result of accumulation of water. 2-Nitropropane which was also tested was less stable than nitromethane. The decomposition pathways of nitroalkanes in aprotic solvents are determined not only by the conditions but also by the availability of α -hydrogen.

The decomposition mechanism of hot liquid nitromethane at various compressions was modeled using reactive force field molecular dynamic simulations [243]. A competition between two different initial thermal decomposition schemes was observed, depending on pressure: At low densities, unimolecular C–N bond cleavage was the dominant route, producing $\cdot\text{CH}_3$ and $\cdot\text{NO}_2$ fragments. As density and pressure rose approaching the C–J detonation conditions (~30% compression, >2500 K) the dominant mechanism switched to the formation of the CH_3NO fragment via H-transfer and/or N–O bond rupture. The change in the decomposition mechanism of hot liquid nitromethane leads to a different kinetic and energetic behavior, as well as different products distribution.

3.3.5 Rapid Thermal Decomposition of Liquid Nitromethane

Shock compression of liquid nitromethane is a thoroughly studied initiation mechanism leading to detonation of nitromethane. Chemical changes occurring in liquid nitromethane during rapid compression and leading to initiation of detonation can be traced by rapid spectrophotometric methods, both in absorption and emission spectra. Observation of light emission during excitation and initiation and propagation of detonation of nitromethane is a very useful diagnostic method and several publications referenced in this chapter deal with this method. Because there are so many publications dealing with optical observation of detonating nitromethane, we were almost ready to assign a dedicated heading to a sub-section on optical diagnostic methods, but then decided to integrate it with the rapid thermal decomposition topic at hand. Rapid compression of diluted nitromethane vapors in a shock tube is a widely used method to study the kinetics of rapid decomposition at different shock compression ratios and temperatures. Shock tube decomposition of nitromethane vapors will be discussed in a following section.

The light from detonation of some explosives is suppressed under pressure from an externally produced shock wave. Similar behavior was observed in nitromethane where the homogeneous liquid can be considered to be free of voids, which may interfere with the emitted light [244]. A somewhat more indirect experiment has been described wherein a detonating nitromethane charge was observed normal to the direction of travel of the compression wave. With under-energetic boosting, weak light emission was observed which, after an induction time, suddenly changed to the normal detonation light intensity. The weak light was attributed to predetonation of material compressed by the initiating shock wave.

The emission radiation spectra of a detonation front in nitromethane in the area of 3800–8000 Å were obtained on a spectrograph of average dispersion [245, 246]. The spectra were continuous with no lines or molecular bands. Preliminary measurements have shown that the distribution of energy in the spectrum differs from that predicted by the Planck theorem.

The effects of pressure and temperature on the melting point and thermal decomposition rate were studied using a diamond anvil cell in conjunction with an optical polarizing microscope for melting point observation and an automated FTIR for thermal decomposition monitoring [247–249]. The nitromethane decomposition rate has a positive pressure dependence, leading to a bimolecular reaction mechanism that results from increased intermolecular interactions. Both pressure and temperature were found to increase the rate of thermal decomposition. The mechanism was very complex and varied over large changes in pressure but appeared to be a bimolecular reaction mechanism. A mechanism was proposed which explained the bimolecular nature of the reaction and also accounted for the observed pressure dependence of the decomposition rate and products.

Time-resolved UV-visible absorption spectroscopy was used to examine chemical decomposition in neat liquid nitromethane subjected to stepwise shock loading

to 19 GPa [155]. Up to a peak pressure (temperature) of 13.8 GPa (854 K), no sign of chemical reaction was observed in the absorption band centered at 270 nm. For shock compression resulting in peak temperatures above 940 K, extensive reaction was indicated by irreversible red-shift of the absorption band edge that occurred after peak pressure was reached. This red-shift was followed by a loss of transmission through the sample, which was attributed to the formation of absorbing reaction products. In a series of similar tests, time-resolved Raman spectroscopy instead of UV-visible absorption spectroscopy was used to examine chemical decomposition in neat liquid nitromethane subjected to stepwise shock loading to 14–17 GPa [250]. After a peak pressure at 14 GPa was reached, no changes in the CN (917 cm^{-1}), NO_2 (1400 cm^{-1}), and CH_3 (2968 cm^{-1}) symmetric stretching modes were observed. After a peak pressure at 16 GPa was reached, time-dependent changes were observed during the induction period reported in previous absorption experiments. At this peak pressure, the extent of reaction was small, and the observed changes in the CH_3 and CN modes indicated prereaction changes in the sample bulk. The broadening of the CH_3 peak and the softening of the CN mode observed in this work suggested strong intermolecular interactions. These interactions led to a reaction precursor involving proposed head-to-tail intermolecular associations with decomposition proposed to follow through a bimolecular reaction.

The mechanism of amine sensitization of shocked nitromethane was investigated using time-resolved optical absorption spectroscopy in the visible range [251]. Neat nitromethane and mixtures of nitromethane with six different primary, secondary, tertiary, and di-amines were shocked to within 12–17 GPa peak pressure using step wave loading. Despite the small amine concentrations, profound differences were observed in the absorption spectra of neat and sensitized nitromethane. The changes in the absorption spectrum of reacting neat nitromethane consisted of irreversible broad band (450–650 nm) loss of transmission through the sample after a short induction time. The intermediate is most likely a radical anion of nitromethane, $\text{CH}_3\text{NO}_2^{\bullet-}$.

Time-resolved emission spectra were obtained from neat and ethylenediamine-sensitized nitromethane shocked to 12–17 GPa peak pressures using step wave loading [252]. Broad band emission identified as chemiluminescence from nitrogen dioxide was observed due to reactions in both neat and amine-sensitized nitromethane. When laser light at 514 nm was present, fluorescence in addition to chemiluminescence was observed in shocked nitromethane/ethylenediamine mixtures, but no such fluorescence was found in neat nitromethane. The fluorescing species were assigned to an intermediate formed in the first stage of decomposition in nitromethane/ethylenediamine mixtures, possibly a radical anion of nitromethane, $^{\bullet}\text{CH}_3\text{NO}_2^-$.

At the borderline between low-velocity detonation (LVD) and high-velocity detonation (HVD), the transition from mechanical shock to detonation and the transition from deflagration to detonation (DDT) is of interest. Ultrafast spectroscopic methods by spectral analysis in the range 0.3–0.85 μm can resolve the chemical and physical processes occurring at the front of the shock wave. Experiments used plane shock im-

pact on explosive targets at 8.6 GPa. Shocked nitromethane remained transparent and its temperature was higher than 2500 K because of local chemical reactions [253].

A spectral analysis in the range 0.3–0.85 μm , with a 28-nm resolution, during experiments of plane shock impacts on nitromethane targets at 8.6 GPa was made to study the shock-to-detonation transition of liquid nitromethane [254]. The time-resolved radiant spectra showed that the detonation front, the reaction products produced during the superdetonation and the detonation products were semitransparent. The temperature and absorption coefficient profiles were determined from the measured spectra. Shocked nitromethane reached at least 2500 K, showing the existence of local chemical reactions after shock entrance. The temperature of superdetonation and steady-state detonation can be determined in this way.

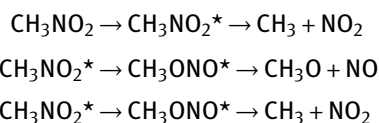
3.3.5.1 Computer Modeling of Thermal Decomposition of Nitromethane

Computational chemistry can predict not only properties of the stagnant molecules, but also excited molecules in predissociative states and reactive intermediates. The thermal decomposition of nitromethane is important for its use as a monopropellant or to predict the threshold of thermal explosions. The thermal decomposition starts at the weakest link in the molecule. This section contains references to computer modeling of slow and fast decomposition and to detonation of nitromethane.

Quantum mechanical model calculations for photodissociation of CH_3NO_2 assumed dissociation along the C–N axis with the molecule being restricted to a flexed angular geometry [255]. In addition, the internal degrees of freedom of CH_3 were assumed frozen. The photofragmentation rate as a function of the total energy showed sharp IR band structures and oscillations associated with the existence of a barrier in the dissociative potential energy surface.

Ab initio calculations on predissociative energy levels in nitromethane showed the multi-configurational nature of the ground and first excited singlet states [256]. The potential surfaces relative to the C–N bond lengths showed that each of the excited states studied is strongly predissociative. The results were compared to picosecond UV photolysis experiments in terms of the calculated potential surfaces and the primary photoreaction leading to electronically excited nitrogen dioxide and methyl radicals.

Classical trajectories were used to investigate the unimolecular decomposition of nitromethane on three model potential energy surfaces [257]. The surfaces differed mainly in the barrier height for the isomerization of nitromethane to methyl nitrite. The energies at the barrier to isomerization for the 3 surfaces were assumed as 905, 230, and 199 kJ/mol (216.4, 55.1, and 47.6 kcal/mol). Three primary decomposition pathways were observed:



where * designates an excited state. The dynamic results also showed that there were two mechanisms for isomerization of nitromethane to methyl nitrite. Isomerization via the dissociation-recombination mechanism occurred only on the surface with a large barrier height ($905 \text{ kJ/mol} = 216.4 \text{ kcal/mol}$) that prevented direct isomerization.

In a study of the decomposition mechanism of nitromethane, using the Bond-Additivity-Corrected Moller-Plesset 4th-order perturbation (BAC-MP4) method and extending previous work with calculated rate constants, a detailed reaction mechanism for nitromethane ignition and decomposition was developed [258, 259]. Unimolecular bond fission was believed to be the initial decomposition step to provide a source of CH_3 and NO_2 radicals for the gas-phase reactions. The C—N bond dissociation activation energy for nitromethane was calculated to be 246 kJ/mol (58.9 kcal/mol). The reactions involved in the first-stage ignition process were essentially thermoneutral, yielding very little temperature rise, with the majority of the heat release occurring in the second-stage ignition, which converted NO to N_2 . The ignition delay times ranged from several nanoseconds to tens of microseconds.

The fully optimized potential energy curves for the unimolecular decomposition of the lowest singlet and triplet states of nitromethane through the C— NO_2 bond dissociation pathway were calculated using various DFT and high-level *ab initio* electronic structure methods [260]. Calculation results demonstrated that the triplet state of nitromethane is bound (not dissociated). The adiabatic curve of this state exhibited a 33 kcal/mol energy barrier. Other DFT methods located this barrier at a shorter C—N bond distance with 12–16 kcal/mol lower energy than a multi-configuration self-consistent field method.

The complex potential energy surface for the unimolecular isomerization and dissociation of nitromethane, including 10 isomers, 46 interconversion transition states and 16 major dissociation products was probed theoretically [261]. The geometries and relative energies for various stationary points were determined and were in good agreement with available experimental values. It was shown that the most feasible decomposition channels for CH_3NO_2 unimolecular decomposition were those that lead to $2\text{CH}_3 + 2\text{NO}_2$, $2\text{CH}_3\text{O} + 2\text{NO}$, $\text{H}_2\text{CO} + \text{HNO}$, and $\text{HCNO} + \text{H}_2\text{O}$. Among them, 2CH_3 and 2NO_2 were predicted to be produced by the direct C—N bond rupture of nitromethane, while the formation of the latter three products is most likely initiated by CH_3NO_2 rearranging first to methyl nitrite or to *aci*-nitromethane. The C—N bond dissociation energy for nitromethane was calculated to be 259 kJ/mol (61.9 kcal/mol), lower than the nitromethane $\rightarrow$ methyl nitrite and nitromethane $\rightarrow$ *aci*-nitromethane isomerization barriers by 11.3 and 8.8 kJ/mol (2.7 and 2.1 kcal/mol), respectively. The CH_3NO_2 isomerization pathways seem to be kinetically disfavored in view of the relatively high activation barriers in excess of 251 kJ/mol (60 kcal/mol). The nitromethane decomposition occurred either via the C—N bond rupture or via concerted molecular eliminations.

Density functional molecular dynamic simulations to determine the early chemical events of hot ($T = 3000 \text{ K}$) and dense ($\rho = 1.97 \text{ g/cm}^3$, $V/V_0 = 0.68$) nitromethane showed that the first step in the decomposition process is an intermolecular proton

abstraction mechanism that leads to the formation of $\text{CH}_3\text{NO}_2\text{H}^+$ and the *aci*-ion H_2CNO_2^- [262]. An intramolecular hydrogen transfer that transforms nitromethane into the *aci*-acid form, $\text{CH}_2\text{NO}_2\text{H}$, accompanies this event. The decomposition mechanism was followed up to the formation of H_2O as the first stable product.

Detonation theories for homogeneous, condensed energetic materials have focused on one-dimensional analysis in which the detonation ignition physics is the most difficult part. The classical models consider detonation ignition through a frozen shock transition followed by an induction period, in which the shock temperature induces vibrational, rotational, and electronic excitation followed by molecular dissociation (i.e., thermal decomposition). The frozen shock assumption has been the topic of debate and an alternative model has been proposed whereby detonation ignition arises from excitation of translational degrees of freedom in the shock front. *Ab initio* molecular dynamic simulations of nitromethane under shock initiation conditions offer an alternative approach to elucidate possible mechanisms of detonation ignition [263]. Molecular dynamic simulations of bimolecular collisions using density functional theories serve as a most simplified model for shock-induced dissociation, while multi-molecular collisions including neighborhood molecules serve as a simple model for shock dissociation in bulk liquids.

Ab initio molecular dynamic simulations indicated that during rapid thermal decomposition, solid nitromethane undergoes multiple chemical reactions at about 2200 K under ambient pressure [264]. The initiation of reactions involved both proton transfer and commonly known C–N bond cleavage. About 75 species and 100 elementary reactions were observed with the final products being H_2O , CO_2 , N_2 , and CNCNC .

A global potential energy surface for nitromethane based on fitting density functional theory electronic energies gave a permutationally invariant fit to these energies [265]. Properties of the potential energy surface and quasi-classical trajectory calculations led to a roaming isomerization pathway to the CH_3ONO isomer and then to the $\text{CH}_3\text{O} + \text{NO}$ products. Theoretical and experimental translational energy distribution and rotational energy distributions in the products $\text{CH}_3\text{O} + \text{NO}$ from the unimolecular dissociation of nitromethane were compared to one another [266]. Calculations on a global potential energy surface revealed the detailed roaming isomerization dynamics in this process, and these were supported by experimental observations. Calculations found production of vibrationally excited CH_3O , which was consistent with experiments. This continues to challenge the conventional idea in transition state theory of a localized transition state that was considered a cornerstone of chemical reaction theory.

The kinetics for the thermal unimolecular decomposition of CH_3NO_2 and its structural isomer CH_3ONO have been investigated by statistical theory calculations based on a potential energy surface, including product branching [267]. The results showed that for the decomposition of CH_3NO_2 at pressures less than 2 Torr, isomerization to CH_3ONO via the roaming transition state is dominant in the entire temperature range

studied, 400–3000 K; however, at higher pressures the formation of the commonly assumed products $\text{CH}_3 + \text{NO}_2$, becomes competitive and at pressures higher than 200 Torr the production of $\text{CH}_3 + \text{NO}_2$ is exclusive. The predicted rate constants for 760 Torr and the high-pressure limit with Ar as diluent in the temperature range 500–3000 K, producing solely $\text{CH}_3 + \text{NO}_2$, can be expressed by

$$k_{d760}(\text{CH}_3\text{NO}_2) = 2.94 \times 10^{55} T - 12.6 \exp(-35500/T) \text{ s}^{-1}$$

and

$$k_{d\infty}(\text{CH}_3\text{NO}_2) = 5.88 \times 10^{24} T - 2.35 \exp(-31400/T) \text{ s}^{-1}$$

In the low-pressure regime, the decomposition reaction takes place exclusively via internally excited CH_3ONO , giving rise to both $\text{CH}_3\text{O} + \text{NO}$ and $\text{CH}_2\text{O} + \text{HNO}$ with the second-order rate constant

$$k_{d0}(\text{CH}_3\text{NO}_2) = 1.17 \times 10^{31} T - 10.94 \exp(-32400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

For CH_3ONO decomposition, a roaming transition state connecting to the $\text{CH}_2\text{O} + \text{HNO}$ products has been located, lying 28.4 kJ/mol (6.8 kcal/mol) below the well-known four-member ring tight transition state and 2.9 kJ/mol (0.7 kcal/mol) below $\text{CH}_3\text{O} + \text{NO}$. The rate constants predicted by similar calculations gave rise to the following expressions for the thermal decomposition of CH_3ONO in He:

$$k_{d760}(\text{CH}_3\text{ONO}) = 8.75 \times 10^{41} T - 8.97 \exp(-22600/T) \text{ s}^{-1}$$

and

$$k_{d\infty}(\text{CH}_3\text{ONO}) = 1.58 \times 10^{23} T - 2.18 \exp(-21100/T) \text{ s}^{-1}$$

in the temperature range 300–3000 K. These results were in very good agreement with available experimental data obtained under practical pressure conditions. The branching ratios for the formation of $\text{CH}_3\text{O} + \text{NO}$ and $\text{CH}_2\text{O} + \text{HNO}$ in the decomposition of both CH_3NO_2 and CH_3ONO are different.

The thermal decomposition of nitromethane provides a classical example of the competition between roaming-mediated isomerization and simple bond fission. Laser schlieren densitometry was used to explore the variation in the effect of roaming on the density gradients for CH_3NO_2 decomposition in a shock tube for pressures of 30, 60, and 120 Torr at temperatures ranging from 1200 to 1860 K [268]. A complementary theoretical analysis provided an exploration of the effects of roaming on the thermal decomposition kinetics. The analysis focused on the roaming dynamics in a reduced dimensional space consisting of the rigid body motions of the CH_3 and NO_2 radicals. A high-level reduced-dimensionality potential energy surface was developed from fits to large-scale multi-reference *ab initio* calculations. The theoretical predictions were compared with prior theoretical predictions, with a related statistical model, and with the extant experimental data for the decomposition of CH_3NO_2 , and for the reaction of CH_3 with NO_2 .

3.3.5.2 Kinetics and Initiation of the Detonation of Nitromethane

The detonation of nitromethane is of practical interest for more than one reason. The main concern is the inadvertent accidental detonation of nitromethane in railroad tank cars. The other area of interest is in the use of nitromethane as a liquid explosive. Nitromethane can be used as a propellant in pulsed detonation engines and rotating detonation engines, which is another reason why detonation of nitromethane is discussed here from both a theoretical and experimental point of view.

It was attempted to identify the rate-determining steps in the ignition of shocked, condensed nitromethane by theoretical calculations [269, 270]. The time t_{pv} required for activation of the internal modes with values of $t_{pv} < 1 \mu s$ were identified with the most efficient transfer of energy when the molecules interact and react bimolecularly in a head-to-tail configuration. These times were consistent with those found in shock experiments and those calculated by other techniques. A minimum pressure of 58 kbar is required for the initiation of high-velocity detonation of homogeneous nitromethane.

A time-of-flight mass spectroscopic study of the chemical reaction zone in base-sensitized detonating liquid nitromethane revealed mass spectra of the reaction zone region for cases where normal CH_3NO_2 and isotope-labeled forms of nitromethane, $^{13}CH_3NO_2$ and CD_3NO_2 , were detonated [271]. The detonation process was initiated by a slapper detonator system. The nitromethane explosives were confined in steel, and the charge geometry was chosen such that the detonations were traveling steadily by the time the detonation wave reached the end of the charge. For the base-sensitized nitromethane explosive, the steady two-dimensional chemical reaction zone was ca. $50 \mu m$ in spatial extent and had a time duration of ca. 7 ns.

The processes involved in the shock initiation of detonation in nitromethane have been the subject of many experimental and theoretical studies. These generally support the classical homogeneous model, although some details of the pressure build-up process are still controversial. In order to clarify these points, plate impact experiments were performed to study the initiation of nitromethane detonation under conditions of steady one-dimensional strain for shock pressures ranging from 8.5 to 12 GPa [272]. The experimental results confirmed the main steps of the classical homogeneous model, but also showed that the build-up process is more complex than previously assumed.

Bimolecular and higher interactions during the initiation of nitromethane are impossible. The most widespread concepts of the primary steps of this initiation, i.e. formation of *aci*-nitromethane anion $[CH_2=NO_2]^-$ by intermolecular hydrogen transfer in the neat nitromethane submitted to shock and formation of this anion by action of an amine, have been scrutinized by a dynamic field theory computational method and evaluated as thermodynamically disadvantageous [273]. Also, the 1,3-intramolecular hydrogen shift in the nitromethane molecule was characterized as a higher barrier process. Two other favorable primary mechanisms of fission in the nitromethane initiation and propagation of its detonation were investigated by calculations: homolysis

of the C—NO₂ bond in neat nitromethane and homolysis of the N—OH bond in its *aci*-form. The second pathway was found to be the thermodynamically most preferable mechanism of fission.

3.3.5.3 Shock Tube Decomposition of Nitromethane Vapor

Although the kinetics of nitromethane vapor decomposition in shock tubes have been studied for a very long time and one would think that all there is to know about nitromethane decomposition has by now been discovered, this topic continues to attract researchers, as indicated by the recent date from some of the publications.

The decomposition of nitromethane in shock waves was followed by spectroscopic observation of the γ system of NO at 2200–2400 Å in a shock tube at temperatures above 1200 K and mixtures consisting of argon and 1.5–10% nitromethane [274]. Initial pressures were 1.3–6.6 kPa (10–50 mm Hg). The kinetic rate equations could not be extrapolated from low temperatures to high temperatures and vice versa, which indicated that different mechanisms were at work.

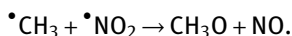
The thermal decomposition of nitromethane highly diluted in Ar has been studied in shock tubes at $900 < T < 1500$ K and $1.5 \times 10^{-5} < [\text{Ar}] < 3.5 \times 10^{-4}$ mol/cm³ [58]. Concentration/time profiles of unreacted nitromethane and reaction product NO₂ were recorded. The unimolecular first-order reaction was found to be in its fall-off range. Limiting low pressure rate constants of

$$k_0 = [\text{Ar}] \times 10^{17.1} \exp(-42 \text{ kcal/mol}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

in the range $900 < T < 1400$ K and limiting high pressure rate constants of

$$k_\infty = 10^{16.25} \exp(-(58.5 \pm 0.5 \text{ kcal/mol})/RT) \text{ s}^{-1}$$

have been derived. A rate constant of $1.3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was found for the first subsequent reaction



The decomposition of nitromethane in a shock tube was studied by using a frequency-stabilized CW CO laser to measure the real-time production of NO and CO, two of the key decomposition products [275]. Highly diluted CH₃NO₂/Ar mixtures (0.15–0.75% CH₃NO₂) were used in incident shock experiments over the temperature range from 940 to 1520 K and pressure range from 40 to 101 kPa (0.4–1.0 atm). A mechanism consisting of 37 chemical reactions was used to model the formation of these two products over the entire range of experimental conditions employed. The NO profiles could be quantitatively modeled over the entire temperature range, whereas those of CO could be accounted for only by adjusting some values of the rate constants.

A detailed chemical mechanism describing ignition of high-temperature pure gaseous nitromethane was compiled and tested in a shock tube in the range 1000–1600 K and 1–10 atm [276, 277]. Measurements were made of the time evolution of the pressure at the end wall as well as of the simultaneous pressure and NO

absorption at a short, fixed distance from the end wall. Mass and IR spectroscopy were used to identify the final products. In the reaction mechanism proposed, initiation started with the C—N bond breaking, which yielded $\cdot\text{CH}_3$ and $\cdot\text{NO}_2$. Methoxy and $\cdot\text{CH}_2\text{NO}_2$ radicals then propagate the reaction through two major parallel pathways, both producing CH_2O . Formaldehyde is then reduced to HCO and carries the reaction towards completion. A detailed mechanism of 48 reactions was developed, and calculated induction times showed good agreement with measured values. It was assumed that initiation started with C—N bond breaking with an E_a of 176 kJ/mol (42 kcal/mol), although a fit of the calculated times yielded a global Arrhenius parameter of 162 kJ/mol (38.6 kcal/mol). After the initial decomposition, the reaction takes two major parallel pathways to CH_2O through methoxy $\text{CH}_3\text{O}\cdot$ and $\cdot\text{CH}_2\text{NO}_2$ radicals. The reaction of $\cdot\text{NO}_2$ with $\cdot\text{H}$ was found to be key in generating highly reactive $\cdot\text{OH}$ radicals. The calculations showed that the nitro radical is the key to explosion: $\cdot\text{NO}_2$ produces $\cdot\text{OH}$ through its reaction with $\cdot\text{H}$ radicals. Hydroxyl reactions, which are fast and exothermic, lead to an accelerated consumption of the explosive with heat release. Comparison with the experiments showed that the mechanism predicted correct induction times for the pressure and temperature range of the experiments.

The thermal decomposition of nitromethane was studied spectrophotometrically in incident and reflected shock waves at temperatures in the range 1050–1400 K at total pressures of 0.2–40 atm [278, 279]. Ar, He, CO_2 , and CF_4 were used as collision partners. Under the experimental conditions used, the thermal decomposition of nitromethane occurred in the fall-off region. The pressure dependence of the rate constants was derived from the data. The rate constants in the low-pressure $k_{d,0}$ and high-pressure $k_{d,\infty}$ limits were represented by the following expressions (the activation energy is given here in kJ/mol)

$$k_{d,0(\text{Ar})} = 10^{17.3} \exp(-175.7/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_{d,\infty} = 10^{16.2} \exp(-249.8/RT) \text{ s}^{-1}.$$

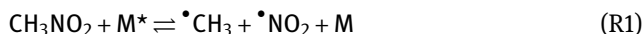
Ignition delay times of exploding nitromethane/oxygen/argon mixtures behind reflected shock waves in a 24-mm diameter, 2.7-m length shock tube but the operating pressure was not stated [280].

The decomposition of nitromethane was measured over the temperature range 1000–1100 K in reflected shock waves and undecomposed CH_3NO_2 and the reaction products were analyzed by gas chromatography (GC) [281]. The derived gross rate constant and activation energy for the disappearance of CH_3NO_2 was consistent with literature data. A reaction mechanism consisting of 99 chemical reactions was developed to simulate the experimental data. Good agreement between experiments and simulations was achieved. It appeared that significant amounts of CH_3NO_2 were destroyed through secondary reactions that involved highly reactive free radicals ($\cdot\text{H}$, $\cdot\text{OH}$, and $\cdot\text{CH}_3$), suggesting the need for redetermining the true unimolecular decay

rate constant for CH_3NO_2 . The loss of nitromethane due to pyrolysis was measured by recording its UV absorption, with a beam directed axially along a small-diameter shock tube.

A re-evaluation of the thermal decomposition mechanisms of gaseous nitromethane and methyl nitrite, where for each system a much simplified mechanism was developed, and the fragmentation/reaction sequence leading to the final products was made more transparent, showed that free radicals ($\cdot\text{CH}_3$, $\cdot\text{H}$, $\cdot\text{OH}$, $\text{HCO}\cdot$, $\text{HNO}\cdot$, $\text{CH}_3\text{O}\cdot$, etc.) played critical roles at different stages of these pyrolysis reactions [282]. A comparison of the products generated by nitromethane with those produced by methyl nitrite showed that the contribution of a nitro-nitrite isomerization reaction in the nitromethane pyrolysis was negligible.

The thermal decomposition of nitromethane under highly diluted conditions in shock tubes has been analyzed in terms of a detailed chemical kinetic model [283]. The experimental data which were adopted from the literature covered the temperature range 1000–1400 K and pressures from 0.5 to 6.0 bar. Based on these experimental results from other sources, rate constants for the reactions

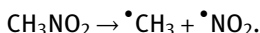


and



have been re-examined. The high and low pressure limits for reaction (R1) determined by others have been shown to be consistent with more recent shock tube data. A reinterpretation of the shock tube results together with room temperature measurements indicated that the rate constant for (R14) decreased slightly with temperature, as $k_{14} = 4.0 \times 10^{13} T^{-0.2} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. At high temperatures and atmospheric pressure this reaction was more than an order of magnitude faster than recombination of $\cdot\text{CH}_3$ and $\cdot\text{NO}_2$ to form nitromethane. Based on the available data for the forward and reverse rates of reaction (R1), a value of $279 \pm 8.4 \text{ J mol}^{-1} \text{ K}^{-1}$ ($66.7 \pm 2.0 \text{ cal mol}^{-1} \text{ K}^{-1}$) for the entropy S_0^{298} of CH_3NO_2 was estimated.

The kinetics of nitromethane decomposition and the rate constant of the process were measured behind reflected shock waves using absorption spectroscopy at $\lambda = 230 \text{ nm}$, temperatures of 1060–1350 K, pressure of $\sim 40 \text{ atm}$, and initial reactant concentrations within 30–100 ppm [284]. It was observed that at the initial stage, nitromethane decomposed exponentially without autoacceleration. The results of numerical simulations with the help of three most known kinetic schemes of nitromethane decomposition were in close agreement with experimental data over the entire temperature range covered. It was demonstrated that the measured rate constant was identical to the rate constant of the dissociation reaction



The temperature dependence of k_1 was approximated by the Arrhenius equation

$$k_1 = 2.57 \times 10^{14} \exp(-52.85/RT) \text{ s}^{-1}$$

where the activation energy is in kcal/mol, which suggested that the nitromethane dissociation proceeds in the fall-off pressure region. In a similar later study, the temperature dependence of k_1 was expressed by the Arrhenius equation

$$k_1(\text{NO}_2) = (6.3 \pm 2) \times 10^{12} \exp(-48.9 \pm 2/RT) \text{ s}^{-1}$$

where the activation energy again is in kcal/mol [285].

Ignition delay times of nitromethane ignition behind reflected shock waves were measured using the chemiluminescence emission from the $A^2\Sigma^+ \rightarrow X^2\Pi$ transition of the excited-state hydroxyl radical (OH^*) in a stainless steel shock tube [286]. The driver section was 2.46 m long (76-mm i. d.), and the driven section was 4.72 m long (152-mm i. d.). Post-reflected shock conditions were obtained using the extrapolated incident shock wave speed in conjunction with shock relations and the initial conditions in the test region. Wide ranges of conditions were investigated in terms of temperature (875–1595 K), pressure (1.8–34.3 atm), equivalence ratio ($\phi = 0.5, 1.0$, and 2.0) and dilution (99, 98, 95, and 90% Ar). Increasing ϕ led to an increase in t_{ign} at around 1420 K, t_{ign} was increased by a factor >3 when ϕ was doubled, from 0.5 (135 μs) to 1.0 (450 μs). For additional shock tube experiments, see also [287, 288].

3.3.6 Photodissociation (Photolysis) of Nitromethane

Nitromethane would normally be stored in the dark. Storage in clear containers in direct sunlight may induce photolytic decomposition. Nitromethane vapors that escaped from storage or nitromethane formed from pollutants in the atmosphere is photolyzed by sunlight. Laser photolysis of nitromethane may be useful to initiate controlled decomposition of nitromethane in a rocket engine, in particular those operating in pulse mode with multiple starts. Photolysis of unreacted nitromethane ahead of the detonation wave, caused by radiation emanating from the combustion zone, may be a predissociation step that presensitizes nitromethane to the subsequent detonation. Laser beams may be used to detect traces of nitro compounds in areas where they do not belong and where they might cause harm.

The photolysis of nitromethane in a matrix of solid argon at 20 K gives methyl nitrite [289]. All other products can be explained in terms of the secondary photolysis of methyl nitrite. The primary products of photolysis of methyl nitrite under these conditions are formaldehyde and nitroxyl, HNO .

The photolysis and pyrolysis of nitromethane and methyl nitrite have been studied by flash photolysis and kinetic spectroscopy [290]. The results showed that photolysis of nitromethane yields methyl radicals and nitrogen dioxide, and that these fragments undergo recombination and disproportionation reactions to form methyl nitrite, methoxyl, and nitric oxide. In the presence of added nitric oxide the methyl

radicals reacted principally with nitric oxide to form nitrosomethane, which subsequently dimerized and also reacted further with nitric oxide to yield nitrogen dioxide. Light absorption by methyl nitrite resulted not only in photolysis, but also in the formation of an isomer of the nitrite, which then reverted slowly to the stable form.

Photolysis of nitromethane in gas phase at 313 nm was studied at 328 K (55 °C) [291]. Methyl nitrite, formaldehyde, nitrosomethane, and NO were obtained as main products, their quantum yields were $\phi_{\text{CH}_3\text{ONO}} = 0.22$, $\phi_{\text{HCHO}} = 0.20$, $\phi_{\text{CH}_3\text{NO}} = 0.06$, and $\phi_{\text{NO}} = 0.10$. The dependence of the quantum yields on the pressure of quenching gases such as ethylene or NO were investigated. The quantum yield of triplet nitromethane was determined and compared with that by product analysis. Both gave the identical value: 0.6. Since ϕ_{HCHO} was not affected by any quencher, it was concluded that formaldehyde was formed directly from singlet excited nitromethane.

The dissociation of nitromethane following the excitation of the $\pi^* \leftarrow \pi$ transition at 193 nm has been investigated by two independent and complementary techniques: product emission spectroscopy and molecular beam photofragment translational energy spectroscopy [292]. The primary process was shown to be cleavage of the C–N bond to yield $\cdot\text{CH}_3 + \cdot\text{NO}_2$ radicals. The translational energy distribution for this chemical process indicated that there are two distinct mechanisms by which $\cdot\text{CH}_3 + \cdot\text{NO}_2$ radicals are produced. The dominant mechanism releasing a relatively large fraction of the total available energy to translation probably gives $\cdot\text{NO}_2$ radicals in a vibrationally excited 2B_2 state.

Atmospheric photodissociation rate coefficients and photodissociation lifetimes for nitromethane were calculated as a function of altitude from their measured visible and near ultraviolet photoabsorption cross-sections at 298 K [293]. From 0 to 50 km the lifetime of nitromethane varies from 10 to 0.5 h, while that of the more abundant methyl nitrate changes from 5.3 to 0.09 days.

The cross-section for photodissociation of nitromethane at 193 nm is $(1.7 \pm 1.0) \times 10^{-17} \text{ cm}^2$. From this it was inferred that the quantum yield for the process is nearly unity [294]. Photofragments of the dissociation were observed at masses 15, 16, and 30 corresponding to CH_3 , O, and NO, but only a very small number of fragments at mass 46 (NO_2) was measured. Time-of-flight spectra were obtained for all fragments except for mass 46. The data can be explained by assuming that two sequential absorptions of photons occur. The first photon dissociates CH_3NO_2 to CH_3 and NO_2 . The second photon is absorbed by the NO_2 fragment to give $\text{NO} + \text{O}$. About 30% of the NO_2 participate in the second absorption and the rate determining step is the primary absorption.

Photodissociation of nitromethane at 266 nm under collision-free conditions resulted in the single photon production of electronic ground state $\text{OH}(X^2\Pi_j)$ [295]. A rotational “temperature” of $1750 \pm 50 \text{ K}$ can describe the rotational distribution of the nascent OH radical. The quantum yield for the photolytic pathway producing the OH radical was 0.004 ± 0.001 .

It appears that UV irradiation of nitromethane produces the *aci*-form which is more susceptible to detonation than the regular form [296]. The activating effect of UV irradiation is similar to the addition of organic amines: both produce the *aci*-anion which is responsible for rapid detonation of nitromethane [297].

Laser-induced fluorescence of decomposing nitromethane vapors can be used as a sensitive analytical method to detect nitromethane vapors in air, for instance in the vicinity of improvised explosive devices. The system used a pulsed laser beam to photolyze molecules of a nitromethane vapor sample introduced into a vacuum chamber [298]. Emission fluorescence of the fragments produced by photodissociation by excimer laser photolysis of nitromethane at 193 nm could be quantified and calibrated. The principal fragment emission occurred at 431 nm.

Polarized emission spectra from photodissociating nitromethane excited at 200 and 218 nm showed a strong progression in the NO₂ symmetric stretch [153]. At 200 nm a weak progression in the NO₂ symmetric stretch in combination with one quantum in the C—N stretch also contributed to the spectra. Measurements of the angular distribution of emitted photons in the strong emission features from the relative intensity ratio between photons detected perpendicular to *versus* along the direction of the electric vector of the excitation laser showed anisotropy. The anisotropy was substantially reduced from the 2 : 1 ratio expected for the pure CH₃NO₂ transition with no rotation of the molecular frame. The intensity ratios for the features in the NO₂ symmetric stretching progression were near 1.5–1.6 for 200 nm excitation and 1.7 for 218 nm excitation. The analysis of the photon angular distribution measurements and consideration of the absorption spectrum indicated that the timescale of the dissociation was too fast for molecular rotation to contribute significantly to the observed reduction in anisotropy. It was suggested that a reassignment of the minor dissociation channel, first evidenced in photofragment velocity analysis experiments which detected a pathway producing slow CH₃ fragments, to the near threshold dissociation channel $\bullet\text{CH}_3 + \bullet\text{NO}_2(^2\text{B}_2)$ should be made.

Multi-photon ionization spectroscopy and time-of-flight mass spectrometry have been used to determine nascent photofragment energy distributions for several of the products of the 193 nm photolysis of nitromethane [299]. Internal energy distributions have been obtained for CH₃ and NO, and translational energy distributions for CH₃, NO and O(³P). The production of two NO electronic states (*X* and *A*) and the appearance of two peaks in the translational energy distributions of the CH₃ and O fragments are consistent with a two-channel dissociation. The major channel produced CH₃ and NO₂(²B₂), some of the latter having sufficient internal excitation to further dissociate to NO and O. The minor channel is believed to produce NO₂ in a different electronic state, which subsequently absorbs a second 193 nm photon and dissociates to yield NO and O.

The direct photolysis of liquid nitromethane was observed after pulse excitation at 299 nm using a sub-picosecond coherent anti-Stokes Raman spectroscopy (CARS)

instrument [300]. From the dynamic behavior under excitation of three main ground-state Raman lines it was deduced that the excited state disappeared with a lifetime of 1.1 ps and a photolysis quantum yield at 299 nm of 24%.

The photochemistry of nitromethane has been studied extensively for many years. Although it is generally agreed that the principal photodissociative process is cleavage of the C–N bond to yield the methyl radical and nitrogen dioxide, there is some evidence of minor competing dissociation channels. Femtosecond laser pulses have been used as a diagnostic method to study multi-photon ionization and photodissociation of nitromethane and led to the efficient production of intact molecular ions [301]. Femtosecond laser mass spectrometry (FLMS) could provide added information on the dissociation pathways of nitromethane. Laser pulses of 90 fs time duration at wavelengths of 375 and 750 nm, coupled to a time-of-flight mass spectrometer have been used and contrary to photoexcitation using nanosecond (ns) pulses, a large parent ion, 61 (CH_3NO_2^+), was detected together with strong peaks at $m/e = 15(\text{CH}_3^+)$, 30 (NO^+), 46 (NO_2^+) as well as a number of other minor peaks. This fragmentation pattern can be explained by a predominant ionization followed by dissociation route.

The isotope-selective IR multi-photon dissociation of nitromethane molecules in the region of stretching vibrations of the NO_2 group with IR free-electron-laser irradiation in a mixture with the natural content of the ^{15}N isotope of 0.4% showed that the content of the ^{15}N isotope in the products of NO dissociation was dependent on and varied within 0.1–1.6% as a function of the laser radiation frequency [302].

The dynamics of oxygen atom formation in the gas-phase photolysis of nitromethane was studied using the pulsed laser photolysis/laser-induced fluorescence (LIF) pump-and-probe technique [303]. Room temperature CH_3NO_2 vapor molecules were excited at 2 UV photodissociation laser wavelengths of 248 and 266 nm. Nascent O photofragments were detected via LIF in the vacuum UV spectral region under collision-free conditions. Narrow-band probe laser light, tunable over the wavelength range 130.2–130.6 nm, was used to monitor the fine-structure state distribution of nascent O atom product. The quantum yields for O atom formation were $\phi(\text{O}) = 0.18 \pm 0.03$ at 248 nm and $\phi(\text{O}) = 0.13 \pm 0.04$ at 266 nm.

The relevant low-lying singlet and triplet potential energy surfaces in the photolysis of nitromethane were studied by using the multi-state extension of the multi-configurational second-order perturbation theory in conjunction with large atomic natural orbital type basis sets [304]. The proposed mechanism for the photolytic decomposition of CH_3NO_2 provided a consistent and re-interpreted picture of the available experimental results. Two reaction paths were found in the photolysis of nitromethane after excitation at 193 nm. No ionic species were predicted in any dissociation path. The low-lying Rydberg states of nitromethane and nitrogen dioxide were then compared since both are present in the reacting mixture.

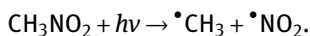
The photodissociation dynamics of nitromethane starting at the S(3) excited state has been studied at the complete active space self-consistent field level of theory in

conjunction with atomic natural orbital type basis sets [305]. The energies of all the critical points and the energy profiles connecting them have been recomputed with a multi-configurational second-order perturbation method. It was found that the key step in the reaction mechanism is a radiationless decay through an S(3)S(2) conical intersection.

Measurements of the nascent $\bullet\text{OH}$ product from photodissociation of nitromethane and nitroethane vapor at 266 nm were performed using the single-photon laser-induced fluorescence technique [306]. The $\bullet\text{OH}$ fragment was found to be vibrationally cold for both systems.

Photodissociation of nitromethane has been investigated for decades both theoretically and experimentally; however, the dissociation dynamics for nitromethane were still disputed for decades, although many different mechanisms have been proposed. To make a revised interpretation of these different mechanisms, photolysis of nitromethane at 226 and 271 nm under both collisional and collision-free conditions was investigated at nanosecond and femtosecond time scales [307]. These two laser wavelengths correspond to the $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ excitations of nitromethane, respectively. In nanosecond 226 nm ($\pi^* \leftarrow \pi$) photolysis experiments, CH_3 and NO radicals were observed as major products employing resonance-enhanced multi-photon ionization techniques and time-of-flight mass spectrometry. A few OH and CH_3O radicals were observed as dissociation products employing laser-induced fluorescence spectroscopy. The CH_3O product was only observed under collisional conditions. In femtosecond 226 nm experiments, CH_3 , NO_2 , and NO products are observed. These results confirmed that rupture of the C—N bond should be the main primary process for the photolysis of nitromethane after the $\pi^* \leftarrow \pi$ excitation at 226 nm, and the NO_2 molecule should be the precursor of the observed NO product. Formation of the CH_3O radical after the recombination of CH_3 and NO_2 species under collisional conditions ruled out a nitro-nitrite isomerization mechanism for the generation of CH_3O and NO from $\pi\pi^*\text{CH}_3\text{NO}_2$. Combined with the 271 nm nanosecond pump-probe experiments, in which none of the CH_3 , NO_2 , CH_3O or OH fragments were observed, it was suggested that all the fragment ions generated in 271 nm femtosecond laser experiments were derived from the parent ion, and dissociation of nitromethane from the $n\pi^*$ excited electronic state does not occur in a supersonic molecular beam under collision-free conditions.

A primary dissociation reaction takes place at 193 nm



Total cross-sections and asymmetry parameters for single-photon ionization from the highest occupied molecular orbitals of nitromethane were computed with a single-channel, frozen-core approximation for photon energies between 0.5 and 20 eV [308]. One-electron resonant processes in the ionization channels and recoil frame photoelectron angular distributions were studied based on a local model potential.

The photodissociation dynamics of nitromethane, following photoabsorption at 213 nm in the $\pi^* \leftarrow \pi$ transition, have been studied using ion imaging [309]. The state-resolved velocity and angular distributions were measured for the CH_3 , NO, and O atom fragments. The CH_3 velocity distribution consisted of two peaks with different angular distributions. The slow and fast components showed isotropic and anisotropic distributions, respectively. The NO and O fragments also showed slow components with isotropic angular distributions. The results observed consistently indicated that these slow photofragments were possibly produced by a concerted three-body dissociation channel.

The photodissociation of nitromethane at 193 nm was reviewed in terms of stereodynamic information provided by the measurement of the first four Dixon's bipolar moments using slice imaging [310]. The measurements indicated that after one-photon absorption by an allowed perpendicular transition, two reaction pathways can compete with similar probability, a direct dissociation process yielding ground-state CH_3 and $\text{NO}_2(1^2\text{A}_2)$ radicals and an indirect dissociation through conical intersections in which NO_2 radicals are formed in lower-lying electronic states. The low recoil energy part of the methyl fragment translational energy distribution presents a contribution with parallel character, irrespective of the experimental conditions employed that was attributed to parent cluster dissociation.

The techniques of infrared multi-photon dissociation (IRMPD) and state selective ion imaging were combined to probe roaming dynamics in the unimolecular dissociation of nitromethane and methyl nitrite [311]. Theoretical calculations suggested a roaming-mediated isomerization pathway of nitromethane to methyl nitrite prior to decomposition. State-resolved imaging of the NO product coupled with infrared multi-photon dissociation was carried out to examine this unimolecular decomposition near the threshold. The IRMPD images for the NO product from nitromethane were consistent with the earlier IRMPD studies that first suggested the importance of an isomerization pathway. The experimental observations were compared to the results of parallel quasi-classical trajectory calculations for nitromethane and methyl nitrite. The observation of distinct methoxy vibrational excitation for trajectories from nitromethane and methyl nitrite dissociation at the same total energy showed that the nitromethane dissociation bears a non-statistical signature of the roaming isomerization pathway, and this is possibly responsible for the nitromethane Λ -doublet propensity as well.

Photodissociation pathways of nitromethane following $\pi \rightarrow \pi^*$ electronic excitation via the potential energy surfaces for four lowest singlet states, and structures of many intermediates, dissociation limits, transition states and minimum energy conical intersections were determined using an automated searching algorithm [312]. Geometries were finally optimized and energies were computed. The calculated preferable pathways and important products were able to qualitatively explain most experimental observations. The major photodissociation products CH_3 and $\text{NO}_2(^2\text{B}_2)$ are formed by direct dissociation from the S_1 state. Important

pathways involving S_1 and S_0 states for production of various dissociation products $\text{CH}_3\text{NO} + \text{O}(^1\text{D})$, $\text{CH}_3\text{O}(\text{X}^2\text{E}) + \text{NO}(\text{X}^2\Pi)$, $\text{CH}_2\text{NO} + \text{OH}$, and $\text{CH}_2\text{O} + \text{HNO}$, as well as various isomerization pathways have been identified. Three roaming processes also have been identified: the O atom roaming in O dissociation from CH_3NO_2 , the OH radical roaming in OH dissociation from $\text{CH}_2\text{N}(\text{O})(\text{OH})$, and the NO roaming in NO dissociation from CH_3ONO .

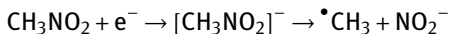
Solid nitromethane along with its isotopically labeled isotopologue D_3 -nitromethane (CD_3NO_2) ices were exposed to Lyman α photons from a hydrogen discharge lamp to investigate the mechanism involved in the decomposition of energetic materials in the condensed phase [313]. The chemical processes in the ices were monitored online and *in situ* via IR spectroscopy complimented by temperature programmed desorption studies utilizing highly sensitive reflectron time-of-flight mass spectrometry coupled with pulsed photoionization at 10.49 eV. The IR data revealed the formation of *cis*-methyl nitrite (CH_3ONO), formaldehyde, water, carbon monoxide, and carbon dioxide. Upon sublimation of the irradiated samples, three classes of higher molecular weight products, which are uniquely formed in the condensed phase, were identified: **(1)** nitroso compounds, nitrosomethane (CH_3NO), nitrosoethane ($\text{C}_2\text{H}_5\text{NO}$), nitrosopropane ($\text{C}_3\text{H}_7\text{NO}$), **(2)** nitrite compounds, methyl nitrite (CH_3ONO), ethyl nitrite ($\text{C}_2\text{H}_5\text{ONO}$), propyl nitrite ($\text{C}_3\text{H}_7\text{ONO}$), and **(3)** higher molecular weight molecules, $\text{CH}_3\text{NONOCH}_3$, $\text{CH}_3\text{NONO}_2\text{CH}_3$, $\text{CH}_3\text{OCH}_2\text{NO}_2$, and $\text{ONCH}_2\text{CH}_2\text{NO}_2$. The decomposition of nitromethane in the condensed phase is more complex compared to the gas phase under collision-free conditions opening up not only hitherto unobserved decomposition pathways of nitromethane (hydrogen atom loss, oxygen atom loss, retro carbene insertion), but also the blocking of several initial decomposition steps. Similar tests were later performed using fast electrons instead of ultraviolet light. See also [314, 315].

3.3.7 Electron Bombardment of Nitromethane

Electron bombardment of nitromethane takes place in the inlet portion of mass spectrometers. The appearance potential of decomposition products is an indication of the stability of the molecule. The adiabatic electron affinity of nitromethane is 0.50 ± 0.02 eV and the C–N bond dissociation energy is 2.67 ± 0.1 eV. For nitromethane, the calculated bond dissociation energy is $D(\text{CH}) = 4.42$ eV, electron affinity is $\text{EA}(\text{CH}_2\text{NO}_2) = 2.45$ eV, and gas-phase acidity is $\text{GPA} = 15.4$ eV [316, 317].

Nitromethane has a positive adiabatic electron affinity. Photoelectron measurements led to a value of 0.26 ± 0.08 eV. Dissociative electron attachment in nitromethane and its anionic states has been investigated using optical and electron scattering methods [318]. The nature and dissociation dynamics of the low-lying anionic states of nitromethane were explained in the light of these experiments and compared to results of *ab initio* molecular orbital computations and qualitative,

simplified potential energy diagrams of energy vs. C—N bond length. It seems that despite the complexity of the dynamics and the large excess of energy, the processes following electron capture by nitromethane are not statistical. Excited anionic states have been probed mostly through dissociative electron attachment processes such as



Dissociative electron attachment measurements to nitromethane in the gas phase have been made by use of a high mass-resolution sector field mass spectrometer [319, 320]. Anion efficiency curves for 16 negatively charged fragments were measured in the electron energy region from about 0 to 16 eV with an energy resolution of ~1 eV. Eight previously unseen anions have been detected: CH_2NO_2^- , CHNO_2^- , CH_2NO^- , H_2NO^- , CH_3^- , CH_2^- , CH^- , and H^- . The five most dominant product anions were NO_2^- , O^- , OH^- , CN^- , and CNO^- , all of them featuring two high-energy resonances at about 5 and 10 eV. Formation of CH_2NO_2^- at low electron energies has been explained in terms of dissociative electron attachment to highly vibrationally excited molecules.

Low energy electron-induced dissociation in multi-layer films of deuterated nitromethane (CD_3NO_2) was investigated by high resolution electron energy loss spectroscopy (HREELS) and by the electron stimulated desorption (ESD) of neutral species [321]. The HREELS measurements showed that the lowest electronic states of the condensed molecule are very similar to those seen in the gas phase. Desorbed neutrals were detected using combined non-resonant multi-photon ionization at 355 nm and time-of-flight mass spectrometry. The most intense signals detected were those of CD_3^+ and NO^+ and were attributed primarily to the desorption of CD_3 and NO_2 fragments following molecular dissociation via low-lying electronic excited states of nitromethane. By varying the time delay between the incident electron pulse and the ionizing laser pulse, it was possible to measure the kinetic energy distributions of desorbing fragments. The kinetic energy distributions above ~5 eV appeared invariant with incident electron energy, indicating that the same desorption process (dissociation via low-lying electronic states) operates at all the studied incident energies. At energies less than ~5 eV, contributions from dissociative electron attachment were also observed in the yield of CD_3 and other neutral fragments.

Icy films of nitromethane or its isotopologue D_3 -nitromethane (CD_3NO_2) were exposed to ionizing radiation (instead of Lyman α line UV light as above) to investigate the mechanisms in the decomposition of (D_3)-nitromethane [322]. The radiation-induced modification of the ices was followed during the radiation exposure *in situ* via IR spectroscopy (condensed phase) and via temperature-programmed desorption (TPD) exploiting reflectron time-of-flight mass spectrometry joined with single photon ionization of the subliming molecules at 10.49 eV (gas phase). The IR spectroscopic and kinetic studies revealed the formation of methyl nitrite via isomerization of nitromethane as well as the presence of formaldehyde, nitrosyl hydride (HNO), and radical decomposition pathways (forming methoxy radical CH_3O and nitrogen monoxide NO), altogether accounting for about 85% of all products formed. The TPD studies

with time-of-flight mass spectroscopy revealed three classes of complex molecules: (i) nitroso compounds, (ii) nitrites and (iii) higher molecular weight products with the synthesis of the homologue series of nitroso and nitrite compounds likely governed by a stepwise molecular growth via carbene (CH_2) insertion. Three decomposition pathways of solid nitromethane were identified, which do not take place in the gas phase: (i) the fragmentation of nitromethane to the nitromethyl radical (CH_2NO_2) plus suprathreshold atomic hydrogen (H), (ii) formation of nitrosomethane (CH_3NO) plus atomic oxygen (O), and (iii) generation of singlet carbene (CH_2) plus nitrous acid (HONO).

Thin films of homogeneously mixed normal nitromethane (CH_3NO_2) and D_3 -nitromethane (CD_3NO_2) frozen ices were exposed to energetic electrons and Lyman α UV photons [323]. The isotopically mixed reaction products were probed *in situ* via time-of-flight mass spectrometry coupled with pulsed photoionization during temperature programmed desorption, providing information on three high energy decomposition pathways, which had not been previously observed under collision-free conditions in the gas phase. These were (1) decomposition of nitromethane via atomic oxygen loss to nitrosomethane (CH_3NO), (2) fragmentation of nitromethane and/or methyl nitrite (CH_3ONO) via carbene (CH_2) loss, (3) and C–H bond rupture processes in nitromethane and/or methyl nitrite.

Absolute dissociative ionization cross-sections of nitromethane from threshold to 200 eV have been measured using Fourier transform mass spectrometry [324]. In the production of positive ions by electron impact ionization 13 ions were detected, including the parent ion CH_3NO_2^+ and the 4 most important fragment ions CH_3NO^+ , NO_2^+ , NO^+ , and CH_3^+ . In the production of negative ions by dissociative electron attachment to nitromethane, three anions were detected: CH_2NO_2^- , NO_2^- , and CN^- .

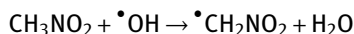
3.3.8 Radiolysis of Nitromethane

It is unlikely that nitromethane would ever be used as a rocket propellant in outer space on long-term missions, where it would be exposed to cosmic radiation that triggers decomposition. The radiolysis of nitromethane produces free radicals that promote decomposition, similar to photolysis, but under more controlled, selective conditions than during thermal decomposition. The same free radicals observed during radiolysis also play a role in the thermal decomposition of nitromethane [325–327].

Initial 100-eV radiolysis yields and effects of dose on the rates of formation of 12 products of the ^{60}Co γ -ray-induced decomposition of pure, air-free, liquid nitromethane have been measured at constant dose rate ($9 \times 10^{17} \text{ eV g}^{-1} \text{ min}^{-1}$) at 273 K (0 °C) and at room temperature. The *cis*-dimer of nitrosomethane, methyl nitrite, and formaldehyde were the major initial products [328]. Mechanisms now identified in the radiolysis of nitromethane may be the same as those occurring in the radiolysis of other commercially more important nitro compounds.

3.3.9 Oxidation of Nitromethane

The reaction of nitromethane vapor with oxygen has been studied in the temperature range from 700 to 740 K in a constant volume, static vessel outside the explosion limit [329]. The explosion limit was markedly lowered due to addition of oxygen, when compared with the case of nitromethane alone and was determined as a function of temperature and/or of O₂ concentration. A simulation of the 121-step “simplified mechanism” gave results that seemed to match experimental data well, not only for the oxidation of nitromethane but also for its pyrolysis, provided that a new way of formation of HCN was introduced. The simulations allowed an estimation of the order of magnitude of several rate constants, the values of which were not precisely known. For example, the rate constant of the reaction



may be about 2.4×10^{11} – 3.0×10^{11} cm³ mol⁻¹ s⁻¹ in the temperature range 700–740 K.

3.3.10 Analytical Methods for Nitromethane

Nitromethane that is to be used as a solvent for electrochemical or spectrophotometric measurements must be purified of contaminants commonly introduced during its manufacture. Apart from water, which is easily removed by distillation down to concentrations near 0.001M owing to the formation of a water-nitromethane azeotrope ($t_b = 356\text{ K} = 83^\circ\text{C}$ at 1 atm), nitromethane contains relatively high concentrations of homologues, which have little effect on the chemical properties of the solvent but which lower its density and raise its viscosity. Different concentrations of the homologues undoubtedly caused the large variations in density (1.1230–1.13124 g/cm³) and viscosity (6.08–6.275 mPa s) reported by various authors. The best method for purification of nitromethane is crystallization from a solution in diethyl ether at low temperatures [92]. This paper also contains a good summary of physical properties of pure nitromethane. Contaminants commonly found include not only nitroethane and 2-nitropropane at concentrations near 0.1M, but also propionitrile at concentrations near 0.1M.

3.3.10.1 Analysis of Bulk Nitromethane

Samples were taken at random from 60 barrels of nitromethane which had been stored at Yuma Proving Grounds in Arizona under varying environmental conditions and sent to Southwest Research Institute for analyses by atomic absorption, mass spectroscopy, gas chromatography, and FTIR [330]. The nitromethane content was determined along with contaminant analyses for nitroethane, 2-nitropropane, water, and metals. The results showed: nitromethane >98%, nitroethane <1.1%, 2-nitropropane <0.2%, water <0.11, and metals <10 ppb.

3.3.10.2 Analysis of Nitromethane in the Air

Nitromethane is quite volatile and vapor pressure may cause hazardous concentrations to build up in areas where work is done with nitromethane. The air in workspaces needs to be monitored to make sure the concentration is below the Threshold Limit Value-Time Weighted Average (TLV-TWA) [331]. Laser-induced fluorescence of decomposing nitromethane vapors can be used as a sensitive analytical method to detect nitromethane vapors in air, for instance in the vicinity of improvised explosive devices. An experimental system used pulsed laser beam photofragment molecules of a nitromethane vapor sample introduced into a vacuum chamber [298]. Emission fluorescence of the fragments produced by photodissociation by excimer laser photolysis of nitromethane at 193 nm can be quantified and calibrated. The principal fragment emission occurred at 431 nm. The limit of detection for nitromethane was 1.6×10^8 molecules, corresponding to an interrogated sample volume of 0.0375 cm^3 and a chamber pressure of $1.3 \times 10^{-7} \text{ mm Hg}$ (i.e., a concentration of 4.2×10^9 molecules/ cm^3). The linear dynamic range extended over 3.5 decades in nitromethane pressure (relative standard deviation of less than 4%).

The acquisition of an analyte from the atmosphere by a nebulization process and electrochemical detection of nitromethane used a gold screen-printed electrode in a flow-thru cell where a detection limit of $4.5 \mu\text{M}$ was achieved and it was selective toward nitromethane amidst a large panel of interfering compounds. Square wave voltammetry was used for this purpose with a gold working electrode and a phosphate buffer at pH 7.5. The limits of detection were $2.3 \mu\text{M}$ without dissolved oxygen in the solution and $12.5 \mu\text{M}$ in air [332, 333]. Detection times of less than 1 min were obtained for nitromethane contents of 8 and 90 ppm.

Nitromethane, nitrobenzene, and some nitro-rich triazole derivatives vapors in air can be detected using a pulsed photoacoustic technique [334]. UV light at 266 nm wavelength i.e. fourth harmonic of Q-switched Nd:YAG laser having pulse durations of 7 ns and 10 Hz repetition rate was used to record the time-resolved photoacoustic spectrum. The photoacoustic fingerprint was produced due to absorption of incident UV light by the molecule itself and photodissociation of nitromethane.

3.4 Strand Burning of Nitromethane

Strand burning of nitromethane and other nitro and nitrate compounds will be discussed in the monopropellant section in *Encyclopedia of Monopropellants*, chapter “Organic Monopropellants”, in connection with rocket engines using such propellants. Nitromethane is underoxidized but it is unlikely to be used as a fuel in bipropellant rocket engines. Combustion of nitromethane in an oxidizing atmosphere will be discussed in a future *Encyclopedia of Non-hypergolic Bipropellant Combinations*.

3.5 Storage Stability of Nitromethane

At higher temperatures, at 322K (49°C) and above, nitromethane undergoes a slow decomposition with evolution of nitrogen dioxide. Therefore, storage temperatures this high should be avoided. According to some sources, the thermal stability can be improved by adding boric acid, hydroquinone, sulfuric acid, or phosphoric acid.

3.6 Materials of Construction for Nitromethane

Nitromethane can be stored in containers made of many common materials of construction. In metals, in the presence of moisture, the rate of corrosion may be accelerated because nitromethane exists in two tautomeric forms, of which the *aci*-form is the more corrosive. The rates of corrosion were measured in stainless steel 0.0025 mm/year, aluminum 0.0025 mm/year and copper 0.0076 mm/year [169]. Stainless steel is a specific catalyst for the decomposition of nitromethane and increased the reaction rate 40-fold [221].

3.7 Handling of Nitromethane

3.7.1 Equipment for Handling of Nitromethane

It was recommended to use slowly closing, non-steel valves in nitromethane systems to prevent water hammer effects and rapid compression of entrained bubbles which might lead to explosions [335].

3.8 Accident History of Nitromethane

For a long time nitromethane was considered safe enough to be shipped all over the United States in railroad tank cars and tanker trucks. That changed dramatically in 1958 when two explosions occurred in two separate incidents with railroad tank cars holding 37000 L of nitromethane [336, 337].

One explosion occurred in a railroad switching yard near Niagara Falls, NY, on 22 January 1958, causing 200 injuries. A rail tank car containing 35 tons of nitromethane detonated, forming a crater 15 × 26 m (50 × 85 ft) wide and 4.8 m (16 ft) deep. Damage extended out to 4.8 km (3 miles) from the explosion center.

The second explosion of 43 tons of nitromethane occurred near Mt. Pulaski, IL on 1 June 1958, and caused 2 fatalities and 4 injuries. The material damage amounted to several million dollars (1958 dollars). The crater was 12 m deep and had a diameter of 30 m [338].

A nearly empty drum of nitromethane exploded at a facility of Dynamit Nobel in Germany in May 1989. In another part of the world, experiments were performed in an effort to determine the cause of an explosion that occurred during a nitromethane manufacturing and rectification process in China [339]. Test samples were collected from the accident site and analyzed by GC and DSC, including reaction product, crude product, 99% pure product and raffinate. A sample evaporating experiment recorded the reaction phenomena occurring at low liquid level in the sump of the still. Based on the experimental results, excess heat released by the decomposition of overheated raffinate was pinpointed as the most likely cause of the explosion.

3.9 Toxicity of Nitromethane

Because nitromethane is finding widespread application as a paint solvent, the vapor toxicity has been thoroughly investigated, in particular after it became apparent that nitromethane is a human (not only an animal) carcinogen. Although nitromethane has not found application as a rocket propellant, its toxic properties are reviewed here because they are related to the toxicity of other more energetic nitro compounds that are used as plasticizers in rocket propellants.

A detailed summary of various aspects of the toxicity of nitromethane has been published as a monograph chapter by the International Agency for Research on Cancer (IARC) [340]. The toxicity of nitromethane is distinctly different from the toxicity of the aromatic nitro compound, nitrobenzene. Absorption of nitromethane into the body leads to the formation of methemoglobin which in sufficient concentration causes cyanosis. The onset of symptoms may be delayed for 2–4 h or longer after ingestion. Table 30 is a summary of lethal dose and lethal concentrations of nitromethane determined in animal exposure tests.

Rabbits and guinea pigs (2 of each species) survived exposures to 30000 ppm for 15 min or 10000 ppm for 1 h, but all died when exposed to 30000 ppm for 2 h or 10000 ppm for 6 h. In a short-term subchronic study, a monkey exposed to 1000 ppm nitromethane in air died after 8 daily 6-h exposure periods. At 500 ppm, the lowest concentration used in this study, 2 rabbits, and 1 monkey survived a total exposure period of 140 h (administered in daily 6-h periods).

Rats exposed to 13000 ppm nitromethane in air died after 6 h [341]. At 2500 ppm, rats survived 4 consecutive 6 h/day exposures but died on the fifth day.

In a study for NIOSH [342], groups of rats and rabbits were exposed to air containing 98 or 745 ppm of nitromethane for 7 h/day, 5 days/week, for periods up to 24 weeks. Groups of 10 rats were sacrificed after 2, 10 days, and 1, 3, and 6 months of exposure. All animals survived the exposure at both concentrations and only mild to moderate symptoms of toxicity were observed in the rats and rabbits. Effects of nitromethane exposure were: decreased weight gain in rats following 8 weeks of exposure to 745 ppm

Table 30: Toxicity of nitromethane based on animal exposure tests.

Route	Species	Dose, mg/kg	Response
Oral	Rats	1210	LD50
Oral	Rats	940	LD50
Oral	Mice	1440	LD50
Oral	Mice	950	LD50
i.p.	Mice	110	LD50
Oral	Rabbits	750	LDLo
Oral	Dogs	125	LDLo
s. c.	Dogs	565	LDLo
i. v.	Rabbits	750–1000	LD50
i. v.	Dogs	800	LDLo
Inhalation	Monkeys	1000 ppm	LCLo
Inhalation	Monkeys	980 ppm	LCLo

Data sources: [83, 84]

and a thyroid effect in rabbits that was indicated by increased thyroid weight and decreased serum thyroxin levels. No exposure-related gross or microscopic alterations were found in any of the tissues examined in the rats and rabbits exposed to either 98 or 745 ppm nitromethane.

Chronic exposure tests of animals to low levels of nitromethane vapor in air extended for over 2 years showed significantly increased frequency of tumors in liver tumors. The results are summarized in Table 31.

Table 31: Chronic exposure animal inhalation test results with nitromethane.

Animal	Concentration, ppm	Frequency	Duration
Rat	188	6h/day	2 years
Mouse	750	6h/day	2 years

Groups of rats were housed in inhalation chambers and exposed to vapors of nitromethane at either 100 or 200 ppm for 7 h/day, 5 days/week for 2 years [343]. The animals were observed daily for signs of pharmacologic or toxic effects and body weights were recorded periodically. At the 2-year termination of the exposure period, serum chemistry and hematology tests were performed on selected animals and all surviving animals were sacrificed. All animals were necropsied and subjected to a thorough histopathologic examination. During the study there were no pharmacologic effects from exposure to nitromethane at either 100 or 200 ppm. There was no effect on mortality at either exposure level. There was no effect of exposure of rats to either level of nitromethane on hematology. There were no clinically significant

effects on serum chemistry. There were no effects of exposure to nitromethane on organ weights. There were no significant differences in the non-neoplastic or neoplastic pathology related to exposure to nitromethane.

Although nitromethane is not expected to be a contaminant in the atmosphere of crewed spacecraft, the National Aeronautics and Space Administration (NASA) has compiled a 20-page summary with 20 literature references of the toxicity considerations for nitromethane should it inadvertently find its way into space station atmospheres by an undefined and unexpected pathway [344]. Toxicity topics summarized include lethality, symptoms, thyroid toxicity, hematological changes, pulmonary toxicity, effects on reproductive function, carcinogenesis, and genotoxicity. The Spacecraft Maximum Allowable Concentration was set at 25 ppm for 1 h and 5 ppm for 180 days.

Toxicology and carcinogenicity studies were conducted by inhalation administration of nitromethane to groups of 50 F344/N rats of each sex at exposures of 0, 94, 188 or 375 ppm and 50 B6C3F1 mice of each sex at exposures of 0, 188, 375 or 750 ppm for 6 h/day, 5 days/week, for 103 weeks [345]. Under the conditions of these 2-year inhalation studies, there was no evidence of carcinogenic activity of nitromethane in male F344/N rats exposed to 94, 188 or 375 ppm. There was clear evidence of carcinogenic activity of nitromethane in female F344/N rats based on increased incidences of mammary gland fibroadenomas and carcinomas. There was clear evidence of carcinogenic activity of nitromethane in male B6C3F1 mice on increased incidences of Harderian gland adenomas and carcinomas. There was clear evidence of carcinogenic activity in female B6C3F1 mice, based on increased incidences of liver neoplasms (primarily adenomas) and Harderian gland adenomas and carcinomas. Increased incidences of alveolar/bronchiolar adenomas and carcinomas in male and female mice exposed to nitromethane were also related to chemical administration. Exposure to nitromethane by inhalation for 2 years resulted in increased incidences of nasal lesions including degeneration and metaplasia of the olfactory epithelium and degeneration of the respiratory epithelium in male and female mice.

The potential of nitromethane to induce morphological transformation in the Syrian hamster embryo cell transformation assay using a 24-h exposure protocol was tested with doses of 2000, 2500, 3000, 3500, and 4000 g/mL [346]. Both the 4000 and the 5000 g/mL dose groups showed a statistically significantly greater increase in morphological transformation frequency compared to the concurrent controls.

The environmental fate and transport processes with spilled nitromethane were reviewed in detail [347]. The fate of nitromethane in water will depend on its ability to undergo chemical, photochemical, and biological reactions, and on partitioning (transport) from the water column into air or sediment. It appeared that the nitroalkanes (including nitromethane) are not hydrolyzed to any measurable extent by the action of water alone. Environmental decay through photolysis is likely to occur, but data concerning photolysis rates in aqueous solution or under environmental wa-

ter conditions could not be found. Nitromethane is fairly reactive and therefore does not persist in the environment. The half-life time of nitromethane is ~4–9 h in air and ~1 day in water. The fate and transport of nitromethane in soil has received very little attention and biodegradation mechanisms are unclear. The relatively high vapor pressure and the high evaporation rate of nitromethane indicated that it may evaporate quite rapidly from dry soil surfaces at a spill site. If nitromethane is spilled into surface water, aquatic toxicity seems to be low. Nitromethane concentrations of 659 ppm were not lethal to fathead minnows (*Pimephales promelas*) over a 96-h exposure, although “severe sublethal effects” were observed. The reportable quantity in cases of a nitromethane spill was set at 1000 lb. For additional information on carcinogenicity and teratogenicity of nitromethane, see [348, 349].

3.9.1 Maximum Allowable Exposure Limits for Nitromethane

Based on animal exposure data, nitromethane has been categorized as a group 2B carcinogen by the IARC Carcinogen List criteria. The recommended exposure limits (REL) are:

- 1993–1994 American Conference of Governmental Industrial Hygienists (ACGIH) TLV: 100 ppm (250 mg/m³) TWA
- 2000 ACGIH TWA 20 ppm
- USA OSHA PEL TWA 8 h/day 100 ppm (250 mg/m³)
- NIOSH REL: The 1989 OSHA PEL may not be protective to workers.
- Original NIOSH (Standards Completion Program, SCP) Immediately Dangerous to Life and Health (IDLH): 1000 ppm

The original NIOSH IDLH was later revised downward to 750 ppm [350, 351]. The chosen IDLH was based on earlier observations that with concentrations above 1000 ppm, if the product of this concentration and the time of exposure was greater than 1 (e.g., 1000 ppm for 3 h) some of the animals, including 1 monkey, had died.

3.10 Safety Properties of Nitromethane

The monopropellant qualities of nitromethane and other nitroalkanes and alkyl nitrates will be discussed in a later volume. The data summarized here deal only with the handling, storage, and transportation safety properties of these compounds.

During a comprehensive search of the literature in order to identify hazards associated with the planned use of nitromethane in the Tactical Explosive System (TEXS), the information was grouped into several categories: adiabatic compression, detonation, tests, change in properties, health hazards and other problems [352]. This is a good source of information for the safe handling of nitromethane.

3.10.1 Transportation Hazard Classification of Nitromethane

Storage and transportation regulations for nitromethane were critically reviewed at a time when the US Army anticipated using larger quantities of this material for a TEXS for minefield clearing. At one time the US Department of Transportation (DOT) and OSHA classified nitromethane only as a flammable liquid. This classification seems to ignore the explosion accidents that have occurred with this material. The US Department of Defense classified nitromethane as a mass-detonating explosive. Liquid nitromethane hazard classification parameters and hazards classification of various slurry mixtures with nitromethane were re-examined in preparation for an anticipated more widespread use of nitromethane in a TEXS [353].

3.10.2 Flash Point and Lower Limit of Flammability

The open cup flash points and the lower limits of flammability in air of nitroalkanes are summarized in Table 32. The upper limits of flammability in air cannot be determined because the vapor is combustible or even detonable all the way to 100% vapor.

Table 32: Flash point and lower limit of flammability of nitroalkanes.

Compound	Open cup flash point		Closed cup flash point		Lower flammable limit in air
	K	°C	K	°C	vol.-%
Nitromethane	317	44	317.6	44.4	7.3 7.3 at 33 °C
Nitroethane	314	41			4.0 3.4 at 30 °C
1-Nitropropane	322	49			2.6 2.2 at 34 °C
2-Nitropropane	311	38			2.6 2.5

Data source: W. R. Grace Datasheet [354]

The autoignition temperature of nitromethane in air is 713 K (440 °C). Other sources give the autoignition temperature as 691 K (418 °C = 785 °F). The flash point by the Abel-Pensky method is 308–310 K (35–37 °C) and its fire point by the Marcusson method is 315–316 K (42–43 °C) [355].

3.10.3 Explosive Sensitivity of Nitromethane

Nitromethane can be used as a rocket propellant or as an explosive, depending on the modes of initiation, the charge geometry, and the presence or absence of sensitizers such as amines, gas bubbles or microballoons. If one uses nitromethane as a rocket propellant, unintended accumulation of unburned nitromethane in the combustion

chamber may lead to explosions. After shutting off an engine at the end of the intended mission, unburned nitromethane in the injector passages, valves, and feed lines may overheat from heat soaking back into the injector and explode. For this reason this book contains a fairly detailed summary of safety and detonation properties of nitromethane.

Nitromethane can be used as the fuel in pulse detonation rocket engines or rotating detonation rocket engines. Sensitivity, detonation velocity, and critical diameter are important properties for evaluating nitromethane as a propellant for these applications. This is one of the reasons why nitromethane explosive properties have been included in such detail in this book. Nitromethane has been considered as a rocket propellant for a long time, but its sometimes unpredictable sensitivity to accidental explosion has prevented any widespread use [356, 357].

The detonation of condensed explosives may not be of similar nature to that of gaseous detonations [358]. Pulsating detonations of condensed and gaseous explosives are similar in nature and are initiated by oblique shock collisions in the detonation wave front [359].

The detonation kinetics and explosion reaction mechanisms in a variety of systems consisting of nitromethane, molecular oxygen, and water vapor were studied using reactive molecular dynamics to simulate reactions in time domain, as they would occur in real life [360]. The high polarity of the nitromethane molecule plays a key role, driving the first exothermic step of the reaction. Rapid temperature and pressure growth stimulate the subsequent reaction steps. Oxygen is important for faster oxidation, whereas its optimal concentration is in agreement with the proposed reaction mechanism. Addition of water (50 mol %) inhibited detonation; however, water did not prevent detonation entirely.

3.10.3.1 Drop Weight Impact Sensitivity of Nitromethane

There are contradicting reports on the drop weight sensitivity of nitromethane in the literature, most likely caused by using a different apparatus or using propellant samples of dubious purity. One source reports that nitromethane did not explode with a 2-kg weight dropped from 1.95 m [361]. Other sources report that dropping a 200-g weight from 20 cm resulted in an event in 20% of the tests, and that a 200-g weight from 40 cm resulted in an event in 90% of the tests [362]. Metal acetylacetonate salts can change the drop weight sensitivity of nitromethane in either direction, cobalt or chromium acetylacetonate increase the sensitivity, whereas copper or nickel acetylacetonate reduce the sensitivity.

Nitromethane or tetranitromethane could not be made to explode under the maximum impact load of the apparatus used when tested for impact sensitivity in comparison to glycerol trinitrate, ethylene glycol dinitrate, and other energetic liquids [363].

The drop weight sensitivity and detonability of nitromethane is reduced by addition of diluents like alcohols (methanol, ethanol, isopropanol) or phlegmatizing ad-

ditives (copper acetylacetonate) [364, 365]. The drop weight impact sensitivity of nitromethane with a 5-kg mass with rebound impact was 160 cm [78].

3.10.3.2 Adiabatic Compression Sensitivity of Nitromethane

One danger associated with the operation of nitromethane rocket engines is that on occasion explosions will occur at the start of a run. This seems to be due to the fact that nitromethane will detonate spontaneously if it is heated to temperatures above $561 \pm 28 \text{ K}$ ($550 \pm 50^\circ \text{ F}$). This heat probably comes from adiabatic compression of gas bubbles [366]. Sudden compression of nitromethane to 18.8 MPa (136 atm) has caused sudden explosions, whereas compression to 9.4 MPa (93 atm) did not trigger any hazardous reactions as long as there were no bubbles in the liquid.

Some of the adiabatic compression sensitivity testing has been done by including a bubble with a known gas filling and a well-defined size. The adiabatic compression sensitivity of nitromethane was tested in an adiabatic compression sensitivity tester developed by Aerojet in comparison to that of *n*-propyl nitrate, methylacetylene and a mixture of 60% ethyl nitrate/40% propyl nitrate [367]. The apparatus consisted of a pneumatically driven piston rapidly compressing a gas bubble above a liquid propellant sample. In a few cases, especially for nitromethane, the apparatus was also inverted, pushing the liquid upward into the gas (vapor) bubble. The sensitivity was

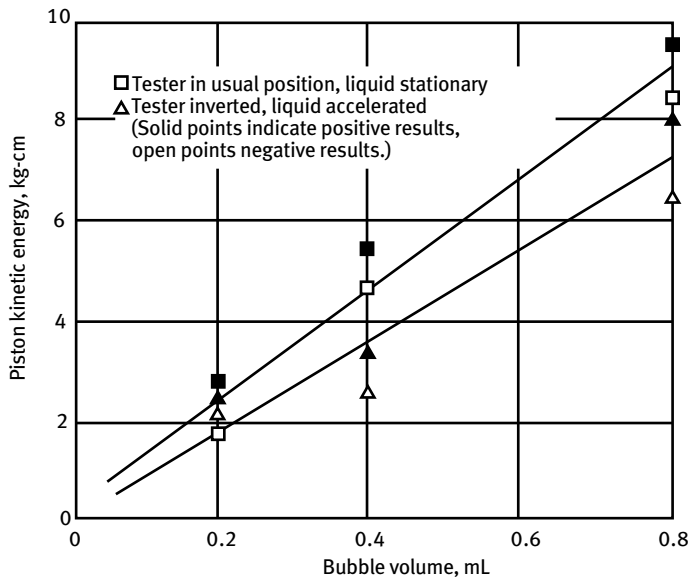


Figure 7: Adiabatic compression sensitivity of nitromethane (republished and modified from [367], with permission of © 1959 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

expressed in terms of the piston kinetic energy divided by the size of the gas bubble, which is the slope of a straight line separating the go-no go areas in an x-y chart (Figure 7). The results are summarized in Table 33. Nitromethane was of intermediate sensitivity in this series of tests.

Table 33: Adiabatic compression sensitivity of nitromethane in comparison to other monopropellants.

Compound	Adiabatic compression sensitivity, kg cm mL ⁻¹
Mixture of 60% ethyl nitrate/40% propyl nitrate	4.0 ± 0.8
<i>n</i> -Propyl nitrate	6.7 ± 1.2
Nitromethane	10.4 ± 1.7
Methylacetylene	86 ± 12

Data source: [367]

Hydrazine, hydrogen peroxide, ethylene oxide or unsymmetrical dimethylhydrazine (UDMH) could not be made to explode at the maximum capable compression rate of this machine (>144 kg cm mL⁻¹). If nitromethane is pushed into a dead-end cavity of a tubing, an explosion will result if the push pressure is 5.88 MPa (58 atm), even if the gas space contains only nitrogen instead of air. See also [368, 369]. Note that in all these tests, not the push pressure, but the pressure rise rate is the important criterion.

“Secondary ignition” was defined as any ignition due to sources other than the desired direct initiation when using nitromethane in rocket engines or explosives dispensing systems.

A study of the shock initiation to detonation transition of nitromethane by itself in the absence of bubbles by a nearly rectangular relatively long-duration, 60-kilobar amplitude shock showed that the time to the appearance of detonation in 3 experiments with shocks of nominal initial pressures of 65, 62, and 60 kilobars was approximately 10, 16, and 20 μs, respectively [370]. Chemical reactions in or near the shock front appeared to accelerate the shock front and reduce the time to initiation.

A series of experiments was conducted in which liquid nitromethane was dynamically compressed to peak pressures in the order of 10 kbar [371]. The compression chamber consisted of a high-strength steel cylinder divided into two compartments by a tightly fitting steel piston. An explosive pressurization charge was placed in one compartment and the sample of nitromethane in the other. The pressure pulse in the nitromethane consisted of a damped oscillation with rise time in the order of 50 s. An initiation and non-detonating decomposition of the nitromethane was repeatedly observed. Diagnostic instrumentation was not sufficiently precise to accurately determine the onset of the decomposition process, but it occurred no later than 200 s after onset of the pressure pulse. Alternative initiation mechanisms were discussed, and it

was shown that initiation by adiabatic compression of air bubbles appears to be the most likely explanation. A theoretical expression for the chemical induction time of nitromethane heated by compressed air bubbles was then derived. The calculations were based on rapid adiabatic compression of air (using a real-gas EOS), a laminar heat conduction process at the gas-liquid interface, and an Arrhenius reaction rate in the decomposing nitromethane.

Adiabatic compression initiation characteristics of liquid propellant nitromethane under dynamic fill conditions in a TEXS were measured in the laboratory and formed the basis for design change recommendations for a nitromethane dispensing system [335]. Nitromethane drawn from four 208-L (55-gallon) barrels was combined in a 833-L (220-gallon) tank for mixing and dispensing. The conditions tested at Princeton Combustion Research Laboratories (PCRL) included:

- Liquid non-bubbly NM
- Liquid nitromethane with fine cavitation bubbles
- Liquid nitromethane with fine air bubbles
- Liquid nitromethane with large air pockets

Calculations were for a 37-mm (1.5-in.) diameter hose with flow rates up to 3780 L/min. (100 gal/min.) Tests were conducted at 293, 328, and 336 K (20, 55, and 63 °C), using the PCRL tester and 2.5 mL in a U-tube test with 6-mm (1/4-in.) O.D. CRES tubes and push pressures up to 9.3 MPa (1350 psi) and cavity pressures up to 103 MPa (15000 psi). The U-section had a radius of 75 mm (3 in.) and the length of the straight section of the dead-end tube was 114 mm (4.5 in.) The PCRL tester achieved pressurization rates of up to 172 MPa/ms (25000 psi/ms).

Spectroscopic methods and rapid-response thermocouples can be used to measure the temperature rise preceding the detonation in shocked nitromethane [372].

The section on *n*-propyl nitrate in chapter “Nitrate Esters” contains a comparison of the adiabatic compression sensitivities of nitromethane, nitroethane, and *n*-propyl nitrate [373]. Nitromethane was the intermediate sensitive liquid of the three liquids tested, with energy required to initiate an explosion in 50% of the tests being between that of nitroethane and *n*-propyl nitrate.

In a U-tube adiabatic compression sensitivity test apparatus with variable, preselected push pressure and constant bubble size, nitromethane could not be made to explode and the push pressure required to explode nitromethane or trinitromethane was beyond the maximum energy input capability of the apparatus, much higher than that of methyl nitrate, glycerol trinitrate, or ethylene glycol dinitrate (EGDN) [374].

3.10.3.3 Bullet Impact Sensitivity of Nitromethane

Bullet impact tests with nitromethane resulted in explosions, but only sporadically. There are too many variables in this test. Under certain conditions (container size, ullage size, wall thickness of 6 mm, container material) nitromethane has been exploded

on impact of 0.50 caliber high-velocity bullets. In similar tests with thin-walled containers (such as 17E drums) no explosions occurred. In the absence of a vapor space above the liquid, it was difficult to achieve detonations even in thick-walled containers.

3.10.3.4 Cap Sensitivity of Nitromethane

Data from an experimental investigation of the shock initiation of liquid nitromethane with shock pressures from 7.5 to 9.5 GPa and temperatures in the unreacted liquid from 900 to 1100 K supported the thermal ignition model of one-dimensional shock initiation of nitromethane [375]. The kinetic parameters in a first-order overall rate law for the initiation-decomposition reaction in nitromethane were

$$k_1 = 2.6 \times 10^9 \exp(-23000/RT) \text{ s}^{-1}$$

which was appreciably different from the rate constant for the unimolecular bond-scission reaction. The data supported the conclusion that radical reactions significantly influence the overall initiation reaction in liquid nitromethane.

The shock and adiabatic compression sensitivity of nitromethane depends largely on the uniformity and gas content of the sample. It is known that inhomogeneities in the form of gas bubbles or suspended solid particles may result in sensitization and sustained LVD. The hot spot theory for propagation of LVD in liquids has been derived in large part from experiments with nitromethane [376, 377]. The optical observations made during the build-up to detonation and the measured shock sensitivities supported a model of initiation for heterogeneous explosives. For studies on the shock initiation of nitromethane explosions, see also [272, 378–383].

3.10.3.5 Card Gap Sensitivity of Nitromethane

Nitromethane has often been used to calibrate test methods for the determination of the sensitivity of liquid explosives; however, its sensitivity depends on the amount of dissolved gases and the eventual addition of sensitizers like amines or hydrazine [384, 385]. Unfortunately, the type and amount of sensitizer has not always been documented in the literature. The card gap sensitivity has been measured in mixtures of nitromethane (gelled with 2% dissolved polymethylmethacrylate, PMMA) with solids as hot spot generators [386]. The detonation velocity of the 2% PMMA/98% nitromethane gel was 6350 m/s. The 50% go-no go point gap width of the 2% PMMA/98% nitromethane gel was 31 mm. See also [387, 388].

3.10.3.6 Shaped Charge Penetration Sensitivity of Nitromethane

It is unlikely that nitromethane tanks in rockets will be penetrated by shaped charge jets, but this may be a special method for initiation and may be similar to meteorite impacts in outer space. This mode of initiation would be more a matter of concern if nitromethane was transported in a military vehicle in hostile territory. It may also be a method for deliberate disposal of surplus or contaminated nitromethane.

The hypervelocity jet initiation threshold criteria for neat nitromethane and homogeneously and heterogeneously sensitized nitromethane mixtures have been determined experimentally over a range of failure diameters, jet velocities from 2–9 mms and different jet diameters in two test configurations [389, 390]. The effect of temperature on failure diameter was measured. These criteria were used to define detonation and failure conditions in nitromethane and the nitromethane mixtures as a function of contact-and bow-shock conditions. A favorable correlation of threshold values was achieved by normalization of the criteria with the failure diameters.

3.10.3.7 Cook-off and Time-to-Explosion Sensitivity of Nitromethane

Thermal explosion times as a function of temperature have been measured for nitromethane, perdeuteronitromethane and 6 dinitroalkanes at 1, 10, and 50 kbar [391]. For a constant thermal explosion time of 30 s, the thermal explosion temperatures were: nitromethane (1 kbar) 627 K = 354 °C, (10 kbar) 551 K = 278 °C, and (50 kbar) 457 K = 184 °C. At 10 kbar and 546 K = 273 °C, the thermal explosion time of perdeuteronitromethane was about 10 times more than that for nitromethane. Using thermal explosion theory, for nitromethane the following Arrhenius parameters were obtained: at 1 kbar, $\log A_s$ ($A_s = A/s^{-1}$) = 40, $E = 531$ kJ (mol = 127 kcal/mol; at 10 kbar, $\log A_s = 5.3$, $E = 92$ kJ/mol = 22 kcal/mol; at 50 kbar, $\log A_s = 6$, $E = 84$ kJ/mol = 20 kcal/mol. At 50 kbar and 498 K = 225 °C the first-order rate constant for nitromethane decomposition was by a factor of more than 10^7 greater than for C–N bond fission.

Thermal explosion times were measured for nitromethane at 50 kbar and for 1,1-dinitropropane, 1,2-dinitropropane and 2,2-dinitropropane at 10 kbar in the temperature range from 423 to 623 K (150–350 °C) [392].

3.11 Explosive Performance of Nitromethane

The primary interest in this book is in nitromethane as a rocket propellant and not in nitromethane as an explosive; however, accidental explosions of nitromethane have occurred when attempting to use it as a rocket propellant, and the conditions leading to unintended initiation of explosion need to be better understood. Most of the publications on detonation of nitromethane referenced here were motivated by the use of nitromethane as an explosive or as a model substance for other explosives. Learning more about the detonation of nitromethane gives us a better understanding of the (often unwanted) detonation of other energetic materials that are used as rocket propellants. Summarizing all publications that have dealt with detonation of nitromethane would fill an entire book in its own right. We are sampling here just a random collection of publications that deal with the detonation of nitromethane, but we probably only scratched the surface of the treasure of information that can be collected if this was the main objective of a literature study. Many of the experiments described

here were done in academic settings and because nitromethane was readily available. Some investigators have failed to provide information if nitromethane was sensitized by chemical additives or not.

In the context of this book, explosions of nitromethane are more likely to be accidental than intentional, but nevertheless we are including at least a tiny fraction of all the literature available on nitromethane as an explosive. Before starting to re-evaluate nitromethane as a rocket propellant, one has to have a thorough understanding of the explosive behavior of nitromethane in order to avoid any unpleasant surprises. Rocket propellant chemists looking for more energetic rocket propellants often are treading a thin line, which is the borderline between a more energetic rocket propellant and a poor explosive. Reading the following sections will give the reader a more solid understanding of where the borderline is.

Sensitized nitromethane can be used as a liquid explosive (the acronym PLX stands for **P**icatinnny **L**iquid **E**Xplosive). The chemical sensitizer used most frequently is ethylene diamine [393, 394], but the disadvantage is that the mixture may segregate into two layers on standing. Mechanical sensitization can be achieved through the use of microballoons, hollow glass spheres or other suspended particles.

Time-resolved vibration spectroscopy with picosecond tunable mid-IR pulses was used to measure the rates and investigate the detailed mechanisms of multi-phonon up-pumping and vibrational cooling in nitromethane [395]. Both processes occurred on the 100 ps time scale under ambient conditions. The mechanisms involved sequential climbing or descending the ladder of molecular vibrations. Efficient intermolecular vibrational energy transfer from various molecules to the symmetric stretching excitation of NO₂ was observed, which helped to understand shock initiation to detonation and the sensitivities of energetic materials to shock initiation.

3.11.1 Detonation of Nitromethane Mixtures

Various additives have been evaluated to reduce the detonation sensitivity of nitromethane to make it safe for transportation and eventual use as a rocket propellant. The additives may or may not prevent the formation of the more sensitive *aci*-form of nitromethane. One of the more thoroughly investigated additives and diluents is methanol because it is used in nitromethane/methanol mixtures as a fuel for model airplane engines.

A ternary nitromethane mixture called NTN consisted of a 5/1/1 mol ratio mixture of nitromethane, tetranitromethane, and 1-nitropropane [396]. It remained liquid over the range 219–347 K (–65 to +165 °F).

Acetone has often been used as a diluent for nitromethane for academic detonation studies to slow down the detonation velocity and make it easier to observe with instruments that cannot handle the higher velocities of undiluted nitromethane [397].

The detonation of nitromethane-tetranitromethane mixtures can propagate at low and high detonation velocities [398].

The effect of acetone, nitroethane or tetrachloromethane on the detonation velocities and critical diameters of nitromethane detonation in brass tubes was tested [399]. Acetone, nitroethane, chloroform, and carbon tetrachloride were mixed with nitromethane and critical diameters in brass tubes were determined for these mixtures at 298 K (25 °C). Detonation velocities at infinite diameter and coefficients of diameter dependence of the detonation velocity were also estimated by applying a least squares method to the values obtained by accurate measurements in various charge diameters. The CJ detonation parameters were calculated and compared with the observed velocities. The lighter the diluent liquid was, the more it affected the critical diameter. Most effective was acetone, least effective was CCl_4 , nitroethane was in between. Nitroethane behaved as if it was an inert liquid on the detonation of nitromethane. The least squares fit of these data gives the following equation for the detonation velocity of nitromethane at 298 K (25 °C):

$$D = 6.2601 - 0.0405 \times (1/\phi)$$

where D is the detonation velocity in km/s and ϕ is the charge diameter in cm. The detonation velocity in infinite diameter of nitromethane would be 6260 ± 5 m/s at 298 K (25 °C) which leads to 6343 ± 5 m/s at 277 K (4 °C). This value was about 30 m/s lower than the value of 6374 m/s reported by other sources.

An experiment was devised to simulate the development of explosive reactions in a large mass of cavitated liquid in which a massive steel piston was propelled into a container (diameter 10 cm) filled with a liquid explosive into which bubbles have been introduced [400]. Most of these substances are usually assessed as “non-detonable” in the card-gap test since they have a critical diameter greater than the diameter in which the card-gap test is normally performed, usually 2.5 cm. In this experiment, transition to “detonation” has resulted using nitromethane and other marginally detonable liquids at initial piston velocities of 24–90 m/s. With further increase in scale size, abrupt accelerations of the order of those occurring in a transport container may suffice to produce explosion. A mathematical model was developed by which the hazard potential of deflagration-to-detonation transition in large masses of a reactive liquid subjected to cavitating conditions and pressure surges can be assessed from burning rate data or from small-scale experiments such as that described. A marginal explosive is any material not intended to be used as an explosive and that cannot be detonated by a No. 8 blasting cap but that is at least theoretically capable of reacting with energy release. The marginally explosive liquid was contained in a steel cylinder of 10.2-cm inside diameter, 15.2-cm length, and 1.27-cm wall thickness. Air bubbles were introduced into the liquid by means of a 15-cm length of polyvinyl chloride tubing which had two rows of pinholes at 21 bars. It was hoped that a correlation could be established between the bubbled detonation hazard and a simple bench-top test measuring the linear strand burning rate (Table 34) but that seemed to be far-fetched.

Table 34: Comparison of nitromethane experimental results with liquid strand burning rates.

Material	Composition	Threshold velocity m/s	Burning rate at 11 MPa cm/s
Nitromethane	100%	24 ± 2	0.27
Amine nitrate aqueous solution	88% ^a	24 ± 6	1.5 ^b
<i>n</i> -Propyl nitrate	100%	91.5 ± 1.5	0.21–0.12
Dinitrotoluene	100%	52.5 ± 4.54	0.29
Nitromethane/1-nitropropane mixture	52/48	~90	0.026
Nitromethane/2-nitropropane mixture	53/47	>119	0.028
Nitromethane/methanol mixture	55/45	>91	0.031

^a Proprietary composition, presumably methylammonium nitrate^b At 7 MPa

Data source: [400]

The effects of dilution of nitromethane with acetone, methanol, nitroethane, nitrobenzene, chloroform, carbon tetrachloride or bromoform on detonation velocities were examined in confined samples [401]. Several of these otherwise inert diluents actually participated in the detonating reaction.

In order to study the influence of oxygen ratio and density on the radiative properties of detonation fronts, brightness temperature measurements have been performed in nitromethane-tetranitromethane mixtures using a four-color pyrometer [402]. The experimental results showed that for the condensed nitromethane-tetranitromethane mixtures the detonation front behaved like a black body. The observed results were compared with calculated ones using several different EOS. The experiments were performed in nitromethane-tetranitromethane mixtures with the following molar proportions: $\text{CH}_3\text{NO}_2 + \alpha\text{C}(\text{NO}_2)_4$ where $\alpha = 0.071, 0.12, 0.25$, and 0.5 . A stoichiometric mixture is obtained for $\alpha = 0.25$ and when reaction partners are in such proportions that $\alpha < 0.15$, the detonation products contain solid carbon which radiated intensely.

The light emitted from the detonation front from nitromethane diluted with acetone is not very bright, and the light amplification available with an image intensifier camera is needed to make sufficiently short exposures possible. Dark waves in the detonation front of nitromethane-acetone mixtures have been photographed using pairs of image intensifier cameras, triggered at slightly different times [403]. The photographs showed the motions and changes of a complex wave structure where the average brightness did not change as much from center to edge as simple theory would predict, showing that the bright regions are high temperature regions, not just areas where less absorbing material is present ahead of the light-emitting layer.

Nitromethane is offered by some commercial nitroalkane producers as a solution in methanol. Detonation tests in mixtures of nitromethane with methanol as an inert (non-explosive) additive in steel tubes of various diameters provided information on the effect of the degree of dilution on detonability [404–406]. Mass velocity pro-

files with a chemical spike characteristic of detonation waves were recorded at the unsteady detonation front in all mixtures studied. This made it possible to distinguish the CJ state and obtain a fairly complete set of detonation parameters. Diluting the explosive with an inert liquid will slow down the detonation and make it possible to observe some of the reactions on an expanded time scale.

The shock wave sensitivity and initiating shock wave pressures of binary mixtures of nitromethane with <38% methanol and <43% nitrobenzene were determined by measurements of particle velocities by an electromagnetic method [407]. The limit initiating pressure dependences on non-explosive liquid content was linear. In both mixtures the dilution of nitromethane with non-explosive components resulted in decreasing shock wave sensitivity.

Historically, dilution of liquid explosives with inert solvents was shown to affect a degradation in the detonation performance properties of any explosive, and result in a rapid increase in the critical diameter with increasing diluent concentration. The results of a series of gas gun-driven plate impact experiments on nitromethane-methanol solutions of several concentrations, using *in situ* electromagnetic gauging to measure the initial shock state (Hugoniot) of the mixture, as well as the overtake-time-to-detonation, surprisingly, showed that the shock sensitivities did not fall off dramatically with increasing methanol concentration [408]. In fact, at some concentrations methanol appeared to sensitize nitromethane, relative to the sensitivity of neat nitromethane.

Addition of hydrazine (or any other base) will increase the sensitivity of nitromethane and addition of methanol will decrease it. It would thus be interesting to identify the point where the sensitization by hydrazine is compensated by dilution with methanol. This can be done experimentally or it can be predicted by computation [409]. An EOS of binary solutions of hydrazine and nitromethane was taking into account a possibility of formation of associated molecules due to interactions between hydrazine and nitromethane molecules. Thermodynamic calculations of detonation parameters of hydrazine-nitromethane binary systems were done for a wide range of hydrazine contents in explosive mixture. (From 0 to 75 mass-%) and for a few ternary (hydrazine-nitromethane-methanol) mixtures. Nitromethane made inert with methanol could be safely transported to the point of usage and then sensitized immediately prior to use by addition of ethylenediamine.

A study of the detonation propagation in liquid mixtures of nitromethane with azidoethanol revealed that high-velocity detonation of the mixtures of nitromethane containing less 70% azidoethanol propagated steadily in thick-walled steel tubes [410]. Addition of 20% azidoethanol to nitromethane decreased the failure diameter from 13 to 9 mm (in glass tubes).

The heat of detonation and the combustion products formed during detonation of nitromethane were compared to those obtained from detonation of HMX, TNT, and bis[2,2-dinitro-2-fluoro-ethyl]-formal (FEFO) [411, 412].

3.11.2 Measured Lead Block Indentation of Nitromethane

Nitromethane is remarkably insensitive to shock. When it does detonate, however, it was found to be a very powerful explosive, with a lead block value of 135 cm^3 [413].

3.11.3 Measured Detonation Velocity of Nitromethane

The detonation velocity of nitromethane is 6650 m/s [413]. When comparing information on the detonation velocity of nitromethane, it is important to know if the nitromethane was sensitized by adding a trace of amine. Also, some reports failed to provide information on the type of confinement in steel pipes or other container materials.

The detonation velocity of nitromethane has been measured for various charge radii and confining materials. The detonation velocity and critical diameter as a function of temperature was measured for detonation of nitromethane in glass tubes [414]. Unconfined nitromethane in a 44-mm diameter charge had a detonation velocity of 6280 m/s , but confined samples in a 40-mm O.D. steel pipe detonated with 6320 m/s [378]. A critical diameter of 27 mm for the detonation of unconfined nitromethane has been found. In a 30-mm O.D. aluminum tube with 2.5 mm wall thickness the detonation velocity was $6600 \pm 130 \text{ m/s}$ [93].

The mass velocity profile of detonating nitromethane was measured with an electromagnetic sensor that registered changes in electromotive force (e.m.f.) of a metal probe entrained in the detonation front [415]. It was concluded that detected e.m.f. was due to electrochemical processes in the vicinity of the electrode surface. The probe was made from 0.03 mm thick aluminum foil. The oscillograms showed that the leading edge of the hypervelocity wave was very steep.

Nitromethane, because it is one of the most studied liquid explosives, and is also inexpensive, was used mainly to check out an experimental procedure. A few experiments were conducted on its isomer, methyl nitrite [416]. Reaction times for shock initiation were measured for some liquid explosives using a high-speed smear camera and a modified gap-test. In all cases the reaction times decreased as the initiating shock pressure increased in the range 70 to 130 kbar, and as the pre-shock temperature was raised in the range from 278 to 313 K (5–40 °C). For constant shock pressure, the reaction time for liquid methyl nitrite was significantly less than the reaction time for nitromethane. This was consistent with thermal explosion theory, because the $\text{CH}_3\text{O}-\text{NO}$ bond strength is more than 83.7 kJ/mol (20 kcal/mol) weaker than the CH_3-NO_2 bond. Graphs were used to illustrate the effect of pre-shock sample temperature and purity of nitromethane on reaction time. The reaction time at 298 K was 0.6 s at a peak pressure of 88 kbar and 2 s at a peak pressure of 80 kbar.

The change of electrical signals arising on two metallic electrodes which are submerged in detonating nitromethane can be used to measure the detonation velocity of nitromethane [417, 418]. The electrodes were thin flat-parallel bands of magnesium, aluminum or zinc. It was concluded that the detected emf. was due to electrochemical

processes in the vicinity of the electrode surface. Electroconductivity of detonation products behind the detonation front is mainly ionic. The electrode of readily oxidizable metal sends its cations into detonation products and is therefore negatively charged and this change can be recorded.

Nitromethane did not behave according to the Campbell-Travis model for detonation in liquid explosives but showed a behavior of liquid explosives very similar to that of solid polycrystalline explosives [419]. There was no evidence for a so-called superdetonation, which would start behind and overtake the pressure shock wave.

Deuterating the methyl group in nitromethane affects the processes that occur in the detonating liquid material. A study of diameter-effect curves (i.e., inverse charge internal radius vs. steady detonation speed) for pure CH_3NO_2 and pure CD_3NO_2 revealed large differences in the infinite medium (i.e., plane wave) detonation speed and in the failure diameter of the two materials [420]. The observed large decrease in CD_3NO_2 infinite medium detonation speed, relative to the protonated material, was interpreted in terms of the theory of steady-state detonation. The increases in nitromethane's failure diameter and its steady one-dimensional chemical reaction zone length due to deuteration depend on the quantity of NM *aci*-ions present.

One group of experimenters measured a failure wave velocity of 4.75 mm/ μs for nitromethane [421], but Stanford Research Institute (SRI) measurements of 3.881 mm/ μs [422] were much closer to the 3.72 mm/ μs measured by Davis and reported by Enig and Petrone [423].

3.11.4 Critical Diameter of Nitromethane Detonations

The critical diameter of unconfined nitromethane detonations was 27 mm [378]. With moderate confinement the critical diameter dropped to below 12 mm. Propagation of detonation of unsensitized nitromethane in 12-mm diameter pipe was often incomplete and can be interrupted by orifices, right-angle bends or sudden expansion into a larger diameter pipe. This phenomenon is often used in the design of detonation traps. For nitromethane sensitized with 5% ethylene diamine, the minimum propagating thickness was 1.6 mm.

The "unconfined" failure diameter of nitromethane was found to be greater than 11.76 mm [423]. Other investigators measured failure diameters of 18 mm at 293 K (20 °C) and 15.7 mm at 303 K (30 °C) for nitromethane with weak (glass) confinement [414].

Studies of detonation failure diameters were made on four liquid nitroalkanes (nitromethane, 1,1-dinitroethane, 1,1-dinitropropane, and 2,2-dinitropropane) under extreme conditions of lead block confinement and weak shell confinement [424]. Shock-induced reaction times and failure wave velocities in decaying detonation waves were measured and used to calculate the failure diameters of these unconfined liquids. The values of the unconfined failure diameters were acceptable when the CJ pressures were accurately known and the experimental shock-induced reaction times and failure wave velocities were used in the calculations.

The critical detonation failure diameter of nitromethane detonations below which the detonation is either slowed down, switches to a low-velocity detonation mode or is quenched altogether depends on many variables, such as type and amount of sensitizer, type and amount of diluents, gas saturation, pressure and temperature [425, 426]. It also depends on the sequence and timing of multiple shocks (incident and reflected) [427].

A magnetodynamic method for determining the particle velocity was used for the measurement of the velocities of detonation products of low-order liquid explosives (nitromethane and isopropyl nitrate) [428]. The objective was to determine the approach to equilibrium in the reaction medium. By an assay using the characteristics of the media in the presence and the space-time diagram of the sensor, it was shown that the profile-characteristic speeds highlight three areas. Characterized by the first acceleration sensor in the explosive charge, the second related to the re-ignition mechanism of the detonation front near the sensor, the third due to relaxation effects of the detonation products.

Taking advantage of the phenomena of nitromethane electric polarization under shock, the relation between pressure and particle velocity and the influence of pressure conditions on induction delays of the explosive were measured [429]. The pressure was generated either by an incident shock wave or by a shock wave reflected within a medium prepressurized by a first shock wave. It was observed that nitromethane compressed at 11 GPa by means of two shock waves did not detonate (during the observation time of about 0.5 μ s), while in the case of a single shock wave of the same amplitude the induction delay was lower than 0.1 μ s. These results showed the important role of temperature, as opposed to that of pressure.

3.11.5 Theoretical Prediction of Detonation Properties of Nitromethane

When studying the effects of replacing one of its hydrogen atoms with bromine or all its hydrogen atoms with deuterium, it was found that the failure diameter of deuterionitromethane in glass was more than double that of normal nitromethane. Similarly, critical diameters and diameter effect curves for nitromethane, bromonitromethane, and deuterionitromethane confined in brass were measured and deuterionitromethane had a larger critical diameter in brass than either nitromethane or bromonitromethane [430].

3.11.6 Hot Spot Theory for Detonation of Nitromethane

Small particles can be added to nitromethane to obtain a well-characterized heterogeneous explosive for experimental studies of shock initiation due to **hot spots**. Computational simulations of hot-spot initiation require a model with a good set of chemical reaction rates and an EOS with good thermal properties. Detonation wave properties of a model were compared with experimental data, also for an underdriven or CJ detonation wave in pure nitromethane [431].

3.11.7 Low Velocity Detonation of Nitromethane

Instrumented detonation tests showed that nitromethane is able to undergo a low-velocity detonation (LVD) reaction if confined in a steel tube and subjected to a shock wave of appropriate strength [432]. It was concluded that the occurrence of LVD in nitromethane requires such conditions as to enable both cavitation of the liquid and sufficient time for explosive reaction. The latter condition means a rather strong confinement, because of the relatively slow reaction rate of nitromethane. The results may lead to an improved design of a card gap test for the investigation of the shock wave sensitivity of liquids.

It is well known that in liquid explosives, propagation is by HVD or LVD, depending on the level of the initiating shock pressure. Two physical models emphasizing either the role of cavitation by precursor waves or the role of a Mach disc have been proposed to describe the propagation of LVD in liquid explosives like nitromethane. The structure of LVD in nitromethane was investigated optically using high-speed photography [433, 434]. Stable LVD in clean nitromethane was not observed, although a transient LVD was found. The generation of cavitation bubbles and the formation of a Mach disc play an important role in the propagation of LVD in nitromethane.

It was proposed that the propagation mechanism of LVD in liquid explosives is not a self-reactive detonation, but rather a supported-reactive detonation from the cavitation field generated by precursor shock waves; however, the detailed structure of LVD in liquid explosives has not yet been fully clarified. High-speed photography was used to investigate the effects of the precursor shock waves on LVD propagating in nitromethane held in various container materials [435]. Stable LVD was not observed in all containers, although transient LVD was observed. The interaction of multiple precursor shock waves, multiple oblique shock waves, and the cavitation field make the structure of LVD very complicated.

Some liquid explosives have two different types of detonation behaviors: HVD or LVD. The detonation behavior (LVD or HVD) depends on the energy of the initiating shock pressure. Multiple shock waves propagating in non-detonating nitromethane were observed for shock pressures below the range required for LVD, while above the LVD threshold range, HVD prevails [436].

The detonation velocities of nitromethane are 6700 m/s in HVD and 2500 m/s in LVD mode. In liquid explosives, the highest pressure of LVD changes with the type of explosive and conditions and has destructive power equivalent to C-J HVD. In an instrumented card gap test with PMMA gap width from 0 to 200 mm, both LVD and HVD could be observed, depending on the gap width [437]. The detonation velocity was the same if the tests were conducted in copper or aluminum cylinders.

3.11.8 Sensitizers for Nitromethane as an Explosive

There are two methods for sensitization of nitromethane: chemical sensitization and mechanical sensitization. The mechanism of chemical sensitization is based on the

formation of *aci*-salts of nitromethane, which are much more sensitive than their parent compound. Sensitized nitromethane can be used as a liquid explosive (e.g., PLX). The sensitizer used most frequently is ethylene diamine. The mechanism of mechanical sensitization is due to inhomogeneities of materials with different sonic velocities, where shock waves may focus like light focuses optically in a biconvex lens and the elevated pressure initiates and propagates a detonation. Hollow glass spheres called microballoons have been added which collapse under the high pressure of a shock wave and propagate the detonation by adiabatic compression of the gas in the bubble.

3.11.8.1 Chemical Sensitization of Nitromethane

Amines are known to sensitize nitromethane to shock initiation. Data from a series of initiation experiments in which nitromethane was sensitized with diethylenetriamine (DETA, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$) showed some of the quantitative aspects of this amine sensitization [438, 439]. Testing different amines there was a correlation between the base strength $\text{p}K_{\text{a}}$ of the amine and the card gap width needed to prevent detonation. It was shown that the time delay to the appearance of a detonation front in nitromethane can be reduced from 18 μs to less than 1 μs with 0–5% DETA, and it was also seen that an overdriven detonation velocity appeared in solutions containing from 0.02% to 0.1% DETA. This overdriven detonation appeared to average as high as 6.76 mm/ μs over a run distance of about 10 cm at 0.05% DETA. The results of 1-in. cylinder tests were compared with calculated data. When testing different amines, there was a correlation between the base strength $\text{p}K_{\text{a}}$ of the amine and the card gap width.

The sensitivity of nitromethane and other nitroalkanes after addition of small amounts of amines was measured in a Naval Ordnance Laboratory (NOL) large-scale gap test [440].

Thermal decomposition experiments yielded substantially lower activation energies and an empirical sensitization factor for nitromethane mixtures that decreased as the nitromethane *aci*-anion concentration increased. Kinetic deuterium isotope analysis pointed to C–N bond scission as the rate-determining step in the thermal decomposition of nitromethane and nitromethane-amine mixtures [441, 442]. Laser ionization mass analyses of the solid nitro compound-amine mixtures indicated significant changes in the fragmentation patterns, with removal of the nitro group occurring in all cases as the first step in the breakdown of the mixtures, which was not the case for the pure materials. New absorption bands appeared in the UV/visible spectra of all the sensitized materials. These bands were ascribed to an intermolecular charge transfer from the nitrogen of an amine group to the anti-bonding orbital of the nitro group. It was shown that with small amounts of amines present, each amine molecule can form a complex with as many nitro compound molecules as there are amino groups on it. Combined with the assumption that the C–N bond breakage is the rate-determining step in the thermal decomposition of these materials, and the suggestion that

the dominant mechanism in their ignition/detonation is most likely thermal in origin, the sensitization mechanism can be explained.

Electronic and chemical changes in shock-compressed nitromethane and a mixture of nitromethane with ethylenediamine (0.1 mass-%) have been examined using time-resolved optical absorption spectroscopy under stepwise pressure loading to 14 GPa [443]. Despite the low amine concentrations, profound differences were observed in the absorption spectra of pure and sensitized nitromethane. The changes in the absorption spectrum of pure nitromethane involved a maximum absorption edge shift of 20 nm and were completely reversible. In contrast, the mixture showed an irreversible time-dependent shift in the absorption edge of up to 90 nm toward longer wavelengths. A substantial component of the shift took place after the sample had reached peak pressure. The time dependence and irreversibility of the absorption edge shift must be caused by a chemical change with the sensitization of nitromethane in the presence of amines.

The concentration of *aci*-anions in nitromethane/DETA mixtures can be measured by UV absorption and electrical conductivity [444]. The *aci*-anion is air-sensitive and its concentration will decrease if exposed to air.

The effect of varying the explosive sensitivity for a heterogeneous explosive charge formed of a packed bed of glass beads impregnated with liquid nitromethane sensitized with DETA was investigated [445]. The changes in the dependence of critical charge diameter on bead size was investigated at concentrations of 5, 10, and 15% DETA over a range of bead diameters from 66 μm to 2.4 mm. Additional measurements are also performed on the critical diameter of the homogeneous liquid explosive itself without any beads inserted.

The mechanism of sensitization of nitromethane by amines has been investigated by means of a computational density functional theory method [446]. Of the various possibilities examined, the most reasonable was that one involving the *aci* (nitronate) ion in an activated form which can interact with the amine eventually yielding another amine and the nitrite ion. The key features of this process are firstly an activation barrier less than the C—NO₂ dissociation of nitromethane, secondly a net release of energy and thirdly products that can sustain the reaction.

The critical diameter for detonation was measured for nitromethane sensitized with two different amines: DETA and triethylamine (TEA) [447]. The critical diameter in glass and polyvinylchloride tubes was found to decrease rapidly as the amount of sensitizer was increased, then increased past a critical amount of sensitizer. The critical diameter reached a minimum at an optimum concentration of sensitizer. It was also found that the critical diameter was lower with DETA than with TEA.

The effect of the addition of small amounts of DETA on the chemical reaction zone length of detonating liquid nitromethane was studied by making accurate measurements of the detonating materials' diameter-effect curves (i.e., detonation speed versus lateral charge size) as a function of the amount of chemical sensitizer added [448]. Detonation speed experiments were performed with additions of the organic base in

amounts between 0.00 and 0.25 mass-%. Reductions in the chemical reaction zone length of as much as 25% were produced by base addition. Most of the reduction in length was produced by very small amounts of base addition, i.e., ca. 0.05 mass-% of base or less (i.e., 1 molecule of the base per 3300 nitromethane molecules or less). Detonation speeds were measured for five compositions of nitromethane and base as a function of the charge internal diameter.

In addition to ethylene diamine, other amines used as sensitizers are DETA [449]. It was shown that small (0.0125–15%) additions of DETA lead to a qualitative change in the flow pattern in the reaction zone of detonating nitromethane. After the shock passed through, the mass flow rate continued to increase for about 10 ns, reached a maximum, and only then decreased. This is due to a sharp increase in the initial reaction rate.

Initiation of the shock-driven chemical reactions and detonation of nitromethane can be sensitized by the addition of weak bases; however, the chemical mechanism by which sensitization occurs remains somewhat unclear. The shock-driven chemical reaction in nitromethane and in nitromethane sensitized with DETA, using a sustained 300 ps shock was monitored with visible transient absorption spectra and measured interface particle and shock velocities of the nitromethane solutions using ultrafast dynamic ellipsometry [450]. Reaction occurred at an interface particle velocity of >2.4 km/s for neat nitromethane and >2.2 km/s for nitromethane with 5% DETA. The chemical reaction mechanisms for shocked nitromethane and nitromethane with DETA seems to be the same.

3.11.8.2 Mechanical Sensitization of Nitromethane

Another method to achieve mechanical sensitization of nitromethane is the addition of microballoons, hollow glass spheres. Another method of sensitization would be to create a nitromethane foam with many bubbles suspended in the (gelled) liquid.

Shock interactions at density discontinuities in nitromethane compressed by a planar shock wave can reduce the induction time for initiation of detonation [451]. The initiating efficacy of the discontinuity formed by a solid inclusion immersed in nitromethane strongly depends on the material used (silica) and the particle size.

Local hot spots behind inhomogeneities apparently produce an effective chemical reaction rate, which allows a stable steady-state flow at a much smaller charge size than is possible in homogeneous nitromethane confined in Pyrex tubes. Detonation-velocity measurements were carried out on cylindrical charges at a number of radii thus generating diameter-effect curves [452]. Silica particles with a known particle-size distribution were added to the nitromethane to produce a heterogeneous material and were held in suspension with a guar-gum gelling agent.

Mixtures of nitromethane and PMMA containing glass microballoons exhibited detonation properties more like solids than liquids because under shock conditions the heterogeneities produced hot spots which increased the energy release rate in

the nitromethane. Experiments were undertaken to determine **(1)** the relationship between steady-state detonation velocity and reciprocal charge size (the diameter effect curve) and **(2)** the critical diameter for mixtures of nitromethane-PMMA containing different concentrations up to 4.36% of glass microballoons with well-defined diameters in the range 37–50 μm [453]. Sets of experiments were performed in steel and plastic tubes to determine how the diameter effect curve and critical diameter of these mixtures.

The critical (i.e., failure) charge diameter and detonation velocity of liquid nitromethane sensitized with 15 mass-% of DETA in densely packed beds of solid spherical glass beads 66 μm –2.4 mm in diameter were systematically measured in unconfined charges over a wide range of bead sizes [454, 455]. It was found that there exists a critical bead size above which the critical diameter decreases with increasing bead size and below which it decreases with decreasing bead size. This indicated an abrupt change in the mechanism of propagation at the critical bead size.

Any inhomogeneity, solid or gaseous, will enhance LVD sensitivity. Nitromethane-silica mixtures containing size-selected silica beads at 6 mass-% were subjected to accurate shock input pressures [456]. The addition of beads was found to influence the shock sensitivity of the mixtures, with the smaller beads being more sensitizing than the larger beads, lowering the shock initiation threshold for the same run distance to detonation compared with neat nitromethane.

3.11.9 Explosive Performance of Nitromethane Mixtures

There are many nitromethane mixtures that have been evaluated as two-component explosives. Most of these are mixtures of nitromethane with liquid or solid oxidizers. These mixtures were formulated to be near stoichiometric for combustion to CO_2 . Mixtures can be homogeneous or heterogeneous (slurry or suspension). Other homogeneous mixtures with inert solvents were made to desensitize nitromethane and make it safe for transport.

Examples for stoichiometric liquid-liquid mixtures of nitromethane are those of nitromethane with nitric acid or tetranitromethane.

Liquid-solid explosive combinations are those of nitromethane with ammonium nitrate or ammonium perchlorate, also used commercially for demolition and excavation applications.

The critical diameter of nitromethane/acetone mixtures depends on the strength of the confining shell. The ratio of critical diameters of unconfined vs. confined 92 nitromethane/8 acetone mix is 20. The critical diameter of liquid explosives as a function of the wall thickness decreased sharply at comparatively thin wall thicknesses [457].

The width of the dark zone in streak-camera records defines the reaction zone region in detonating liquid explosives. A strongly boosted solution of 75/25

nitromethane/acetone showed a shortened reaction zone out to about 25 cm of free run [458]. The steady-state reaction time of diluted nitromethane was 0.4 μ s. The measured reaction time in undiluted nitromethane was 22 ns [459].

The effect of additions of HNO_3 , HClO_4 , CH_3COOH , methyl nitrate, triethylamine, diethylamine, acetone, methanol, CCl_4 or HCCl_3 on the detonation properties (detonation velocity and critical diameter) of nitromethane was studied in glass and steel tubes [460].

The detonation of mixtures of concentrated (94–100%) nitric acid with nitromethane was studied and the detonation failure diameter was measured in glass tubes [461]. For mixtures of nitric acid with nitromethane the minimum values of critical diameter were smaller than 1 mm and occurred at zero oxygen balance of the mixtures (stoichiometric ratio).

Mixtures of 2-nitropropane and nitric acid or mixtures of nitromethane with ammonium perchlorate (AP) are highly detonable and could be used as two-component explosives. The propagation and extinction of detonation in heterogeneous mixtures of spherulized AP with mean diameters of 9, 35, 90, 200, and 400 μ m were measured to study the effect of charge diameter, equivalence ratio of the mixture and the size of particles on the detonation velocity and critical diameter [462].

Sensitized nitromethane can be used as a field-filled homogeneous filling in shaped charges for the disposal of unexploded ordnance for both commercial and military applications [463].

Ultrafast optical interferometry was used to measure the Hugoniot pressure curve of an oxygen-balanced mixture of nitromethane and hydrogen peroxide (NM/HP) and to compare it with Hugoniot data for pure nitromethane and a 90% hydrogen peroxide/water mixture, as well as theoretical predictions [464, 465]. Unlike the Hugoniot of either HP or nitromethane, in which measured shock speeds deviate to values greater than the unreacted Hugoniot for piston speeds larger than the respective reaction thresholds, in the NM/HP mixture the shock speed deviations were lower than the unreacted Hugoniot. If this is a signature of chemical initiation, it would suggest that the process may not be kinetically limited.

3.11.10 Applications of Nitromethane

Nitromethane is widely used as a solvent. Solvent applications include polymers and coatings, as extraction or partition solvents, as reaction media or solvent in crystallization of organic compounds.

Large quantities of nitromethane are used as a paint, lacquer, and adhesive solvent. It is used as the solvent for cyanoacrylate polymers in “super glue”.

Nitromethane is sometimes used as a racing fuel additive in internal combustion engines in dragsters [466–468]. For that application it is usually mixed with methanol and sold under various brand names. One kilogram of nitromethane needs only 1.7 kg of air to burn. The same amount of gasoline needs 14.6 kg of air for optimum com-

bustion. That means that the cylinder of an engine can burn roughly 8.7 times more nitromethane on a stroke, generating 2.3 times more power than gasoline, but this is hard on the pistons and bearings, and the engines may not last very long. Some foolhardy racing car enthusiasts attempted to push the performance even further by adding hydrazine to the nitromethane, not realizing that the mixture is highly explosive. Nitromethane mixtures are used as the fuel in glow-plug model airplane engines (often with castor oil as the lubricant, giving that characteristic odor of model airplane engine exhaust). In model airplane engines and glow-plug fuel, the primary ingredient is generally methanol with some nitromethane mixed in (10–65%, but rarely over 30% since nitromethane is more expensive than methanol) and 10–20% lubricants (usually castor oil and/or synthetic oil). Nitromethane has been evaluated as the fuel for miniature combustion piston engines for use in unmanned aerial vehicles (UAV).

Nitromethane has been tested in many laboratories as a rocket propellant in static firings but has not (yet) found any practical applications (see *Encyclopedia of Monopropellants*). The detonation of nitromethane is of practical interest for more than one reason. Nitromethane can be used as a propellant in pulsed detonation engines and rotating detonation engines, which is another reason why detonation of nitromethane is discussed here from both a theoretical and experimental point of view.

Sensitized nitromethane can be used as a liquid explosive (PLX). Nitromethane in combination with ammonium nitrate has been used as a blasting agent which is more energetic but also more expensive than ammonium nitrate fuel oil (ANFO).

Nitromethane-based liquid explosives have been evaluated by the military for minefield clearance and tunnel destruction and excavation [469, 470]. Extensive safety tests on nitromethane were done to support such military applications. Such safety tests can benefit other applications of nitromethane. In the patent literature there are numerous patents on gelled nitromethane with addition of oxidizers like ammonium nitrate or metals with high heat of combustion like aluminum flakes. A preferred gelling agent for nitromethane is galactomannan cyanoethyl ether (US Pats. 3666577, 3755292, and 3806465).

Nitromethane has been evaluated as a liquid gun propellant. In order to reduce its sensitivity, nitromethane was diluted with methanol [471, 472].

Nitromethane is miscible with high proportions of aromatic hydrocarbons and only sparsely miscible with aliphatic hydrocarbons at low concentrations. It is therefore a suitable solvent for the separation of aromatics from aliphatics in petroleum distillates by solvent extraction techniques. Nitromethane may also be incorporated into diesel fuels with up to 2% by mass to help increase power and to reduce exhaust smoke and improve the cetane number.

4 Dinitromethane

Dinitromethane, $\text{H}_2\text{C}(\text{NO}_2)_2$, DNM, CAS RN [625-76-3] is a volatile liquid with a sharp, acrid odor. It is unstable at room temperature and decomposes with evolution of nitrogen dioxide. It can be kept for longer periods only at temperatures below 273 K (0 °C) or in solution in inert solvents like benzene or tetrachloromethane. Although it has a higher oxygen content than nitromethane, it is not useful as a rocket propellant. Some of its salts are more stable than the parent compound. Dinitromethane is formed as an undesirable byproduct during the production of 1,1-diamino-2,2-dinitroethene (DADNE, FOX-7).

Treatment of the potassium salt of dinitromethane with hydrogen fluoride in ether gave a fairly stable dinitromethane that could be distilled [473, 474].

4.1 Physical Properties of Dinitromethane

The boiling point of dinitromethane is 312–313 K (39–40 °C) at 26 Pa (2 mm Hg), the refractive index n_D^{20} is 1.4480 (but another source listed 1.4732) and the density at 293 K (20 °C) is 1.524 g/cm³.

4.1.1 Thermodynamic Properties of Dinitromethane

Dinitromethane is rarely mentioned in the literature. The heat of combustion is 574 ± 0.8 kJ/mol (137.2 ± 0.2 kcal/mol), from which an enthalpy of formation of -105 ± 0.8 kJ/mol (-25.2 ± 0.2 kcal/mol) can be derived for the liquid. The enthalpy of formation of gaseous dinitromethane was estimated at -59.4 kJ/mol (-14.2 kcal/mol) [173]. An experimental enthalpy of formation of the vapor, $\Delta H_{298} = -61.5$ kJ/mol = -14.7 kcal/mol taken from Knobel et al. was recommended by NIST 97. It is not known what type of correction was applied to those data.

4.1.2 Molecular Structure of Dinitromethane

The molecular structure of dinitromethane was modeled by computational chemistry using different computational methods and compared to the structures of other nitromethanes.

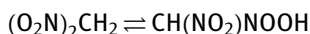
The molecular geometries of dinitromethane and trinitromethane were optimized and their harmonic force fields were calculated [475]. The force fields obtained made it possible to reliably interpret the vibrational spectra of dinitromethane, trinitromethane, and a number of isotopomers of trinitromethane. The hybrid density functional method used was shown to accurately predict the structural parameters and vibrational frequencies for polynitromethanes.

A quantum-chemical study of reactions leading to the formation of *aci*-dinitromethane and its decomposition with elimination of water employed an *ab*

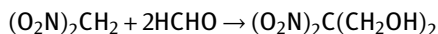
initio RHF method with inclusion of electron correlation, a density functional theory approach and a semiempirical method [195]. For dinitromethane, the barrier to reaction was substantially lower than for nitromethane. The estimates of the heights of the energy barriers to formation found from DFT calculations (218.5 kJ/mol for *aci*-DNM) were suggested to be the most reliable.

4.2 Chemical Properties of Dinitromethane

Dinitromethane can exist in two tautomeric forms:



Similar to trinitromethane, dinitromethane is an acid and forms a variety of salts which are only a little more stable than the parent acid. Dinitromethane reacts with two molecules of formaldehyde to form the diol



which can be used to form thermally more stable esters.

Gaseous products of the thermal decomposition of dinitromethane and potassium dinitromethanide were investigated by simultaneous DTA/FTIR analyses under isothermal or non-isothermal DTA conditions [476]. Nitrous oxide and carbon dioxide were detected by FTIR.

4.2.1 Salts of Dinitromethane

Seven salts of dinitromethane with organic bases were prepared by two different methods: either by neutralization of dinitromethane solutions with the appropriate base or by metathesis reactions between dinitromethane sodium salt and a respective organic base salt [477]. Crystal structures of formamidinium dinitromethanide, acetamidinium dinitromethanide, and propionamidinium dinitromethanide and ^1H and ^{13}C chemical shifts of all compounds were determined by XRD and NMR and their thermal stabilities were determined by DSC. These salts are more stable than the parent acid and are potentially useful as propellant ingredients.

Single crystals of the potassium, rubidium, and cesium salts of dinitromethane were examined by XRD, and the structure of the dinitramidate anion was derived from the Weissenberg XRD diagrams [478]. The N—C—N bond angle is 121° . The space group of all three salts is $P\bar{1}$. The nitro groups of the anion are rotated about 10° out of the plane of the N—C—N bonds. The potassium salt is less stable than the rubidium salt.

Guanidinium, triazolium, and tetrazolium dinitromethanide salts are thermally stable and can be relatively insensitive to impact [479].

4.2.2 Salts of Dinitrosomethane

Dinitrosomethane is an acid like dinitromethane, it also forms salts with a wide range of metals and bases. The blue color indicates that they may contain free radicals. Alkali dinitrosomethanides $M[HC(NO)_2]$ [$M = Li, Na, K, Cs$ K(18-crown-6-polyether)] were prepared, fully characterized, and are stable at ambient temperature [480]; however, alkali dinitrosomethanides are heat-sensitive and shock-sensitive and are highly explosive. It is doubtful if they can ever be used as rocket propellants.

5 Trinitromethane

Trinitromethane, also known as nitroform, NF, $HC(NO_2)_3$, CAS RN [517-25-9] is an oxidizer. Trinitromethane by itself is not typically used as an oxidizer or monopropellant. It is a net oxidizer since its oxygen balance is +37.1%. The physical and safety properties of trinitromethane are summarized here while applications of its salts as monopropellants are discussed in *Encyclopedia of Monopropellants*, and applications of its salts as solid propellant oxidizers will be discussed in future volumes of this series of *Encyclopedia of Rocket Propellants*. Trinitromethane may be an intermediate in the preparation of trinitromethanide salts and therefore its physical, chemical, and safety properties must be known. Trinitromethane is useful for introducing the trinitromethyl group into other moieties.

5.1 Production of Trinitromethane

Tetranitromethane is easier to obtain than trinitromethane and is a starting material for trinitromethane. The synthesis of trinitromethane is the removal of one nitro group from tetranitromethane by a reducing agent. Trinitromethane and its alkali metal salts can be prepared from tetranitromethane by reaction with an alkali metal nitrite and some alkali metal hydroxide or hydrogen carbonate which later regenerates some of the nitrite [481]. The reaction mixture at 323 K with 50/50 methanol/water as a solvent turns from colorless to red to yellow and becomes homogeneous within 20 min.

The various steps of the production of trinitromethane from acetylene involve nitration of acetylene, isolation of trinitromethane and recovery of concentrated nitric acid and oxides of nitrogen. The economic aspects and the layout of a production plant capable of producing 60 tons per year operating one shift per day were optimized [482].

Although nitroform is usually used up quickly at the same place where it is produced, it can be transported as a stabilized aqueous solution with urea, a water-soluble carbamic acid alkyl ester or a mixture of urea and a water-soluble carbamic acid alkyl ester as stabilizing agent [483].

4,6-Dihydroxypyrimidine (DHP) is a useful intermediate for the synthesis of trinitromethane without unwanted byproducts. DHP was prepared via cyclocondensation of dimethyl malonate and formamide as raw materials. Nitroform could then be obtained via nitration hydrolysis reactions of DHP [484]. Nitration of 4,6-dihydroxypyrimidine in sulfuric acid gave nitroform as the sole product by the formation of an intermediate, 5,5-dinitro-4,6-dihydroxypyrimidine, that underwent hydrolysis in the nitrating acid to *gem*-dinitroacetyl formamidine. This compound was further nitrated in the same reaction mixture to trinitroacetylformamidine, which finally underwent hydrolytic cleavage to nitroform. The *gem*-dinitroacetyl ureas were also able to produce nitroform on nitration.

Optimization studies showed that for up to 80% yield, the optimal reaction conditions were the molar ratio of nitric acid to DHP = 5 : 1, the molar ratio of sulfuric acid to nitric acid = 3.5 : 1.0, a reaction temperature of 318 K (45 °C) and a reaction time of 2 h [485]. Subsequently, hydrazinium nitroformate (HNF) with a purity of 98.9% was synthesized from the nitroform that was made by this method.

Trinitromethane can be made by incomplete nitration of acetic anhydride. Complete nitration would lead to tetranitromethane.

Trinitromethane can be made by treating acetone with an excess of nitrating acid at 333–373 K (60–100 °C) [486]. Instead of acetone, one can start with isopropanol, which most likely becomes oxidized to acetone and undergoes subsequent nitration [487, 488]. The effect of the nitronium NO_2^+ ion on the preparation of nitroform from isopropanol was investigated by using white fuming nitric acid (WFNA) and $\text{H}_2\text{SO}_4/\text{HNO}_3$ as nitrating agents. The results indicated that WFNA showed a better efficiency for the studied reaction. Furthermore, the effect of specific factors, such as reaction temperature, reaction time and molar ratio of nitrating agent to isopropanol, on the yield of nitroform was investigated. Pure nitroform could be obtained under optimized condition with a yield of 51%.

Nitroform can be prepared from a series of α -methyl carbonyl compounds such as acetylacetone as substrates using WFNA as the nitrating system [489]. Operating parameters such as additives, reaction temperature and time were optimized. Optimized conditions gave a nitroform yield of 40.8%.

Nitroform can be prepared by reaction of isopropanol with WFNA and concentrated sulfuric acid in dichloroethane as the solvent [490]. The reaction mixture was allowed to cool down and poured into ice water. Steam distillation gave trinitromethane in 25% yield which was washed first with diluted alkali and then with water. The product was then dried over anhydrous sodium sulfate.

5.2 Physical Properties of Trinitromethane

Physical and safety properties of trinitromethane are described in [491]. The physical properties of trinitromethane are summarized in Table 35.

Table 35: Physical properties of trinitromethane.

Property	S.I. units	Other units	Source	References
Molecular mass	151.0353 g/mol	6.621 mol/kg	NIST	[91]
Melting point	295 K 292 K	22 °C 19 °C	72 °F	Lewis and Smyth 1939 [492]
	299.4 K	26.3 °C	Konkova and Matyushin	[493]
	287.4 K	14.3 °C	Anonymous NIOSH 1981	[84]
Boiling point at 23 mbar pressure	321 K	48 °C	118 °F	Meyer, Koehler and Homburg [96]
Boiling point at 22 mm Hg pressure	318–320 K	45–47 °C	Kaye-Fedoroff Vol. 8	[491]
Density at 293 K		1.479 g/cm ³	Anonymous NIOSH 1981	[84]
Density at 298 K		1.59 g/cm ³	Meyer, Koehler and Homburg	[96]
Density at 297.4 K		1.5967 g/cm ³	Kaye-Fedoroff Vol. 8	[491]
Refractive index $n_D^{24.3}$		1.44174	Kaye-Fedoroff Vol. 8	[491]
Enthalpy of formation ΔH_f°	–38.5 kJ/mol	–254.9 kJ/kg	–9.21 kcal/mol JANA F 1964	[494]

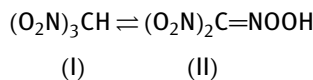
Trinitromethane is quite soluble in water: 16.7 g/100 mL water at 273 K = 0 °C and 193.8 g/100 mL water at 333 K (60 °C). It is only sparsely soluble in ethanol: 5.29 g/L ethanol.

5.2.1 Crystal Structure of Trinitromethane

Trinitromethane crystallizes in space group C_3 . Surprisingly, no intermolecular C—H $\cdots$ O hydrogen bond bridges are formed [495]. Recrystallization of $(O_2N)_3CH$ from dioxane forms a 2 : 1 adduct $(O_2N)_3CH\cdots O(CH_2CH_2)_2O\cdots HC(NO_2)_3$ with dioxane which exhibits the shortest C—H $\cdots$ O bonds with a C—O distance of only 2.94 Å [496].

5.2.2 Molecular Structure of Trinitromethane

Trinitromethane (nitroform) can exist in two tautomeric isomers: a nitro form (I) and an *aci*-form (II):



The colorless form (I) exists in solutions acidified with hydrochloric or sulfuric acid and also in anhydrous benzene, carbon disulfide, or ether. Aqueous and basic solutions are intensely yellow due to the presence of the form II.

Trinitromethane has a propeller-like arrangement of its nitro groups, the symmetry of which is possibly relating to its lower than predicted (although still high) acidity, its *aci*-tautomerization, and the absence of expected very short C—H...O intermolecular bridges in the crystal is unusual [497]. A combination of crystallographic and computed data was used to explain the anomalous acidity which can be attributed to intramolecular and/or intermolecular electrostatic interactions. Decomposition via C—NO₂ bond scission may occur before *aci*-tautomerization can take place.

The dipole moment of trinitromethane is 2.71 D in accordance with its unsymmetrical tetrahedral structure [492].

The molecular geometries of dinitromethane and trinitromethane were optimized and their harmonic force fields were calculated [475]. The force fields obtained made it possible to reliably interpret the vibrational spectra of trinitromethane and a number of isotopomers of trinitromethane. The hybrid density functional method used was shown to accurately predict the structural parameters and vibrational frequencies for polynitromethanes.

Equilibrium angles, barriers to internal rotation and electronic structure of trinitromethane and its halo derivatives were described in [498].

5.2.3 Optical Properties of Trinitromethane

5.2.3.1 Infrared Spectra of Trinitromethane

The vibrational spectrum of trinitromethane was interpreted in terms of the additive interatomic interaction model on the basis of experimental IR and Raman spectra of HC(NO₂)₃, DC(NO₂)₃, HC(¹⁵NO₂)₃ and normal coordinate analysis [499]. The frequency assignment results were used in discussing its structure. It was shown that the symmetry of trinitromethane is below C₃ in the liquid state.

5.2.4 Thermodynamic Properties of Trinitromethane

Up until 1998, data reported in the literature for the enthalpy of formation of trinitromethane were quite contradictory. Older sources reported an enthalpy of formation of -77.8 kJ/mol (-18.6 kcal/mol) or -25.9 kJ/mol (-6.2 kcal/mol) for solid

trinitromethane and -21.3 kJ/mol (-5.1 kcal/mol) or -9.2 kJ/mol (-2.2 kcal/mol) for molten trinitromethane. The *NIST Chemistry WebBook* lists three different enthalpies of formation for liquid trinitromethane ranging all the way from -77.95 to -68.0 ± 3.1 to -32.1 kJ/mol but does not judge which one is the most accurate. The JANAF ingredients database (Jan 1964) listed an enthalpy of formation of -38.5 kJ/mol (-9.21 kcal/mol) for liquid trinitromethane.

The heat of combustion of trinitromethane was first reported as -458 kJ/mol ($-109.58 \text{ kcal/mol} = 726 \text{ cal/g}$) based on a single calorimeter run [15].

For the heat of combustion of trinitromethane, Holcomb and Dorsey gave a value of 458.6 kJ/mol (109.6 kcal/mol) and Picatinny Arsenal reported 521 kJ/mol (124.5 kcal/mol). An interpolation from a graphic method gave 526 kJ/mol (125.75 kcal/mol) [180].

Later, the heats of combustion of solid and liquid trinitromethane were determined in a microcalorimeter as $792.2 \pm 3.2 \text{ cal/g}$ and $816.5 \pm 2.8 \text{ cal/g}$, respectively [500, 501]. From these numbers the enthalpy of formation of solid nitroform at standard conditions have been calculated as being $-48.12 \pm 2.1 \text{ kJ/mol}$ ($-11.5 \pm 0.5 \text{ kcal/mol}$) for the solid, and for the liquid phase $-33.05 \pm 1.67 \text{ kJ/mol}$ ($-7.9 \pm 0.4 \text{ kcal/mol}$). From the relationship of the pressures of the saturated vapor over solid and over liquid trinitromethane the heat of sublimation was calculated as being $46.0 \pm 0.4 \text{ kJ/mol}$ ($11.0 \pm 0.1 \text{ kcal/mol}$), and the heat of fusion as being $32.6 \pm 0.4 \text{ kJ/mol}$ ($7.8 \pm 0.1 \text{ kcal/mol}$). The energy of dissociation of the C-H bond in trinitromethane was determined to be $420 \pm 12 \text{ kJ/mol}$ ($100.5 \pm 3 \text{ kcal/mol}$).

Enthalpies of formation of trinitromethane and its salts, C-N bond energies in nitromethanes, nitro group substituent effects on atomization enthalpies and formation enthalpies of nitromethyl radicals were summarized and reviewed on the basis of literature data and new thermochemical measurements [502].

The kinetics of thermal decomposition of nitromethanes provided a set of energies of dissociation of C-NO₂ bonds based on enthalpies of formation from research and literature data [37, 38]. These values enabled one to determine the enthalpies of formation of nitromethyl free radicals and the energy of dissociation of C-H bonds and the energies of dissociation of -NO₂ groups from radicals of the three nitro derivatives of methane.

The standard enthalpies of formation at 298 K and heat capacities and entropies in the temperature range of 300–5000 K for trinitromethane and a range of other nitro compounds were computed by means of a density functional theory in quantum chemistry [41].

The heat of vaporization of trinitromethane was estimated at 54.8 kJ/mol but this contradicts a heat of sublimation of $46.0 \pm 0.42 \text{ kJ/mol}$ reported in the same source (NIST). The heat of sublimation should be higher than the heat of vaporization, the difference being the heat of fusion. A more probable heat of vaporization is 32.6 kJ/mol .

5.3 Chemical Properties of Trinitromethane

The most remarkable property of trinitromethane is that it is an acid. The acidity of nitromethanes increase in the order nitromethane, dinitromethane, trinitromethane. As such, it can form salts with a variety of bases and these salts have been tested as solid propellant ingredients. The salts of trinitromethane are sometimes called “trinitromethides” or “trinitromethanides”.

One of the most thoroughly investigated trinitromethide salts is the hydrazinium(1+) salt, hydrazinium nitroformate, also abbreviated as HNF. The properties of HNF are described in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salts”. Several solid propellant formulations have been prepared with HNF. HNF is not very soluble in water, but nevertheless its solutions have been evaluated as “green” monopropellants (*Encyclopedia of Monopropellants*). Other nitroformate salts of organic amines are described in the chapters of the parent amine from which they were derived.

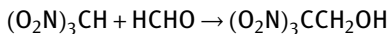
The other remarkable property of trinitromethane for its use as a rocket propellant ingredient is its oxidizing power and the excess oxygen in the molecule. Trinitromethane has an oxygen balance of +37.1% and a nitrogen content of 27.83 mass-% N.

5.3.1 Reactions of Trinitromethane

Trinitromethane is an acid and forms salts with a variety of bases. The salt formed from reaction with hydrazine (hydrate), hydrazinium trinitroformate, has been tested as a monopropellant and in solid propellant formulations. Trinitromethane is highly reactive and can add to unsaturated compounds and other organic compounds.

Trinitromethane adds readily in a Michael type of addition to α,β -unsaturated compounds such as acrylic acid and its esters, hydroxymethyl vinyl ketone, or nitroethylene. This reaction is used in the synthesis of 2-nitro-3-acetoxy-1-propene by way of a unique reaction of 1,1-dinitroethane and nitroform [503]. 4,4,4-Trinitrobutyric acid was converted to 3,3,3-trinitropropyl isocyanate and 3,3,3-trinitropropyl amine hydrochloride. Trinitromethyl carbamates were prepared by the addition of 2,2,2-trinitroethanol to various isocyanates and the addition of different alcohols to 3,3,3-trinitropropyl isocyanate. Trinitromethyl amines were prepared by the Mannich condensation of 2,2,2-trinitroethanol with various primary amines and the reaction of 3,3,3-trinitropropyl amine with nitroalcohols. Trinitromethyl heterocyclic compounds and 2,2,2-trinitroethyl esters are energetic compounds potentially useful as rocket propellants. Trinitromethane adds to activated double bonds, such as of α,β -unsaturated carbonyl compounds and vinyl ethers. It forms a complex with dioxane containing two mols of trinitromethane to one of dioxane, with a m.p. of 317.1–317.6 K (44–44.5 °C) and b.p. at 1 kPa (8 mm Hg) of 334–335 K (61–62 °C). It forms complexes with benzene and methylbenzenes.

The reaction of trinitromethane with formaldehyde gives 2,2,2-trinitroethanol which can be used for the synthesis of other energetic compounds.



The esterification of trinitroethanol with acetic anhydride gives trinitroethyl acetate which is more stable than trinitromethane itself and can be used as a solvent for nitro-cellulose. 2,2,2-trinitroethanol is described in *Encyclopedia of Oxidizers*, chapter "Nitroaliphatic Compounds".

The nucleophilic Michael addition of nitroform to acrylamide creates 4,4,4-trinitrobutanamide in the first step that can be converted to trinitropropylamine and salts containing the trinitropropylammonium cation, $[(\text{NO}_2)_3\text{CCH}_2\text{CH}_2\text{NH}_3]^+\text{X}^-$ [504]. For $\text{X}^- = \text{ClO}_4^-$, $(\text{NO}_2)_2\text{N}^-$, IO_4^- , or amino-bistetrazolate, these salts are of interest as propellant ingredients [505].

The reaction of trinitromethane with urea and acetaldehyde forms *N,N'*-bis(1,1,1-trinitroprop-2-yl)urea which can be converted to 1,1,1-trinitroprop-2-yl carbamate and 1,1,1-trinitroprop-2-yl nitrocarbamate which can be used as energetic additives or explosives [506].

5.3.2 Thermal Stability of Trinitromethane

5.3.2.1 Thermal Decomposition of Trinitromethane

The decomposition of trinitromethane (nitroform, NF) is of practical interest because trinitromethane is an intermediate in the production of hydrazinium nitroformate (HNF) and is a product of thermal decomposition and an intermediate in the combustion of HNF. There are several publications on decomposition of HNF which closely relate to the decomposition of NF. Nitroform is thermally unstable and decomposes already at its melting point of 287.4 K (14.3 °C) and is therefore not useful as a rocket propellant by itself.

When studying the decomposition of vapors of trinitromethane, fluorodinitromethane, and chlorodinitromethane under static conditions, it was noted that a significant influence on the rate is exerted by reactions proceeding on the surface of the reaction vessel [507]. A consideration of this reaction permits a determination of the characteristics of homogeneous decomposition, which, in the case of trinitromethane and fluorodinitromethane, indicates a radical mechanism of decomposition. The theory that H and F atoms have the same effect on the energy of cleavage of the C—N bond in nitro compounds studied was confirmed. The gas phase thermal decomposition of trinitromethane below 443 K (170 °C) and at an initial pressure of trinitromethane above 2.6 Pa (20 mmHg) proceeds with self-acceleration and has a pronounced induction period. With the addition of NO and NO₂ the decomposition rate of trinitromethane increased considerably and the induction period completely disappeared. In view of this, the acceleration of the reaction was attributed to the catalytic effect of the decomposition products

NO and NO₂. The gas phase decomposition of trinitromethane yields products typical for a monomolecular radical decomposition of polynitro compounds. The gas phase decomposition of trinitromethane followed a first-order equation. In the range 453 K < *T* < 473 K (180 °C < *T* < 200 °C), the reaction can be characterized by the following kinetic parameters: $E_{\text{act}} = 172\text{--}184 \text{ kJ/mol}$ (41–43.9 kcal/mol) and $\log A = 15.32\text{--}16.69 \text{ s}^{-1}$.

A hybrid method of density functional theory was used to compute optimized geometries of trinitromethane and some intermediates of its decomposition [CH(NO₂)₂, CH(NO₂)₂ONO, CH(NO₂), and HC(O)NO] and to locate the transition states of the dissociation and isomerization reactions involving these species [508]. The heat of formation of nitroform and of the intermediates of its decomposition and the Gibbs energies of activation of the reactions examined were calculated using *ab initio* multi-level procedures. The high-pressure limits of the rate constants of these reactions in the temperature range 300–2000 K were calculated using transition state theory or its variational analogue.

5.3.3 Radiolysis of Trinitromethane

Trinitromethane is formed during the radiolysis of tetranitromethane when the trinitromethyl radical abstracts a hydrogen atom from a solvent. The radiolytic decomposition of trinitromethane in solution by ⁶⁰Co γ-radiation has been measured by the decrease in the optical density at 350 nm [509]. The initial yield of this decolorization in molecules/100 eV was shown as a function of the pH. In strongly alkaline solutions the decolorization proceeded with a yield of 2.8 molecules/100 eV. It increased with increasing hydrogen ion concentration up to the value of 8.2 at pH 0. This high radiation sensitivity of trinitromethane in acidic solutions may be responsible for the low yields of trinitromethane in radiolysis of acid solutions of tetranitromethane. In alkaline solutions the absorption maximum of the C(NO₂)₃[−] ion at 350 nm not only became less intense but also was shifted to longer wavelengths. This indicated the formation of dinitromethane.

5.3.4 Trinitromethane Salts

Trinitromethane is a strong acid and forms salts with a variety of inorganic and organic bases. The salts are thermally more stable than the parent acid itself. The salts are potentially useful as oxidizers for solid propellants or, if dissolved in a solvent, as monopropellants. The most thoroughly investigated salt of trinitromethane is hydrazinium(1+) trinitromethide, also called hydrazinium(1+) trinitromethanide or hydrazinium nitroformate. A separate chapter has been devoted to this compound in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salts”.

Single crystals of potassium, rubidium or cesium trinitromethanide are unstable at room temperature and decompose within a few hours. The crystal structures of the three salts were determined by XRD [510].

The enthalpies of formation of the ammonium salts of trinitromethane and 1,1-dinitropropane have been determined by calorimetric measurements in a combustion bomb [511].

A combined method for determination of the standard enthalpies of formation of trinitromethane and its salts used the enthalpies of dissolution of trinitromethane and its ammonium, hydrazinium, guanidinium and potassium salts in water [512]. The enthalpy of combustion of hydrazinium salt of nitroform was determined by combustion calorimetry, and its standard enthalpy of formation was calculated. The enthalpy of formation of trinitromethyl anion in infinitely diluted aqueous solution was -24.94 ± 0.79 kJ/mol. Standard enthalpies of formation of trinitromethane and its salts are given in Table 36.

Table 36: Thermochemical properties of trinitromethane and its salts.

Compound	Enthalpy of solution, kJ/mol	Enthalpy of formation, kJ/mol
$\text{HC}(\text{NO}_2)_3$	19.71 ± 0.08	-44.65 ± 1.13
$\text{NH}_4\text{C}(\text{NO}_2)_3$	39.87 ± 0.08	-197.90 ± 0.88
$\text{N}_2\text{H}_5\text{C}(\text{NO}_2)_3$ ^a	50.04 ± 0.08	-76.86 ± 1.13
$\text{CN}_3\text{H}_6\text{C}(\text{NO}_2)_3$	49.12 ± 0.04	-213.14 ± 1.18
$\text{KC}(\text{NO}_2)_3$	64.10 ± 0.08	-341.18 ± 0.80

Data source: [493]

^a Heat of combustion is 1031.23 kJ/mol

The solid-state structures of three nitroformate salts were determined using single crystal X-ray crystallography [513]. The trinitromethanide anion was found to be a non-planar moiety which adopts either the commonly observed C_{2v} conformation or distorted propeller conformation (D_3) in the case of the silver salts or a C_2 conformation in the case of the potassium salt. This latter C_2 conformation has been uniquely observed for potassium trinitromethanide. All structures exhibited cation-anion interactions that influence the structure of the anion. The ^{13}C and ^{14}N NMR spectra of the trinitromethanide anion showed broad singlets, which indicated the equivalence of the nitro groups in solution within the NMR time scale. The gaseous decomposition products of potassium trinitromethanide at 298 K (25 °C) were detected using IR and mass spectrometry.

Guanidinium trinitromethanide is a relatively stable salt with a melting point of 401 K (128 °C) for the anhydrous salt, but it is usually obtained as the hydrate which melts at 395–397 K (122–124 °C). The anhydrous salt has a density of 1.643 g/cm^3 and a detonation velocity of 8200 m/s. The drop weight impact sensitivity with a 2.5-kg weight 50% point is at 17 cm.

Methylammonium trinitromethanide is a yellow solid with an m.p. (with decomposition) of 399–401 K (126–128 °C). It has been patented as a rocket propellant and explosive ingredient [514]. The vacuum stability of a 0.5-g sample of methylammonium trinitromethanide during 48 h at 333 K was 1.02 mL gas.

Tetra-*n*-butylammonium trinitromethanide is well crystallized and its crystal structure was determined by XRD, supported by ^{13}C and ^{14}N NMR spectra [515]. The trinitromethanide anion was found to be a non-planar system. The sum of dihedral angles between the central (C–N₃) plane of the anion and the planes of the individual nitro groups varies from 60 to 100°. The C–N and N–O interatomic distances in the trinitromethanide anion can be correlated with the dihedral angles of the corresponding nitro groups.

Trinitromethane was combined with oximes of cyclopentanone, cyclohexanone, and diphenylcyclopropenone and with melamine and two 1,3-dialkyl-2,4-dialkylimino-1,3-diazetidines to give simple trinitromethanide salt adducts [516]. Tricyanomethane was added to diphenylcyclopropenone oxime to give hydroxylamino-2,3-diphenylcyclopropenylium tricyanomethanide.

5.3.5 Other Trinitromethane Derivatives

Comparing the gas phase thermal decomposition of $\text{RC}(\text{NO}_2)_3$ compounds, where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$, it was found that the reactions are unimolecular and are characterized by high pre-exponential factors [517]. The activation energy is determined by the strength of the C–N bond. The effect of substituents R and molecular structure on the Arrhenius parameters for the radical decomposition of nitro compounds can thus be quantified.

Tetranitromethane, iodotritinitromethane, and *gem*-trinitroethane decompose in the liquid state with the same rates as in the gaseous phase [518]. The mechanism of decomposition in both states is identical.

The composition of the decomposition products of tetranitromethane, 1,1,1-trinitroethane, chloro-nitroform, bromo-nitroform, and iodo-nitroform in the gas phase as determined by GC-MS confirmed a radical non-chain mechanism of the decomposition, the first step of which is cleavage of the C–N bond [519]. A detailed decomposition mechanism has been proposed, considering the reactions of nitroalkyl radicals in systems containing NO and NO₂.

The theoretical molecular structures of trinitromethane derivatives $\text{XC}(\text{NO}_2)_3$ with $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{NC}, \text{NF}_2$ or N_3 were studied using a density functional theory method [520]. Graphs showed the dependence of the C–X bond length on the nature of X. In the sequence H, F, Cl, Br, the C–X bond length increased from 1.1 to 1.9 Å but the C–N bond changed only moderately. A similar correlation exists with X-CH_3 compounds. Corresponding compounds with X = iodine could not be studied.

Spectroscopic parameters of trinitromethane derivatives $\text{RC}(\text{NO}_2)_3$ with $\text{R} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{NC}, \text{NF}_2$ or N_3 were determined experimentally and compared to computational predictions [521]. The experimental IR and Raman spectra of all trinitromethane derivatives were very similar. The most intense IR bands were observed at 1600, 1300, and 800 cm^{-1} while the most intense Raman lines were observed at 1350, 850, and 375 cm^{-1} . Their positions varied only slightly going from one compound to another. The calculated frequencies and the potential energy distributions over vibrations were tabulated, with the most detailed results obtained for $\text{FC}(\text{NO}_2)_3$ and $\text{ClC}(\text{NO}_2)_3$.

The trinitromethyl or trinitroethyl functionality is an important tool for the design of energetic materials. Theoretical calculations are capable of predicting some material properties. The synthesis, characterization, energetic properties and structure properties of several new promising trinitroethyl compounds possessing energetic material properties were reported and compared to standard explosives currently used [522, 523]. Based on a review of trinitroethyl-containing compounds available in the literature, it was observed that high density can generally be obtained in a more targeted manner in energetic materials taking advantage of non-covalent bonding interactions.

Trinitromethyl chloride is a useful chemical for the introduction of the trinitromethyl group into other molecules and the synthesis of energetic materials. The $\text{C}-\text{Cl}$ bond in trinitromethyl chloride is much shorter than in methyl chloride.

An evaluation of the potential use of trinitromethyl ethers, with the linkage $(\text{O}_2\text{N})_3\text{C}-\text{O}-\text{CR}_3$, a class of compounds that might have promise as superior oxidizers to replace ammonium perchlorate, did not result in the hoped for compounds [524]. Trinitromethyl ethers, trinitromethyl triazoles and non-anitroisobutane lacked the necessary stability.

Ten theoretical salts based on the nitroformate anion and various nitrogen-rich cations were designed and their molecular structure geometries were optimized using a density functional computational method [525]. The oxygen balance, enthalpies of formation, densities, detonation velocities and detonation pressures of these salts were calculated.

5.3.6 Combustion of Trinitromethane Derivatives

Because trinitromethane itself is not used as a rocket propellant, no strand burning data of pure trinitromethane are in the literature, but the burning behavior of many trinitromethane derivatives that are potential rocket propellant ingredients or explosives was studied in detail.

Hydrogen bonding affects the heat of sublimation and thermal stability, as evidenced by universal force field calculations [526]. The explosive properties of bis(2,2,2-trinitroethyl) nitramine (BTNEN) are shown in Table 37 in comparison to those of other common explosives. It is unique among other explosives in that it has a positive oxygen balance of +16.7%.

Table 37: Properties of BTNEN in comparison to other explosives.

Name	ρ g/cm ³	ΔH_f kcal/mol	P_{Det} GPa	V_{Det} km/s	Energy density kJ/cm ³	h^a cm	Oxygen balance %
BTNEN	1.96	−175.9	39.080	9.157	8.861	5	+16.7
For comparison:							
HMX	1.90	17.8	38.080	9119	8.858	26	−21.62
RDX	1.80	14.7	34.240	8786	8.321	24	−21.62
PETN	1.77	−129.0	33.130	8.686	8.157	12	−10.13
Nitroguanidine (NQ)	1.77	−22.0	27.010	7.843	6.650	177	−30.77
2,4,6-Trinitro- phenylmethyl- nitramine (tetryl)	1.73	8.0	26.290	7.792	6.590	32	−47.38
TNT	1.65	−18.0	20.540	6.991	5.336	160	−74.00

^a h = drop weight impact sensitivity, cm

Data source: [526]

5.4 Safety Properties of Trinitromethane

Trinitromethane would ordinarily not be handled in large quantities in the pure state by itself. Most applications would prefer it to be used only in solution while it is used as an intermediate in the synthesis of other chemicals. The safety and explosive properties of trinitromethane were determined only in comparison to that of other nitromethanes, to study the effect of progressive replacement of hydrogen atoms on methane by nitro groups.

5.5 Toxicity of Trinitromethane

Although trinitromethane is rarely used as such, the toxicity of trinitromethane has been studied and compared to the toxicity of nitromethane and tetranitromethane. The oral LDLo of trinitromethane in mice was 150 mg/kg and the oral LD50 was 300 mg/kg [527]. The exposure of mice to inhalation of trinitromethane for 2h gave an LDLo of 0.7 mg/L (113 ppm), an LC50 of 0.8 mg/L (130 ppm) and an LD100 of 1.0 mg/L (162 ppm). Symptoms observed prior to death included irritation of mucous membranes of the eyes and respiratory tract, dyspnea, excitability, motor incoordination, convulsions, and narcosis. Threshold concentrations of 0.04–0.05 mg/L (8 ppm) were noted in cats and rats where changes in conditioned reflexes and neuromuscular activity were observed. In continuation of this study, subchronic exposure by daily inhalation of 0.12 mg/L (19 ppm) trinitromethane vapor for 2h over a period of

2 months altered excitability of the nervous system, increased reticulocytes in the blood, produced 6–9% methemoglobinemia, and resulted in death of 46% of the rats. Inhalation of 0.002–0.01 mg/L (0.3–1.6 ppm) trinitromethane vapor for 4 h/day for 7 months altered the threshold of nervous excitability. See also reference [528].

5.6 Other Applications of Trinitromethane

Of particular interest is the use of nitroform as a starting material for the preparation of bis(2-fluoro-2,2-dinitroethyl) formal (FEFO) and 1,3-bis(fluorodinitroethoxyl)-2,2-bis(difluoroamino) propane (SYEP). Both FEFO and SYEP are energetic plasticizers that were evaluated in formulating solid propellants (*Encyclopedia of Oxidizers*, chapter “Nitroaliphatic Compounds”). Low-cost processes for their production were sought. This, of course, necessitated starting their production with low-cost nitroform. For instance, fluorotrinitromethane can be prepared by direct fluorination of trinitromethane in aqueous solution with diluted elemental fluorine [529].

6 Tetranitromethane

Tetranitromethane, $C(NO_2)_4$, CAS [509-14-8], in the following often abbreviated as TNM, would be a good rocket propellant oxidizer if one could deal with its shock sensitivity and toxicity problems. The oxygen balance of TNM is +49%. It has also been tested as an explosive ingredient in mixture with various fuels. Its sensitivity to explosions and the high melting point have prevented the use of TNM as an oxidizer in its own right. It is now only of historical interest when compiling a list of chemicals that have been considered as rocket propellants at one time or another. TNM has a very high density (1.64 g/cm^3) which makes it attractive for storable liquid propellants in pressure-fed systems. The volume-specific useful oxygen content (1.07 kg/L) expressed in kg of useful oxygen per liter, is the highest of all storable oxidizers and approaches that of liquid oxygen (1.14 kg/L). Oxygen atoms are packed in the nitro groups more densely than in liquid oxygen.

A comprehensive summary of information on the methods of preparation, physical and chemical properties and toxicity of tetranitromethane, summarizing literature that appeared in print up to 1974 and including a list of 317 references is available in reference [530]. This includes information on the various reactions of tetranitromethane with unsaturated compounds that lead to other energetic chemicals. Additional properties of TNM are summarized in reference [531].

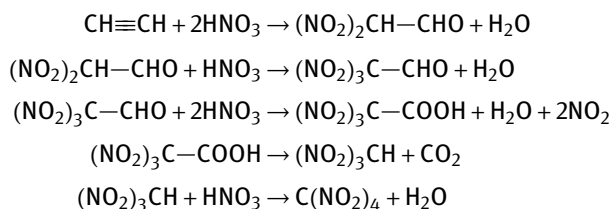
6.1 Production of Tetranitromethane

Tetranitromethane is formed as a by-product during nitration of aromatic hydrocarbons with concentrated acids at high temperatures, as a result of ring opening. During times of high demand of TNT, it may be difficult to get rid of the excess TNM.

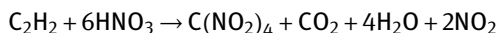
6.1.1 Production of Tetranitromethane from Acetylene

The main method for production of TNM proceeds by reaction of acetylene with nitrating acid in the presence of mercury(II) nitrate as a catalyst [532]. An apparatus was designed capable of producing 10 kg TNM/day. Similar reactions can be performed with ethylene and nitrating acid [533]. Acetylene or ethylene is absorbed with great ease into white fuming nitric acid and the TNM separates from the mixture [534, 535].

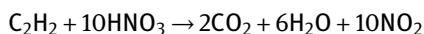
During World War II the Germans manufactured tetranitromethane by this method on a semi-commercial scale, after they had developed and improved the industrial process. The reaction takes place in the presence of mercury(II) nitrate as a catalyst at temperatures ranging from 318 to 323 K (45–50 °C) (max. 333 K = 60 °C):



The overall reaction may be presented as:



The yield of TNM is reduced by an unwanted side-reaction



Both reagents are readily available in industrial quantities. Just how to react a gaseous fuel (acetylene in itself is already detonable) with a liquid oxidizer without causing an explosion, that is not an easy task. See also reference [536].

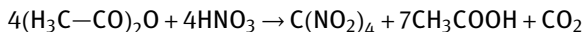
6.1.2 Production of Tetranitromethane from Acetic Anhydride

It was found earlier that tetranitromethane is formed when fuming nitric acid is reacted with acetic acid, but for the preparation of tetranitromethane on the laboratory scale the method using acetic anhydride instead of acetic acid is preferred [537–539].

Of the many methods for the preparation of TNM, the reaction between acetic anhydride and nitric acid seems the most promising [540]. The reaction is best carried out in all-glass equipment consisting of a flask, mechanical stirrer, dropping funnel,

thermometer, and reflux condenser. Commercial WFNA can be used with success, but the yield of TNM is higher if the nitric acid is first purified by vacuum distillation. No advantage is gained in purifying the acetic anhydride. The optimum temperature of reaction is 293–298 K (20–25 °C), and the yield is enhanced by the presence of chipped glass. The yields of a considerable number of experiments averaged 61–62%.

Another method consists of treating acetic anhydride with fuming nitric acid at room temperature or below. After a few days of standing the homogeneous solution is poured into water, causing the oily tetranitromethane to separate. The reaction equation for the production of TNM from acetic anhydride and nitric acid is:

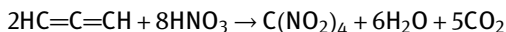


This method was applied in the USA. on a larger scale by Nitroform Products Co., Inc., Newark, N.Y.; however, the plant was completely destroyed by an explosion that occurred in the manufacture of tetranitromethane. Until 1953, TNM for the US Navy's research and development needs was available from the Nitroform Products Company, East Orange, N.J. In February 1953, the Nitroform Company facility was destroyed by an accidental explosion which killed all of the key personnel. The only other commercial supplier at that time was Johnson and Scudder, Bloomfield, N.J., but they were not interested in supplying larger quantities. Therefore, the US Navy began making it themselves for their own needs. Several hundred pounds of TNM have been prepared by the reaction of 96–98% nitric acid with acetic anhydride on a semi-pilot scale which was capable of producing 160 lb/month [541]. This somewhat hazardous reaction requires care and many precautions to conduct safely on an enlarged scale. The yields averaged 50% based on nitric acid and 35% based on acetic anhydride. After mixing WFNA and Ac_2O in an agitated and cooled kettle, the mixture was transferred to another kettle for the 5-day aging cycle. The kettles used for the aging cycle were cooled by circulating tap water. The temperature during the aging cycle was controlled at 298 K (25 °C) by adjusting the water flow to remove the heat of reaction. The impact sensitivity of the reaction mixture was measured immediately after the addition of nitric acid 1 day later, 5 days later, and that of the crude product after drowning and separation. All of these materials appeared to be insensitive and gave no explosion on the drop weight sensitivity testing machine with a 2.5 kg weight dropping from a height of up to 320 cm.

The acetic anhydride method is more expensive than the acetylene method and can be used for smaller scale production. This is the method that was used at IG-Farben during WWII when the German rocket development center in Peenemünde began to develop interest in this oxidizer [542–544]. When the reaction mixture is poured into ice water, tetranitromethane separates out. An alternate method is the reaction of acetic anhydride with N_2O_5 instead of WFNA.

6.1.3 Other Methods for Production of Tetranitromethane

Tetranitromethane may also be prepared by introducing a slow stream of ketene into cooled 100% nitric acid [545]:



When the reaction mixture is poured into ice water, tetranitromethane separates out. Tetranitromethane can also be produced by nitration of trinitromethane. The reaction of silver nitrite with iodotrinitromethane yields tetranitromethane. Another method is the reaction of nitryl chloride with sodium trinitromethanide.

TNM is formed as an undesirable byproduct during the production of TNT by nitration of toluene, following opening of the ring. It is a constituent of the so-called red water which is the waste stream of TNT production that is difficult to dispose of in an environmentally acceptable manner. Therefore, it is desirable that formation of TNM during nitration is minimized for safety and health reasons. Indeed, there is evidence that a reduction in the meta-isomer content of lower nitrated toluenes (MNTs and DNTs) will be effective in reducing TNM formation. Over 80% of all the TNM formed in the production of TNT is derived from such meta-isomers. Isotope labeling has shown that most of the TNM is formed from carbon atoms that were part of the benzene ring where the methyl group was attached. TNM also forms as an unwanted byproduct during the production of dinitrotoluene which is an intermediate for the production of toluene diisocyanate, an important building block for polyurethane polymers.

TNM is an unwanted byproduct of many industrial nitration processes. There are numerous patents describing the removal of TNM contamination from TNT and other nitration products. An attempt was made to effectively remove TNM from the effluent gas stream from TNT manufacturing operations and convert it to nitroform [546]. The TNM was efficiently removed by passing the gas through a column scrubber containing an aqueous solution of sodium carbonate and stabilized hydrogen peroxide. The resulting sodium nitroformate solution is a marketable by-product. See also [9, 547, 548].

Spent nitrating acid that is coming out of nitrating reactors may contain TNM that may accumulate in other locations of the process if it is not removed before the acid is recycled or neutralized. The removal of TNM from spent nitrating acid can be done by sparging with air or solvent extraction, followed by destruction [549].

In the recovery of acids from the nitration of toluene to TNT, it is possible under certain conditions to obtain mixtures of nitroaromatic compounds, primarily mononitrotoluene and dinitrotoluene with nitrogen tetroxide and/or tetranitromethane. These mixtures have the potential of being highly sensitive liquid explosives. Studies showed that such odd mixtures are not exceptionally sensitive to mechanical impact and friction or thermal initiation but at oxygen balanced proportions, are extremely sensitive to induced shock and are capable of propagating explosive reactions at film thicknesses of less than 0.5 mm [550].

For kinetic studies of reactions involving TNM, it may be useful to have isotope-labeled TNM. ^{15}N labeled tetranitromethane, $\text{C}(^{15}\text{NO}_2)_4$, can be prepared from ^{15}N labeled anhydrous nitric acid and acetic anhydride [551].

6.2 Physical Properties of Tetranitromethane

Rocket propellant chemists already started measuring and collecting the physical properties of TNM in the early days of rocket development in Peenemünde in Germany during the 1940s. Subsequently, several summaries of the properties of TNM were published [552] and some of the data from these sources are summarized here.

Physical properties of tetranitromethane were summarized in [553–555]. Other data came from manufacturer's marketing literature, data sheets that are no longer available.

6.2.1 Freezing Point and Phase Diagrams of Tetranitromethane

Freezing point data for tetranitromethane are summarized in Table 38.

Table 38: Summary of literature freezing point data for tetranitromethane.

Freezing point temperature			Data source	References
K	°C	°F		
286.95	13.8	56.8	Nicholson 1949	[554]
286.9	13.75	56.75		
287.286	14.136	57.44	Taylor	[556]

Tetranitromethane undergoes a phase transition in the solid state at 174.95 K [557]. The cryoscopic constant of TNM is 14.3 °C mol solute/kg TNM [558].

6.2.2 Boiling Point of Tetranitromethane

One must not attempt to distil TNM at sea level pressure because this may result in explosions. The boiling point of TNM at 760 mm is 126 °C = 259 °F [559, 560]. TNM can be distilled safely by steam distillation.

6.2.3 Density of Tetranitromethane

Literature data for the density of tetranitromethane are summarized in Table 39.

Table 39: Density of tetranitromethane.

Temperature		Density	Data source	References
K	°C	g/cm ³		
288	15	1.649	Nicholson 1949	[554]
293	20	1.630	Nicholson 1949	[554]
285.3	12.2	1.638	Hummel 1962	[561]
288	15.0	1.65	Hummel 1962	[561]
298	25.0	1.64	Hummel 1962	[561]
298	25	1.62294	Lewis and Smyth 1939	[492]
298	25	1.65	Taylor 1955	[541]
286	13	1.650	Dobratz 1972	[562]

6.2.4 Vapor Pressure of Tetranitromethane

Literature data for the vapor pressure of tetranitromethane are summarized in Table 40. It is the high vapor pressure and the toxicity of TNM that makes safe handling of this chemical as a rocket propellant a very difficult task.

Table 40: Vapor pressure of tetranitromethane.

Temperature		Vapor pressure		Data source	References
K	°C	kPa	mm Hg		
273	0	0.25	1.9	Nicholson 1949	[554]
287	13.8	0.76	5.7	Nicholson 1949	[554]
293	20	1.12	8.4	Nicholson 1949	[554]
303	30	1.98	14.9	Nicholson 1949	[554]
313	40	3.43	25.8	Nicholson 1949	[554]
293	20	1.12	8.4	Hummel 1962	[561]
303	30	1.98	14.9	Hummel 1962	[561]
313	40	3.52	26.5	Hummel 1962	[561]
343	70	14.4	108	Hummel 1962	[561]
373	100	45.1	339	Hummel 1962	[561]
313	40	3.52	26.5	Edwards 1950, 1952	[563, 564]
323	50	5.75	43.3	Edwards 1950	[563]
333	60	9.04	68	Edwards 1950	[563]
343	70	14.4	108	Edwards 1950	[563]
353	80	21.8	164	Edwards 1950	[563]
363	90	31.8	239	Edwards 1950	[563]
373	100	45.1	339.6	Edwards 1950	[563]

The TNM vapor pressure data of Nicholson can be expressed by the equation

$$\log p = 8.63 - 2260/T$$

where p is the vapor pressure in mm Hg and T is the temperature in kelvin. The same data in the form of the Antoine equation for the temperature range from 273 to 313 K are represented by the equation:

$$\log_{10}(P) = 1.75688 - [498.772/(T - 158.538)]$$

where P is the vapor pressure in bar and T is the temperature in kelvin. The TNM vapor pressure data of Edwards can be expressed by the equation [564]:

$$\log p = 7.23 - 2130/T$$

where p is the vapor pressure in mm Hg and T is the temperature in kelvin. The same data in the form of the Antoine equation for the temperature range from 313 to 373 K are represented by the equation:

$$\log_{10}(P) = 4.54919 - [1582.071/(T - 49.74)]$$

where P is the vapor pressure in bar and T is the temperature in kelvin.

6.2.5 Viscosity of Tetranitromethane

The viscosity data for liquid TNM are somewhat divergent, one source reporting a viscosity of 1.76 cPs at 293 K (20 °C) [559] and another source showing a viscosity of 1.19 cPs at 288.2 K (15.1 °C) on a graph [565].

6.2.6 Surface Tension of Tetranitromethane

Literature data for the surface tension of tetranitromethane are summarized in Table 41.

Table 41: Surface tension of tetranitromethane.

Temperature		Surface tension	
K	°C	dyn/cm	N/m
293	20	30.47	0.0305
298	25	29.44	0.0294
303	30	28.98	0.0290
308	35	28.74	0.0287
323	50	26.45	0.0264

Data source: Gmelin Handbook of Inorganic and Organometallic Chemistry

Note: 10^5 dyn = 1 N; 1 dyn/cm = 10^{-5} N/cm = 10^{-3} N/m

6.2.7 Optical Properties of Tetranitromethane

6.2.7.1 Infrared Spectra of Tetranitromethane

The IR spectrum of tetranitromethane is of importance for quality control of the oxidizer to make sure it is free from contaminants. The IR spectrum of tetranitromethane is the key to the operation of monitoring instruments that monitor the air in human-occupied work spaces in propellant and explosive factories. The IR spectra of tetranitromethane were obtained at 298 K = 25 °C (vapor), 291 K = 18 °C (liquid), 233 K = -40 °C (solid I), 185 K = -88 °C (solid I), 169 K = -104 °C (solid II) and 147 K = -126 °C (solid II) [566], Figure 8. Cooling curve IR spectral investigations showed that a transition between two crystalline forms of tetranitromethane occurred at 173.3 K = -99.8 °C and its character suggested an order-disorder transformation. The spectra of the vapor were best interpreted by a molecule with $S_4-\bar{4}$ symmetry whereas reported Raman spectra indicated a $D_{2d}-\bar{4}2_m$ symmetry in the liquid. A total of 25 fundamental frequencies were assigned to fundamental vibrations and additional frequencies not interpreted as fundamentals were also tentatively assigned to other movements in the molecule.

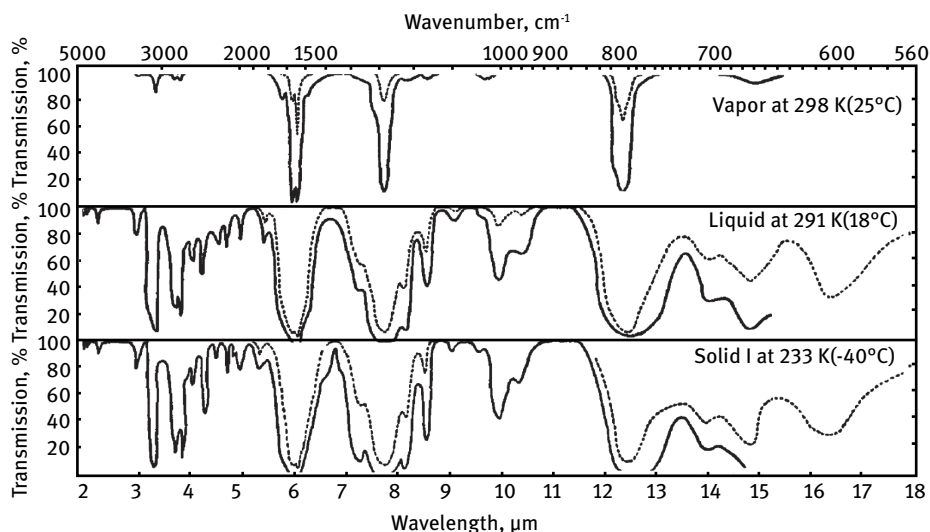


Figure 8: IR spectra of tetranitromethane (republished and modified from [566], with permission of © 1953 American Institute of Physics; permission conveyed through Copyright Clearance Center Inc.) Legend: Top: vapor at 298 K in 5-cm cell, solid line: vapor in equilibrium with liquid, dashed line: low pressure <0.5 mm Hg; Center: liquid at 291 K, solid line: 0.15 mm cell, dashed line: <0.03 mm film; Bottom: solid at 233 K

6.2.7.2 UV Spectra of Tetranitromethane

The UV absorption of TNM has a $\lambda_{\max}$ at a wavelength of ca. 275 nm with $\log \varepsilon = 2.2$.

6.2.7.3 Index of Refraction of Tetranitromethane

Literature data for the index of refraction of TNM are summarized in Table 42.

Table 42: Index of refraction of tetranitromethane.

Temperature		Index of refraction	Source	References
K	°C	n_D		
290	16.9	1.4398	Hummel 1962	[561]
293	20	1.4384	Nicholson 1949	[554]
298	25	1.4358	Nicholson 1949	[554]
298	25	1.43822	Lewis and Smyth 1939	[492]
298	25	1.4351	Taylor 1955	[567, 568]

6.2.8 Electrical Properties of Tetranitromethane

The dielectric constant of TNM at 25 °C is 2.251. The specific electric conductance of TNM at 25 °C is $1.0 \times 10^{-8} \text{ Ohm}^{-1} \text{ cm}^{-1}$ (*Gmelin Handbook of Inorganic and Organometallic Chemistry*).

The dipole moment of tetranitromethane is <0.7 D which indicates that it has a symmetrical tetrahedral structure [492]. The dipole moment of the perfectly symmetrical tetranitromethane molecule should, of course, be zero, while that of trinitromethyl nitrite (a suspected contaminant or isomer) would depend on rotation around the single O—N bond of the nitrite group and would vary from 3.4 to 0 with variation in the angular position around this bond.

6.2.9 Thermodynamic Properties of Tetranitromethane

Thermodynamic properties of TNM are summarized in Table 43.

6.2.9.1 Heat Capacity of Tetranitromethane

Phase changes of TNM in the solid state can be identified by IR spectra and by abrupt changes in the heat capacity [557].

6.2.9.2 Heat of Formation of Tetranitromethane

The heat of combustion of TNM in an atmosphere of CO is -2130 kJ/mol (-508.7 kcal/mol), from which number the standard enthalpy of formation of liquid TNM was calculated as $+36.8 \text{ kJ/mol}$ ($+8.8 \text{ kcal/mol}$) [569].

The originally measured value of $\Delta H_f^{298}(\text{L})$ of $+37 \pm 2 \text{ kJ/mol}$ was later revised by Cox and Pilcher [179] based on different calibrations as $+41.2 \pm 4.2 \text{ kJ/mol}$ [571]. Other sources report an uncorrected heat of formation of $+38 \pm 2 \text{ kJ/mol}$ [572].

Table 43: Thermodynamic properties of tetranitromethane.

	SI units		Other units		Data source	References
	kJ/mol	kJ/kg	kcal/mol	cal/g		
Enthalpy of formation, ΔH_{298}^f liquid	+36.82	+187.8	+8.8	+44.89	Gardner and Grigger 1963	[569]
Enthalpy of formation, ΔH_{298}^f liquid	+38.5	+196.4	+9.2	+46.9	Meyer, Koehler and Homburg	[96]
Heat of fusion (ΔH)melt	9.422	48.06	2.252	11.49	Sarner 1966	[570]
Heat of evaporation (ΔH)evap	43.09	219.8	10.3	52.54	Nicholson 1949	[554]
Heat of decomposition ($\rightarrow \text{CO}_2 + 2\text{N}_2 + 3\text{O}_2$)	374.5	1910	89.5	456.6	Tschinkel 1956	[559]
Enthalpy of formation, ΔH_{298}^f liquid	54.4	+277	+13.0	+66	Dobratz 1972	[562]

NIST molecular mass: 196.0329 g/mol = 5.1012 mol/kg

6.2.9.3 Heat of Fusion of Tetranitromethane

The heat of fusion of TNM is 9.42 ± 0.25 kJ/mol (2.25 ± 0.06 kcal/mol) [541].

6.2.9.4 Heat of Evaporation of Tetranitromethane

From the vapor pressure data, the latent heat of evaporation was calculated as 43.1 kJ/mol (10.3 kcal/mol) [554]. Similar calculations resulted in a heat of evaporation of 40.6 kJ/mol (9.7 kcal/mol) [563]. The Edwards data were later revised to match different calibrations and shown as 43.1 ± 2.1 kJ/mol at 313 K. Other sources showed a heat of evaporation of 43.9 ± 0.4 kJ/mol [572]. The heat of sublimation of solid TNM is 47.4 kJ/mol between 255 and 286 K.

6.2.10 Molecular Structure of Tetranitromethane

Tetranitromethane has four equivalent nitro groups attached to the central carbon atom and the bonds are at tetrahedral angles, $109^\circ 28'$. The C—N bond length of 1.46 Å and the N—O bond length of 1.21 Å are similar to those in nitromethane [573, 574].

The IR spectra of gaseous TNM indicated an S_4 symmetry of the molecule, thus proving an earlier hypothesis about an unsymmetrical trinitromethyl nitrite isomer to be wrong [575].

Infrared and Raman spectra of tetranitromethane have been recorded in the liquid and vapor phases as well as in solutions of TNM in several different solvents [576]. The bands were assigned to $-\text{NO}_2$ asymmetrical stretching, $-\text{NO}_2$ symmetrical stretching, $-\text{CN}$ stretching, $-\text{NO}_2$ bending, wagging and rocking, $-\text{NCN}$ bending and $-\text{NO}_2$ torsions. The measured vibrational frequencies were compared to predictions from two different computational methods, a semiempirical method and an *ab initio* method. The agreement between experimental data and predicted data was better for the *ab ini-*

tio method. The computed vibrational frequencies fit the experiment within $\pm 2\text{cm}^{-1}$. See also Figure 8.

Computational chemistry methods were again applied to study the mechanism of thermolysis of TNM and identify possible reaction channels [577]. The first step in the thermal decomposition of TNM involves dissociation of a C—N bond. Computed values for the activation energy and pre-exponential factors satisfactorily agreed with experimental ones.

The structure and vibrational frequencies for tetranitromethane were calculated using three different methods [578]. The structural parameters obtained from density functional theory were compared to results obtained with more conventional methods and to experimentally determined values. It was found that molecular geometries were best calculated using Møller-Plesset second order perturbation theory (MP2), local and hybrid density functional methods. The non-local density functional methods produced unacceptably long values for the C—N bonds. Hybrid density functional theory produced the best agreement of vibrational frequencies.

The C—NO₂ bond dissociation energies and the heats of formation of nitromethane and polynitromethanes (dinitromethane, trinitromethane, and tetranitromethane) in the gas phase at 298 K were calculated theoretically using density functional theory and other methods in combination with different basis sets [46]. As the number of NO₂ groups on the same C atom was gradually increased, one functional performed better than the other functional. Predictions for the enthalpy of formation in the gas phase were accurate with deviations of <2 kcal/mol from experimental data for CH₂(NO₂)₂ and CH(NO₂)₃. For the C(NO₂)₄ molecule, a different basis set augmented with polarization functions and diffusion functions was required to yield a good result.

It was sometimes difficult to obtain a molecular structure for the highly symmetrical molecule of tetranitromethane that was consistent with results from diffraction experiments and spectroscopic analysis, but the structure has now been determined more accurately both in the gas phase and in the solid state [579]. For the gas phase, a new approach based on a four-dimensional dynamic model for describing the correlated torsional dynamics of the four C—NO₂ units was necessary to describe the experimental gas phase electron diffraction intensities. A model describing a highly disordered high-temperature crystalline phase was established, and the structure of an ordered low-temperature phase was determined by XRD.

6.3 Properties of Tetranitromethane Mixtures

6.3.1 Solubility of Tetranitromethane

Tetranitromethane is sparsely soluble in water, but soluble in alcohol and ether. The solubility of TNM in water is 0.85 g/L at room temperature. Solubility of TNM and trinitromethane must be known to prevent the accumulation of these unwanted contaminants in process streams of nitration facilities [548].

6.3.2 Freezing Point of Tetranitromethane Mixtures

A number of additives were evaluated to lower the freezing point of TNM to where it can be handled as a liquid propellant over a wider temperature range. It was difficult to find additives that will lower the freezing point without increasing the shock sensitivity of TNM.

The most thoroughly examined oxidizer mixture with TNM is the mixture with dinitrogen tetroxide which was already discussed in *Encyclopedia of Oxidizers*, chapter „Dinitrogen Tetroxide“ [580–582]. Here we discuss mixtures of TNM with other organic compounds, which were added mostly with the intention of lowering its freezing point; however, in many cases the shock sensitivity of the mixtures was prohibitively increased and none of the mixtures has found practical application. Table 44 gives the freezing points of tetranitromethane/nitromethane mixtures.

Table 44: Freezing points of tetranitromethane/nitromethane mixtures.

Mass-% CH_3NO_2	Mol fraction TNM	Freezing point		Freezing point depression, °C
		K	°C	
2.0	0.938	283.6	10.5	3.3
5.0	0.855	279.6	6.5	7.3
15.0	0.638	271.8	−1.3	15
25.0	0.438	264.6	−8.5	22
50.0	0.237	247	−26	40

Data source: [559]

In addition to binary mixtures, also ternary mixtures of 33–95 mol-% N_2O_4 , 5–41% TNM and 0–56.5% MeNO_2 are candidate liquid oxidizers [583]. An oxygen-rich ternary mixture containing 53 mol-% N_2O_4 , 25 mol-% $\text{C}(\text{NO}_2)_4$, and 22 mol-% CH_3NO_2 freezes at 233 K (−40 °C), while the most oxygen-rich ternary mixture freezing at 223 K (−50 °C) contained about 47 mol-% N_2O_4 , 19 mol-% $\text{C}(\text{NO}_2)_4$, and 34 mol-% CH_3NO_2 . A mixture of 20% TNM and 80% dinitrogen pentoxide freezes at 267 K (−7 °C) and has been proposed as a hypergolic oxidizer [584].

Mixtures of TNM with aliphatic difluoroamino compounds, such as bis(difluoroamino)ethane $\text{C}_2\text{H}_4(\text{NF}_2)_2$, tris(difluoroamino)propane $\text{C}_3\text{H}_5(\text{NF}_2)_3$, tetrakis(difluoroamino)tetrahydrofuran, tetrakis(difluoroamino) butane $\text{C}_4\text{H}_6(\text{NF}_2)_4$, pentakis(difluoroamino) pentane $\text{C}_5\text{H}_7(\text{NF}_2)_5$ have been patented as rocket propellant oxidizers [585]. The inventor failed to verify that the two liquids are miscible over the entire range of mixture ratios and will not segregate on cooling. Mixtures of TNM with various aromatic hydrocarbons and aromatic nitro compounds were tested as potential liquid explosives. The less energetic ones in this list might be suitable as monopropellants as long as they are not too sensitive to thermal and mechanical stimuli [586]. Melting points of several such mixtures are summarized in Table 45.

Table 45: Eutectic points in binary mixtures with tetranitromethane.

Mixture component A	Eutectic point at		
	Component A, mass-%	K	°C
Benzene	30	257.0	−16.1
Nitrobenzene	43	253.7	−19.4
<i>o</i> -Nitrotoluene	58.5	244.6	−28.5
<i>p</i> -Nitrotoluene	17.5	274.6	+1.5
α -Nitronaphthalene	10.0	282.6	+9.5
<i>m</i> -Dinitrobenzene	30	284.8	+11.65
Trinitrotoluene	30	285.5	+12.36

Data source: [586, 587].

6.3.3 Shock Sensitivity of Tetranitromethane Mixtures

Stoichiometric nitromethane/TNM mixtures are less shock sensitive than hydrocarbon/TNM mixtures. Several of the nitromethane/TNM mixtures have been patented [588–591]. These will be discussed again in *Encyclopedia of Monopropellants*. For mixtures of TNM with benzene, a two-component liquid explosive, see also [592].

Table 46: Density and oxygen balance of propellant mixtures with TNM.

Fuel component	Fuel, mass-%	TNM, mass-%	Oxygen balance λ for combustion leading to:		Density at 20 °C, g/cm ³
			CO	CO ₂	
Methanol	100	—	—	—	0.792
Methanol	48	52	0.770	0.572	1.085
Methanol	46	54	0.800	0.588	1.100
Methanol	37	63	1.000	0.742	1.175
Methanol	26	74	1.429	1.000	1.265
Ethylene glycol monomethyl ether	100	—	—	—	0.965
Ethylene glycol monomethyl ether	43	57	0.742	0.572	1.260
Ethylene glycol monomethyl ether	41.5	48.5	0.800	0.606	1.270
Ethylene glycol monomethyl ether	33	67	1.000	0.742	1.332
Ethylene glycol monomethyl ether	23	77	1.409	1.000	1.413
Nitromethane	100	—	0.800	0.572	1.136
Nitromethane	81.3	18.7	1.000	0.705	1.205
Nitromethane	55.5	44.5	1.450	1.000	1.316

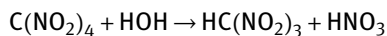
Data source: [559]

Mixtures of TNM with methanol or ethylene glycol monomethyl ether were considered as monopropellants, see Table 46; however, insufficient data are available on their shock sensitivity and they may be too sensitive for practical applications. These mixtures may only be detonable at the stoichiometric mixture ratio but may be safe monopropellants at off-stoichiometric mixture ratios.

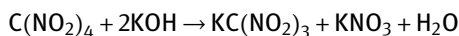
6.4 Chemical Properties of Tetranitromethane

6.4.1 Reactions of Tetranitromethane with Inorganic Compounds

TNM hydrolyzes slowly with water to form trinitromethane (nitroform):



Pure TNM is colorless, but hydrolysis in the presence of moisture will cause it to turn yellow. With potassium hydroxide it forms the potassium salt of nitroform:



Reaction of TNM with alkaline species leads to formation of trinitromethane. The preferred alkali for this reaction is potassium ethylate or potassium hydroxide. The rate constant of trinitromethane formation by solvolysis of tetranitromethane in various polar and non-polar solvents can be determined by measuring the absorbance of the nitroform anion $\text{C}(\text{NO}_2)_3^-$ as a function of reaction time [593]. Two mechanisms involving heterolytic C—N bond rupture in water and homolytic C—N bond cleavage in the less polar solvents were proposed to account for the solvolysis reactions.

6.4.2 Reactions of Tetranitromethane with Organic Compounds

Tetranitromethane reacts with organic compounds having double bonds to form intensely yellow colored adducts. This reaction is very sensitive and may be used for detecting traces of unsaturated olefins in saturated paraffin fractions.

Tetranitromethane can be used for nitration of enol silyl ethers and aromatic compounds. It is also employed in the controlled photo-oxidation of sulfides to sulfoxides.

The fact that one of the four nitro groups reacts preferentially was the cause for some speculation that TNM might exist in the form of an isomer trinitromethyl nitrite $(\text{O}_2\text{N})_3\text{C}(\text{ONO})$ but this hypothesis has been eliminated by proving that TNM is a symmetric molecule [575].

Addition of solid ferrocene to pure liquid TNM caused a violent, exothermic explosion accompanied by an intense flash [594].

In the reaction of two mols of styrene with one mol of TNM, the heterocyclic compound *N*- α -phenyl- β -nitroethoxy-3,3-dinitro-5-phenylisoxazolidine was formed [595].

The kinetics and products for the reaction of TNM with inorganic ions and primary, secondary and tertiary alcohols have been investigated [596]. It seems that re-

action of an RO^- ion with TNM starts the sequence of reactions to yield RONO_2 as product.

The electrolytic reduction of polynitroalkanes by electrolysis of tetranitromethane or 1,1,1-trinitroethane is a method for the electrochemical denitration of polynitroalkanes, and it was shown that this method can be used for preparative purposes employing cathodes made from various materials [597]. It was proposed to use the electrochemical denitration method for the separation of mixtures of polynitroalkanes, and also for the removal of accompanying impurities from polynitroalkanes.

Many reactions of TNM with unsaturated compounds and oxiranes lead to nitrosubstituted heterocyclic compounds, many of which are suitable as propellant ingredients [598].

6.4.3 Analysis of Tetranitromethane

Tetranitromethane has been analyzed colorimetrically by its reaction with benzidine. It can be analyzed volumetrically by titration of the iodine liberated when TNM reacts with iodide in aqueous solutions. The reaction with hydrazine liberates an accurate amount of nitrogen gas that can be captured in a gas burette and measured [599]. The reaction that takes place is:



The trinitromethanide anion formed has a strong absorption at 350 nm and can be determined spectrophotometrically [600]. In a 1-cm path length cell, TNM can thus be determined at concentrations down to 2×10^{-5} M in air or in solution.

6.4.3.1 Analysis of Tetranitromethane in the Air

Tetranitromethane is a by-product of the nitration of toluene, a process performed on a large industrial scale. The air in work spaces where TNM may be present should be monitored to make sure that the tolerable concentration of TNM is not exceeded. Air samples can be passed through an impinger filled with ethanol and the absorbed TNM is reacted with benzidine. The color reaction was performed by adding a measured amount of benzidine solution in ethanol (1 g/L) to the TNM solution in ethanol, the pH of which was brought to 6 by means of pyridine [601]. The absorption of the solution is then measured at 400 nm in a spectrophotometer and compared to a calibration curve. The dye formed is sensitive to light and not very stable.

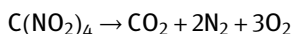
The NIOSH recommended method for analysis of TNM in air is with impingers with ethyl acetate as the absorbent, followed by GC analysis [602].

6.4.4 Decomposition of Tetranitromethane

6.4.4.1 Slow Thermal Decomposition of Tetranitromethane

Tetranitromethane is indefinitely storable at 273 K (0 °C). Above 303 K (30 °C), which is a warm room temperature in a tropical climate, it will decompose slowly under evolution of nitrous fumes. Above 313 K (40 °C) in a sealed container there will be a noticeable increase of pressure due to gaseous decomposition products.

Pure TNM can be heated to 373 K (100 °C) without exploding. The exothermic decomposition starts normally at 523 K (250 °C) which is substantially above its boiling point of 399 K (126 °C). In the presence of contaminants the autodecomposition reaction



may start at lower temperatures.

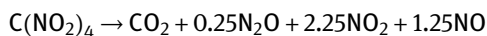
The thermolysis of tetranitromethane has been studied experimentally and computationally by semiempirical methods starting with the stable molecules and ending with the final products NO, NO₂, CO and/or CO₂ [603]. In agreement with the experimental data, the rate-limiting step has been found to be the monomolecular activation of a C—N bond, which can proceed either towards dissociation or towards isomerization to nitrite. A detailed reaction mechanism was proposed and every transition state was identified. The activation energy and the pre-exponential factor in the rate constant have been computed and found to be in good agreement with experimental results.

Tetranitromethane vapor at a partial pressure of 1 mm Hg diluted with helium to atmospheric pressure was passed through a stirred-flow reactor and the rate of conversion as a function of dwell time was monitored by GC [604]. Mass spectrometric analysis of the decomposition products showed NO, NO₂, N₂O, and CO₂.

The rates of thermal decomposition of tetranitromethane, chlorotrinitromethane, bromotrinitromethane and 1,2-dichlorotetranitroethane were determined in selected solvents at various temperatures [605, 606]. The results of this study were used to derive a mechanism for the decomposition. The rate equation for decomposition of TNM is:

$$k = 10^{16.5} \exp[(-38400 \pm 1400)/RT]$$

and the products of the reaction are:



The gas phase decomposition of tetranitromethane, hexanitroethane, chlorotrinitromethane, bromotrinitromethane, iodotrinitromethane and dichlorodinitromethane has been studied over a temperature range from 373 to 433 K (100–160 °C) using a manometric method [607]. The reactions were found to be homogeneous and first order. The rates were independent of vapor pressures and of nitric oxide, nitrogen peroxide and iodine additions. The parameters of the Arrhenius equation

have been determined and a qualitative analysis of the decomposition products has been carried out. The results were interpreted in terms of a radical non-chain mechanism, the C—N bond scission being the first step.

6.4.4.2 Rapid Thermal Decomposition of Tetranitromethane

A solution of tetranitromethane in benzene in the liquid phase decomposed at high pressure at a rate significantly exceeding the rate of decomposition of pure tetranitromethane under the same conditions [608]. The addition of toluene or nitromethane to tetranitromethane did not influence the rate of its decomposition in gas mixtures. This observation can be explained by the formation of charge transfer complexes in a solution of tetranitromethane in benzene. The thermal decomposition of tetranitromethane vapor was measured in shock waves [609].

6.4.5 Photolysis of Tetranitromethane

Tetranitromethane in polar or non-polar solvents was electronically excited with 248 nm, 15 ns pulses from an excimer laser and the transient species formed were detected and characterized by nanosecond time-resolved absorption spectroscopy [610, 611]. In aerated or deaerated polar solvents the NO_2 radical and the nitroform anion $(\text{NO}_2)_3\text{C}^-$, with absorption maxima at 350 nm, were formed. In non-polar solvents, electronic excitation of TNM lead to the formation of the NO_2 radical and a transient species with absorption at 307 nm, which was attributed to the trinitromethyl radical, $(\text{NO}_2)_3\text{C}^\bullet$. Prolonged irradiation of TNM in non-polar solvents resulted in the formation of nitroform with an absorption maximum at 290 nm, which is generated by $(\text{NO}_2)_3\text{C}^\bullet$ via H abstraction from the solvent. See also reference [612].

The products of the photolysis of TNM were monitored in the 10^{-8} – 10^{-3} s range by recording the optical absorption and electrical conductivity of the solutions [613]. In polar solvents, the anion of nitroform, $\text{C}(\text{NO}_2)_3^-$, was formed during the 20 ns laser pulse. The yields of $\text{C}(\text{NO}_2)_3^-$ were highest in ethanol and lowest in aqueous solutions. In water, ionic dissociation of tetranitromethane was the main photolytic decomposition mode. In the alcohols and acetone a two-step mechanism was proposed involving C—N bond rupture to form the trinitromethyl radical, which subsequently picked up an electron from the solvent to form $\text{C}(\text{NO}_2)_3^-$ and an electron deficient solvent state.

The principal result for the decomposition of tetranitromethane during pulse photolysis using a UV laser is the formation of trinitromethane anions [614]. The quantum yield for the photodecomposition of tetranitromethane in methanol or in 96% aqueous ethanol is higher than in the vapor phase.

The photolysis of TNM has developed into a useful synthesis tool for nitration of organic compounds and the synthesis of trinitromethyl-substituted energetic compounds, as described in a series of publications that continued for up to 45 sequels, with a few examples quoted here [615–618]. Aromatic nitration by TNM was shown

to be photochemically initiated but mixtures of TNM with pyridine may explode accidentally [619].

The photofragmentation dynamics of TNM were explored by spin-unrestricted time-dependent excited-state molecular dynamic computations [620]. The leading order process was represented by the molecule undergoing cyclic excitation and de-excitation. During excitation cycles, kinetic energy was assumed to accumulate to overcome the dissociation barriers in the reactant and subsequent intermediates. The dissociation pathway included the ejection of NO_2 groups followed by the formation of NO and CO.

6.4.6 Radiolysis of Tetranitromethane

Because it is unlikely that tetranitromethane-based rocket propellants would be used in outer space where they are subjected to cosmic radiation, one would not worry about the lack of radiolytic stability of TNM. It was discovered that TNM acts as a free radical scavenger similar to NO in some radiolytic reactions where free radicals maintain a decomposition reaction [621]. One must be careful to avoid the formation of explosive mixtures during radiolysis experiments with TNM.

6.5 Strand Burning of Tetranitromethane and Tetranitromethane Mixtures

Encyclopedia of Monopropellants contains a comprehensive discussion of the strand burning of tetranitromethane and tetranitromethane mixtures, also with reference to accidental explosions of such mixtures.

6.6 Materials of Construction for Tetranitromethane

Glass, stainless steel, lead or aluminum are not attacked by dry TNM. Plain iron, copper, bronze, or zinc are not suitable for use in contact with TNM. PVC, polyisobutylene, butyl rubber or latex rubber are not suitable for use with TNM, which will either degrade their mechanical properties or permeate through the materials.

6.7 Explosive Safety Properties of Tetranitromethane

6.7.1 Shock Sensitivity of Tetranitromethane

Pure TNM is not shock sensitive to mechanical impact but the presence of organic contaminants can dramatically lower its shock sensitivity to a point where it has to be handled with the same precautions as a liquid explosive.

Pure TNM is a relatively non-explosive liquid. The impact sensitivity on the Explosives Research Laboratory (ERL) drop-weight impact machine with 2.50 kg weight was above 320 cm (for comparison: TNT = 160 cm) [541].

Tetranitromethane could not be made to explode under the maximum impact load of the apparatus used when tested for impact sensitivity in comparison to glycerin trinitrate, ethylene glycol dinitrate, and other energetic liquids [363].

6.7.1.1 Shock Sensitivity of Tetranitromethane Mixtures

Mixtures of TNM with hydrocarbons like toluene have been reported as being explosive and more sensitive to shock than nitroglycerine. Preliminary studies of the sensitivity of TNM when mixed with nitromethane or nitrobenzene showed that the impact sensitivities of these mixtures do not bear out the extreme sensitivity reported in the literature [622]. Mixtures of TNM and nitrobenzene were found to be much more sensitive than mixtures with nitromethanes. With both substances the maximum sensitivity occurred at the stoichiometric composition for explosion to CO₂, see Table 47.

Table 47: Drop weight impact sensitivity of tetranitromethane mixtures.

Diluent	Mass-% TNM	Impact sensitivity with 2.5-kg mass, cm
Nitromethane	44.6	109
Nitromethane	21.2	196
Nitromethane	65	180
Nitromethane	85	210
Nitrobenzene	42.6	264
Nitrobenzene	61.7	44
Nitrobenzene	76.3	22
Nitrobenzene	82.8	47
For comparison:		
Nitroglycerine		4–5
RDX		22
TNT		160
Pure TNM		>320

Data source: [541]

In 1920 at the University of Münster in Germany during a chemistry class lecture a massive iron gas burner containing a residue of 10 g of a TNM/toluene mixture suddenly exploded. The detonation splintered the container, and of the 300 students in the area 10 were killed and 20 were injured (see additional information on this accident later).

The card gap sensitivity of TNM/benzene, TNM/methyl glycol, and TNM/nitromethane mixtures was determined over a wide range of mixture ratios [623]. The

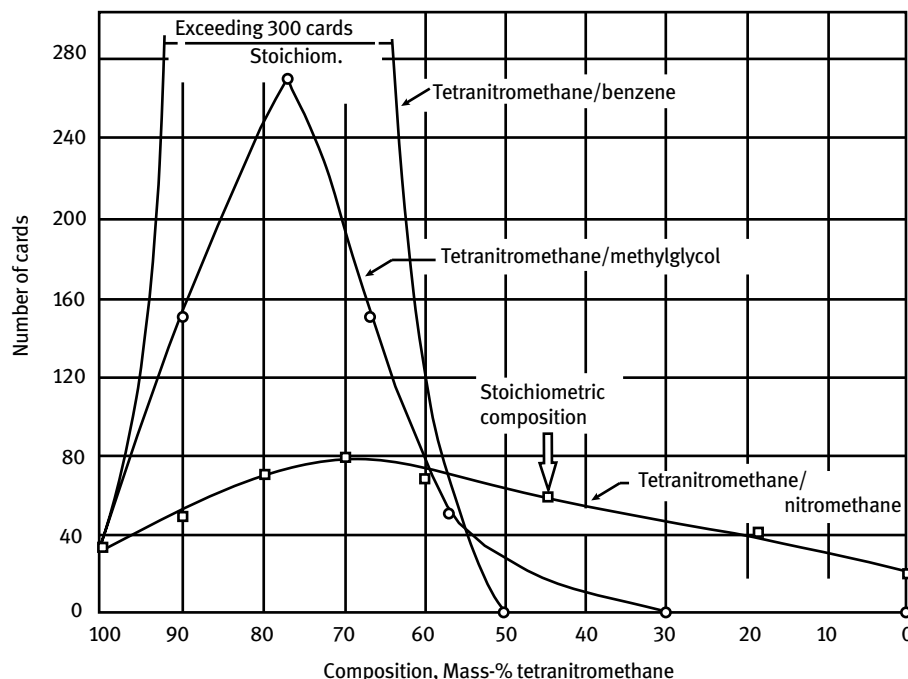


Figure 9: Card gap sensitivity of tetranitromethane mixtures (reproduced and modified from [623], with permission from © 1958 American Chemical Society; permission conveyed through RightsLink.)

higher the number of cards to prevent explosion, the more sensitive the explosive mixture is. The results are illustrated in Figure 9. While TNM/methyl glycol and TNM/nitromethane mixtures showed a maximum of sensitivity within the capability of the test method (<300 cards), a wide range of TNM/benzene mixtures required more than 300 cards to obtain a no go result and the maximum of the sensitivity could not be determined.

6.7.2 Adiabatic Compression Sensitivity of Tetranitromethane

Ethyl nitrate and *n*-propyl nitrate were used to calibrate an adiabatic compression U-tube test apparatus in preparation for additional tests with tetranitromethane and difluoroamino compounds [624]. The average 50% probability pressure ratio derived from a probit plot using the up-and-down method for ethyl nitrate was 7.81 ± 0.71 . Five tests were conducted to evaluate the sensitivity of TNM at ambient temperature ($\sim 294\text{ K} = \sim 70^\circ\text{F}$). In all cases, dry air in the gas bubble and the maximum driving pressure of 12.4 MPa (1800 psi) were used. The gas bubble was partially evacuated during some tests to obtain higher driving pressure ratios. No positive reactions were obtained up to the maximum driving pressure ratio of 256.

6.8 Detonation Properties of Tetranitromethane

The detonation velocity of pure TNM is $6360 \text{ m/s} = 20900 \text{ ft/s}$ at $\rho = 1.637 \text{ g/cm}^3$. Other sources give a detonation velocity of 6400 m/s for pure TNM with a density of 1.64 g/cm^3 [562].

The detonation front structure and parameters in solid and liquid tetranitromethane were investigated using a Doppler Fabry-Perot velocimeter, recording the particle velocity of explosion products braking on the high explosive/window interface [625]. A smooth front of the detonation wave and concave negative-going particle velocity profile were observed for liquid TNM. The experimental records indicated that because of solid TNM heterogeneity, turbulization occurred behind the detonation wave front, which became evident in the form of velocity fluctuations in the $U(t)$ profile.

6.9 Explosive Performance of Tetranitromethane

In the Trauzl lead block test, pure TNM gave an indentation that was 21.4% of that of TNT.

6.9.1 Detonation of Tetranitromethane Mixtures

The explosive properties of mixtures of tetranitromethane and nitrobenzene have been known for a very long time but little is known about their actual use in the field. Mixtures of tetranitromethane with fuels are more suitable as explosives than as rocket propellants. The adiabatic explosion temperature of TNM is 2948 K (2675°C), the detonation velocity in 21-mm diameter steel pipes is 6400 m/s [626].

Mixtures of tetranitromethane with pyridine may explode accidentally [619].

The detonation velocities and the Trauzl lead block indentations of the same TNM/organic compound mixtures studied in the first part of this two-part publication (see mixtures listed in Table 45) were measured in 9.5 and 22-mm diameter charges [627]. The highest detonation velocities were observed with mixtures of 78.7% TNM and 21.3% *p*-nitrotoluene (8170 m/s) or 80.3% TNM and 19.7% α -nitronaphthalene (8160 m/s). The highest lead block expansion (650 cm^3) was achieved with a mixture of 65.95% TNM and 34.05% *m*-dinitrobenzene.

Lead block indentations of TNM mixtures are compared to those obtained with glycerin trinitrate and TNT in Table 48.

Mixtures of TNM with organic fuels are shock sensitive and detonable. A mixture of TNM and toluene detonated in an auditorium during chemistry classes taught at the University of Münster in Germany, resulting in several fatalities [628–630]. This explosion occurred in the overcrowded lecture hall on 27 May 1920, when in a lecture on combustion with combined oxygen a cutting torch device employed in the first year of

Table 48: Lead block indentations of TNM and TNM mixtures

Detonator size	Pure TNM	70 mass-% TNM + 30 mass-% N ₂ O ₄	87 mass-% TNM + 13 mass-% benzene (stoichiometric)	For comparison	
				TNT	Glycerin trinitrate
1	12	0	413	0	171
2	44	0	404	0	172
3	65	13	404	218	379
4	86	48	—	268	407
5	71	37	445	332	397

Trauzl block, 10 g sample, widening of a 20 cm³ bore measured in cm³ as a measure for explosive power, from [559]

World War I for cutting-burning through barbed wire entanglements of front line barricades and in which toluene was the fuel and C(NO₂)₄ the supporter of combustion, was demonstrated. This device consisted of a piece of steel tube 20 cm long by 2.8 cm in diameter closed at one end. When filled with 15 g of cotton or cellulose wadding the stuffing will absorb 75 mL of a mixture of 7.5 mL of toluene and 67.5 mL of C(NO₂)₄ without any of the liquid running off. This material burns quietly and slowly at the regular rate of about 4 cm in 3/4 min., giving a very hot flame containing an excess of oxygen. The time for complete burning of the charge in the apparatus was about 3 1/2 min. On the day of the accident the charge had behaved as expected for about 3 min., the demonstration in wire cutting, etc., was finished and the quiet burning out of the remainder was awaited as usual when a violent explosion occurred, rending the steel burner tube into many small pieces, killing 5 students outright and wounding 5 others fatally. In all, 30 out of the 300 present were struck. The damage to the apparatus and building was extensive. Investigation showed that the lecture journal from which the assistant secured his instructions had recently been rewritten and that the unit of gram had been inadvertently entered instead of mL in recording the quantities of the components to be used in this mixture. Hence in this fatal experiment the mixture consisted of 7.5 g of toluene and 67.5 g of C(NO₂)₄. As the specific gravity of toluene is 0.8 and that of C(NO₂)₄ is 1.65, the weight of toluene in this mixture was nearly double that intended.

The shock sensitivity of TNM/toluene mixtures was measured in a gap test that used water instead of plastic cards to fill the gap between the donor and acceptor charge [631].

The minimum gas pressure of an oxygen/methane mix in the donor section to initiate detonation of a TNM/benzene mixture (1.5 TNM/1 benzene by volume) in a 30-mm O.D. Plexiglas tube was 2 atm, where two out of three tests resulted in a detonation [632]. Using an incrementally higher gas pressure of the oxygen/methane mix in the

donor section, the detonation time lag in the liquid explosive decreased from 350 to 10 μ s.

Rapidly cooled mixtures of TNM and benzene will contain small crystals (5–10 μ m) of TNM suspended in benzene. At even lower temperatures, both oxidizer and fuel will freeze. The detonation velocity of TNM/benzene mixtures was measured at different temperatures [633]. The detonation velocity of the liquid homogeneous 70 TNM/30 benzene solution at room temperature was 7680 m/s, but the two-phase, inhomogeneous, rapidly cooled mixture detonated at varying speeds between 3340 and 6500 m/s, depending on the temperature.

The detonation of tetranitromethane/ethyl iodide mixtures with volume ratios ranging from 27/73 to 30/70 was tested in flat channels of constant depth but varying diameters to determine critical diameters and propagation through narrow passages or sharp bends where the detonation wave would be attenuated or quenched [634].

The effects of hexane, propylene oxide, chloroform, and tetrachloromethane on the detonation properties of TNM were studied experimentally in 25-mm charges [635]. The densities of TNM mixtures with these additives were measured at 283–303 K. The density as a function of the TNM concentration and temperature was linear for mixtures all except those with CCl_4 . The detonation velocities for mixtures containing hexane or propylene oxide had a maximum at the stoichiometric composition. A TNM/hexane mixture containing a mol fraction of 0.715 TNM had a density of 1.3473 g/cm³ and a detonation velocity of 7207 m/s. The critical diameters below which detonation would no longer propagate were determined for all four mixtures [636]. Measured detonation velocity data were compared with those calculated by using a Becker-Kistiakowsky-Wilson EOS.

A laser interferometer was used to measure mass velocity profiles in steady-state detonation waves in tetranitromethane and its mixtures with methanol [637, 638]. In the experiments with tetranitromethane, the chemical spike pressure was found to be 1.7 times higher than the CJ pressure. A 50% increase in methanol concentration led to instability of the detonation front manifested in oscillations in the mass velocity profiles. The detonation velocity of TNM/MeOH mixtures increased from 5400 m/s at 0% MeOH to a maximum of 7100 m/s at 20% MeOH which corresponds to a small positive oxygen balance (equal to + 9%), and then dropped to a low of 5800 m/s at 60% MeOH. The detonation became unsteady when the MeOH content was increased beyond 40%. Stoichiometric zero oxygen balance corresponds to a TNM/methanol ratio of 75.4/24.6.

The effect of dilution of tetranitromethane by methanol on the process of detonation was studied over a wide range of diluent concentrations [639]. Experiments on the ignition of mixtures in steel tubes of various diameter were performed to obtain data on the critical (limiting) diameters. The results were compared with those from previous studies of mixtures of nitromethane with methanol and nitrobenzene. There may be chemical interactions of tetranitromethane as an active oxidizer with methanol as a fuel component in the reaction zone. The detonation velocity depen-

dence on methanol concentration goes through maximum near stoichiometric compositions calculated for total oxidation of fuel elements [640].

6.10 Toxic Properties of Tetranitromethane

The toxicity of TNM has been known for 100 years [641]. Tetranitromethane is very poisonous and has been the cause of several accidental fatal poisonings, mostly in connection with the production and storage of trinitrotoluene where it is formed as a volatile by-product [642–644]. Some toxicity publications erroneously still report that TNM is used as a rocket propellant, when actually it is no longer used as such. A long time ago it has been evaluated as a rocket propellant but that is now history.

The acute toxicity of TNM is first and quickly noticeable in the form of irritation of the mucous membranes in the eyes, nose and respiratory tract. The next symptoms are increased salivation, inflammation of the nose and upper respiratory passages, accompanied by headache or nausea. Repeated exposure leads to chronic poisoning evidenced by headaches, continued fatigue, sleeplessness, slowing of the heartbeat (bradycardia), methemoglobinemia, carboxyhemoglobin formation and respiratory distress, accompanied by anomalies of the central nervous system and irregular heartbeat. Skin irritations were rarely observed.

Inhalation of tetranitromethane causes nasal passage irritation and pulmonary carcinogenesis in rodents [645]. A very detailed summary of the toxicity of TNM has been published as part of an IARC monograph [646]. The animal test acute toxicity levels are summarized in Tables 49 and 50.

Summaries of toxicity information for trinitromethane and tetranitromethane were compiled in a government report [649]. Oral and inhalation toxicities and the degree of histological damage increase with increasing molecular weight of the compounds. The following Table 51 gives TNM acute toxicity data obtained from animal exposure tests.

Table 49: Acute toxicity animal tests with tetranitromethane.

Animal	Mode of administration	LD50, mg/kg	LC50, ppm
Rat	p.o.	130	
Rat	Inhalation		18
Rat	i.v.	12.6	
Mouse	p.o.	375	
Mouse	Inhalation		54
Mouse	i.p.	53	
Mouse	i.v.	63.1	
Cat	Inhalation		100

Data source: [84]

Table 50: Toxicity of tetranitromethane in rodent animal tests.

Species/Sex	Route	Measure	Value
Rat, Sprague-Dawley male	Oral	LD50	130 mg/kg (83–205)
Mice, CF-1 male	Oral	LD50	375 mg/kg (262–511)
Rat, Sprague-Dawley male	Intravenous	LD50	12.6 mg/kg (10.0–15.9)
Mice, CF-1 male	Intravenous	LD50	63.1 mg/kg (45.0–88.7)
Rat, Sprague-Dawley male	Inhalation	LC50	17.5 ppm (16.4–18.7) 0.14 mg/L
Mice, CF-1 male	Inhalation	LC50	54.4 ppm (47.0–61.7) 0.44 mg/L

Data source: [647, 648]

Table 51: Toxicity of tetranitromethane as determined by animal exposure tests.

Route	Species	Dose	Response
Oral	Rats, male	130 mg/kg	LD50
Oral	Mice	380 mg/kg	LD50
Inhalation	Rats, male	18 ppm for 4 h	LC50
Inhalation	Mice	54 ppm/for 1 h	LC50

Data source: [650]

Chronic exposure tests to low levels of TNM extended over 2 years showed significantly increased frequency of tumors in bronchiogenic carcinoma. Based on these data, TNM has been categorized as a group 2B carcinogen by the IARC Carcinogen List criteria. It may also be a mutagen and cause DNA damage.

The mechanisms underlying carcinogenesis induced by TNM have not yet been clarified. It was previously revealed that nitrosotyrosine and nitrosotyrosine-containing peptides caused Cu(II)-dependent DNA damage in the presence of P450 reductase, which is considered to yield nitroreduction. Since TNM is a reagent for nitration of tyrosine in proteins and peptides, it was hypothesized that TNM-treated tyrosine and tyrosine-containing peptides induce DNA damage by the modification of tyrosine. DNA damage induced by TNM-treated amino acids or peptides using 32P-5 end-labeled DNA fragments obtained from the human p53 tumor suppressor gene and the c-Ha-ras-1 protooncogene was detected [651]. Time-of-flight mass spectrometry confirmed that reactions between Lys-Tyr-Lys and TNM yielded not only Lys-nitroTyr-Lys but also Lys-nitrosoTyr-Lys. Therefore, it was speculated that the nitrosotyrosine residue can induce oxidative DNA damage in the presence of Cu(II) and NADH.

For government regulatory agency activities, in particular those affecting drinking water quality in the vicinity of explosives manufacturing plants, there was a deficiency of data on TNM based on which safe contaminant levels of TNM in drinking water could be established and Drinking Water Health Advisories could be issued [652]. This report contains a good summary of toxicity data on TNM as they were known at that time.

Inhalation of tetranitromethane by rats (20 animals in each group) at 3 levels of concentration, 1230, 300, and 33 ppm, caused death in 50% of the animals in 36.3 min, 60 min, and 5.8 h [653]. Successive signs of toxicity observed were considerable preening, increased respiration which was deeper, closed eyes, and gasping respiration, lacrimation, and rhinorrhea and salivation. Animals appeared cyanotic and suffered short tonic convulsions and coma prior to death. In the same investigation, effects of chronic exposure were: inhalation of 6.35 ppm tetranitromethane by 2 dogs and 19 rats (with equal numbers of control animals) for 6 months on a 6 h/day, 5 days per week basis produced 11 deaths (57%) in the rats and no deaths among the dogs. Only one death occurred in the control group of rats. Temporary symptoms in the dogs after the first 2 days of exposure included occasional coughing, lethargy, unthrifty appearance and refusal to eat at the termination of each exposure. A yellowish discoloration of the fur persisted in all animals. There was occasional blood-tinged exudate on the nares of the rats. The target organ for chronic TNM toxicity was the central nervous system and heart. The time to 50% death in TNM-exposed rats was 36 min. at 1230 ppm, 60 min. at 300 ppm, and 518 h at 33 ppm [643]. At the highest exposure concentration, rats exhibited rapid and severe respiratory distress, which was followed by cyanosis, convulsion, coma, and death. Similar but less severe dose-related symptoms appeared at lower exposures. At 6.35 ppm, exposure for 6 h/day, 5 days/week, the ET50 was 133 days, and there were no specific signs of toxicity or alterations in blood chemistry.

Male Sprague-Dawley rats and CF-1 mice were exposed to TNM vapor generated by a diffusion tube system for 4 h. Groups of 10 rats were exposed to 6 concentrations between 10 and 23 ppm and groups of 10 mice were exposed at 8 concentrations between 14 and 76 ppm [647]. The LC50 values for rats and mice were 17.5 and 54.5 ppm, respectively. All exposed animals remained inactive and had breathing difficulties, and eye and nose irritation at toxic levels of exposure. Deaths that occurred following exposure were generally in the first 12 h. Rats at non-lethal exposure levels lost weight for 4 days but recovered weight gain by the end of the 14-day observation period. Weight loss was more severe in survivors at the higher (partially lethal) doses. Scattered weight losses were seen in surviving mice. The animals that died showed moderate to severe lung congestion and areas of alveoli hemorrhaging at necropsy. Survivors showed mild lung congestion. In the same test series, groups of 100 male Sprague-Dawley rats were exposed continuously for 14 days to 3.5, 5 or 7.5 ppm TNM by inhalation. No mortality was seen at 3.5 ppm; at 5 ppm, mortality at 10 and 14 days was 5 and 15%, respectively, and at 7.5 ppm mortality was 3, 23, and 65% at 7, 10, and 14 days. At termination, mean body weights of survivors were 15, 25, and 55% lower than controls at 3.5, 5, and 7.5 ppm exposure groups; mean wet weights of lungs were about 20, 35, and 65% greater than controls at the same exposure levels. No dose-related decreases were seen in liver or kidney weights. Lung irritation and edema were noted on gross examination. The incidence of lung edema increased with exposure level as did the severity of symptoms. Evaluation of pulmonary lesions was

complicated by chronic murine pneumonia in all animals in the colony. Bronchiolitis, bronchitis, and tracheitis appeared related to exposure. Based on decreases in body weight and increases in lung weight (edema), the lowest observed adverse effect level (LOAEL) was 3.5 ppm, but a no observed adverse effect level (NOAEL) was not established.

Rats and mice were subjected to inhalation exposure at 0.2, 0.7, 2.0, 5.0, and 10 ppm TNM in air for 6 h/day, 5 days/week for 13 weeks [648, 654]. At the highest dose tested, final mean body weights of male and female rats were 15 and 6% lower than controls, respectively. At necropsy, lungs were found infiltrated with mononuclear inflammatory cells with minimal fibrosis of the interstitium surrounding bronchioles. Focal metaplasia was found in 4/10 females at 10 ppm. These observations on lung pathology were not found at lower exposures. Increased mean absolute liver weights and liver to body weight ratios observed in both sexes were not dose-related nor was there any accompanying liver microscopic pathology. Mice exposed under identical conditions as rats displayed lethargy and dyspnea. The final mean body weights of males were 5 and 12% lower than controls at 5 and 10 ppm, respectively; in females weight loss was 9 and 12% at 5 and 10 ppm, respectively. Necropsy findings revealed mild inflammation of nasal mucosa, serous exudate, focal metaplasia of the nasal and bronchiolar epithelium.

In the same series of tests, life-time exposure studies also were carried out in rats and mice by exposing animals to inhalation of TNM in air at 0, 5, and 10 ppm for 104 weeks (2 years). The decrease in survival at the high exposure level was significant ($p < 0.001$). Mean survival time was 664, 660, and 616 days for male rats and 647, 691, and 657 days for females at 0, 2, and 5 ppm, respectively. Mean body weights at 100 weeks at 5 ppm were 17 and 15% lower than controls for males and females, respectively; at 80 weeks the weights were similar to controls in both sexes. Hyperplasia of the alveolar bronchiolar epithelium occurred at increased incidence in exposed rats, and in organs other than lungs no exposure-related non-neoplastic changes were seen. In all four test groups there was clear evidence of carcinogenic activity of TNM. In mice treated under similar conditions, mean survival time was 709, 650, and 633 days for males and 672, 688, and 673 days for females at 0, 2.0, and 5.0 ppm, respectively. Mean survival time was significantly lower ($p < 0.001$) in males exposed to 2.0 ppm. At 2.0 ppm exposure, the mean body weights at termination were 9 and 19% less than controls in males and females, respectively. Non-neoplastic lesions observed in the nasal passages of mice were similar but less severe than those observed in rats treated under identical conditions of exposure.

Groups of Fischer 344 rats and B6C3F₁ mice were exposed for 2 years to vapors of tetranitromethane at concentrations below (0.5 ppm) and slightly above (2 or 5 ppm) the current US recommended occupational exposure limit [655]. Under the conditions of exposure of 6 h/day, 5 days/week, tetranitromethane was found to cause mild irritation and hyperplastic lesions in the nasal passages, but no nasal cavity neoplasms. In contrast, nearly all animals exposed to the higher TNM concentrations, and the

majority of animals exposed to the lower concentrations, developed alveolar/bronchiolar adenoma or carcinoma. Squamous cell neoplasms of the lung also occurred in exposed rats. The extent of the lung tumor response, and the low concentrations of tetranitromethane required to bring about this response are significant, compared to effects of other toxic agents tested at the National Toxicology Program (NTP).

6.10.1 Carcinogenicity of Tetranitromethane

Dominant transforming genes were detected in lung tumors from rats and mice chronically exposed by inhalation to tetranitromethane [656]. The rat lung neoplasms were classified as adenocarcinomas, squamous cell carcinomas (epidermoid carcinomas) or adenosquamous carcinomas. The mouse lung tumors were classified as papillary adenocarcinomas or adenomas. In both species the tumors were morphologically similar to lung tumors in humans. Analyses indicated that the transforming gene was an activated K-ras proto-oncogene in both species. All of the rat tumors tested and all of the mouse tumors tested had a mutated allele with the GC→AT transition mutation present. Tetranitromethane may exert its carcinogenic action by both activation of the K-ras oncogene and stimulation of cell proliferation by its irritant properties.

6.10.2 Mutagenicity of Tetranitromethane

Mutagenicity of tetranitromethane was tested in *Salmonella typhimurium* strains TA97, TA98, TA100, and TA102, using the standard plate method or a preincubation method with or without S9 activation (0.5 mL rat S9/plate) [657]. Tetranitromethane was mutagenic in all strains. Activity was independent of an activation system with maximum mutagenic activity occurring at concentrations of 16–32 µg TNM/plate. Activation reduced the mutagenic and toxicity effect of TNM; at 130 µg/plate all strains except TA97 showed distinct mutagenicity without toxicity. Using the preincubation assay, background was reduced and maximum mutagenicity was seen (without activation) at 16 µg/plate. Strains TA100 and TA102 were sensitive to base-pair substitution mutagens, whereas strains TA97 and TA98 were sensitive to frame-shift mutagens. The results of these studies indicated that TNM reverts base substitution as well as frame-shift mutation.

6.10.3 Workplace Maximum Allowable Concentrations Established by Regulatory Agencies

The most likely occurrence of tetranitromethane (TNM) at the work place would be as a contaminant in TNT. The occupational exposure standard recommended by ACGIH (1981) for tetranitromethane was a TLV-TWA of 1 ppm (8 mg/m³). This limit has remained unchanged for several decades, although additional data have become available in the interim that indicate that TNM is a very toxic chemical with long-lasting effects.

AEGLs recommended by the National Advisory Committee for Acute Exposure Guideline Levels (AEGLs) for Hazardous Substances in 1999 were superseded by the more restrictive guideline levels issued in 2007 and listed in Table 52 for short-term exposure to TNM [658].

Table 52: Summary of proposed AEGL values for tetranitromethane.

Classification	30 min.	1 h	4 h	8 h	Endpoint
AEGL-1	Not recommended due to insufficient data				
AEGL-2	0.66 ppm (5.3 mg/m ³)	0.52 ppm (4.2 mg/m ³)	0.33 ppm (2.6 mg/m ³)	0.17 ppm (1.4 mg/m ³)	Pulmonary irritation in rats [647]
AEGL-3	2.2 ppm (18 mg/m ³)	1.7 ppm (14 mg/m ³)	1.1 ppm (8.8 mg/m ³)	0.55 ppm (4.4 mg/m ³)	NOEL for lethality in rats [647]

As of 2005, the NIOSH REL was 1 ppm (8 mg/m³). As of 2005, the OSHA PEL TWA for 8-h exposure remained at 1 ppm (8 mg/m³), in spite of the fact that in 2004 ACGIH had recommended a drastic lowering of the TLV/TWA down to 0.005 ppm and classified it as A3 chemical (confirmed animal carcinogen with unknown relevance to humans). The NIOSH IDLH limit was at one time 5 ppm, but later it was lowered to 4 ppm.

6.10.4 Protective Equipment for Handling of Tetranitromethane

Tetranitromethane is not absorbed by common filters in gas masks. It is a very symmetrical nonpolar molecule and passes right through high-surface area materials that effectively retain other molecules.

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Nitrous Oxide

The topic of nitrogen oxides had to be distributed over seven chapters because it would have been a very large chapter, which would have made it more difficult for readers to find information on a specific compound. It would also have been difficult to distribute 30 chapters among 5 subvolumes and make each subvolume about the same size. That arrangement was made easier by dealing with smaller increment chapters. The other six chapters in this series are titled Nitrogen Oxides, Nitric Oxide, Dinitrogen Trioxide, Nitrogen Dioxide, Dinitrogen Tetroxide, and Dinitrogen Pentoxide.

Nitrous oxide, N_2O , CAS RN [10024-97-2], also called dinitrogen monoxide, nitro-gen(I) oxide, diazene 1-oxide, hyponitrous acid anhydride, laughing gas, or factitious air is the nitrogen oxide with the lowest state of oxidation of nitrogen, N^{+1} . In French, N_2O is called “*protoxyde d’azote*”. Nitrous oxide occurs naturally as the result of biological processes in the nitrogen cycle. Atmospheric air now contains 314 ppb N_2O . While fairly accurate measurements exist about the antropogenic increase of atmospheric CO_2 , there have been no such historic measurements for N_2O for the same time period since the beginning of the Industrial Age.

Nitrous oxide as the oxidizer in the hybrid rocket engines propelling the Scaled Composite/Virgin Galactic SpaceShipTwo, VSS Unity, to suborbital speeds has opened a new era of space tourism.

1 General Information on Nitrous Oxide

1.1 Summary and Review of Publications on Nitrous Oxide

A very comprehensive review of nitrous oxide chemistry was published in 2001, containing 329 literature references on various applications and reactions of nitrous oxide [1]. This is a good source of information for an in-depth study of this chemical. We have included several of those 329 references in our book here.

An excellent 17-page summary of properties and applications of nitrous oxide, including 145 references, was published in 2009 [2], but it failed to include the earlier published Leontev et al. [1] summary in its list of references. We have included several of those 145 references from the Gaidei [2] summary in our book here.

2 Preparation of Nitrous Oxide

2.1 Natural Occurrence of Nitrous Oxide

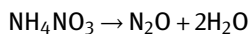
Nitrous oxide is the third most abundant minor constituent of the unpolluted atmosphere, exceeded in its concentration only by carbon dioxide. There are insufficient measurements of the historical evolution of nitrous oxide concentration in the atmosphere to decide whether anthropogenic nitrous oxide is a major contribution to global warming. Initially, there were more measurements of carbon dioxide than of nitrous oxide, but more recently sensitive remote sensing methods have been developed for nitrous oxide as well.

The analysis of air samples taken from air bubbles trapped in glacier ice demonstrated that the nitrous oxide content of the atmosphere remained rather constant (~280 ppb) over the past thousand years. From the mid-eighteenth century, the growth in industrial pollution caused a progressive increase in the N_2O content in the atmosphere. Presently, the concentration of N_2O in the Northern Hemisphere has reached 330 ppb and continues to increase at a rate of 0.5–0.9 ppb per annum. The nitrous oxide content of the atmosphere increases by 0.2 to 0.3% annually. Processes of nitrification and denitrification in soils of tropical and temperate regions and in oceanic waters are the major natural contributors of N_2O . It is assumed that these processes are responsible for 45–85% of all natural emission of N_2O . Heating and power plants, motor transport, some industrial chemical processes (12%), and agriculture (70%) are recognized to be the major sources of anthropogenic N_2O [1]. As of 2010, it was estimated that about 29.5 Mton of N_2O enter the atmosphere each year, of which 64% were natural and 36% due to human activity. Efforts to remove NO_x (NO and NO_2) from stack gases may inadvertently lead to the formation of the less visible, colorless N_2O as a byproduct. Nitrous oxide, ammonia, and methane are formed in manure piles under the action of ammonia-oxidizing bacteria. Some of the nitrogen fertilizer applied to agricultural lands in the form of ammonia or ammonium nitrate ends up as nitrous oxide in the atmosphere.

Carbon dioxide (“dry ice”) deposits have been identified on Mars and other extraterrestrial bodies. It is a safe assumption that wherever carbon dioxide deposits, such as in the polar caps of Mars, some nitrous oxide will deposit along with it. The formation of nitrous oxide, $\text{N}_2\text{O}(\text{X}^1\Sigma^+)$, in interstellar space and in ices on Pluto and Triton has been experimentally investigated. A molecular dinitrogen and carbon dioxide ice mixture was irradiated at 10 K with 5-keV electrons to simulate the electronic interaction effects of Galactic cosmic-ray bombardment of extraterrestrial ice samples over a time of 5×10^6 years [3]. By monitoring the experiment with an FTIR spectrometer on line and *in situ*, the temporal evolution of the 2235 cm^{-1} absorption band of nitrous oxide was found to follow pseudo-first-order kinetics; see Section 6, Environmental Impact of Nitrous Oxide.

2.2 Industrial Production of Nitrous Oxide

Nitrous oxide is commercially produced by controlled, slow thermal decomposition of ammonium nitrate:

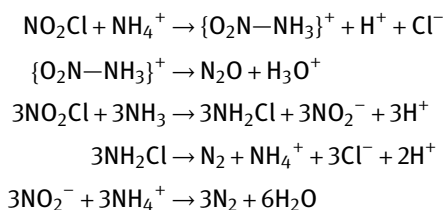


Everybody knows that heating ammonium nitrate to beyond its melting point is a hazardous operation. There have been several industrial accidents when AN exploded instead of slowly decomposing during the production of N_2O [4]. The Compressed Gas Association has issued guidelines for the safe production of nitrous oxide by decomposition of ammonium nitrate [5].

In one version of the AN decomposition process, AN is decomposed in an aqueous, chloride-containing solution in nitric acid at 383–398 K (110–125 °C), while an ammonia atmosphere is maintained above the reaction mixture [6]. The atmosphere of ammonia is maintained by introducing at least part of the required ammonia into the gas volume of the reaction vessel. The decomposition of the AN and the formation of N_2O are enhanced by the presence of catalytically active ions of manganese, copper, cerium, lead, cobalt, and nickel, especially in their bivalent forms.

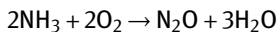
According to a similar patent, N_2O is produced by continuous decomposition of ammonium and nitrate ions fed into an aqueous, strongly acidic (4–6 M in H^+) reaction liquor containing 0.1–0.2M chloride ion as catalyst, at a temperature from 378–393 K (105–120 °C) [7]. The temperature is so maintained that the reaction liquor boils at the reaction temperature, the excess water being continuously removed. N_2O and water are continuously removed, and the N_2O gas that is withdrawn overhead is scrubbed with alkaline solutions to remove chlorine contamination.

A study of the decomposition of the aqueous ammonium nitrate at elevated temperatures and pressures as a function of chloride, nitrate, and total acidity showed that catalysis by both chloride and acid took place in solutions containing 20 mass-% NH_4NO_3 at 453 K (180 °C) [8]. Nitrous oxide and dinitrogen were generated in a 4 : 1 ratio below 0.2M H^+ . A mechanism based on the intermediacy of NO_2Cl was proposed for the chloride catalysis and contrasted to the radical-based pathways operational in molten NH_4NO_3 decompositions. Isotope labeling experiments using $^{15}\text{NH}_4\text{NO}_3$ led to the formation of ^{15}NNO -labeled nitrous oxide and the dinitrogen products $^{15}\text{N}^{15}\text{N}$ and $^{14}\text{N}^{15}\text{N}$ in a 1 : 3 ratio. Decomposition of $\text{NH}_4^{15}\text{NO}_3$ produced only $^{14}\text{N}^{15}\text{NO}$ and $^{14}\text{N}^{15}\text{N}$. This agreed with the reaction sequences:



A website shows pictures of equipment for production of N_2O by decomposition of ammonium nitrate in India [9]

A promising method for the production of N_2O is the thermocatalytic method of direct oxidation of ammonia by oxygen, where platinum-rhodium alloy, oxides of manganese, bismuth, cobalt, and others are recommended as catalysts:



However, the catalysts first proposed in 1928 were insufficient by activity and selectivity on the desired product (less than 84%), produced a high yield of unwanted NO, and were of low mechanical strength. It was, therefore, uneconomical to develop the industrial technology of production N_2O by this method. A process for the preparation of nitrous oxide by reaction of ammonia with oxygen in the presence of steam using a copper-manganese oxide catalyst gives a gas containing nitrogen, oxygen, and nitrous oxide, such that formation of unwanted NO_x byproducts is kept to a minimum [10–13]. Other catalysts patented for this reaction are ceramic mixed metal oxides [14]. For instance, a patent disclosed a process for preparing N_2O by catalytic partial oxidation of NH_3 with oxygen using a catalyst composed of manganese oxide, bismuth oxide, and aluminum oxide, which leads to dinitrogen monoxide with high selectivity [15]. The catalyst composition was: manganese(IV) oxide 5.0–35.0 mass-%, bismuth oxide 4.5–30.0%, and aluminum oxide 35.0–90.5% with a Brunauer-Emmet-Teller (BET) surface area of 5–80 m^2/g .

Many N_2O production patents recover N_2O from the off-gas of another chemical process where it can be directed to a useful purpose instead of venting it above the roof. For instance, the offgas stream of an adipic acid plant may contain from 0.8 to 1.0 mol of N_2O per mol of adipic acid formed by oxidation of cyclohexanol/cyclohexanone mixtures with nitric acid. Nitrous oxide is widely used for the selective oxidation of olefins and unreacted nitrous oxide can be recovered from the product mix and recycled [16].

It has been speculated that oxidation of ammonia by nitrous oxide under carefully controlled (non-combustion) conditions may even result in the formation of hydroxylamine.

2.2.1 Purification of Nitrous Oxide

Nitrous oxide produced by industrial processes may contain nitrogen, oxygen, and other oxides of nitrogen as contaminants, which need to be removed to obtain medical grade nitrous oxide. In a cylinder with nitrous oxide of inadequate purity, nitric oxide, NO, is released at the beginning of drawing gas from the cylinder, while contaminating nitrogen dioxide, NO_2 (in equilibrium with dinitrogen tetroxide) accumulates in the tank residue and is released when the tank is nearly empty. Nitrous oxide can be purified by distillation under high pressure [17]. The effective separation coefficients for nitrous oxide/impurity systems were determined experimentally. The distillation process at high pressure gave a very pure product.

Several other N_2O purification and separation processes have been patented. Another purification method liquefies the impure gas mixture first and then contacts it in

a bubble column with a countercurrent stream of a high-boiling, non-volatile organic solvent such as *N*-methylpyrrolidone, dimethylformamide, dimethyl sulfoxide, propylene carbonate, sulfolane, nitrobenzene, or dimethyl phthalate [18]. The presence of CO_2 in the raw feed gas would be desirable since it dilutes the otherwise potentially explosive mixtures in the first stage of the process. Because the physical properties of N_2O and CO_2 are so similar, it would be difficult to separate the gases by simply physical methods, but CO_2 can be washed out by an alkaline aqueous solvent.

A patent describes a process for purifying N_2O , wherein NO , NO_2 , CO_2 , and H_2O are initially removed, and the gas mixture is subsequently liquefied by compressing it from 40 to 300 bar and cooling to as low as 185 K (-88°C) [19]. From this liquefied gas mixture, dinitrogen monoxide can then be removed. Although this method achieves a purification and concentration of the N_2O , it is economically unattractive owing to the required high pressure (60 bar), the low temperatures 188 K (-85°C), and the associated high capital costs. Similar processes would be useful also for recovering and purifying nitrous oxide that has become contaminated during rocket cold flow testing.

3 Physical Properties of Nitrous Oxide

Several physical properties of nitrous oxide are very similar to those of carbon dioxide. Both molecules are linear molecules with a very small dipole moment and identical molecular mass (44). Both have a very narrow liquidus range, which makes it difficult to handle them in the liquid state without accidentally freezing the contents of tanks and lines.

A very good 22-page summary of physical properties of nitrous oxide was compiled in Appendix B of [20]. A more recent and very complete summary of the physical properties of nitrous oxide can be found in [21]. That report gives most physical properties as a function of temperature and is much more complete than the brief summary on physical properties of nitrous oxide offered here. It provides evaluated thermophysical properties data for nitrous oxide. Equations based on a critical evaluation of experimental data in the literature are given for the variation with temperature along the saturation line for the following liquid and vapor properties: density, specific enthalpy, specific heat capacity at constant pressure, dynamic viscosity, and thermal conductivity.

3.1 Physical and Mechanical Properties of Nitrous Oxide

The molecular mass of N_2O with a natural isotope distribution is 44.013 (1983 IUPAC atomic masses, compared to that of carbon dioxide, which is 44.010). NIST gives a molecular mass of 44.0128 for N_2O .

3.1.1 Freezing Point and Phase Diagrams of Nitrous Oxide

Table 1 gives a summary of literature data on the freezing (melting) point of nitrous oxide.

Table 1: Summary of literature data on the freezing (melting) point of nitrous oxide.

Author(s)	Year	Freezing point		References
		K	°C	
Mitchell, Melvold, and Quaglino	1973	182.26	−90.89	[20]
Blue and Giauque	1935	182.26	−90.89	[22]
		Triple point		
Atake and Chihara	1974	182.407 ± 0.002	−90.74	[23]

3.1.1.1 Phase Changes at Very High Pressures

The phase stability of simple molecular solids is generally predicated on a well-defined separation in energy scale between strong intramolecular interactions and relatively weak intermolecular bonds. A phase diagram for nitrous oxide was derived from *in-situ* high-pressure and temperature Raman and XRD studies [24]. Two new phases (II and IV) were discovered above 600 K between 18 and 50 GPa, and both were quenchable to ambient temperature. The crystal structures and stability fields of N₂O phases are similar to those of CO₂ below 50 GPa and 800 K. However, subtle

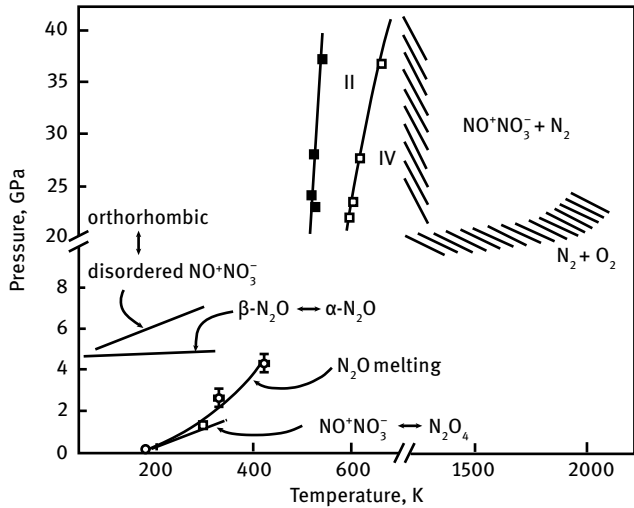
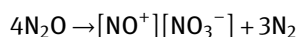


Figure 1: Schematic phase and reaction diagram of N₂O and [NO⁺][NO₃[−]]. (Republished and modified from [25], with permission from © 2005 Elsevier, permission conveyed through Copyright Clearance Center, Inc.) (based on data from several other sources)

differences in their physical properties and crystal structures were found to exist, indicating an increased disparity (or ionicity) between N—N and N—O bonds in bent N₂O-IV (*Pbcn*). At higher pressures and temperatures, N₂O disproportionates into ionic NO⁺NO₃[−] and N₂, whereas CO₂ polymerizes into an extended covalent solid.

Although feed pressures in rockets very rarely reach the gigapascal range, it is worthwhile mentioning that at very high pressures (10–50 GPa), N₂O undergoes several phase changes [25]. From atmospheric pressure to ~5 GPa N₂O crystallizes in the same configuration as CO₂ as Phase I (α) with *Pa3* configuration and above 5 GPa as Phase III (β) with *Cmca* configuration (Figure 1). Phases II and IV exist only above 23 GPa and 500 K.

At 10–30 GPa and with laser heating, N₂O disproportionates irreversibly into nitrosonium nitrate (similarly to the behavior of NO):



3.1.1.2 Melting Point at Very High Pressures

Like water ice, but in the opposite direction, the melting point of dinitrogen monoxide is pressure dependent. This dependency is similar to that of carbon dioxide, which has been investigated more thoroughly than dinitrogen monoxide. Up to a pressure of 25.25 MPa (250 atm), the melting point of N₂O follows the equation

$$T = 182.24 + 1.716 \times 10^{-1}p - 1.91 \times 10^{-6}p^2$$

where *T* is the temperature in kelvin and *p* is the pressure in atm [26]. The phase conditions of melting N₂O are similar to those of CO₂, which is why phase properties for both solids are listed together in Table 2 for comparison.

Table 2: Phase density near the melting point of nitrous oxide at high pressures.

Compound	Initial slope of (<i>dp/dT</i>) in atm/K	Volume change, cm ³ /mol	Phase density g/cm ³		$\rho_{\text{liquid}}/\rho_{\text{solid}}$ at melting point
			liquid	solid	
Carbon dioxide	45.9	8.05	1.178	1.501	1.274
Dinitrogen monoxide	58.3	6.075	1.229	1.480	1.204

Data source: [26]

3.1.2 Boiling Point of Nitrous Oxide

Table 3 gives a summary of literature data on the boiling point of nitrous oxide.

Apparently not only nitrous oxide by itself but also mixtures of nitrous oxide with ethane have been evaluated as refrigerants to replace fluorocarbons, which were the main refrigerants until their adverse environmental impact was recognized. Calculated binary interaction parameters were used to derive the vapor-liquid equilibrium for nitrous oxide/ethane mixtures, which revealed strong positive

Table 3: Summary of literature data on the boiling point of nitrous oxide.

Author(s)	Year	Boiling point		References
		K	°C	
Blue and Giauque	1935	184.59	−88.56	[22]
Hoge	1945	184.695	−88.465	[27]
Atake and Chihara	1974	184.81	−88.34	[23]
Corvaro et al.	2006	184.67	−88.48	[28]
Lemmon and Span	2006	184.68	−88.47	[29]
Ferreira and Lobo	2009	184.646	−88.50	[30]

deviations from Raoult's law with a positive azeotrope at around $X_{\text{C}_2\text{H}_6} = 0.65$ at $T = 243.15 \text{ K}$ [28]. We were amazed to read this publication and not find any precautionary note to warn potential users that this is a dangerous explosive mixture.

3.1.3 Density of Nitrous Oxide

Figure 2 is a representation of the density of nitrous oxide at very high pressures.

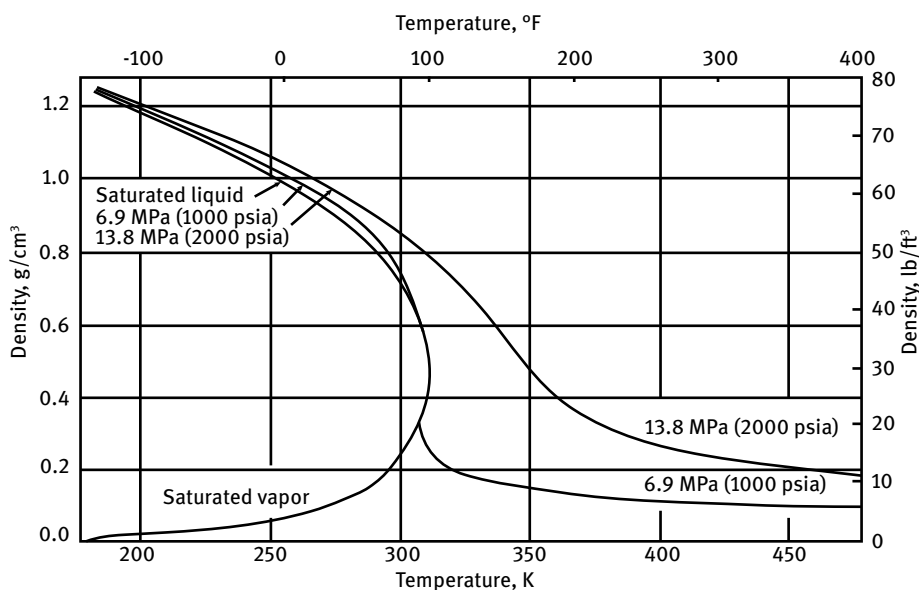
**Figure 2:** Density of liquid nitrous oxide at temperatures below 450 K. (Reproduced and modified from [20].)

Figure 3 is an extension of the data from Figure 2 to higher temperatures. One must anticipate that N_2O will start decomposing explosively under the conditions shown in this graph.

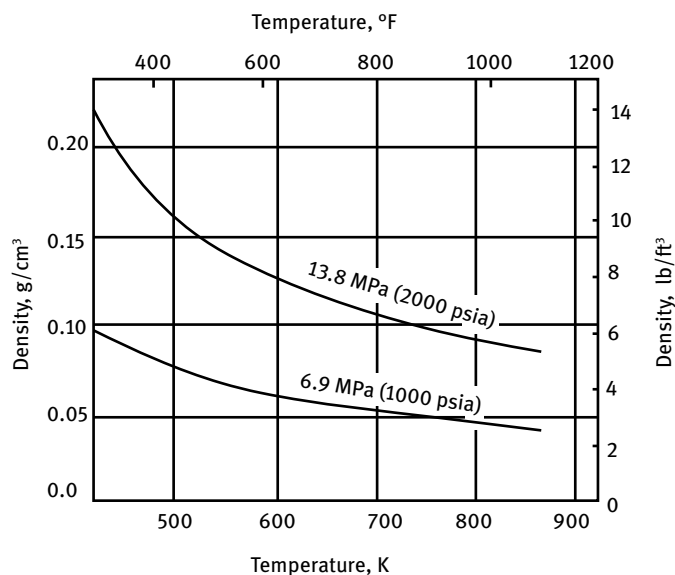


Figure 3: Density of liquid nitrous oxide at temperatures above 450 K. (Reproduced and modified from [20].)

The density and surface tension of liquid nitrous oxide were measured between 182 and 184 K, which is between the freezing point and boiling point of the liquid at atmospheric pressure and are tabulated in Table 4.

Densities of liquid N_2O were measured over a wider range with a high-temperature, high-pressure vibrating tube densimeter system in the sub- and super-critical states [32]. The uncertainty in the density measurement was estimated to be between ± 0.2 and ± 0.3 g/L, depending on the temperature. The densities were measured for temperatures from 473 to 273 K and up to 40 MPa for N_2O (251 data points), which encompassed density ranges between 0.1244 and 1.0511 g/cm³. The liquid densities were correlated with a new three-dimensional density correlation system (TRIDEN) to give a complete set of P - ρ - T data in the sub- and supercritical states and a virial-type equation of state.

The orthobaric density of a compound is the density of coexisting phases (liquid, gas, or solid) at a given temperature. Figure 4 shows the orthobaric densities of nitrous oxide in the temperature range from 183 K to the critical point, based on data points from multiple sources. The solid curve drawn through the numerous values passes well within the scatter of the literature data and joins smoothly with the low-temperature data:

Table 4: Density and surface tension of liquid nitrous oxide.

Temperature K	Density g/cm ³	Temperature K	Surface tension dyn/cm
182.4	1.241	182.5	24.26
182.7	1.241	182.5	24.25
182.6	1.241	182.6	24.23
182.8	1.240	182.8	24.18
183.0	1.239	182.9	24.11
183.1	1.239	183.2	24.07
183.2	1.239	183.4	24.04
183.3	1.237	183.7	24.00
183.4	1.237	183.9	23.95
183.0	1.238	184.0	23.87
183.7	1.238	184.2	23.86
183.9	1.237	184.4	23.85
184.1	1.238		
184.2	1.236		
184.3	1.236		
184.3	1.236		
184.5	1.235		

Data source: [31]

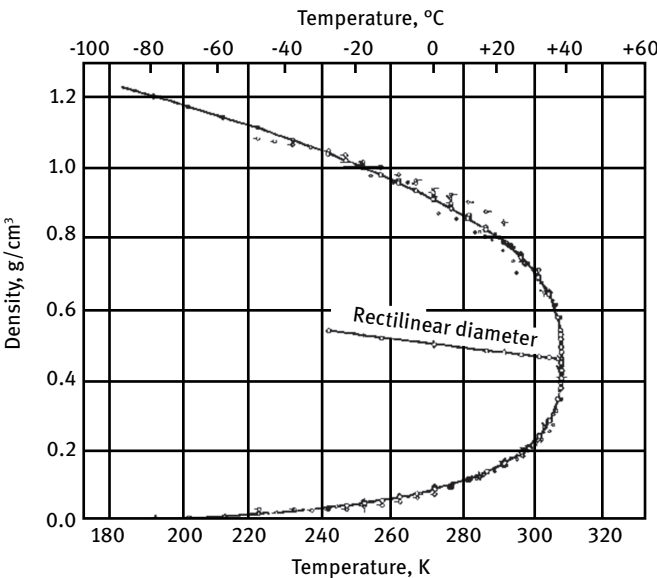


Figure 4: Orthobaric densities of nitrous oxide. (Reprinted and modified from [33] with permission from © 1961 American Chemical Society; permission conveyed through RightsLink.)

The orthobaric density data by Cook [34] (also shown in Figure 4 above as upright triangles, but the data point symbols are too small to recognize) can be expressed by the polynomial equations:

$$\rho_l = 0.452 + 0.00132(t_c - t) + 0.1232(t_c - t)^{\frac{1}{3}}$$

$$\rho_g = 0.452 + 0.00132(t_c - t) - 0.1232(t_c - t)^{\frac{1}{8}}$$

where ρ is the density, subscripts l and g signifying liquid and gas phase, respectively, t is the temperature in °C, and t_c is the critical temperature in °C.

A collection of 51 literature data points on the liquid density of nitrous oxide from five sources taken between 1929 and 1990 was curve fitted to give the following equation [30]:

$$\rho_l = \rho_c \exp\left(c_1 \tau^{\frac{1}{3}} + c_2 \tau^{\frac{2}{3}} + c_3 \tau^{\frac{7}{3}} + c_4 \tau^4\right)$$

where ρ_l is the density in g/cm³, ρ_c is the critical density, T is the temperature in kelvin, and T_c is the critical temperature in kelvin, $\tau = (1 - T/T_c)$, with the parameters $c_1 = 1.6779$, $c_2 = -0.5810$, $c_3 = 1.3148$, and $c_4 = -2.9806$. The standard deviation is ± 0.003 g/cm³.

Other measurements of the density of liquid N₂O showed that the density of liquid N₂O as a function of temperature in the temperature range from 280 to 293 K can be calculated from

$$\rho = 0.9368 - 0.0039t$$

where ρ is the density in g/cm³, and t is the temperature in °C. Another equation covers the density between 252.4 and 297 K:

$$\rho = 0.342 + 0.00166t + 0.0922\sqrt{36.4 - t}$$

A single data point for density at the boiling point at 183.75 K (−89.4 °C) was reported as 1.2257 g/cm³ [35]. See also [36]. The density of frozen N₂O at 78 K is 1.604 g/cm³, [37].

The density and refractive index at 543 nm of frozen nitrous oxide in comparison to frozen oxygen and N₂O₄ are summarized in Table 5.

Table 5: Density and refractive index of solid O₂, N₂O, and N₂O₄ deposited on a Si substrate.

Compound	Temperature, K	Density, g/cm ³	Refractive index at 543 nm
O ₂	16	1.54	1.322
N ₂ O	16	1.16	1.318
N ₂ O ₄	16	1.17	1.316
N ₂ O ₄	60	1.90	1.548

Data source: [38]

3.1.4 Critical Point Properties and the Equation of State of Nitrous Oxide

The critical point properties of nitrous oxide reported during the past 150 years have fluctuated quite a bit, and there was a lot of data scatter due to the different experimental techniques used. The oldest critical point temperature ($309.5\text{ K} = 36.4^\circ\text{C}$) reported in the literature dates back to 1878 and was very close to the value generally accepted today. Table 6 gives a summary of literature data for the critical point properties of nitrous oxide. Because the critical temperature of nitrous oxide is only a few degrees above room temperature, it does not take much change of operating conditions to enter the supercritical regime where heat transfer and phase behavior are totally different from what we are used to for liquids below their critical point pressure and temperature.

The pressure-density-temperature (P - ρ - T) relations in the critical region ($0.996 < T_c < 1.004$ and $0.6 < \rho_c < 1.4$) were determined for N_2O by means of a direct

Table 6: Critical point properties of nitrous oxide.

Property	SI Units	Other units	References
Critical temperature			
	$309.56 \pm 0.15\text{ K}$	$36.41 \pm 0.15^\circ\text{C}$	[39]
	$309.65 \pm 0.2\text{ K}$	$36.5 \pm 0.2^\circ\text{C}$	[40]
	309.49 K	36.34	[41]
	$309.5 \pm 0.5\text{ K}$	36.4°C	[34, 42]
	309.584 K	36.434°C	[33]
	309.52 K	36.37	[43]
	309.548 K	36.398	[30]
	309.56 K	36.41	[44]
Critical pressure			
	$7.238 \pm 0.02\text{ MPa}$	$72.38 \pm 0.2\text{ bar}$	[39]
	$7.27 \pm 0.05\text{ MPa}$	$72.70 \pm 0.5\text{ bar}$	[40]
	$72.346 \pm 0.51\text{ bar}$	71.12 atm	[34, 42]
	72.545 bar	71.596 atm	[33]
	7.2450 MPa	—	[43]
	7238 kPa	—	[30]
	7.238 MPa	—	[44]
Critical volume			
	$0.0955 \pm 0.002\text{ L/mol}$		[40]
		$97.4\text{ cm}^3/\text{mol}$	[34, 42]
		$97.087\text{ cm}^3/\text{mol}$	[30]
	$10.3 \pm 0.1\text{ mol/L}$	—	[39]
	10.2 mol/L	—	[41]
	$10.3 \pm 0.05\text{ mol/L}$	0.452 g/cm^3	[34, 42]
	10.28 mol/L	0.4525 g/mL	[33]
		0.4533 g/cm^3	[44]

Note: Several of these critical point data were also listed on [43] NIST Chemistry WebBook website.

method [39]. The critical properties were determined from a logarithmic plot based on a power law for the vapor-liquid coexistence curve and the P - ρ relation on the critical isotherm for each system. The restricted linear model, one of the simplest scaled equations of state, was applied to describe the P - ρ - T relations in the critical region.

It is hard to believe that anyone would experiment with supercritical mixtures of nitrous oxide and methylamine (a perfect monopropellant and potentially explosive mixture) as a solvent for the extraction of lignin from wood. Given the explosive potential of this mixture, these experimenters were close to death without realizing it [40]. But it would have been interesting to use the same apparatus to characterize the supercritical $\text{N}_2\text{O}/\text{NH}_3$ system, which is also under investigation as a potential monopropellant.

The PVT properties of dinitrogen monoxide were measured by means of two different apparatus: one isochoric apparatus operating in the two-phase region, and the other a two-chamber apparatus operating in the superheated vapor-phase region [45]. The isochoric method was applied in the saturation region, and the Burnett two-chamber method was applied in the vapor region. Isochoric measurements were carried out at temperatures from 219 to 273 K and at pressures from 550 to 3100 kPa. The 18 measurements along the saturated liquid-vapor region were fitted, together with selected literature data, with the Wagner equation. For Burnett measurements, 14 runs along 7 isotherms in a pressure range from 170 to 5200 kPa were made. The second and third virial coefficients were derived, and good consistency was found after comparison with data in the pre-2004 literature. However, the Di Nicola third virial coefficients do not quite match with the set of virial coefficients published later by NIST and shown in Table 7. In a second set of measurements by the same investigators, PVT properties isochoric measurements were carried out at temperatures from 219 to 354 K and at pressures from 550 up to 5400 kPa [46]. For the Burnett measurements, 14 runs along 7 isotherms in a pressure range from 170 to 5200 kPa were performed. The second and third virial coefficients were derived, and good consistency was found after comparison with older literature data in the reduced temperature range of interest ($0.9 < T/T_c < 1.2$).

Numerous experimental values of the coordinates of the triple point and of the critical point of nitrous oxide reported in the literature were reassessed and those judged as most reliable selected for a statistical exercise [30]. Empirical equations were derived for the vapor pressure, sublimation, and fusion curves. The virial coefficients and saturation properties as functions of temperature along the equilibrium curves were described by reduced equations. They were then used in arriving at the molar enthalpies at the triple point and the normal boiling temperature. Equations for the sublimation and fusion curves resulting from the exactly integrated Clapeyron equation compared favorably with the results from the empirical treatment and the various experimental data. For the coordinates at the triple point, a molar volume value of $V_t = 35.847 \pm 0.002 \text{ cm}^3/\text{mol}$, temperature $T_t = 182.293 \text{ K}$, and $p_t = (87.866 \pm 0.001) \text{ kPa}$ were

selected from the average of six independent measurements taken over several years; see also [47, 29].

3.1.5 Compressibility of Nitrous Oxide

Deviations in the compressibility of real gases are indicative of molecule interactions and repulsion. The virial coefficients B of a simple equation of state

$$PV = RT + BP$$

were determined for gaseous nitric oxide and nitrous oxide [48]. The virial coefficient B of nitrous oxide in the range 197–298 K as a function of temperature and pressure can be expressed by the equation

$$B = 32 - \frac{5611.5}{T} + 3.9424 \times \frac{10^6}{T^2} - 3.9145 \times \frac{10^{11}}{T^4} + 3.0747 \times \frac{10^{15}}{T^6}$$

where B is the virial coefficient in cm^3/mol , and T is the temperature in kelvin. Later examination by other investigators showed that the Johnston and Weimer [48] values for N_2O were consistently too low, and for NO the values were consistently too high.

Other gas compressibility measurements covered the range from 243 to 423 K (–30 to +150 °C) for pressures up to 6.56 MPa (65 atm) [49]. Later measurements covered a wider pressure range from 6 to 315 atm [50, 51] Figure 5.

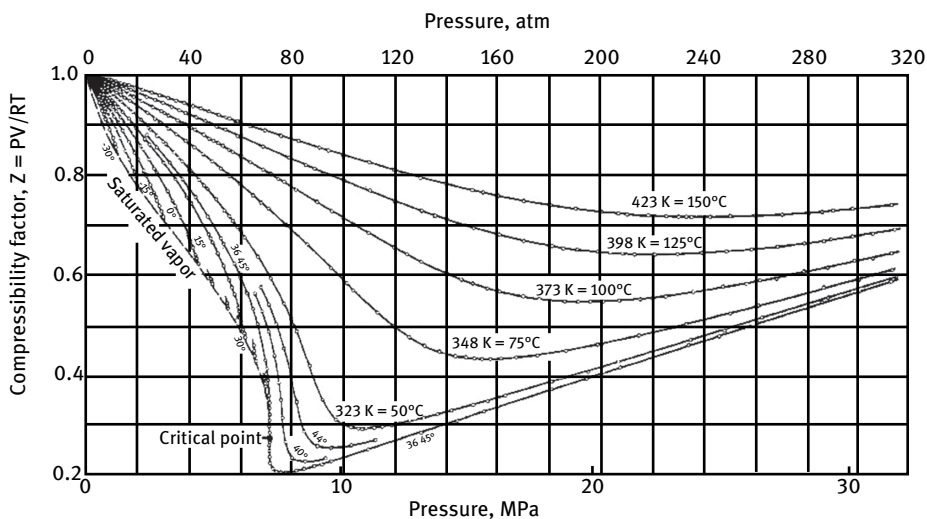


Figure 5: Compressibility factor of gaseous nitrous oxide. (Reprinted and modified from [33] with permission from © 1961 American Chemical Society; permission conveyed through RightsLink.)

From the same set of data, a graph with the pressure-volume isotherms was drawn (Figure 2 on page 230 of [33]).

Because the critical temperature of nitrous oxide is only a few degrees above room temperature, it is very easy to inadvertently slide into supercritical conditions. The pressure-volume isotherms of nitrous oxide near the critical point are, therefore, shown in Figure 6 for conditions near the critical point.

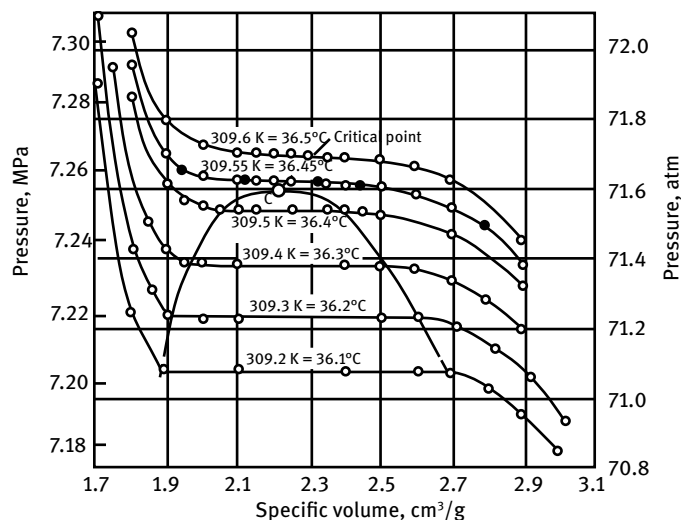


Figure 6: Pressure-volume isotherms of nitrous oxide near the critical point. (Reprinted and modified from [33] with permission from © 1961 American Chemical Society; permission conveyed through RightsLink.)

The compressibility of nitrous oxide gas was measured between 273 and 423 K (0 to 150 °C) and over a number density range of about 18 to 180 amagat¹, which corresponds to pressures of 1.616–16.66 MPa (16–165 atm) [52]. Attempts to measure compressibility of the gas above 423 K (150 °C) were foiled by incipient decomposition of nitrous oxide. The agreement with results of others [51, 33] using somewhat different experimental techniques was satisfactory. The virial coefficients were calculated, and the intermolecular potential of nitrous oxide calculated from the second virial coefficient for several forms of force laws, both spherical and non-spherical. It was attempted to see what information the virial coefficients can yield about the intermolecular forces that cause the deviation from ideal gas behavior. First, a spherical central-force model was used, and then an orientation-dependent model since N₂O is

¹ An amagat is a practical unit of number density. Although it can be applied to any substance at any conditions, it is defined as the number of ideal gas molecules per unit volume at 1 atm (= 101.325 kPa) and 0 °C (= 273.15 K). For nitrous oxide, one amagat unit of number density is equal to 4.4940×10^{-5} mol/cm³.

Table 7: Virial coefficients, thermal conductivity, and viscosity of gaseous nitrous oxide.

References		[54]	[55]	[54]					[54]	[55]	[55, 56]	
		Vapor pressure		Virial coefficients					Thermal conductivity		Viscosity	
Physical state <i>T</i> , K	Gas	Liquid	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas
	$C_p(T)/R$	kPa	$B(T)$, cm ³ mol ⁻¹	$dB/dT \cdot T$, cm ³ mol ⁻¹	$C(T)$, cm ⁶ mol ⁻²	$dC/dT \cdot T$, cm ⁶ mol ⁻²	λ , mW/(m·K)	η , μPa·s				
200	4.04	374.99	-311.9	678.0	-47794	475438	10.9	9.98				
210	4.10	573.1	-280.7	603.9	-28691	317801	14.6	10.47				
220	4.17	840.95	-254.0	542.4	-16447	214933	15.1	10.95				
230	4.23	1192	-231.1	490.7	-8505	146401	15.6	11.43				
240	4.30	1640.2	-211.2	446.9	-3318	99939	16.2	11.92				
250	4.36	2200.2	-193.7	409.4	73	67976	16.7	12.40				
260	4.42	2887.4	-178.3	377.0	2280	45721	17.2	12.88				
270	4.48	3718.6	-164.6	348.8	3695	30079	17.7	13.36				
280	4.54	4713.4	-152.4	324.0	4577	19007	18.2	13.84				
290	4.59	5897.3	-141.4	302.2	5099	11136	18.7	14.32				
300	4.65	—	-131.5	282.8	5377	5529	18.6	14.80				
310	4.70	—	-122.5	265.5	5490	1543	19.4	15.28				
320	4.76	—	-114.3	250.0	5491	-1275	20.2	15.76				
330	4.81	—	-106.9	236.1	5420	-3246	21.0	16.24				
340	4.86	—	-100.0	223.5	5302	-4599	21.8	16.71				
350	4.91	—	-93.7	212.0	5155	-5499	22.6	17.19				
360	4.95	—	-87.9	201.6	4991	-6068	23.4	17.67				
370	5.00	—	-82.5	192.0	4820	-6392	24.2	18.14				
380	5.04	—	-77.5	183.3	4647	-6538	25.0	18.58				
390	5.09	—	-72.8	175.2	4477	-6554	25.8	19.02				

Data source: <https://www.nist.gov/pml/sensor-science/fluid-metrology/database-thermophysical-properties-gases-used-semiconductor-14>

Table 7: (continued)

References	[54]	[55]	[54]	[54]	[54]	[54]	[55]	[55]	[55, 56]
Vapor pressure									
Virial coefficients									
Thermal conductivity									
Viscosity									
Physical state	Gas	Liquid	Gas	Gas	Gas	Gas	Gas	Gas	Gas
T, K	$C_p(T)/R$	kPa	$B(T)$, cm ³ mol ⁻¹	$dB/dT \cdot T$, cm ³ mol ⁻¹	$C(T)$, cm ⁶ mol ⁻²	$dC/dT \cdot T$, cm ⁶ mol ⁻²	λ , mW/(m·K)	η , μPa·s	
400	5.13	—	-68.5	167.8	4312	-6476	26.6	19.45	
410	5.17	—	-64.4	160.9	4154	-6330	27.3	19.88	
420	5.21	—	-60.6	154.5	4003	-6137	28.1	20.30	
430	5.25	—	-57.0	148.6	3861	-5913	28.9	20.72	
440	5.29	—	-53.7	143.1	3728	-5667	29.7	21.14	
450	5.33	—	-50.5	137.9	3604	-5410	30.5	21.55	
460	5.37	—	-47.6	133.1	3488	-5147	31.3	21.96	
470	5.41	—	-44.7	128.6	3380	-4882	32.1	22.36	
480	5.44	—	-42.1	124.4	3280	-4620	—	—	
490	5.48	—	-39.6	120.4	3187	-4362	—	—	
500	5.51	—	-37.2	116.6	3102	-4112	—	—	
550	5.68	—	-26.8	100.7	2764	-2987	—	—	
600	5.82	—	-18.6	88.5	2545	-2091	—	—	
650	5.96	—	-11.9	78.8	2406	-1397	—	—	
700	6.08	—	-6.4	70.9	2323	-863	—	—	
750	6.19	—	-1.7	64.5	2278	-452	—	—	
800	6.29	—	2.3	59.0	2259	-134	—	—	
850	6.38	—	5.7	54.4	2259	112	—	—	
900	6.46	—	8.7	50.5	2271	304	—	—	
950	6.54	—	11.3	47.0	2291	454	—	—	
1000	6.61	—	13.7	44.0	2318	571	—	—	

Data source: <https://www.nist.gov/pml/sensor-science/fluid-metrology/database-thermophysical-properties-gases-used-semiconductor-14>

not a symmetrical molecule. A comparison with the physically similar molecule carbon dioxide showed some differences.

The physical properties of nitrous oxide and carbon dioxide are very similar in several aspects. The compressibility of carbon dioxide and nitrous oxide was measured at pressures under 0.2 MPa (2.0 atm) and over a temperature range of 243–348 K (–30 to –75 °C) [53]. Second virial coefficients were calculated and compared with data presented in the literature for both gases. The compressibility data were estimated to be accurate within $\pm 0.10\%$ of the actual compressibility factor.

The equation of state for a gas can be expressed in the form of a virial exponential equation

$$P = RT\rho[1 + B(T)\rho + C(T)\rho^2 + \dots]$$

where P is the pressure, T is the temperature in kelvin, ρ is the density, $R = 8.314472 \text{ J mol}^{-1} \cdot \text{K}^{-1}$ is the universal gas constant, and $B(T)$ and $C(T)$ are the second and third density virial coefficients. The virial coefficients B and C and their derivatives for gaseous N_2O recommended by NIST are tabulated in Table 7 along with other physical properties. The density virial coefficients were derived from velocity of sound measurements [54].

3.1.6 Velocity of Sound in Gaseous Nitrous Oxide

The velocity of sound was measured in gaseous nitrous oxide and nitric oxide using an acoustic resonance technique over the temperature range from 200 to 460 K and at pressures up to the lesser of 1.6 MPa or 80% of the vapor pressure [54]. All measurements were above the triple point temperature of N_2O . The data were analyzed to ob-

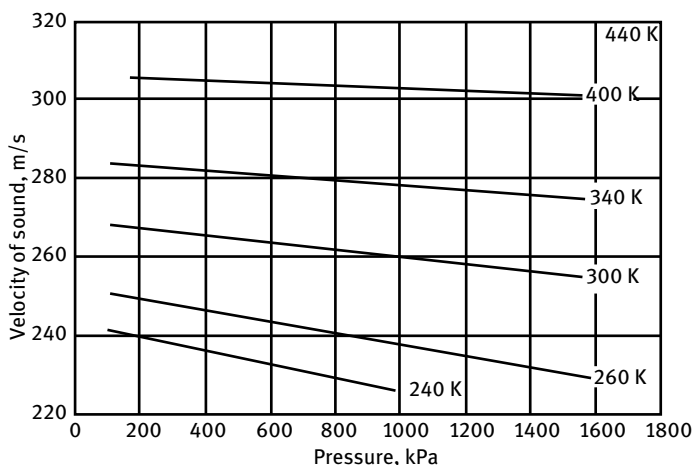


Figure 7: Isotherms of the velocity of sound of gaseous nitrous oxide. (Created by Schmidt 2016, based on data from [54].)

tain the constant-pressure ideal-gas heat capacity C_p^0 as a function of temperature. For N_2O , the values of C_p^0 agreed within 0.1% with those determined from spectroscopic data. The velocity-of-sound data were fitted by virial equations of state to obtain temperature-dependent density virial coefficients. In trying to explain what caused the variation from ideal gas behavior, two virial coefficient models were employed, one based on square-well intermolecular potentials, and the second based on a hard-core Lennard-Jones intermolecular potential. The model reproduced nearly all the sound velocity data to within $\pm 0.01\%$ and may be used to calculate vapor densities. Figure 7 shows isotherms for the velocity of sound of gaseous nitrous oxide at pressures above the triple point and below the critical point.

3.1.7 Vapor Pressure of Nitrous Oxide

Vapor pressure data reported in the literature during the first half of the twentieth century were spread over a wide range and were often inconsistent. An early report [27] gave the following Antoine equation for the vapor pressure of N_2O between 184 and 240 K:

$$\log P = 4.1375 - \frac{656.60}{T - 26}$$

where P is the pressure in atm, and T is the temperature in kelvin. A renewed measurement between 243 and 309 K (-30 and $+36^\circ\text{C}$) [33] gave the following curve fitted equation for the vapor pressure as a function of temperature:

$$\log P = 4.1375 - \frac{656.60}{T - 26}$$

where P is the pressure in atm, and T is the temperature in kelvin. This equation was graphed in Figure 8 from a spreadsheet. The vapor pressure of nitrous oxide at room temperature ($20^\circ\text{C} = 68^\circ\text{F} = 293\text{ K}$) is 49.9 atm (733 psia).

The vapor pressure data reported by Cook [34] are in good agreement with the Couch and Kobe [33] later set of data, although just a bit higher. Cook had determined the vapor pressure of nitrous oxide only over a very narrow range from 285 K (12°C) to the critical point, and the vapor pressure was expressed by the following equation:

$$\log P = 4.6258 - \frac{858.63}{T}$$

where P is the vapor pressure in atm, and T is the temperature in kelvin. The Cook [34] data also agreed well with earlier data reported by Michels et al. [57] and Villard [58]. The vapor pressure data collected by Stull [59] for the temperature range 129.8–

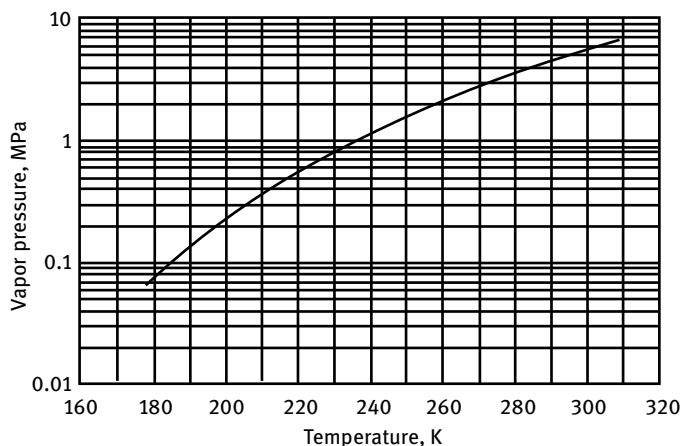


Figure 8: Vapor pressure of nitrous oxide. (Image created by Schmidt 2020, based on data from [33].)

187.7 K have been converted to an Antoine equation and posted on the NIST Chemistry WebBook web site [43]:

$$\log P = A - \left(\frac{B}{T + C} \right)$$

where P is the vapor pressure in bar, T is the temperature in kelvin, and A, B, C are constants: $A = 4.37799$, $B = 621.077$, $C = -44.659$. The data generated from this equation are shown in Figure 9:

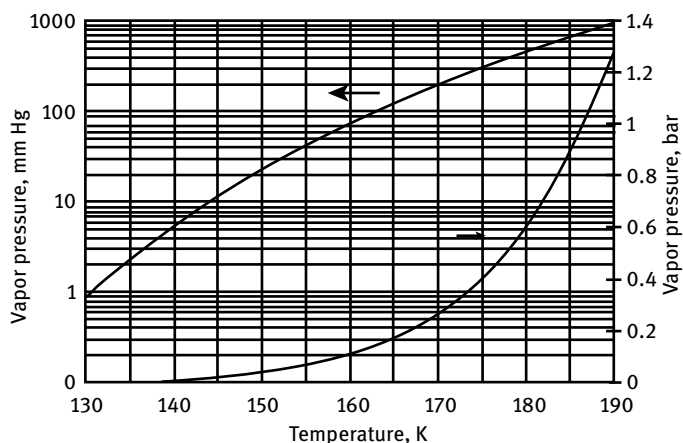


Figure 9: Vapor pressure of nitrous oxide. (Chart created by Schmidt 2016, based on data from [59].)

Saturated vapor pressures were measured in an isochoric apparatus over the temperature range from 219 to 273 K as part of an overall PVT characterization including both two-phase saturated pressure and superheated gas-phase above atmospheric pressure conditions [45]. The raw (unsmoothed) data are tabulated in Table 8 and illustrated in Figure 10.

Table 8: Vapor pressure of nitrous oxide.

Temperature, K	Vapor pressure, kPa
219.24	554.7
222.28	626.3
223.31	652.8
227.32	759.6
227.36	760.6
232.37	912.1
232.43	915.4
237.49	1092.9
242.57	1294.7
247.65	1521.9
252.73	1777
257.8	2061.8
257.87	2065.4
262.9	2379
262.95	2381.8
267.98	2730.6
268.03	2734
273.08	3119.9

Data source: [45]

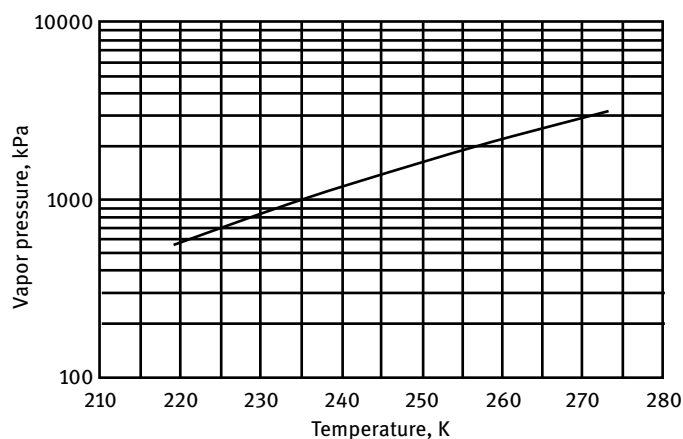


Figure 10: Vapor pressure of nitrous oxide. (Image created by Schmidt 2020, based on data from [45].)

In order to compare the experimental data to previously published literature data, 146 data points from a total of 11 different data sources were examined, and 27 were rejected as outliers, leaving 119 data points to be curve fitted by regression analysis with a Wagner equation in the form:

$$\ln \frac{P}{P_c} = \frac{T_c}{T} [A_1\tau + A_2\tau^{1.5} + A_3\tau^{2.5}]$$

where $\tau = (T_c - T)/T_c$; T_c = critical temperature $T_c = 309.54$ K, P_c critical pressure = 7249.27 kPa and A_1 , A_2 , and A_3 are constants: $A_1 = -6.88269266$, $A_2 = 1.94458967$, and $A_3 = -2.58663757$.

A set of data from multiple literature sources covering a very wide pressure range is shown in Figure 11 copied from Reference [60]. The vapor pressure of N_2O calculated from molecular orbital theory was compared with the experimental data in Figure 25 (Section 3.4.5) [61].

The triple point pressure was given as 0.87890 ± 0.0001 bar (Fonseca and Lobo [62]) bar or 0.8791 ± 0.00008 bar (Calado, Rebelo et al. [63]), as quoted by NIST Chemistry WebBook [43].

Vapor pressure data from 9 different sources, including 296 experimental points collected during a time span from 1935 to 2007, were critically evaluated and combined into a uniform data format, giving the following Wagner vapor pressure equation [30]:

$$P = P_c \exp \left[\frac{(a_1\tau + a_2\tau^{1.5} + a_3\tau^{2.5} + a_4\tau^5)}{(T/T_c)} \right]$$

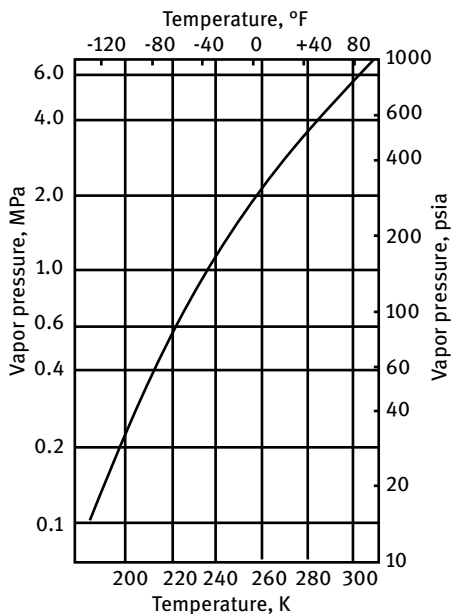


Figure 11: Vapor pressure of nitrous oxide. (Reproduced and modified from [20].)

where P is the vapor pressure in kPa, P_c is the critical pressure in kPa, T is the temperature in kelvin, $\tau = (1 - T/T_c)$, $a_1 = -6.8657$, $a_2 = 1.9373$, $a_3 = -2.6440$, and $a_4 = 0.0387$. In this equation, if one sets $T = T_c$, the critical pressure is $P_c = 7243$ kPa. For $P = 101$ kPa, the normal boiling point is $T_b = 184.646$ K. Because the vapor pressure at the triple point of frozen nitrous oxide is relatively high, and because the liquidus range is so narrow, sublimation of nitrous oxide going directly from the frozen to the vapor state is a likely occurrence. Sublimation pressure data from 7 different sources taken between 1930 and 1983 were combined into one data set of 160 data points and curve fitted to the equation

$$\ln P = \ln P_t + \frac{(e_1\theta + e_2\theta^f)}{(T/T_t)}$$

where P is the sublimation pressure, T_t is the triple point temperature in kelvin, p_t is the triple point pressure in Pascal, $\theta = (1 - T/T_t)$, and e_1 , e_2 and f are numerical adjustable parameters. These parameters are: $e_1 = -6.6551$, $e_2 = -9.8076$, and $f = 1.0364$. The relative average absolute deviation for this curve-fitting exercise was AAD = 4% (in the pressure). The enthalpy of sublimation at the triple point can be calculated by adding the enthalpy of fusion and the enthalpy of evaporation, which resulted in an estimate of 23.205 kJ/mol. A maximum value of the enthalpy of sublimation occurs at $T = 50$ K where it is 25.214 kJ/mol. The sublimation pressure curve occupies the lower 3/4 and the major portion of the phase diagram Figure 12, which shows the pressure versus temperature phase boundary diagram for all three states. This graph is a compilation of data from about 15 different sources from the literature.

Based on sublimation pressure measurements, the entropy of solid N_2O at 0 K was calculated as $S_0 = 5.98 \text{ J mol}^{-1} \text{ K}^{-1} = 1.43 \text{ cal mol}^{-1} \text{ K}^{-1}$, and the enthalpy of solid N_2O at 0 K was predicted as $H_0 = -24.2 \text{ kJ/mol} = -5799 \text{ cal/mol}$ [64].

Fractionated distillation of NO has been used for isotope separation for production of ^{15}N , and the question was whether or not a similar isotope effect has industrial application, but the difference in vapor pressures of N_2O isotopes is less pronounced and most likely cannot be used for ^{15}N production. The vapor pressures of three isotopic samples of N_2O enriched in ^{15}N and ^{18}O were compared with normal N_2O over the temperature range 143–219 K [65]. Over the temperature range studied in the solid and in the liquid in the neighborhood of the triple point, the vapor pressures decreased in the order $^{14}\text{N}_2^{16}\text{O} \geq ^{14}\text{N}^{15}\text{N}^{16}\text{O} \geq ^{15}\text{N}^{14}\text{N}^{16}\text{O} \geq ^{14}\text{N}_2^{18}\text{O}$. Shifts in the internal stretching and bending modes on condensation lead to significant differences in the vapor pressures of the isomers $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{15}\text{N}^{16}\text{O}$.

The vapor pressure of solid nitrous oxide in the range 146–182.4 K (triple point) can be expressed in the form of an Antoine equation

$$\log_{10} P = -\frac{1270.42}{T} + 8.955644 - 00094121 \times T$$

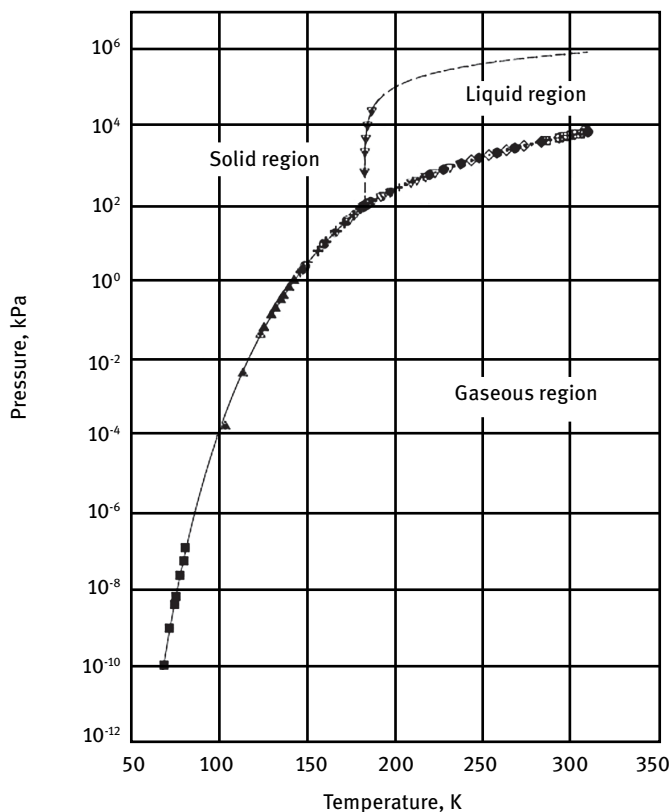


Figure 12: Phase diagram of nitrous oxide. (Republished and modified from [30], with permission of © 2009 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

where P is the pressure in pascal, and T is the temperature in kelvin. The vapor pressure of liquid nitrous oxide in the range 182.4 K (triple point) to 185 K can be expressed by the equation

$$\log P = -\frac{886.293}{T} + 9.803215$$

where P is the pressure in pascal, and T is the temperature in kelvin [23]; see also References [66] and [22].

3.1.8 Viscosity of Nitrous Oxide

3.1.8.1 Viscosity of Gaseous Nitrous Oxide

The viscosity of gaseous nitrous oxide was measured in the temperature range of 373 to 1273 K (100–1000 °C) using a specially constructed transpiration apparatus of fused

silica [67]. Results at the lower temperatures showed good agreement with previously published data, with the viscosity behaving normally up to about 823 K (550 °C), above which the thermal decomposition of nitrous oxide became noticeable, and viscosity measurements became erratic.

Eight sets of experimental viscosity data were taken from the pre-1975 literature and combined into a recommended data set [55]. Graphing the departure of the individual data from the averaged result showed a very irregular pattern, and deviations went in all directions and at all temperatures. The recommended viscosity data for the lower temperature range are summarized in Table 9. The upper temperature data were omitted from this table because they were adulterated by incipient decomposition.

The viscosity and thermal conductivity coefficients of gaseous nitrous oxide and nitrous oxide/carbon dioxide mixtures were calculated for a temperature range 180–900 K and pressures from 0.1 to 23 MPa based on theoretical considerations and the theorem of corresponding states [68]. The viscosity at low pressures as a function of temperature was expressed by a polynomial equation with nine coefficients. The viscosity at 273 K and 101 kPa was predicted as $0.74250 \times 10^{-4} \text{ lb}_m \text{ ft}^{-1} \text{ s}^{-1} = 0.11 \text{ cPs}$. For comparison, data were also offered for $\text{N}_2\text{O}/\text{CO}_2$ mixtures containing 6 or 12% CO_2 .

The dynamic viscosity of gaseous nitrous oxide was measured at atmospheric pressure in the temperature range 300.6–473 K (27.5–200 °C) with an accuracy of $\pm 0.2\%$ [69]. The results can be correlated by a law of corresponding states.

The dynamic viscosity of gaseous nitrous oxide in the temperature range 190 to 310 K can be expressed by the equation

$$\ln \eta = A \ln T + \frac{B}{T} + \frac{D}{T^2} + D$$

where η is the dynamic viscosity in μPs ($1 \mu\text{Ps} = 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1}$), T is the temperature in kelvin, and A , B , C , and D are constants as follows: $A = 0.224485$, $B = -375.3232$, $C = 22927.27$, and $D = 4.721$ [70].

The viscosities of gaseous nitric oxide (372–1015 K) and nitrous oxide (372–733 K) have been measured using a capillary-flow viscometer in a comparative mode, calibrating the instrument with nitrogen gas [71]. Smoothed viscosity data for nitrous oxide are shown in Table 10.

The viscosity of nitrous oxide as a function of temperature can be expressed by the equation

$$\eta = \frac{aT^{1/2}}{1 + b/T + c/T^2}$$

where η is the viscosity in $\mu\text{N s m}^{-2}$, T is the temperature in kelvin, and a , b , and c are constants: $a = 2.064 \mu\text{N s m}^{-2} \text{ K}^{-1/2}$, $b = 597.2 \text{ K}$, and $c = -62380 \text{ K}^2$.

The transport properties of gases in the limit of zero density provide a basis for the prediction of these properties over a wider range of thermodynamic states. In order to extend studies on the viscosity of polyatomic gases to nitrous oxide and to provide

Table 9: Dynamic viscosity of gaseous nitrous oxide.

Temperature, K	Viscosity, $\text{N s}^{-1} \text{m}^{-1} \times 10^{-6}$	Temperature, K	Viscosity, $\text{N s}^{-1} \text{m}^{-1} \times 10^{-6}$
180	9.01	520	24.3
190	9.52	530	24.7
200	10.03	540	25.1
210	10.54	550	25.5
220	11.05	560	25.9
230	11.56	570	26.2
240	12.06	580	26.6
250	12.55	590	27.0
260	13.04	600	27.3
270	13.53	610	27.7
280	14.02	620	28.0
290	14.49	630	28.4
300	14.97	640	28.7
310	15.44	650	29.1
320	15.90	660	29.4
330	16.36	670	29.8
340	16.82	680	30.1
350	17.27	690	30.5
360	17.72	700	30.8
370	18.16	710	31.1
380	18.60	720	31.5
390	19.03	730	31.8
400	19.46	740	32.1
410	19.89	750	32.5
420	20.31	760	32.8
430	20.73	770	33.1
440	21.14	780	33.4
450	21.56	790	33.7
460	21.96	800	34.1
470	22.37	810	34.4
480	22.77	820	34.7
490	23.16	830	35.0
500	23.56	840	35.3
510	23.9	850	35.6

Data source: [55]

a background for a description of the thermal conductivity of these gases, nitrous oxide viscosity data were correlated by kinetic theory [72].

The viscosity of gaseous nitrous oxide was measured with an oscillating-disk viscometer in the critical region between 309.65 and 318.15 K and pressures up to 9.6 MPa [44]. The viscosity of N_2O exhibited an anomalous increase near the critical point. The anomalous increase in viscosity as the temperature approached the critical point also caused more data scatter and was analyzed with a viscosity equation proposed by

Table 10: Smoothed dynamic viscosity data for gaseous nitrous oxide.

Temperature K	Dynamic viscosity $\mu\text{N s m}^{-2} = \mu\text{Pa s}$
400	19.63
500	23.73
600	27.75
700	31.65
800	35.41

Data source: [71]; 1 Pa = 1 N/m²

Busu and Sengers, which was supposed to be able to predict viscosity based on known critical point properties. Figure 13 shows the viscosity as a function of pressure, and Figure 14 shows the same data as a function of density.

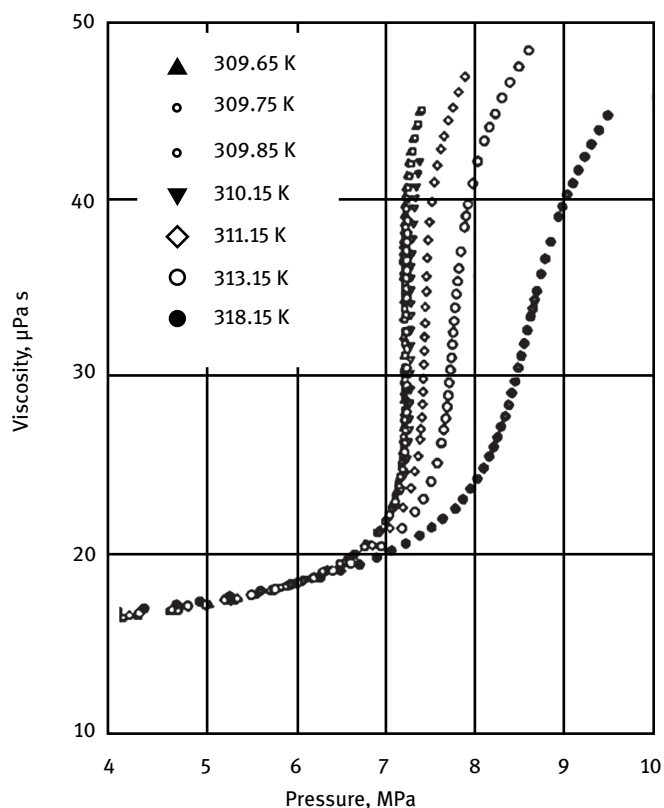


Figure 13: Dynamic viscosity of gaseous N₂O as a function of pressure. (Republished and modified from [44], with permission from © 1994 Springer Nature; permission conveyed through Copyright Clearance Center Inc.)

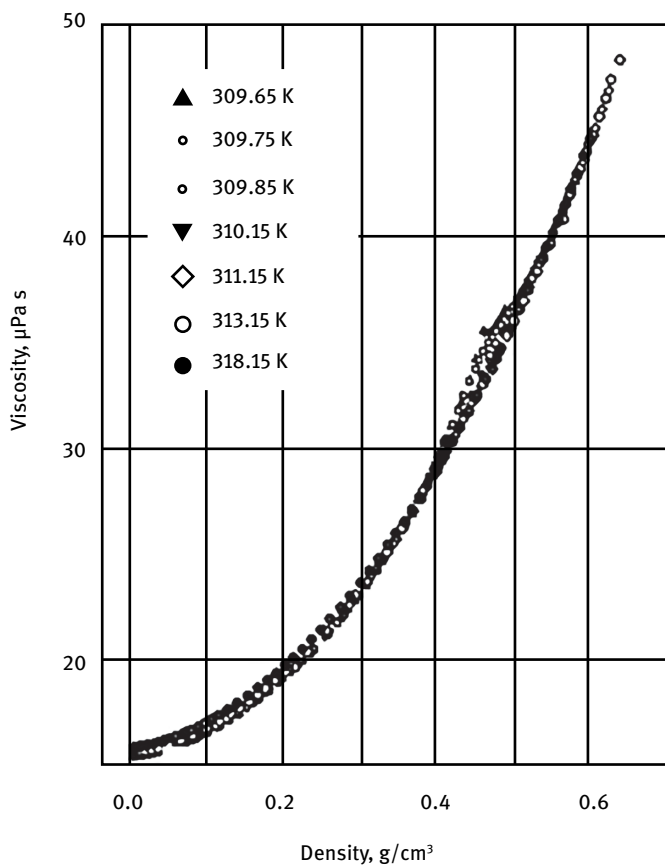


Figure 14: Dynamic viscosity of gaseous N_2O as a function of density. (Republished and modified from [44], with permission from © 1994 Springer Nature; permission conveyed through Copyright Clearance Center Inc.)

Measurements of the viscosity of gaseous nitrous oxide using the same oscillating disk viscometer were then extended to pressures up to 25 MPa and temperatures from 298.15 to 398.15 K [73]. Historical data from 12 previously reported viscosity measurements going back all the way to 1909 were reviewed, and Figure 15 shows the results of plotting the investigator's own viscosity data as a function of pressure and temperature, which showed a substantial difference between the more recent measurements and literature data (dotted lines) from 1975 [74].

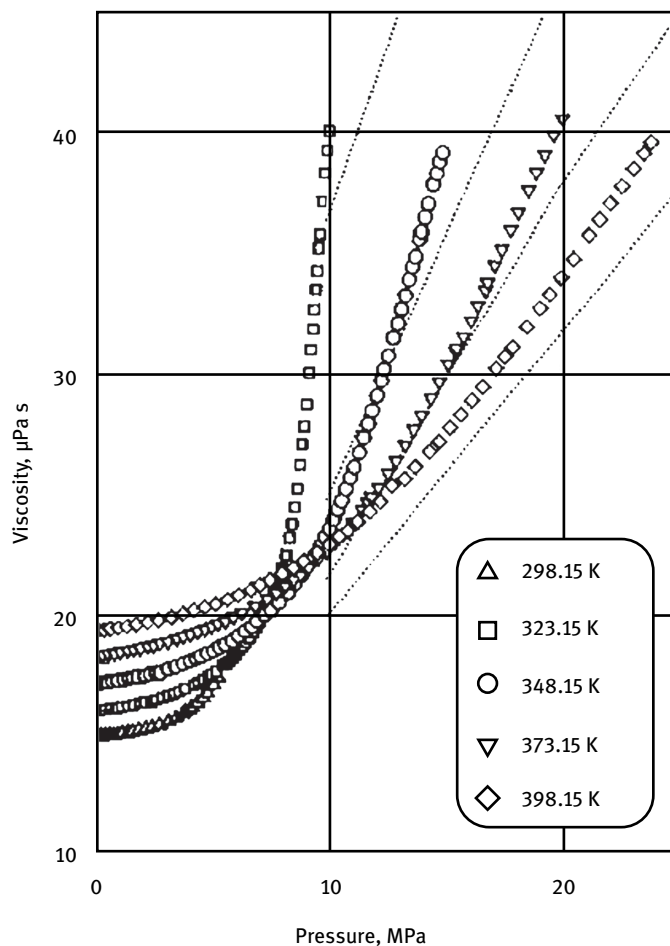


Figure 15: Plots of dynamic viscosity as a function of pressure P for gaseous nitrous oxide for five different temperatures. (Reprinted and modified from [73] with permission from © 1996 American Chemical Society; permission conveyed through RightsLink.)

The experimental results were fitted to an empirical equation that gives the viscosity of N_2O at 101 kPa as a function of temperature:

$$\eta = \frac{(T/\text{K})^{0.5}}{a_1} + \frac{a_2}{(T/\text{K})} + \frac{a_3}{(T/\text{K})^2} + \frac{a_4}{(T/\text{K})^3}$$

where η is the viscosity in $\mu\text{Pa s}$, T is the absolute temperature in kelvin, and a_n ($n=1-4$) are constants: $a_1 = 0.5992$, $a_2 = 0.1770 \times 10^3$, $a_3 = -0.2413 \times 10^4$, and $a_4 = -0.7192 \times 10^6$.

The viscosity and velocity of sound of gaseous nitrous oxide were measured using a Greenspan acoustic viscometer over the temperature range 225–375 K and pressures up to 3.4 MPa [56]. The viscosity isotherms are graphed in Figure 16. The velocity of sound data measured up to 3.4 MPa were fitted by a virial equation of state that predicted gas densities within the uncertainties of the equations of states available in the literature. The velocity of sound data were similar to those already described in Section 3.1.5. Measurements of the velocity of sound in N_2O have been reported previously but only at pressures up to 1.5 MPa. The Hurly [56] measurements agreed with these earlier literature values with maximum relative standard deviations of only 0.025%.

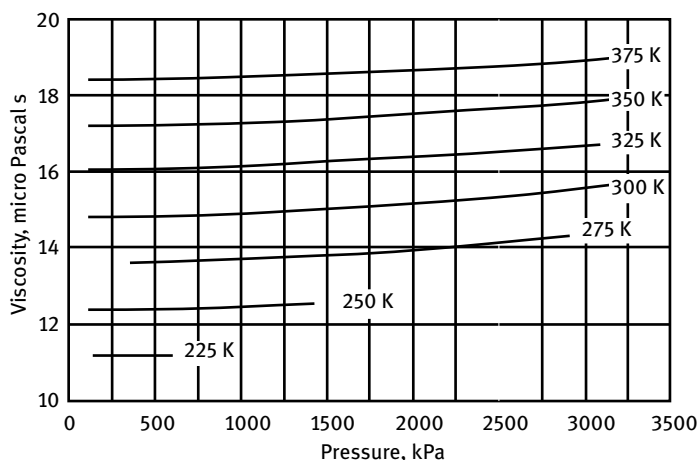


Figure 16: Viscosity isotherms of gaseous nitrous oxide. (Created by Schmidt 2020, based on data from [56].)

From these data a graph showing the viscosity of nitrous oxide gas at atmospheric pressure as a function of temperature can be constructed (Figure 17).

3.1.8.2 Viscosity of Liquid Nitrous Oxide

Because N_2O has such a narrow liquid range, not many measurements of physical properties of the liquid were made in this range.

3.1.8.3 Viscosity of Gas Mixtures Containing Nitrous Oxide

Mixing nitrous oxide with other gases might bring some advantages: dilution with inert gases would reduce the tendency for detonations, mixing with other oxidizers might improve the performance as an oxidizer in rocket engines or lower the freezing point, and mixing with gaseous fuels would increase the performance as a gaseous monopropellant (but may widen the detonable range).

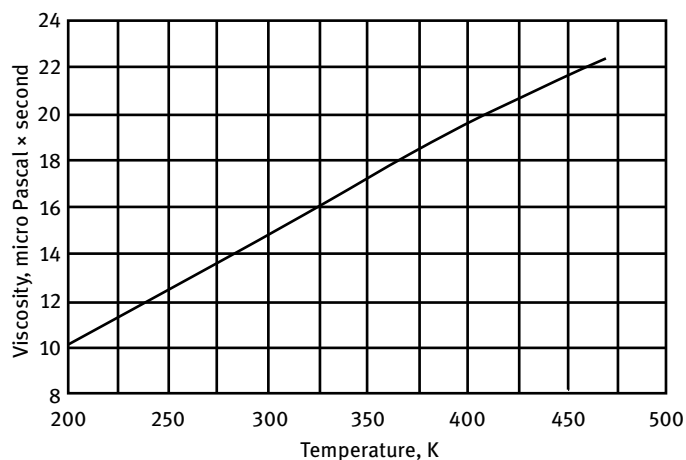


Figure 17: Viscosity of gaseous nitrous oxide at atmospheric pressure. (Created by Schmidt 2020, based on data from NIST.)

The viscosity and diffusion coefficient of binary gaseous systems of nitrous oxide with N_2 , Ar, and CO_2 in the range of temperatures from 298 to 473 K (25 to 200 °C) were measured, and the calculated values of the binary mixtures diffusion coefficients were consistent with the KRW Law of Corresponding States [75]. The viscosity of N_2O/CO_2 mixtures containing 6 or 12% CO_2 was calculated based on the theorem of corresponding states [68].

The viscosity of mixtures of nitrous oxide with nitric oxide was measured between 474 and 788 K (201 and 515 °C) for mixtures containing 25, 50, or 75 vol-% nitric oxide [76]. The results are summarized in Table 11.

Mixtures of nitrous oxide and ammonia have been evaluated as gaseous monopropellants. It is, therefore, of interest to find data for the viscosity of gaseous N_2O/NH_3 mixtures taken with a capillary viscometer at three different temperatures 298, 308, and 353 K (25, 35, and 80 °C) [77]. The dynamic viscosities of N_2O/NH_3 mixtures at 308 K (35 °C) are illustrated in Figure 18. The unit of viscosity used here is ($10^7 \text{ g cm}^{-1} \text{ s}^{-1}$); $1.0 \text{ g cm}^{-1} \text{ s}^{-1}$ corresponds to 100 cPs. For comparison, the values for N_2O by itself (without NH_3) were $1486 \times 10^{-7} \text{ g cm}^{-1} \text{ s}^{-1}$ at 298 K, $1533 \times 10^{-7} \text{ g cm}^{-1} \text{ s}^{-1}$ at 308 K, and $1730 \times 10^{-7} \text{ g cm}^{-1} \text{ s}^{-1}$ at 353 K. It appears that the investigators were unaware of the explosive potential of such oxidizer/fuel mixtures. The solid and dashed lines are predictions from theory. The solid circles are measured data points.

3.1.9 Surface Tension of Liquid Nitrous Oxide

The average of three determinations of surface tension of liquid nitrous oxide at the boiling point (183.75 K = -89.4 °C at an atmospheric pressure of 741.1 mm Hg) was $26.323 \times 10^{-5} \text{ N/cm}$ [35]; see also Reference [78].

Table 11: Viscosity of N₂O/NO mixtures.

Composition, vol.-%									
NO	N ₂ O								
25	75	Temperature, K	508.7	580.7	632.9	651.3	692.7	734.2	778.4
25	75	Temperature, °C	235.6	307.6	359.8	378.2	419.6	461.1	505.3
25	75	Viscosity, g cm ⁻¹ s ⁻¹ × 10 ⁷	2516	2820	2985	3082	3232	3340	3518
50	50	Temperature, K	474.9	532.8	575.5	647.7	700.6	740.7	788.6
50	50	Temperature, °C	201.8	259.7	302.4	374.6	427.5	467.6	515.5
50	50	Viscosity, g cm ⁻¹ s ⁻¹ × 10 ⁷	2485	2712	2871	3106	3354	3471	3678
75	25	Temperature, K	510.3	575	597.8	645.6	699.7	742.1	784.9
75	25	Temperature, °C	237.2	301.9	324.7	372.5	426.6	469	511.8
75	25	Viscosity, g cm ⁻¹ s ⁻¹ × 10 ⁷	2732	3021	3099	3256	3425	3611	3740

Data source: [76]

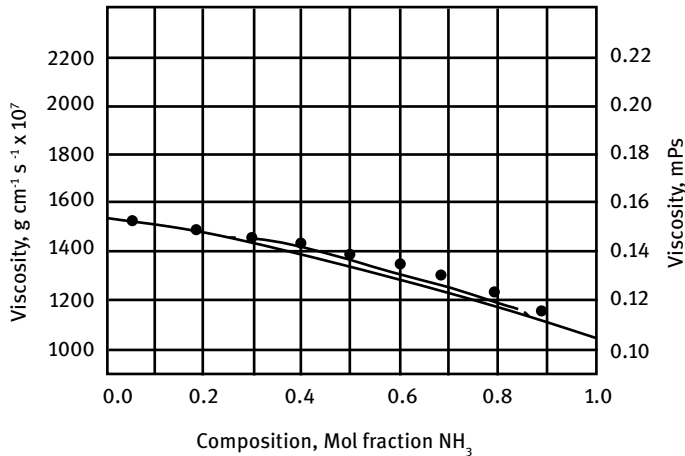


Figure 18: Viscosity of gaseous N₂O/NH₃ mixtures at 308 K (35°C). (Republished and modified from [77], with permission of © 1965 The Royal Society of Chemistry; permission conveyed through Copyright Clearance Center Inc.)

The surface tension of liquid nitrous oxide was measured between 182 and 184 K, which is between the freezing point and the boiling point of the liquid at atmospheric pressure, by a capillary rise method where three capillaries with different diameters (0.2, 0.4, and 2 mm) were interconnected and partially filled with liquid [31]. The data are listed in Table 12.

Table 12: Surface tension of liquid nitrous oxide.

Temperature K	Surface tension	
	mN/m	dyn/cm
182.5	24.26	24.26
182.5	24.25	24.25
182.6	24.23	24.23
182.8	24.18	24.18
182.9	24.11	24.11
183.2	24.07	24.07
183.4	24.04	24.04
183.7	24.00	24.00
183.9	23.95	23.95
184.0	28.87	28.87
184.2	23.86	23.86
184.4	23.85	23.85

Data source: [31]

1 dyn = 10^{-5} N

3.2 Thermal Conductivity and Heat Transfer Properties of Nitrous Oxide

The thermal conductivity of gaseous nitrous oxide goes through a minimum near 330 K (Figure 19). The thermal conductivity of gaseous nitrous oxide listed on the NIST Chemistry WebBook website is tabulated in Table 13 and illustrated in Figure 20.

Gaidei [2] quoted the thermal conductivity of liquid (λ_{liquid} , $\text{W m}^{-1} \text{K}^{-1}$) and gaseous (λ_{gas} , $\text{W m}^{-1} \text{K}^{-1}$) nitrous oxide on the line of saturation at different temperatures from an unidentified source as listed in Table 14. They should have listed the pressures at which these measurements were taken.

The thermal conductivities of two binary systems of non-polar gases, $\text{N}_2/\text{N}_2\text{O}$ and $\text{NO}/\text{N}_2\text{O}$, were measured in the temperature range from 323 to 453 K (50 to 180 °C) [79]. It was found that the presence of NO in N_2O effectively increased the rate of its catalytic decomposition on Fe-ZSM-5 zeolite, and at the same time the NO, CO_2 , and water inhibited the process of homogeneous N_2O decomposition.

Attempts to predict the thermal conductivity of polyatomic gases have not always been successful. Extending the theory to include polyatomic gases having more than one relaxation time showed that in the case of CO_2 , all theories matched equally well with experimental results, while for N_2O there was a poor fit and a different mathematical expression had to be used [80].

The thermal conductivity of gaseous N_2O measurements by Johnston and Grilly [81] were included for comparison in a later graph (Figure 21) created by Richter and Sage [82]. The Johnston and Grilly data tended to be a bit higher than the Richter and

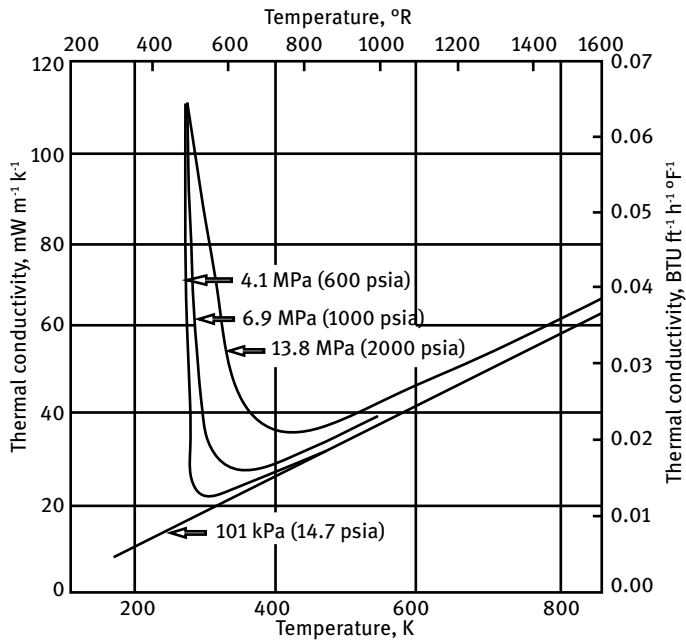


Figure 19: Thermal conductivity of gaseous nitrous oxide. (Reproduced and modified from [20].)

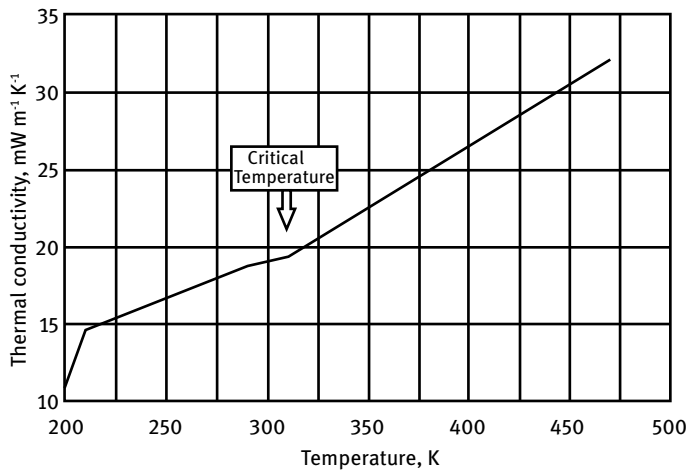


Figure 20: Thermal conductivity of gaseous nitrous oxide. (Created by Schmidt 2020, based on data from [43].)

Table 13: Thermal conductivity of gaseous nitrous oxide.

Temperature K	Thermal conductivity		
	$\text{mW m}^{-1} \cdot \text{K}^{-1}$	$\text{cal s}^{-1} \text{cm}^{-1} \text{ } ^\circ\text{C}^{-1}$	$\text{BTU ft}^{-1} \text{h}^{-1} \text{ } ^\circ\text{F}^{-1}$
200	10.9	2.603E-05	6.302E-03
210	14.6	3.486E-05	8.441E-03
220	15.1	3.606E-05	8.730E-03
230	15.6	3.725E-05	9.020E-03
240	16.2	3.869E-05	9.366E-03
250	16.7	3.988E-05	9.656E-03
260	17.2	4.107E-05	9.945E-03
270	17.7	4.227E-05	1.023E-02
280	18.2	4.346E-05	1.052E-02
290	18.7	4.466E-05	1.081E-02
310	19.4	4.633E-05	1.122E-02
320	20.2	4.824E-05	1.168E-02
330	21	5.015E-05	1.214E-02
340	21.8	5.206E-05	1.260E-02
350	22.6	5.397E-05	1.307E-02
360	23.4	5.588E-05	1.353E-02
370	24.2	5.779E-05	1.399E-02
380	25	5.970E-05	1.445E-02
390	25.8	6.161E-05	1.492E-02
400	26.6	6.352E-05	1.538E-02
410	27.3	6.519E-05	1.578E-02
420	28.1	6.710E-05	1.625E-02
430	28.9	6.901E-05	1.671E-02
440	29.7	7.092E-05	1.717E-02
450	30.5	7.283E-05	1.763E-02
460	31.3	7.474E-05	1.810E-02
470	32.1	7.665E-05	1.856E-02

Data source: NIST http://www.nist.gov/pml/div685/grp02/srd_134_gasesindex.cfm

$1 \text{ mW m}^{-1} \cdot \text{K}^{-1} = 10^{-3} \text{ W m}^{-1} \cdot \text{K}^{-1} = 10^{-5} \text{ W cm}^{-1} \cdot \text{K}^{-1} = 0.000002388 \text{ cal s}^{-1} \text{cm}^{-1} \text{ } ^\circ\text{C}^{-1} =$

$2.388 \times 10^{-6} \text{ cal s}^{-1} \text{cm}^{-1} \text{ } ^\circ\text{C}^{-1} = 0.000578176 \text{ BTU ft}^{-1} \text{h}^{-1} \text{ } ^\circ\text{F}^{-1} = 5.78176 \times 10^{-4} \text{ BTU ft}^{-1} \text{h}^{-1} \text{ } ^\circ\text{F}^{-1}$

Sage data. Table 15 lists the thermal conductivity of gaseous nitrous oxide in comparison to those of nitric oxide and dioxygen.

The thermal conductivity of gaseous nitrous oxide was measured at temperatures from 278 to 444 K (40 to 340 °F) and at pressures up to 34.5 MPa (5000 psia) using an apparatus consisting of two concentric spheres where the fluid under study filled a narrow gap between the two spheres, and the inner sphere was heated electrically and the temperature difference between the two spheres was measured [82]. The thermal conductivity of nitrous oxide at atmospheric pressure is illustrated in Figure 21, and the thermal conductivity at elevated pressures is illustrated in Figure 22.

Table 14: Thermal conductivity of liquid and gaseous nitrous oxide.

Temperature		Thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$	
$^{\circ}\text{C}$	K	λ_{liquid}	λ_{gas}
-13	260	0.1200	0.0176
22	295	0.1276	0.0230
32	305	0.2341	0.0290

Data source: [2]

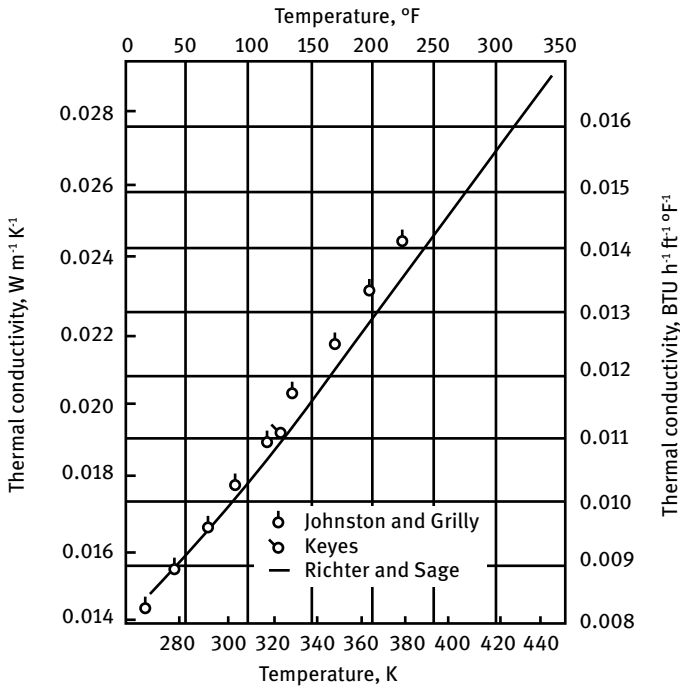


Figure 21: Thermal conductivity of gaseous nitrous oxide as a function of temperature at atmospheric pressure. (Reprinted and modified from [82] with permission from © 1963 American Chemical Society; permission conveyed through RightsLink.)

Experimental measurements of the thermal conductivity of gaseous nitrous oxide were reported for pressures up to 5.343 MPa (775 psia) at 323 K (122 $^{\circ}\text{F}$) [83].

The thermal conductivity of nitrous oxide was measured by the conductivity column method in the temperature range 323 to 1173 K (50 to 900 $^{\circ}\text{C}$) [84]. The data suggested that it is necessary to take into account the relaxation of translational-internal

Table 15: Smoothed thermal conductivities of gaseous nitrous oxide in comparison to those of nitric oxide and dioxygen.

Temperature K	Thermal conductivity					
	cals ⁻¹ cm ⁻¹ °C ⁻¹ × 10 ⁵			SI Units, W m ⁻¹ K ⁻¹		
	N ₂ O	NO	O ₂	N ₂ O	NO	O ₂
80			1.701			7.122E-03
90			1.93			8.081E-03
100			2.159			9.039E-03
110			2.387			9.994E-03
120		2.58	2.614		1.080E-02	1.094E-02
130		2.792	2.84		1.169E-02	1.189E-02
140		3.003	3.064		1.257E-02	1.283E-02
150		3.214	3.287		1.346E-02	1.376E-02
160		3.423	3.508		1.433E-02	1.469E-02
170		3.631	3.728		1.520E-02	1.561E-02
180	2.021	3.838	3.946	8.462E-03	1.607E-02	1.652E-02
190	2.173	4.042	4.162	9.098E-03	1.692E-02	1.743E-02
200	2.33	4.245	4.375	9.755E-03	1.777E-02	1.832E-02
210	2.493	4.445	4.584	1.044E-02	1.861E-02	1.919E-02
220	2.661	4.643	4.79	1.114E-02	1.944E-02	2.005E-02
230	2.823	4.84	4.993	1.182E-02	2.026E-02	2.090E-02
240	3.011	5.035	5.194	1.261E-02	2.108E-02	2.175E-02
250	3.192	5.229	5.392	1.336E-02	2.189E-02	2.258E-02
260	3.377	5.423	5.586	1.414E-02	2.271E-02	2.339E-02
270	3.564	5.615	5.78	1.492E-02	2.351E-02	2.420E-02
280	3.755	5.807	5.97	1.572E-02	2.431E-02	2.500E-02
290	3.949	5.999	6.159	1.653E-02	2.512E-02	2.579E-02
300	4.149	6.189	6.35	1.737E-02	2.591E-02	2.659E-02
310	4.352	6.379	6.547	1.822E-02	2.671E-02	2.741E-02
320	4.562	6.568	6.748	1.910E-02	2.750E-02	2.825E-02
330	4.775	6.756	6.954	1.999E-02	2.829E-02	2.912E-02
340	4.991	6.944	7.164	2.090E-02	2.907E-02	2.999E-02
350	5.206	7.131	7.378	2.180E-02	2.986E-02	3.089E-02
360	5.425	7.318	7.594	2.271E-02	3.064E-02	3.179E-02
370	5.644	7.504	7.812	2.363E-02	3.142E-02	3.271E-02
380	5.861	7.69	8.033	2.454E-02	3.220E-02	3.363E-02
273.1	3.623	5.674	5.839	1.517E-02	2.376E-02	2.445E-02
293.1	4.011	6.057	6.218	1.679E-02	2.536E-02	2.603E-02
298.1	4.11	6.153	6.314	1.721E-02	2.576E-02	2.644E-02

1 cal s⁻¹ cm⁻¹ °C⁻¹ = 418.68 W m⁻¹ K⁻¹

Data source: [81]

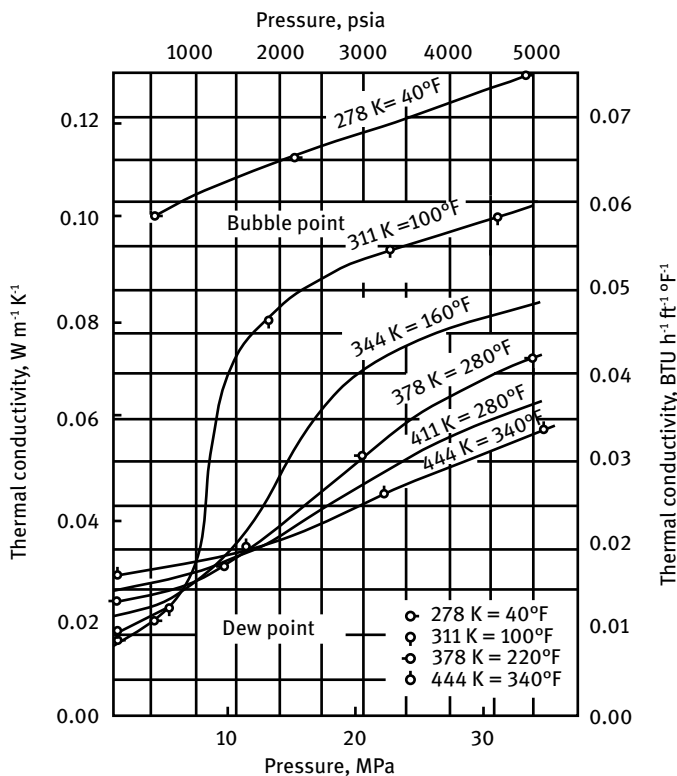


Figure 22: Thermal conductivity of gaseous nitrous oxide as a function of pressure. (Reprinted and modified from [82] with permission from © 1963 American Chemical Society; permission conveyed through RightsLink.)

energy exchange for nitrous oxide in this temperature range for an adequate theoretical interpretation of its thermal conductivity.

The viscosity and thermal conductivity coefficients of gaseous nitrous oxide and nitrous oxide/carbon dioxide mixtures were calculated for a temperature range 180–900 K (330–1600 R) and pressures from 0.1 to 23 MPa (3500 psi) based on theoretical considerations and the theorem of corresponding states [68]. The thermal conductivity at low pressures as a function of temperature was expressed by a polynomial equation with nine coefficients. The thermal conductivity at 273 K and 101 kPa was predicted as $0.584 \text{ BTU h}^{-1} \text{ ft}^{-1} \text{ °F}^{-1} = 0.0024 \text{ cal cm}^{-1} \text{ s}^{-1} \text{ °C}^{-1} = 0.010 \text{ W cm}^{-1} \text{ °C}^{-1}$. Data were also offered for $\text{N}_2\text{O}/\text{CO}_2$ mixtures containing 6 or 12% CO_2 .

Absolute measurements of the thermal conductivity of nitrous oxide were carried out with a transient hot-wire instrument in the temperature range 308 to 430 K and at pressures up to 11 MPa [85]. For nitrous oxide near its critical conditions, the accuracy of measurements was degraded, and the data spread may be as bad as $\pm 2\%$.

The thermal conductivity coefficient of solid N_2O exhibited a surprisingly (compared with simple molecular crystals such as N_2 , CO , or O_2) high value in the temperature range 1.2,40 K, and temperature dependence of the thermal conductivity was determined at temperatures below 23 K [86]. This indicated that relatively low density of dislocations and weak phonon-phonon interaction might be reasons for the good thermal conduction in solid N_2O . The influence of possible low-temperature dipolar ordering on thermal conductivity of nitrous oxide crystal is uncertain, see also Reference [87].

The preferred method for warming liquid nitrous oxide and to prevent it from freezing is to fill a run tank with sufficient ullage volume and allow it to slowly warm up to the desired temperature by circulation of ambient air around the tank. If a faster active heating system must be used, such as for testing in colder climates during the winter, one can run the nitrous oxide through a heat exchanger with a uniform wall temperature such as a coil submerged in a water bath. One must never expose nitrous oxide lines, tanks or components to open flames or other concentrated heat sources. Hot spots in heat exchangers can lead to catastrophic failures even with liquid flow. SpaceDev has conducted several tests on nitrous oxide heat exchangers in association with Purdue University and has demonstrated that it is possible to start a decomposition reaction with liquid nitrous oxide in tubing under a 1/4-in. diameter by exposing it to an extreme, highly concentrated heat source [88]. This should be a warning to all designers working on the design of nitrous oxide feed systems.

3.3 Thermodynamic Properties of Nitrous Oxide

The thermodynamic properties of nitrous oxide were examined in a doctoral dissertation [50].

3.3.1 Heat Capacity of Nitrous Oxide

The heat capacity of gaseous nitrous oxide at 298 K is $38.617 \text{ J mol}^{-1} \text{ K}^{-1}$. The heat capacity of gaseous nitrous oxide as a function of temperature can be calculated from the following polynomial equation

$$C_p^\circ = A + B \times \tau + C \times \tau^2 + D \times \tau^3 + \frac{E}{\tau^2}$$

where C_p is the molar heat capacity in $\text{J mol}^{-1} \text{ K}^{-1}$, τ is the temperature in kelvin divided by 1000, and A, B, C, D, and E are constants listed in Table 16 for two different temperature ranges. One must note that N_2O is unstable at temperatures above 700 K, and the column for the higher temperature range 1100–6000 K is only of academic value. It is not very practical to list thermodynamic data for a compound that is unstable at

Table 16: Thermodynamic property polynomial equation coefficients for gaseous nitrous oxide.

Temperature, K	298–1400	1400–6000
<i>A</i>	27.67988	60.30274
<i>B</i>	51.14898	1.034566
<i>C</i>	−30.64454	−0.192997
<i>D</i>	6.847911	0.012540
<i>E</i>	−0.157906	−6.860254
<i>F</i>	71.24934	48.61390
<i>G</i>	238.6164	272.5002
<i>H</i>	82.04824	82.04824

Data source: [43, 89]

the temperature range listed. It would be much more valuable to have more accurate thermodynamic data for liquid nitrous oxide; see also Reference [22].

The heat capacity of solid and liquid nitrous oxide was measured with an adiabatic calorimeter between 1.9 and 184 K [23]. The anomalous increase of heat capacity below the triple point was interpreted as arising from thermal creation of orientational defects with an enthalpy of formation of 10.8 kJ/mol. The molar heat capacity as a function of temperature is shown in Figure 23, a graph that uses two different scale expansions (which may be confusing at the first glance). Smoothed and interpolated heat capacity of solid nitrous oxide are listed in Table 17.

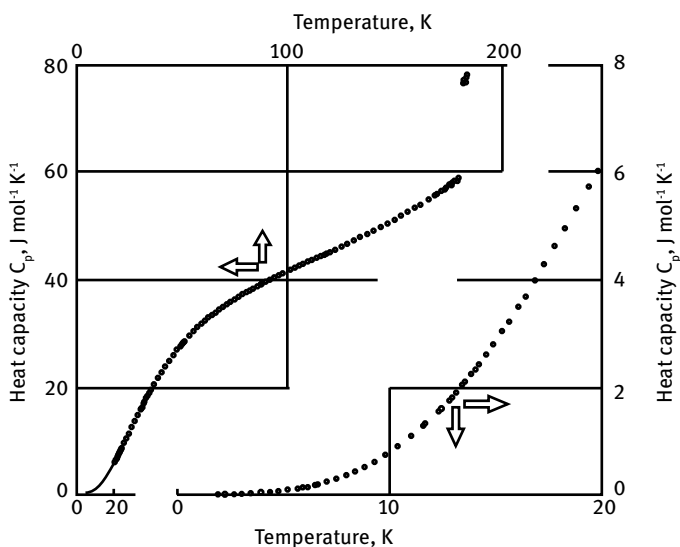
**Figure 23:** Molar heat capacity of nitrous oxide as a function of temperature. (Reproduced and modified from [23], with permission of Chemical Society of Japan.)

Table 17: Smoothed and interpolated heat capacity of solid and liquid nitrous oxide.

Temperature K	Physical state	Molar heat capacity $\text{J K}^{-1} \text{mol}^{-1}$
3	Solid	0.019
5	Solid	0.089
10	Solid	0.822
15	Solid	2.918
20	Solid	6.309
30	Solid	14.40
40	Solid	21.65
50	Solid	27.25
60	Solid	31.47
70	Solid	34.64
80	Solid	37.23
90	Solid	39.41
100	Solid	41.28
110	Solid	43.07
120	Solid	44.86
130	Solid	46.70
140	Solid	48.63
150	Solid	50.70
160	Solid	52.95
170	Solid	55.48
180	Solid	58.28
185	Liquid	77.50

Data source: [23]

3.3.2 Enthalpy of the Formation of Nitrous Oxide

Enthalpy of formation data reported for nitrous oxide in the literature are summarized in Table 18.

Table 18: Enthalpy of formation of nitrous oxide.

Physical state	SI Units	Other units	References
Gas at 298 K	+82.048 kJ/mol	+19.6 kcal/mol	[43]
Gas at 298 K	+82.048 kJ/mol	+19.61 $\pm$ 0.1 kcal/mol	[89]
Liquid at 298 K	+75.595 kJ/mol	+18.068 kcal/mol	
Liquid at NBP	+65 kJ/mol	+15.53 kcal/mol	[90]

The standard enthalpy of formation of N_2O gas is $\Delta H_{\text{f,gas}}^\circ = +82.05 \text{ kJ/mol} = +19.6 \text{ kcal/mol}$ [43]. Note that the enthalpy of formation is highly positive, which

means that nitrous oxide can spontaneously decompose back to the elements from which it was formed and this would be a very exothermic reaction, quite suitable for its proposed use as a monopropellant. The enthalpy of formation of gaseous nitrous oxide as a function of temperature can be calculated from the following polynomial equation

$$\Delta H = H^\circ - H_{298.15}^\circ = A \times \tau + \frac{B \times \tau^2}{2} + \frac{C \times \tau^3}{3} + \frac{D \times \tau^4}{4} - \frac{E}{\tau} + F - H$$

where ΔH is the enthalpy in kJ/mol, τ is the temperature in kelvin divided by 1000, and A, B, C, D, E, F, and H are constants listed in Table 16 above for two different temperature ranges.

The latent heat of vaporization of N_2O at 298 K is 6.455 kJ/mol. Subtracting this from the enthalpy of formation of gaseous N_2O at 298 K (+82.05 kJ/mol) gives the enthalpy of formation of liquid N_2O at 298 K: +75.595 kJ/mol, which is the value we entered into Table 18 above.

3.3.3 Heat of Fusion of Nitrous Oxide

The molar enthalpy of fusion of nitrous oxide at the triple point derived from a Simon equation [30] is 6.720 kJ/mol, which can be compared with the measured enthalpy of fusion of 6.529 kJ/mol, which is the average of the two values reported in the literature [22, 23].

From another source, Gaidei [2] quoted the heat of fusion as $\Delta H_{\text{fus}} = 6.54$ kJ/mol. The heat of fusion at atmospheric pressure was found to be 6.516 ± 0.02 kJ/mol, and the entropy of fusion was 35.7 ± 0.1 J K⁻¹ mol⁻¹ [23].

3.3.4 Heat of Evaporation of Nitrous Oxide

The heat of evaporation of nitrous oxide at the moment one withdraws propellant from a self-pressurizing propellant tank containing liquid N_2O , is the key parameter entering a model that predicts the pressure and temperature history of liquid in a tank that relies on its own vapor pressure for expulsion. Other propellants or working fluids in this category that have been used are propane and propylene. In the case of nitrous oxide, due to its narrow liquidus range, the concern is that one might accidentally withdraw so much propellant that the contents in the tank will freeze. In order to prevent freezing, heat must be supplied from somewhere else in the system. Either the tank has to be wrapped in an electric heating blanket, or, as long as the satellite is in direct sunlight, the albedo of the sun-facing side of the satellite can be controlled by black and white louvers to allow the tank to warm back up. One of the first determinations of the heat of evaporation of N_2O [22] found the latent heat of evaporation to be 3958 ± 3 cal/mol, which converts to 16.56 kJ/mol, similarly to what was found by later investigators.

One of the more accurate determinations of the heat of evaporation of N_2O at the normal boiling point ($184.695\text{ K} = -88.465^\circ\text{C}$) measured the latent heat as $16.55\text{ kJ/mol} = 3.95\text{ kcal/mol}$ [27].

From the vapor pressure data in Figure 8, an equation was derived that gives the latent heat of vaporization as a function of the temperature [50, 33]:

$$\Delta H_{\text{evap}} = a(t_c - t)^b + c(t_c - t) + r_v$$

where ΔH_{evap} is the heat of evaporation in cal/g, t_c is the critical temperature = 36.434°C , t is the temperature in $^\circ\text{C}$, r_v is a residual correction, and a , b , and c are constants: $a = 12.9922$, $b = 0.417796$, $c = -0.082167$. Experimental and smoothed data calculated from this equation are summarized in Table 19 and illustrated in Figure 24.

Table 19: Vapor pressure and heat of evaporation of nitrous oxide.

Temperature		Vapor pressure, atm		Latent heat of evaporation		
K	$^\circ\text{C}$	observed	smoothed	observed cal/g	smoothed cal/g	smoothed kJ/mol
243	-30	13.044	13.041	69.817	69.788	12.851
248	-25	15.267	15.274	67.590	67.575	12.444
253	-20	17.772	17.778	65.280	65.318	12.028
258	-15	20.582	20.571	63.007	62.995	11.601
263	-10	23.665	23.670	60.575	60.573	11.155
268	-5	27.090	27.096	58.013	58.014	10.683
273	0	30.878	30.869	55.274	55.272	10.178
278	5	35.007	35.013	52.247	52.249	9.622
283	10	39.546	39.552	48.853	48.861	8.998
288	15	44.511	44.514	45.001	44.997	8.286
293	20	49.937	49.934	40.494	40.499	7.458
298	25	55.856	55.850	35.056	35.054	6.455
303	30	62.322	62.318	27.958	27.960	5.149
306	33	66.484	66.497	22.018	22.017	4.054
308.5	35.5	70.154	70.173	13.481	13.485	2.483
309.1	36.1	71.082	71.082	9.180	9.152	1.685
309.2	36.2	71.235	71.236	7.989	7.974	
309.3	36.3	71.386	71.389	6.379	6.379	
309.4	36.4	71.540	71.543	3.776	3.776	
309.434	36.434		71.596	0000	0.000	

Data source: [33]

The heat of evaporation of nitrous oxide at normal boiling point of 184.81 K and 101.7 kPa was found to be $16.544 \pm 0.020\text{ kJ/mol}$ [23], which is very similar to a value reported earlier in the literature [22] of $16.564 \pm 13\text{ kJ/mol}$ at 184.59 K .

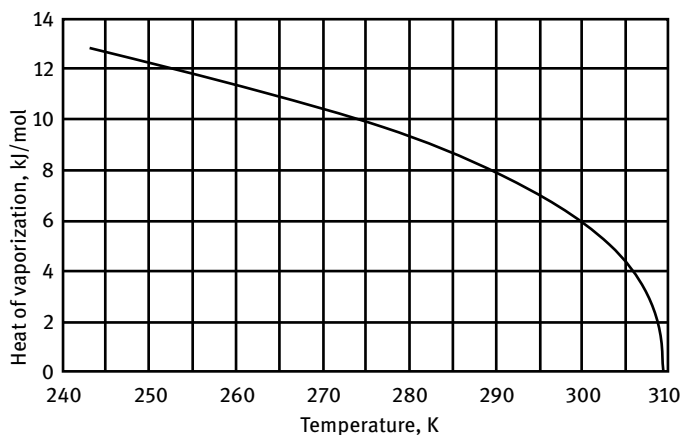


Figure 24: Heat of vaporization of nitrous oxide. (Created by Schmidt 2020, based on data from [33].)

The calculated heat of evaporation of N_2O was compared with experimental data in Figure 26 (Section 3.4.5) [61].

The sudden accidental freezing of liquid N_2O during rapid discharge from an airborne tank and clogging of discharge orifices would prevent the aircraft from dumping the unwanted mass in order to reduce its touchdown mass. The freezing of flowing N_2O has been studied in several oxidizer dump tests [91, 92].

Gaidei [2] quoted the following from other sources: $\Delta H_{\text{evap}} = 16.55 \text{ kJ/mol}$ and heat of liquid nitrous oxide evaporation on the line of saturation at different temperatures: at $T = 260 \text{ K}$ (-13°C) 11.58 kJ/mol ; at $T = 295 \text{ K}$ (22°C) 7.30 kJ/mol ; at $T = 305 \text{ K}$ (32°C) 4.75 kJ/mol .

3.3.5 Entropy of Nitrous Oxide

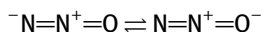
The entropy of gaseous N_2O at 298 K and 1 atm pressure is $S^\circ_{\text{gas}} = 219.96 \text{ J mol}^{-1} \text{ K}^{-1}$ (NIST 1998). The entropy of gaseous N_2O can be calculated from the polynomial equation

$$S^\circ = A \times \ln(\tau) + B \times \tau + \frac{C \times \tau^2}{2} + \frac{D \times \tau^3}{3} - \frac{E}{(2 \times \tau^2)} + G$$

where G is the integration constant in $\text{J mol}^{-1} \text{ K}^{-1}$, τ is the temperature in kelvin divided by 1000, and A , B , C , D , E , and G are constants listed in Table 16 for two different temperature ranges.

3.4 Molecular Structure of Nitrous Oxide

Nitrous oxide (dinitrogen monoxide) can exist in three isomeric forms: an asymmetric linear form NNO, a symmetric linear form NON, and a cyclic triangular form. All measurements support the asymmetric linear form, although computations also indicate the possibility of other forms as short-lived intermediates. Although N_2O has no inversion symmetry, it has been shown to oscillate between two resonant structures with opposing dipole moments, in effect canceling each other



As a result, the net dipole moment of N_2O is negligible compared to its substantial quadrupole moment. The linear shape of the N_2O molecule has a pronounced effect on the collision cross section of N_2O in molecular beams at low pressures.

3.4.1 Bond Lengths and Bond Angles of the N_2O Molecule

The N—N bond (1.128 Å) in nitrous oxide is substantially shorter than the standard N=N bond (e.g., 1.24 Å in $\text{MeN}=\text{NMe}$) and is only insignificantly longer than the $\text{N}\equiv\text{N}$ bond (1.10 Å, N_2). The N—O bond (1.184 Å, N_2O) is quite similar to the standard N=O double bond (1.21 Å, $\text{MeN}=\text{O}$). Therefore, the N—N and N—O bond orders in nitrous oxide are estimated at 2.73 and 1.61, respectively.

3.4.2 Crystal Structure of Frozen Nitrous Oxide

For rocket applications, the rocket engineer would rather not see frozen nitrous oxide clogging the feed lines at any time, but the crystal structure of frozen nitrous oxide is one of the reasons for the narrow liquid range of this oxidizer.

A comparison of Raman ν_1 line intensities expected for a random distribution of the molecular orientations N—N—O and O—N—N in frozen N_2O showed that a small deviation from the equiprobability of these molecular orientations leads to a drastic effect on the spontaneous Raman scattering line shapes [93].

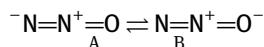
The consequences of head-to-tail disorder in crystalline N_2O have been studied by means of molecular dynamics simulations of the IR and Raman spectra of the lattice vibrations [94]. Single particle and collective mode properties were analyzed, also in relation to the cause of line broadening associated with the head-to-tail disorder. The study was extended to study the effect of dipolar disorder on the internal symmetric stretching mode ν_1 in the IR and Raman spectra of frozen N_2O [95].

Rietveld refinements of angle-resolved powder XRD data indicated that the crystal structure of CO_2 and N_2O phase IV adopts a post-stishovite-type $\alpha\text{-PbO}_2$ structure ($Pbcn$, $Z=4$); $\text{N}_2\text{O-IV}$ ($a=4.236[1]$ Å, $b=5.982(1)$ Å, and $c=4.223(1)$ Å) [96]. In these phases, both CO_2 and N_2O molecules are bent (133° for $\angle\text{N—N—O}$), with relatively long intramolecular bond distances and relatively short intermolecular bond distances. However, in contradistinction to carbon atoms in CO_2 , nitrogen atoms at the center of N_2O maintain the fcc positions of phases I or III.

The lattice dynamics of molecular crystal N_2O can be treated throughout the Brillouin zone within the framework of classical harmonic approximation. Density of states and heat capacity at low temperatures could be obtained by applying a potential computation method [97]. The results were in good agreement with available experimental data. The lattice frequencies of the isomorphous crystallized CO_2 calculated by using the same potential method agreed well with neutron scattering data.

3.4.3 Dipole Moment of Nitrous Oxide

The opposite charge distribution in the resonance forms A and B



accounts for the relatively low dipole moment of the molecule (0.161 D).

The N_2O dipole moment is very sensitive to two bond lengths and to the electron correlation. This can be measured in adducts of N_2O with the strong acid hydrogen fluoride HF [98]. The $\text{N}_2\text{O}\cdots\text{HF}$ adduct has two minima on the energy hypersurface corresponding to bent $\text{NNO}\cdots\text{HF}$ and linear $\text{FH}\cdots\text{NNO}$ structures. The activation energy between the two minima was estimated to be 497 cm^{-1} . The stability and structures of $(\text{N}_2\text{O})_2$ dimers, $\text{N}_2\text{O}\cdots\text{BH}_3$, $\text{N}_2\text{O}\cdots\text{NH}_3$ adducts were also examined. One would assume that two NNO molecules might associate in a “head-to-tail” orientation and form a dimer $(\text{N}_2\text{O})_2$, but measurements have shown that of the two structures, only the one having the oxygen atoms close to one another is experimentally observed.

The proton affinity of N_2O is very low, but protonated N_2OH^+ has been observed in the gas phase. The infrared spectra indicate that the proton would preferentially dwell at the oxygen atom and not at any of the two nitrogen atoms [99].

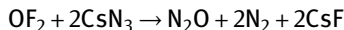
3.4.4 Other Isomers or Oligomers of Nitrous Oxide

Monomeric nitrous oxide may possibly also exist in a short-lived, cyclic form of an oxdiazirane:



Further studies of this structural isomer would be valuable for its potential evaluation as a rocket propellant, if it can be shown that it is more energetic than linear NNO and if it can be stabilized. It might also be possible to decompose this compound spontaneously on a catalyst at room temperature and use it as a monopropellant like hydrazine so that one does not have to preheat the catalyst. The structure of the cyclic molecule is similar to that of ethylene oxide, which can also be used as a monopropellant.

The reaction of OF_2 with NaN_3 or CsN_3 gave dinitrogen and nitrous oxide in a molar ratio of roughly 1:2, but not the expected oxygen azide:



This may proceed by intermediate formation of $\text{O}(\text{N}_3)_2$, which decomposes into N_2O and two equivalents of N_2 . The structure, energy, and vibrational frequencies of the not previously described $\text{O}(\text{N}_3)_2$ were computed by *ab initio* methods [100]. The formation of linear N_2O as the product of the reaction of OF_2 with CsN_3 can best be explained by the intermediate formation of $\text{O}(\text{N}_3)_2$, which then decomposes in a unimolecular reaction to yield N_2 and cyclic N_2O (C_{2v}), the latter of which then rearranges to form the more stable linear isomer of N_2O ($C_{\infty v}$). If cyclic $\text{NON}(C_{2v})$ existed, one would expect it to have the following bond lengths and bond angles: $\text{N}-\text{N}$ 1.214 Å, $\text{N}-\text{O}$ 1.511 Å, $\angle\text{NON}$ 47.4°, $\angle\text{NNO}$ 66.4°.

Clusters of two or more molecules of N_2O survive long enough to be identified if a jet of the gas is expanded into vacuum to form a molecular beam. Supersonic expansions of nitrous oxide seeded in argon were studied by single pass FTIR absorption at right angles with the jet axis [101]. In very dilute mixtures, 0.2% N_2O , dimer bands at 1282.4 and 2228.0 cm^{-1} were observed. Cluster bands (due to clusters of undetermined size) were readily observed in 20–100% N_2O mixtures at 1165.1, 1295.2, 2245.6, 2467.4, 2578.3, 2811.7, and 3505.8 cm^{-1} . All bands were shifted from the corresponding monomer bands more than in the crystal and in the same direction. Changing the dilution from 10 to 20% shifted all cluster bands 1–2 cm^{-1} towards low frequencies but still far away from the crystal frequencies. This was interpreted as being due to cluster melting.

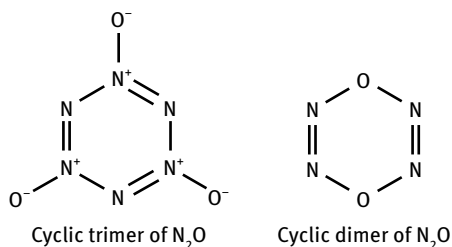
In addition to finding dimers in expanding flows, N_2O dimers can also be found by their IR spectra in cryogenic matrices. The IR spectra of the dimers of carbon dioxide and nitrous oxide have been recorded in nitrogen and argon matrices at about 17 K [102]. The spectra have been interpreted in terms of the presence of weak van der Waals molecular complexes, stabilized in one instance by quadrupole-quadrupole and in the other by dipole-dipole interactions. The structures of the dimers deduced on the basis of the spectra have been compared with those predicted by *ab initio* studies and with those determined in the gas phase and in some earlier matrix isolation studies.

High-resolution IR spectroscopy has been used in conjunction with *ab initio* calculations to identify the structure of a nitrous oxide tetramer [103]. It was possible to observe a non-planar structure in which all four molecules were approximately parallel. The high symmetry of this system made the spectral assignment straightforward. In fact, the *ab initio* calculations and experiment indicated that this system is very nearly a spherical top with rotational constants $A'' = B'' = 0.0248 \text{ cm}^{-1}$ and $A' = B' = 0.02495 \text{ cm}^{-1}$. The C rotational constant could only be roughly estimated to be 0.02 cm^{-1} from the relative intensities of the Q and P, R branches observed in the C -type band.

Clusters of N_2O in a molecular beam can be disassembled selectively by tuning the energy of an electron beam until cluster splitting is observed. The interaction of electrons of carefully controlled energy with a molecular beam of N_2O molecules and clusters has been studied in a pulsed crossed-beam arrangement over the energy range from threshold to 200 eV [104]. A variety of time-resolved techniques was applied to isolate and study many of the dissociative excitation channels that occurred. The degree of clustering in the target beam does not have much effect on the cluster dissociation energy.

Large N_2O clusters containing up to 177 molecules were simulated using a semiempirical computational chemistry method called AM1 [105]. Simulated spectra of different cluster sizes showed excellent agreement with experimental spectra. The vibrational band shape of the strong N—N stretching vibration was more strongly influenced by shape and size than that of the N—O stretching vibration. Stabilization energies and spectral band shapes confirmed a crystal-like structure of N_2O clusters generated in supersonic jet expansions. The AM1 results were compared to experimental and high-level *ab initio* methods, and it was shown that AM1 reproduced experimental results (structure and vibrational frequencies) and MP2 dissociation energies of small N_2O clusters far better than any other quantum mechanical method.

In search of more energetic or easier to store derivatives of nitrous oxide, calculations for hypothetical nitrous oxide oligomers were performed, examining the possibility of the existence of a cyclic trimer (N_2O)₃. The predicted heats of its formation calculated by different methods indicated that there is a small energy barrier before the trimer converts back to the monomer N_2O . Two isomeric structures are possible for the trimer, one is a benzene analog, resonance-stabilized ring structure, and the other is a 1,4-diox-2,3,5,6-tetrazane six-membered ring:



High pressure may facilitate a range of stability for these unusual compounds. A trimer of nitrous oxide has been observed in a molecular beam by IR spectroscopy.

A laser has been used in conjunction with a molecular-beam apparatus to study the infrared vibrational predissociation spectra of nitrous oxide clusters near the $\nu_1 + \nu_3$ vibrational combination band of the monomer [106]. These spectra were recorded as a function of source pressure in order to measure their dependence on cluster size. A frequency shift, corresponding to a gradual transition from the vapor to the solid state, was observed as the cluster size increased. Cluster-size distributions

were estimated using both quadrupole and ion time-of-flight mass spectrometry. The latter technique showed cluster sizes well in excess of $(\text{N}_2\text{O})_{100}$.

The structure of the nitrous oxide dimer was determined from sub-Doppler resolution infrared spectroscopy [107]. An opto-thermal detection method has been used to obtain rotationally resolved infrared spectra for both $(^{14}\text{N}^{14}\text{N}^{16}\text{O})_2$ and $(^{15}\text{N}^{14}\text{N}^{16}\text{O})_2$ dimers. The vibrational band observed in each case correlated well with the $\nu_1 + \nu_3$ band of the N_2O monomer. Isotopic substitution showed that of the two structures, only the one having the oxygen atoms close to one another is experimentally observed. The structural constants were determined to be $r_{\text{N}-\text{N}} = 3.493(4) \text{ \AA}$ and $\angle \text{NNO} = 59.2(5)^\circ$.

3.4.5 Computational Chemistry of Nitrous Oxide Molecules

Computational chemistry has been applied to single N_2O molecules, to N_2O clusters, and to N_2O adducts with other compounds. The objective was to find molecules that are more energetic than N_2O itself.

Multi-local minima on the potential energy surface of the electronic ground state of the N_2O molecule were predicted by various *ab initio* methods [108]. The calculations confirmed that the global minimum of the molecule possesses an N—N—O linear structure with $C_{\infty v}$ symmetry, as experiment and other theoretical calculations have already indicated. Calculations also predicted other local minima on the energy surface: a less stable cyclic isomer with a C_{2v} symmetry and a least stable linear N—O—N isomer with a $D_{\infty h}$ symmetry. The electronic structures of the local minima indicated that the energy of the system increased if the N—N bond of the molecule becomes weak (the cyclic C_{2v} case) or breaks (the linear $D_{\infty h}$ case). The electronic structure and stabilities of the local minima of the N_2O molecule potential energy surface gave a qualitative valence bond representation for the $C_{\infty v} \rightarrow C_{2v} \rightarrow D_{\infty h}$ isomerization energy differentials.

STO-6G calculations indicated that a valence-bond structure for N_2O generates a lower energy than does resonance between two valence-bond structures with π electron configurations [109]. In each of these three structures, the central nitrogen atom is apparently pentavalent. For N_2O , the bond orders that are implied by the structure



were shown to be in qualitative accord with the observed bond lengths. Estimates of the lengths of “normal” N=N and N=O double and triple bonds are 1.24 Å ($\text{H}_3\text{C}-\text{N}=\text{N}-\text{CH}_3$), 1.10 Å (N_2), 1.21 Å ($\text{H}_3\text{CN}=\text{O}$), and 1.06 Å (NO^+). Therefore, the N—N and N—O bond lengths of 1.13 and 1.19 Å for N_2O are only slightly longer than the N≡N triple bond of N_2 and similar to an N=O double bond.

The results of STO-6G valence bond calculations with Lewis-type valence bond structures were reported for the $S = 0$ spin ground states of the linear NNO ($C_{\infty v}$) and NON($D_{\infty h}$) isomers of N_2O [110]. It was shown that the singlet diradical character of the NON isomer is substantially larger than for the NNO isomer. Results of B3LYP/6-

31G(d) density functional calculations were also reported for the $C_{\infty v}$ and $D_{\infty h}$ ground states, the single determinant approximations to the lowest-energy $S = 1$ spin excited states of these two isomers, and for the triangular C_{2v} isomer. The calculated bond lengths were in accord with qualitative valence bond considerations. Molecular orbital calculations for the $O(N_3)_2$ decomposition showed that it can lead to a cyclic isomer of N_2O as a short-lived intermediate.

Lennard-Jones parameters of size and energy of force fields for nitrous oxide and dioxygen were determined by fitting the theoretical results to measured single component vapor/liquid equilibrium data [61]. The force fields accurately described the vapor/liquid two-phase coexistence curves of nitrous oxide, as shown in the vapor pressure plot (Figure 25) and the heat of evaporation plot (Figure 26). In addition to single component phase coexistence simulations, the phase equilibria of binary mixtures including N_2O/O_2 and N_2O/N_2 were simulated without further adjustment of the model parameters and found to be in good agreement with experimental data.

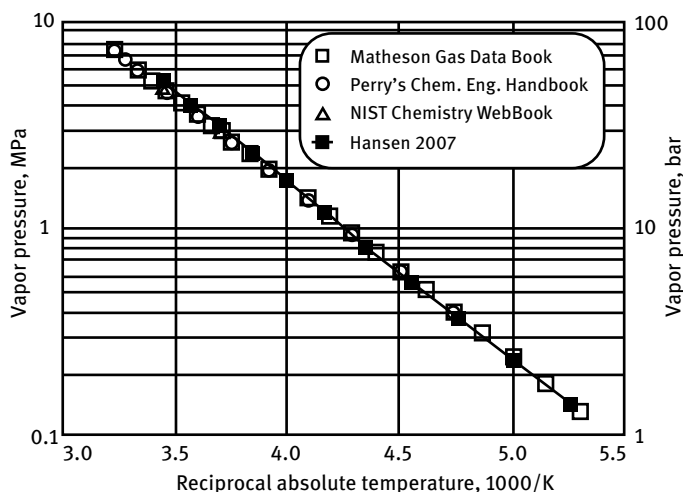


Figure 25: Clausius-Clapeyron plot for calculated vapor pressure of nitrous oxide. (Republished and modified from [61], with permission of © 2007 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

Open symbols represent experimental data and filled symbols the simulation results calculated by [61].

A global potential-energy surface was calculated for the electronic ground state of N_2O [111]. The new form was shown to accurately mimic the *ab initio* points calculated at the multi-reference configuration interaction level. The topographical features of this potential-energy surface were examined in detail and compared with those of other potential functions available in the literature and good agreement with experimental data was observed.

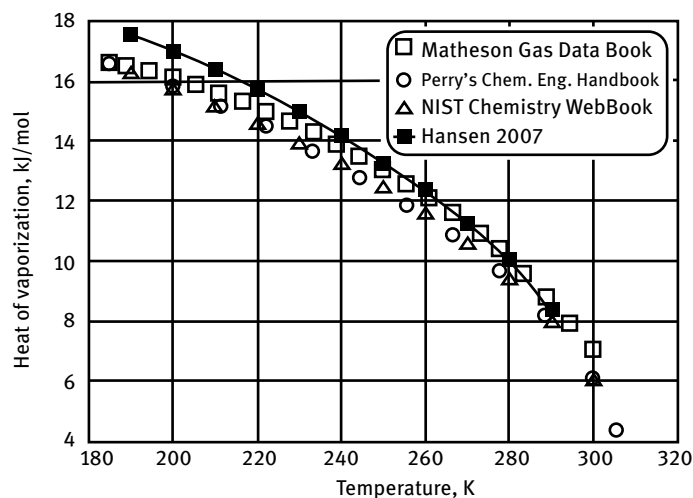


Figure 26: Calculated and measured heat of evaporation of liquid nitrous oxide. (Republished and modified from [61], with permission of © 2007 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

Open symbols represent experimental data and filled symbols the simulation results calculated by [61].

First-principles molecular-dynamics simulations based on density-functional theory were used to study the electronic and optical properties of fluid nitrous oxide under extreme pressure and temperature conditions [112]. Systematic descriptions of the pair-correlation function, the atomic structure, and the charge density distribution were used to investigate the dissociation of fluid nitrous oxide. It was found that the non-metal-metal transition for fluid nitrous oxide can be directly associated to the dissociation and has a significant influence on the optical properties of the fluid.

3.5 Optical Properties of Nitrous Oxide

3.5.1 Ultraviolet Spectra of Nitrous Oxide

Knowledge about the ultraviolet spectrum of nitrous oxide would be useful for laser ignition of nitrous oxide reactions. It is also fundamental in trying to understand the rate of N_2O destruction by photolysis in the stratosphere and calculating the mean lifetime of N_2O once it is released into the atmosphere as the result of anthropogenic industrial and biological processes.

A reinvestigation of the UV absorption spectrum of nitrous oxide agreed with previous results in the range 210 to 235 nm, but contrary to the previous results it indicated

a vanishingly small cross section above 260 nm [113]. The absence of the relatively long wavelength absorption implied a negligible rate of photolysis of nitrous oxide in the troposphere. These results plus the previously estimated atmospheric mean residence times of N_2O indicate that there may be a large, unknown tropospheric sink for nitrous oxide.

The UV absorption spectra of nitrous oxide and its ^{15}N isotope-substituted isomers were measured from 172 to 330 nm [114]. The long wavelength absorption above 265 nm was shown to be almost entirely due to Rayleigh scattering. This reduces the calculated rate of nitrous oxide photolysis in the troposphere to a very small value. Spectra over the wavelength range 172 to 190 nm demonstrated that the diffuse bands are a separate pronounced absorption of nitrous oxide, which is strongly affected by temperature. This banding is the result of transitions to discrete vibronic levels in an upper electronic state.

The UV absorption spectra of nitrous oxide and its ^{15}N isotopologues over the wavelength range 197 to 172 nm and between 150 and 500 K showed a weak continuous absorption and a pattern of diffuse banding that became more pronounced at higher temperatures [115, 116]. Spectra were measured at room temperature, 151, 333, and 485 K. The temperature dependence of the absorption spectrum results from the activation of the ν_2'' bending mode. Deconvolution of the data showed that absorption by molecules in the (010) vibrational mode results in a spectrum of vibrational bands superimposed on a continuum. A weaker and nearly continuous spectrum results from the ultraviolet absorption by molecules in the (000) vibrational mode. No rotational structure could be observed. The spectra of N_2O with natural isotope distribution were compared to those of $^{14}\text{N}^{15}\text{NO}$, $^{15}\text{N}^{14}\text{NO}$, and $^{15}\text{N}^{15}\text{NO}$. Measurement of the ν_2'' isotope shift was used to identify the quantum number of the upper state vibrational levels. Absorption cross section spectra of nitrous oxide for a wavelength range from 173 to 197 nm are shown in Figure 27.

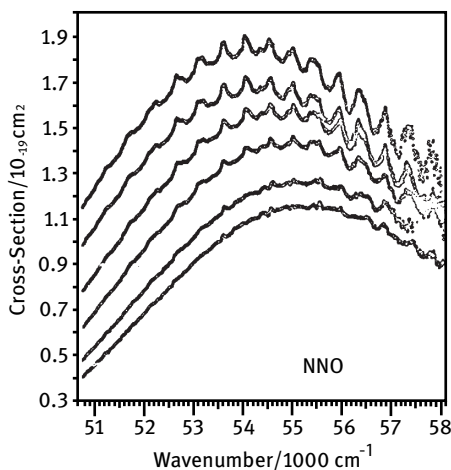


Figure 27: Absorption cross sections for $^{14}\text{N}^{14}\text{N}^{16}\text{O}$ at temperatures listed in the legend: (from bottom to top) 148, 213, 301, 372, 442, and 503 K. (From [115].)

The isotopically substituted nitrous oxide isotopologues $^{14}\text{N}^{14}\text{NO}$, $^{15}\text{N}^{14}\text{NO}$, $^{14}\text{N}^{15}\text{NO}$, and $^{15}\text{N}^{15}\text{NO}$ were investigated by UV absorption spectroscopy, and high-precision cross sections were obtained for the wavelength range 181 to 218 nm at 233 and 283 K [117]. These data were then used to calculate photolytic isotopic fractionation constants as a function of wavelength. The fractionation constants were used in a three-dimensional chemical transport model in order to simulate the actual fractionation of N_2O in the stratosphere, and the results were found to be in good agreement with field studies.

3.5.2 Infrared Spectra of Nitrous Oxide

The nitrous oxide molecule is unsymmetrical and, therefore, should have a dipole moment and an infrared absorption spectrum. The knowledge of IR spectra of N_2O is important for calculating its thermodynamic properties, for detection of N_2O leaks in the atmosphere near rocket test sites using N_2O , and for measuring the greenhouse effect contributions by N_2O in the upper atmosphere. Nitrous oxide, being a polar molecule, may associate to oligomers in the vapor phase at low pressures, typically studied in molecular jets. Infrared spectra of N_2O under these conditions help to determine how many N_2O molecules may have agglomerated in these clusters [103]. It is mostly due to the participation of nitrous oxide in atmospheric chemistry and energy balance that the infrared spectra of this compound have been so thoroughly investigated during the past 20 years, including the use of isotope-labeled molecules to identify the molecular vibrations and rotations that cause certain IR absorption bands. The detection and analysis of nitrous oxide as a rocket propellant benefits from the spectroscopy work done by the atmospheric chemistry researchers. IR spectroscopy would allow us to measure undecomposed N_2O in the rocket plume from a hybrid or monopropellant rocket engine.

On closer examination with a high-resolution spectrometer, all the bands in Figure 27 are revealed to consist of a multitude of very narrow absorption lines that can be assigned to specific vibration and rotation states of the molecule.

A typical wide-range, low-resolution IR spectrum of nitrous oxide gas is shown in Figure 28. The spectrum of gaseous nitrous oxide has been measured with a high-resolution grating spectrometer in the region from 2395 to 3510 cm^{-1} [118]. Long absorbing paths were used in a heated cell, so that it was possible to observe many of the weaker bands, including those with lower vibrational levels ν_2 , $2\nu_2^0$, $2\nu_2^2$, and ν_1 . From the line frequencies, accurate values of the rotational constants have been obtained, including the I -type doubling and variations with ν and I of the centrifugal stretching constant.

In one of the first high-resolution spectra recorded using an antique echelle spectrograph, almost 400 lines from five N_2O absorption bands arising from the ground state of the molecule have been measured [119]. The molecular constants of the above bands were then determined by making use of combination relationships applying

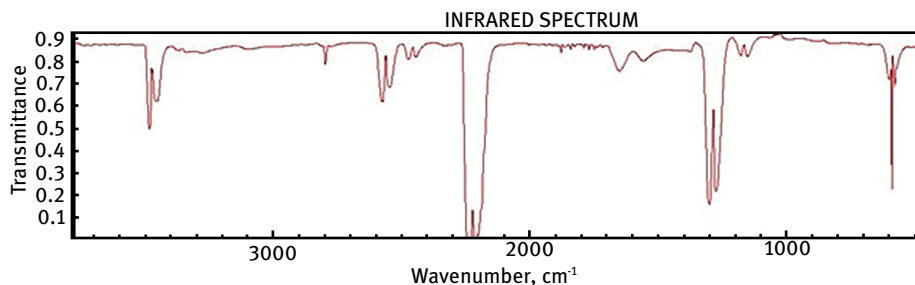


Figure 28: Infrared spectrum of gaseous nitrous oxide. (Reproduced and modified with permission from Coblenz Society, Inc., Evaluated Infrared Reference Spectra in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, <https://doi.org/10.18434/T4D303>, retrieved June 7, 2021)

least-squares methods to the data. The line frequencies were then calculated to four decimal places and presented in tables that contained over 600 line frequencies.

Measurements of the vibration-rotation bands of nitrous oxide occurring at 4.5μ yielded improved values for some of the rotational constants of this molecule [120].

Extending the spectroscopy from N_2O with natural isotope distribution to isotope-labeled N_2O , the IR spectra of $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ and $^{15}\text{N}_2^{16}\text{O}$ were measured with a high-resolution grating spectrometer in the region between 2100 and 4450 cm^{-1} and the spectrum of N_2O with natural isotope distribution $^{14}\text{N}_2^{16}\text{O}$ was remeasured for comparison in order to obtain accurate values of the isotopic shifts [121]. Twelve vibration-rotation bands of each isotopic species were analyzed, and from the rotational constants obtained it was possible to determine improved equilibrium internuclear distances $r_{\text{N-N}} = 1.1282\text{ \AA}$, $r_{\text{N-O}} = 1.1842\text{ \AA}$ for the nitrous oxide molecule.

High-resolution IR spectra of N_2O in the range from 1830 to 2270 cm^{-1} were obtained with optical path lengths of 1.2, 4, and 24 m and pressures ranging from 1 to 200 mm Hg [122]. The 1.2-m cell could either be cooled to 220 K or warmed to 400 K. At that high resolution, the absorption bands in Figure 28 can be resolved into individual rotation bands. The two high-resolution spectra in Figures 29 and 30 remind one of the proverbial “picket fence” spectrum. Once the moments of inertia of the molecule were known, vibration frequencies could be calculated, and the calculated results agreed quite well with the measured frequencies. By comparing the spectra of $^{14}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, and $^{14}\text{N}^{14}\text{N}^{18}\text{O}$, individual bands in the spectra could be assigned to specific modes of vibration and their harmonics.

The zero-order frequencies, and the anharmonic and vibration-rotation coupling constants up to fourth order have been calculated for $^{14}\text{N}_2^{16}\text{O}$ from a careful analysis of all available experimental data on the vibration-rotation energy levels of the molecule [123, 124]. It was found necessary to include the fourth-order constants in the energy expression in order to reproduce the recent accurate measurements to within their experimental uncertainties. Anharmonic interactions influence the energy levels. To

Most of the spectroscopy work discussed here deals with absorption spectra of nitrous oxide. However, when the molecule is excited by other means other than Brownian motion and thermal energy, e.g., in a glow discharge or a DC arc, it will also emit infrared vibrational luminescence radiation in specific frequency ranges. High-resolution measurements have been performed on 19 emission and absorption bands of the nitrous oxide molecule at 4.7 and 2.9 μm , and from these, accurate values of the vibrational and rotational constants of 23 vibration levels could be obtained [133].

Several bands of nitrous oxide occurring in the region of about 5.3 μm were measured by using a high-resolution vacuum infrared spectrograph, and the line frequencies were used to calculate the molecular constants [134].

A high-precision wavenumber calibration has been achieved for the spectrum of N_2O at 4.5 μm [135]. The values of the wavenumbers were reported for the $(00^0_1-00^0_0)$ and for the $(01^1_1-01^1_0)$ transitions in the ν_3 and the $(\nu_2 + \nu_3 - \nu_2)$ bands, giving a new set of molecular constants for the upper and lower levels of these two transitions. In particular, the value of the H constant for the ground state $(-2.02 \pm 0.4) \times 10^{-13} \text{ cm}^{-1}$ reported was significantly different from previous results.

The high-resolution infrared spectrum of N_2O in the region of ν_2 was recorded with an FTIR spectrometer at a resolution of $\sim 0.005 \text{ cm}^{-1}$ [136]. In addition to ν_2 , “hot” bands associated with this band and the bending fundamental ν_2 of $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ were analyzed.

An N_2O spectroscopic database suitable for high temperature and medium resolution applications has been created in the 4.5 μm region [137]. Intensities of $^{14}\text{N}_2^{16}\text{O}$ hot bands were extrapolated from the ν_3 band intensity, and energies of vibrational levels were computed. Pure N_2O spectra were recorded with an FTIR spectrometer at temperatures up to 900 K and with 1 cm^{-1} resolution. At that temperature, N_2O is already in a predissociation stage. A good agreement between these spectra and line-by-line calculations was obtained.

The absorption spectra of a $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ -enriched sample of nitrous oxide were recorded at Doppler-limited resolution with an FTIR spectrometer in the spectral range 3500–9000 cm^{-1} [138]. More than 12000 transitions of $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ were observed and ro-vibrationally assigned on the basis of a global effective Hamiltonian model. The band-by-band analysis led to the determination of the ro-vibrational parameters of a total of 107 bands. Among the 107 bands, 80 were newly observed, and for 27 others the rotational analysis was significantly extended and improved. The effective Hamiltonian parameters were determined from global fitting to the observed line positions. As a result, a set of 117 obtained effective Hamiltonian parameters reproduced 16134 observed line positions of 148 bands with an accuracy of $\pm 0.0014 \text{ cm}^{-1}$.

Vibrational-rotational line positions of the $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ isotopologues of nitrous oxide were fitted using a Hamiltonian approach describing all rovibrational energy levels in the ground electronic state and containing in explicit form all resonance interaction terms due to the approximate relations between

harmonic frequencies [139]. For $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, 124 effective Hamiltonian parameters were fitted to near 28000 observed line positions covering the 0.8–8860 cm^{-1} spectral range. For $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, 121 effective Hamiltonian parameters were fitted to more than 31000 observed line positions covering the same spectral interval. In both cases, the models described all available line positions with precision compatible to the measurement uncertainties.

Using FTIR spectra of the nitrous oxide isotopologue $^{15}\text{N}_2^{16}\text{O}$, the line positions and intensities have been measured for 511 lines of 8 cold bands and 1 hot band lying between 5800 and 7600 cm^{-1} [140]. A multi-spectrum fitting procedure has been used to retrieve line parameters from five experimental spectra recorded at different pressures. The line positions measured and those collected from the literature allowed the global fitting of the effective Hamiltonian parameters for this isotopologue, giving very accurate inertia moments and bond distances.

Cavity ring-down spectroscopy is a form of laser absorption spectroscopy. In cavity ring-down spectroscopy, a laser pulse is trapped in a highly reflective detection cavity [141, 142]. The $6\nu_3$ and $\nu_2 + 6\nu_3 - \nu_2$ bands of ^{15}N -substituted nitrous oxide isotopologues have been recorded by a continuous-wave cavity ring-down spectrometer operated near 0.8 μm [143]. In total, 213, 86, and 191 transitions were observed for the $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, and $^{15}\text{N}_2^{16}\text{O}$ isotopologues, respectively. The ro-vibrational spectroscopic parameters of the upper states were determined from least square fitting of the transitions. The absolute line intensities of the $6\nu_3$ cold bands were retrieved by a multi-line fitting procedure from the spectra for the majority of the unblended lines.

The absorption spectrum of nitrous oxide has been recorded by Intracavity Laser Absorption Spectroscopy between 12760 and 12900 cm^{-1} [144]. The rotational analysis led to an improved determination of rovibrational parameters of the $6\nu_3$ and $6\nu_3 + \nu_2 - \nu_2$ bands of $^{14}\text{N}_2^{16}\text{O}$. The high J rotational levels of the (00^0_6) and (01^1_6) upper states were found perturbed by an anharmonic interaction. Line intensity values of the $6\nu_3$ band were tabulated, and the main effective dipole moment parameter of this molecule was then determined.

3.5.2.1 Infrared Spectra of Solid and Matrix-Isolated Nitrous Oxide

There are hundreds of publications on IR spectra for gaseous N_2O , hardly any for liquid N_2O , and only a few for solid N_2O . Chilling N_2O until it solidifies would also freeze the rotational structure and broaden the other bands due to interaction of closely packed molecules.

The infrared spectrum of solid nitrous oxide was measured at 80 K [145]. In contradistinction to CO_2 , no evidence for splitting due to intermolecular coupling or for reflection peaks in the spectrum was observed. Spectral features assigned to torsional lattice motions (with fundamentals at 80 and 91 cm^{-1}) and to translational lattice motions (as broadening of ν_3) could be seen.

Nitrous oxide was isolated in pressed alkali halide matrices [146]. Its three infrared active fundamentals appeared at room temperature as single peaks and without

the gas phase rotational structures. Cooling of the host matrix caused these bands to sharpen and to shift to higher frequencies. At any given temperature, however, the peak frequencies were essentially independent of the host matrix. The temperature dependence of the most intense ν_3 fundamental was examined in detail, and the results indicated that there were two dominant trapping sites for N_2O in pressed KCl, KBr, or KI matrices.

The IR spectrum of crystalline nitrous oxide showed longitudinal-transverse mode splitting of the three fundamentals and factor group splitting of ν_2 [147]. A large number of internal isotopic and combination bands have been assigned. In the region of combination bands extended two-phonon absorption bands have been observed, which were particularly prominent in the region of $\nu_1 + \nu_3$ and $\nu_2 + \nu_3$. The energy of one- and two-phonon states has been calculated using a resonant dipole-dipole interaction potential. The results of calculation agreed well with experiments. The intensity and profile of the two-phonon bands was calculated using a mechanism of induced dipoles. It was shown that two-phonon bands arise by direct excitation via non-linear terms in the dipole operator.

In studying the temperature dependence of the far infrared active lattice modes of solid nitrous oxide, spectra of solid N_2O were precisely measured in temperature range from 1.8 to 130 K [148]. Remarkable temperature dependence of the absorption bandwidths was obtained and explained by means of the perturbation theory of the anharmonic crystal. The results suggested ways in which the lattice vibration energy is dissipated. No dipole ordering was found by the spectroscopic studies.

The vibrational spectrum of solid N_2O diluted in a frozen nitrogen matrix was compared to the spectrum of N_2O produced after the photolysis of ozone diluted in solid nitrogen [149]. The photolysis of ozone produced atomic oxygen. The small shift observed between the two spectra was found to be due to the formation of a 1 : 1 complex between nitrous oxide and molecular oxygen. Upon increasing the temperature, the complex formed after the photolysis of ozone in nitrogen reacted with an oxygen atom leading to O_3 and N_2O .

Isotopically labeled nitrous oxide has been produced in solid nitrogen matrices using mixtures of nitrogen and water containing ^{14}N , ^{15}N , ^{16}O , ^{17}O , and ^{18}O [150]. All 12 possible N_2O isotopologues and isotopomers were obtained, and their fundamental, overtone, and combination frequencies were assigned by the joint use of infrared spectroscopy and quantum chemical calculations. The nitrogen matrix has some influence upon frequency and anharmonicity of the vibrations.

The physical properties of nitrous oxide are very similar to those of carbon dioxide. Just like there is carbon dioxide snowing at the polar caps of Mars, there might be other celestial bodies where it is snowing nitrous oxide instead. This is why the reflection spectra of solid N_2O in all wavelengths are of astrophysical interest.

Figure 31 is a composite of three spectra of solid nitrous oxide at 16 K taken at three different wavelength ranges. Note that the optical depth ordinate scale is different for each of these three segments.

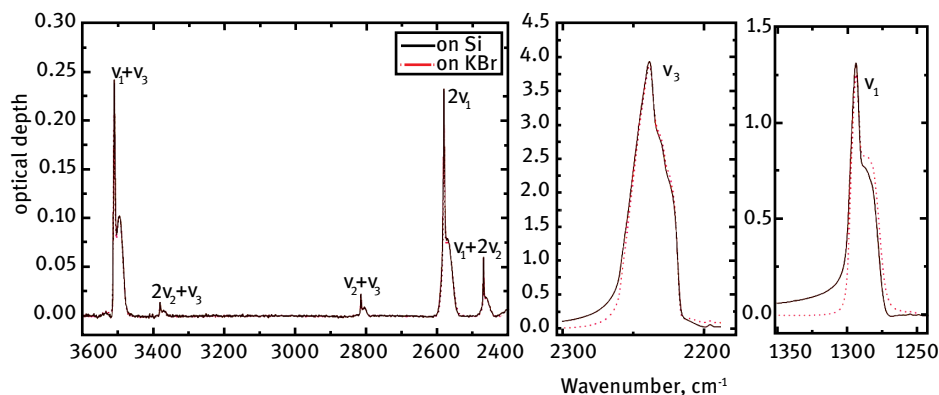


Figure 31: Infrared spectra of solid nitrous oxide at 16 K. (Reprinted and modified from [38], with permission from © 2009 Elsevier; permission conveyed through RightsLink.)

The peak positions and the band assignments from the spectra above are listed in Table 20. Similar spectra were obtained for $\text{NO}_2/\text{N}_2\text{O}_4$ equilibrium mixtures flash-frozen at 16 K.

Table 20: Peak positions of the IR bands of solid N_2O deposited at 16 K and their assignment.

Wavenumber, cm^{-1}	Vibration mode
1166	$2\nu_2$
1295	ν_1
2239	ν_3
2469	$\nu_1 + 2\nu_2$
2581	$2\nu_1$
2814	$\nu_2 + \nu_3$
3380	$2\nu_2 + \nu_3$
3509	$\nu_1 + \nu_3$

Data source: [38]

Table 21 gives a comparison of absorption coefficients of nitrous oxide as a gas at 300 K and dissolved in liquid oxygen (LOX) at 90 K. The frequencies, half-widths, and intensities of bands in the infrared spectra of linear molecules (N_2O) dissolved in LOX were measured at 90 K and compared with the results obtained from the spectra in the gas phase [151]. Solutions whose concentrations were known to be lower than saturated were prepared by liquefaction in a cryostat of standard gas mixtures of the gas with oxygen. On condensation the partial pressure of the gas was lower than the vapor pressure over solid N_2O to avoid N_2O precipitation. The standard mixtures were chosen such that in most cases, the vibrational frequencies underwent a shift to lower

frequencies on going from the gas phase to the LOX solution. Once the absorption coefficient of N_2O at its strongest ν_1 absorption band was known, this method could be used to determine N_2O concentrations in LOX solutions used as rocket propellant.

Table 21: Absorption coefficients of nitrous oxide as a gas and dissolved in liquid oxygen.

Band assignment	Gas at 300K	In liquid oxygen at 90K	Band half-width $\Delta\nu_{1/2}$
	$A \times 10^8, \text{cm}^2 \text{mol}^{-1} \text{s}^{-1}$	$A \times 10^8, \text{cm}^2 \text{mol}^{-1} \text{s}^{-1}$	
$\nu_1 \Sigma$	29.9	29.5 ± 1	2.7
$\nu_2 \Pi$	4.6–2.3	3.3	1.2
$\nu_3 \Sigma$	157 ± 10	164 ± 10	2.7
$2\nu_1 \Sigma$	4.9 ± 0.5	5.1	3.2
$2\nu_2 \Sigma$	1.3–0.9	1.0	2.6
$2\nu_3 \Sigma$	0.18	0.16	3.6
$\nu_1 + 2\nu_2 \Sigma$	1.3 ± 0.2	1.0	2.9
$\nu_2 + \nu_3 \Pi$	0.27	0.3	1.9
$2\nu_2 + \nu_3 \Sigma$	0.22	0.25	3.4
$\nu_1 + \nu_3 \Sigma$	5.1–4.5	5.5	3.4

Data source: [152]

3.5.3 Raman Spectra of Nitrous Oxide

Raman scattering in the lattice region (25 to 200 cm^{-1}) of frozen N_2O at 90 , 120 , and 170 K has been investigated using He-Ne gas laser excitation [153]. The structure of crystals in polycrystalline N_2O lacks a symmetry center, and the site group is C_3 and the space group is T^d ($P2_13$). The greater band widths in the N_2O spectrum (compared to CO_2) may be attributed to crystalline disorder (Table 22). The origin of the shoulder observed near 111 cm^{-1} is uncertain. It may correspond to the band observed at 113 cm^{-1} in the far-infrared spectrum of N_2O at 65 K .

Table 22: Temperature dependence of Raman lattice frequencies of N_2O .

Temperature, K	Wavenumber, cm^{-1} (half-height width in parentheses)		
90	68 (8)	80 (5)	122 (8)
120	64	76	119
170	61 (12)	71 (shoulder)	110 (13)

Data source: [153]

A comparison of Raman stretching mode ν_1 line intensities expected for a random distribution of molecular orientations $\text{N}-\text{N}-\text{O}$ and $\text{O}-\text{N}-\text{N}$ in frozen N_2O showed that a small deviation from the equiprobability of these molecular orientations leads

to a drastic effect on the spontaneous Raman scattering line shapes [93]. It was concluded that N_2O crystals grown from the gas phase were not totally disordered.

The isoelectronic molecules CO_2 and N_2O form crystals of cubic symmetry, with space groups T_h^6 and T^4 , respectively. Laser-excited Raman spectra of polycrystalline solid samples of CO_2 and N_2O (Figure 32) excited by the $5145\text{ \AA}$ line of an argon laser operating at about 433 mW power were measured at 79 and 18 K, and lattice and molecular modes were assigned according to predictions from the known crystal structures, and the observed lattice frequencies were compared with calculated values [154].

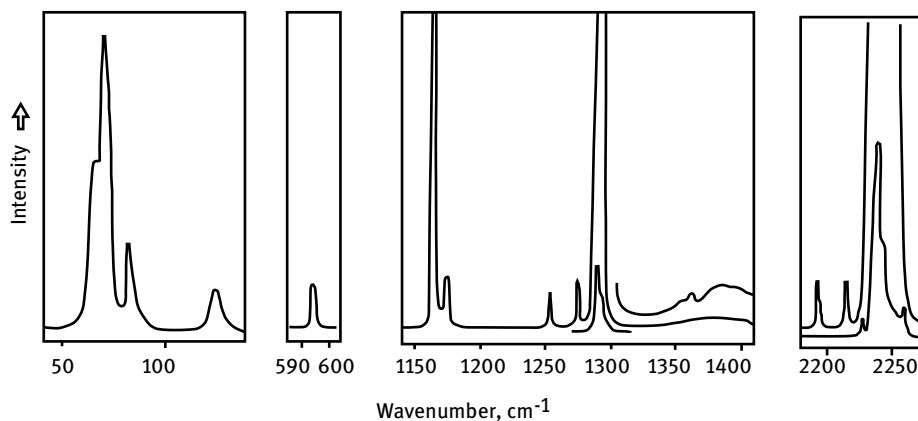


Figure 32: Raman spectra of polycrystalline nitrous oxide at 18 K. (Reprinted and modified from [154] with permission from © 1971 Elsevier, permission conveyed through Copyright Clearance Center, Inc.)

The absence of a center of symmetry in N_2O results in a more detailed Raman spectrum. In the lattice region, besides the three librational modes, four translations are Raman active. However, apart from increases in line widths, the observed spectrum is very similar to that of CO_2 , indicating that the translations are very weakly Raman active, possibly as a result of the residual disorder. All three intramolecular modes of N_2O are Raman active, with two components predicted for each of the stretching vibrations and three for the bending mode.

Raman studies as a function of pressure ($P < 40\text{ GPa}$) and temperature (20–300 K) have been made of the external and internal modes of solid N_2O , and the pressure dependence of external and internal modes was determined [155]. The occurrence of orientational disorder manifested itself in the line shape of the lattice and intramolecular modes. A new high-pressure phase $\text{N}_2\text{O-II}$ was found above 5.5 GPa. The temperature shift of the external mode wave numbers was found to decrease drastically with increasing pressure.

Based on *in situ* high-pressure, high-temperature Raman spectroscopy, two new solid phases were discovered in the phase diagram of nitrous oxide [156]. The two

new solid phases were stabilized by heating the room temperature orthorhombic nitrous oxide at pressures between 12–35 GPa and temperatures above 500 K. Both new phases could be quenched metastably to room temperature, where they remained stable over a wide range of pressures between 5–60 GPa. The appearance and properties of the new phases were similar to those of the high pressure-high-temperature phases of carbon dioxide. However, the similarity between the two isoelectronic molecules ends at temperatures above 1000 K, where nitrous oxide disproportionates to form an ionic solid (nitrosonium nitrate), while carbon dioxide forms a covalent solid.

When β -nitrous oxide ($Cmca$ N_2O) was laser-heated to between 2000 and 3400 K at high pressures (10–55 GPa), it disproportionated into an ionic form of dimeric nitrous dioxide ($NO^+NO_3^-$) and nitrogen [157]. Raman spectra of the quenched products suggested that the ionic phase was stable to 55 GPa at ambient temperature but, upon subsequent heating at pressures below 30 GPa, further dissociated into nitrogen, oxygen, and other nitrogen-oxygen compounds. XRD patterns of the ionic phase indicated that it has an orthorhombic structure ($Z = 4$, $\rho_o = 2.69 \text{ g/cm}^3$), similar to the aragonite phase of calcium carbonate. The results suggested that the primary driver for ionization is densification at high pressures, whereas dissociation between 10 and 30 GPa resulted from the combined effects of densification and entropy increases.

3.5.4 Microwave Spectra of Nitrous Oxide

Rotational lines of N_2O have been measured with high precision in the region of 1 to 3 mm wavelength (100 to 300 GHz) for nine $J \rightarrow J + 1$ transitions between $3 \rightarrow 4$ and $11 \rightarrow 12$. These microwave measurements have given very precise values for the ground-state rotational constant, $B_0 = 12561.63 \text{ MHz}$, $D_J = 5.359 \text{ kHz}$, and the I-doubling constant, $q = 23.73_6$, of the $^{14}N^{14}N^{16}O$ molecule [158].

Rotational transitions observed between 125 and 302 GHz ($J = 4 \rightarrow 5$ to $J = 11 \rightarrow 12$) have provided improved rotational and centrifugal distortion constants for the (00^0_0) , (01^{1c}_0) , (01^{1d}_0) , (02^0_0) , (02^{2d}_0) , (02^{2c}_0) , and (10^0_0) vibrational levels of $^{14}N_2^{16}O$ [159]. The splitting of the (02^2_0) state due to I -type resonance was well resolved, and a correlation between B_v and D_v was studied; B_0 and D_0 were $12561.6338 \pm 0.0006 \text{ MHz}$, and $5.282 \pm 0.004 \text{ kHz}$, respectively.

The submillimeter wave spectrum of N_2O within the 375–565 GHz frequency range included 161 lines belonging to 22 spectroscopically different states of the molecule (specifically, the ground and some excited vibrational states of the five most abundant isotopic species of the molecule in natural abundance) [160]. Rotational and two centrifugal stretching constants could be determined for each spectroscopic species. The total number of the rotational and rovibrational constants exceeded 40.

High-precision microwave absorption measurements of gaseous nitrous oxide were eventually extended up through 1.5 THz [161]. The data set included ground state, ν_2 , $2\nu_2$, ^{15}NNO , $N^{15}NO$, and $N_2^{18}O$ spectra up to $J = 68$, and improved Hamiltonian parameters derived therefrom.

3.5.5 NMR Spectra of Nitrous Oxide

^{15}N nuclear-magnetic-resonance (NMR) measurements on solid ^{15}NNO showed that the anisotropic chemical shift and intramolecular dipole coupling, molecular reorientation resulted in a change in the nuclear-precession frequency [162]. The rate of combined-translation-rotation jumps in this orientationally ordered solid was followed with two-pulse spin echoes, as well as stimulated echoes. Although the rates and activation energies determined by NMR and previously reported dielectric measurements were similar, they were not equal. The data demonstrated that dielectric measurements monitor in-place, head-tail flips, while NMR follows the slightly slower combined-translation-rotation jumps.

3.5.6 Refractive Index of Nitrous Oxide

The refractive index of liquid N_2O at $T = -90^\circ\text{C}$ (183 K) is 1.330.

The refractive index of frozen nitrous oxide at 16 K at 543 nm is 1.318, as shown in Table 5 above [38].

3.6 Electrical Properties of Nitrous Oxide

The dielectric constant of liquid nitrous oxide at 183 K (-90°C) is 1.97, and the dielectric constant of gaseous nitrous oxide at 293 K (20°C) and atmospheric pressure is 1.001028. The dipole moment of nitrous oxide is 0.1608 Debye. The ionization potential of N_2O is 12.6 eV.

3.7 Magnetic Properties of Nitrous Oxide

The magnetic susceptibility of gaseous nitrous oxide is -0.429×10^6 CGS units.

3.8 Solubility of Nitrous Oxide

3.8.1 Solubility of Gases in Liquid Nitrous Oxide

Liquid nitrous oxide is a good solvent for gases and other liquids. Although nitrous oxide as a rocket oxidizer is often used in a self-pressurizing mode, pressurant gases such as helium or oxygen that are applied to prevent it from flashing prematurely into a solid (due to its narrow liquidus range) would readily dissolve in liquid N_2O and alter its behavior in pumps, valves, cavitating venturi, or other orifices. In one application, the N_2O tank was designed contain pressurized helium in the ullage volume, and this He was to force the N_2O out of the tank, through the metering system, and into a combustor. The N_2O absorbs He, and if the absorbed He is subsequently desorbed

during the flow or metering processes, the metering system may not function properly. Supercritical N_2O , similar to supercritical CO_2 , is an excellent solvent for a wide range of substances.

3.8.2 Mixtures of Liquid Nitrous Oxide with Other Oxidizers

Use of gaseous oxygen as the pressurant for other oxidizers eliminates the need for the expensive helium gas. Oxygen gas is quite soluble in liquid nitrous oxide, thus improving its performance and allowing the saturated solution to be used in a self-pressurizing blowdown mode of propellant expulsion.

Liquid nitrous oxide and liquid oxygen are not miscible over the entire range of compositions and temperatures. Studies have been made at either end of the range of composition, studying the solubility of N_2O in LOX and the solubility of gaseous O_2 in liquid N_2O . Mixtures of nitrous oxide, carbon dioxide, and oxygen have been proposed as oxidizers for Mars mission applications [163].

If nitrous oxide is bubbled into a cooled sample of N_2O_4 , a partially saturated solution will contain 9.5 mass-% N_2O , have a freezing point of $255.7\text{ K} = -174^\circ\text{C}$ and a boiling point of 301 K (28°C) [164]. In a similar test, where it was observed that N_2O bubbles bubbling through cooled N_2O_4 were completely absorbed before they reached the surface, the saturated solution contained 41.5 mass-% N_2O and had a freezing point of 222 K (-51°C) and a boiling point of 306 K (33°C). The absorption of N_2O into N_2O_4 was exothermic, suggesting that some sort of chemical reaction may have taken place in addition to forming a physical solution. Many years later, propellant combinations with mixtures of N_2O and N_2O_4 containing between 28 and 52 mass-% N_2O_4 were again patented [165], but there was no reference to prior art such as that described in [164].

3.8.3 Solubility of Nitrous Oxide in LOX

The solubility of nitrous oxide in liquid oxygen will be discussed in detail in *Encyclopedia of Oxidizers*, chapter “Oxygen”.

3.8.4 Solubility of Oxygen in Liquid Nitrous Oxide

Mixtures of gaseous nitrous oxide and gaseous oxygen are widely used in surgery as an anesthetic/analgesic because it was found to be desirable to store the premixed gases in gaseous form in a single cylinder instead of having to meter the two gases from two different cylinders at the point of end use. In a commercial cylinder containing nitrous oxide and oxygen at 293 K (20°C) and a total pressure of 13.8 MPa (136 atm), the maximum percentage of nitrous oxide that can be obtained without the condensation of liquid nitrous oxide is 37% N_2O by volume. For the medical application, it is important that the mixture ratio of the two gases remain the same over the entire period of drawing gases from a cylinder. The nominal composition for anesthesia/analgesia usage is a 50 : 50 mixture by volume of the gases. The composition of the gas mixture

released from evaporating liquid in cylinders that have been stored at low temperatures may deviate from the nominal mixture ratio if the cylinders have not been stored and oriented properly. It is essential that the mixture remain in a homogeneous state during the administration at all times. If liquid N_2O were inside the cylinder, then an oxygen-rich gas mixture would be withdrawn at first, the mixture becoming progressively richer in nitrous oxide until the oxygen concentration fell below 10%. Such a mixture would be dangerous to breathe as it would contain insufficient oxygen to support normal respiration. It was necessary to establish safe procedures for the storage and use of premixed nitrous oxide-oxygen mixtures to prevent phase separation. Unwanted condensation of liquid nitrous oxide may occur inside the full cylinder if it is cooled to a temperature less than about 266 K (-7°C). In the case of premixed cylinders of a 50/50 gaseous nitrous oxide-oxygen mixture used as an analgesic, any liquid phase formed as a result of inadvertently cooling the cylinder to below 233 K (-40°C) can be dispersed and rehomogenized by storing the cylinder horizontally for at least 24 h at a temperature not less than 278 K (5°C). Rolling the cylinder would aid the mixing, and the mixing time is of the order of minutes.

In 2009, a review was undertaken of existing literature to examine the developmental history of these $\text{N}_2\text{O}/\text{O}_2$ mixtures and to examine data to support the position that the contents of a cylinder of a 50 vol.-% nitrous oxide and 50 vol.-% oxygen mixture is in a homogenous single gas phase in a filled cylinder under normal conditions of handling and storage. If phase separation could be made to occur by inadvertent undercooling, there was justification for the instructions given recommending 48-h horizontal storage at temperatures above 283 K (10°C) and repeated inversion of the cylinders before use [166].

The liquid-vapor equilibria for the nitrous oxide/oxygen system have been compared to the behavior of carbon dioxide/oxygen because N_2O and CO_2 are usually very similar in their physical properties and solvent characteristics. The liquid-vapor equilibria for the systems nitrous oxide-oxygen and carbon dioxide-oxygen were measured and presented in the form of isotherms on pressure-composition graphs, and isobars on temperature graphs, up to 20.7 MPa (200 atm) [167]. In Figure 33, the points of known liquid composition give the “liquid curve” or bubble-point curve. If one of these points is approached from outside the loop, it gives the point where the first bubble appears. When the mol fraction of oxygen is zero, the bubble-point and dew-point curves meet at the vapor pressure for pure nitrous oxide at the temperature of the isotherm. The broken line in Figure 33 adjacent to the vapor curve represents the ideal vapor phase composition, assuming that the vapor phase is a mixture of perfect gases obeying Dalton’s law. This assumes that the vapor pressure of nitrous oxide remains constant and independent of the total pressure in the cylinder. In practice, the partial pressure of nitrous oxide found in the vapor phase of these mixtures always exceeded that of pure nitrous oxide. Above a certain pressure, PM (approximately 9.6 MPa (94 atm)), the percentage of nitrous oxide increased rather than decreased as the pressure was raised. This resulted in the liquid and vapor phase compositions be-

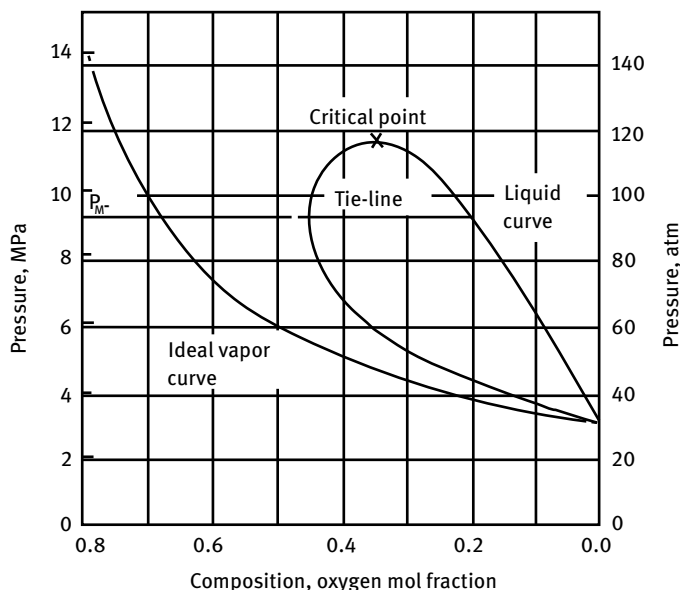


Figure 33: 273 K isotherm for nitrous oxide-oxygen mixtures. (Republished and modified from [167], with permission of IOP Publishing Ltd.; permission conveyed through Copyright Clearance Center, Inc.)

coming equal at a critical point. A horizontal line drawn on the pressure-composition diagram connects positions of equilibrium and is called a “tie-line”.

Measurements taken over a temperature range from 243 to 303 K (−30 to 30 °C) in 5° increments were combined in isobars in a temperature vs. composition plot (Figure 34).

Nitrous oxide that is intended to be used as an anesthesia/analgesia agent must be of extreme purity, and contaminants like nitrogen and methane must be removed. The liquid/vapor equilibria of the binary systems N_2O/N_2 , N_2O/O_2 , and N_2O/CH_4 at low temperatures between 213 and 293 K (−60 and +20 °C) and high pressures up to 9.09 MPa (90 atm), bordering on critical point conditions, were measured to identify the range of compositions where purification by distillation is no longer effective [168]. The same measurements also identified the composition/temperature/pressure ranges where N_2O/O_2 gas mixtures might liquefy and disturb the required composition of the gas mixture withdrawn for medical purposes.

With the advances in computational chemistry it has now become possible to predict miscibility and phase boundaries of binary mixtures of nitrous oxide and oxygen. Simulations have been carried out at five different temperatures based on a Lennard-Jones plus point charge functional form [61]. Figure 35 shows the phase equilibrium data at 253.15 K. The simulations were in good agreement with the experimental data

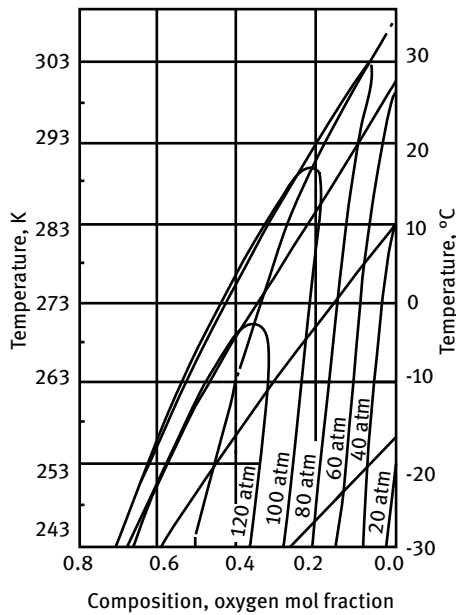


Figure 34: Liquid-vapor equilibrium isobars for nitrous oxide-oxygen mixtures. (Republished and modified with permission of IOP Publishing Ltd. from [167]; permission conveyed through Copyright Clearance Center, Inc.)

in the lower pressure regime. At higher pressures deviations occur for the bubble line. Simulations carried out for pressures higher than 80 bar followed the course of the Bracken et al. isotherm, although the deviations from the experimental data became larger.

The former Space Propulsion Group (Sunnyvale, CA) had applied for a patent [169] for oxidizers based on refrigerated mixtures of nitrous oxide and oxygen that were called “Nytrox” [170], although the claims in the patent were overly broad and diffuse and should have been narrowed to more specific claims before granting a patent. The potential advantages of mixtures of oxygen and nitrous oxide compared with the pure components are:

- partial self-pressurization possible at high densities (eliminates or minimizes the use of expensive helium)
- improved I_{sp} performance compared to N_2O
- unlike liquid oxygen, not cryogenic; oxidizers at 213 to 233 K (−60 to −40 °C) are much easier to manage.
- potentially lower freezing point compared to N_2O useful for space applications

Using oxygen instead of helium as a pressurant for oxygen in bipropellant or hybrid systems would have the advantage that after all liquid oxidizer is consumed, the pressurant gas can be burned with fuel providing additional impulse (assuming that some fuel is left at this point and that the flow rate of both components can be adjusted to account for the change in the physical state of the oxidizer). If there is any concern that

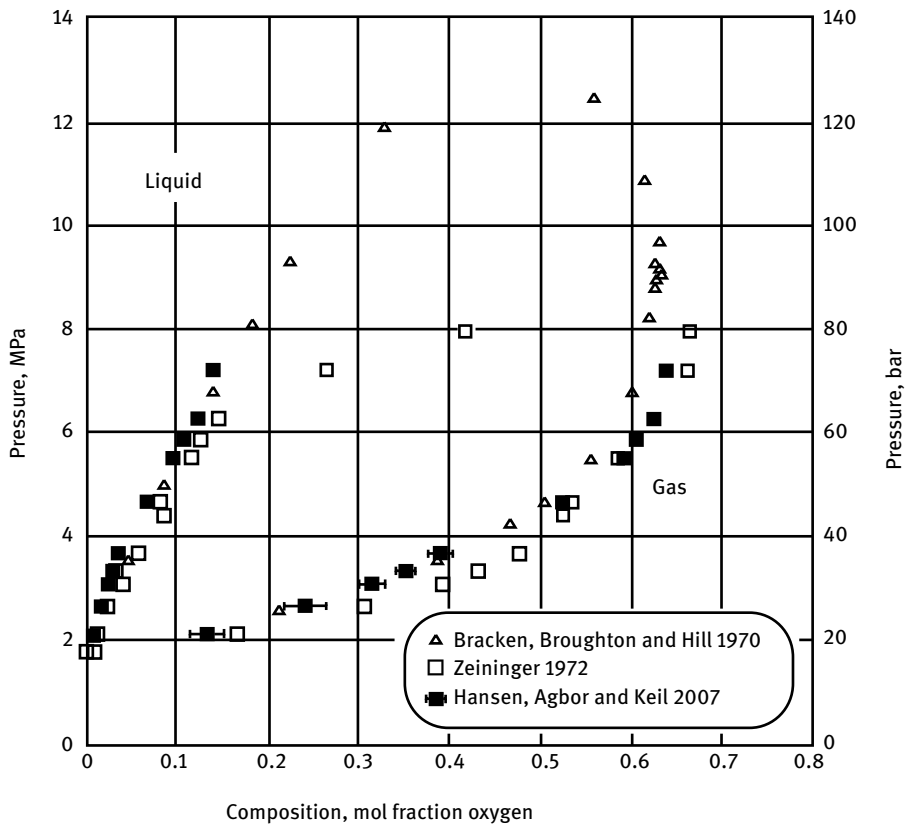


Figure 35: Pressure-composition phase diagram for the oxygen-nitrous oxide binary system at 253 K. (Republished and modified from [61], with permission of © 2007 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.) Experimental data are represented by open symbols, simulated data by solid filled symbols

the residual gaseous nitrous oxide in the oxidizer tank of an all- N_2O oxidizer system at the end of a mission constitutes a potential explosion hazard, then the dilution with oxygen would substantially reduce this hazard, because oxygen dilution increases the energy required to initiate explosive N_2O decomposition in the gaseous state. Because Nitrox is a two-component and two-phase system, a gelling agent would be needed to maintain a homogeneous emulsion of the two liquids. Fumed silica has been proposed as a gelling agent. The Peng-Robinson equation of state can be used to calculate deviations of real mixtures of N_2O and O_2 from the behavior of ideal mixtures and can be used to predict the PVT phase conditions. Figure 36 shows the predicted density of nitrous oxide/oxygen mixtures as a function of pressure and temperature [171]:

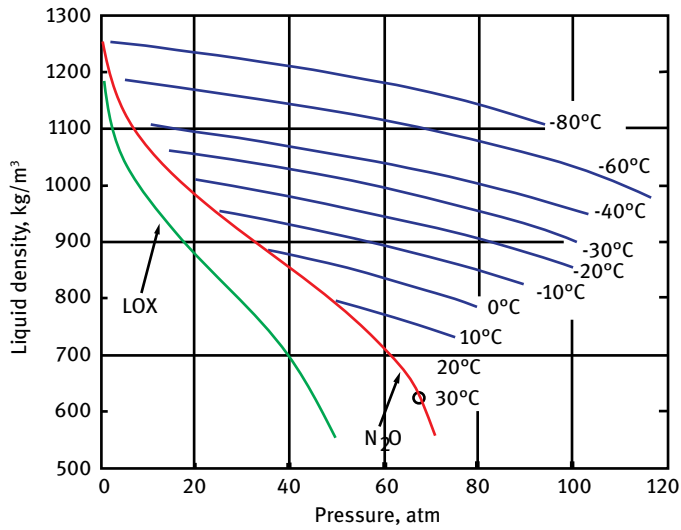


Figure 36: Liquid density as a function of pressure at various temperatures for the O_2/N_2O mixtures. (Reproduced and modified from [171] with permission granted by Dr. Arif Karabeyoglu 29-Apr-2021.)

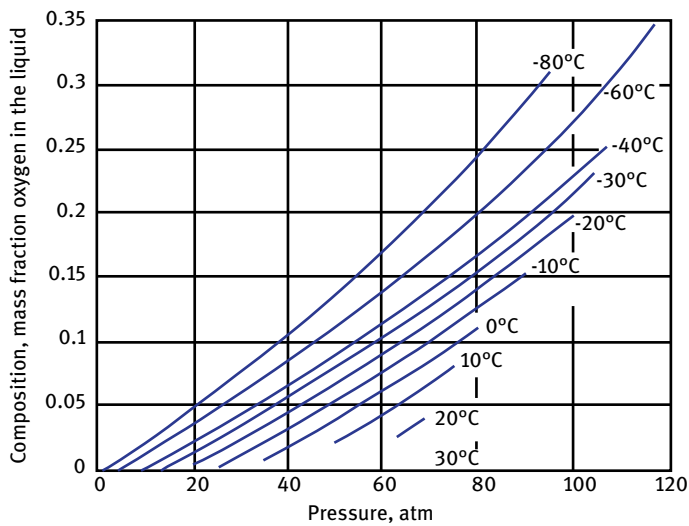


Figure 37: Oxygen mass fraction in the liquid phase as a function of pressure at various temperatures for two-phase O_2/N_2O mixtures. (Reproduced and modified from [171] with permission granted by Dr. Arif Karabeyoglu 29-Apr-2021.)

For application of the $\text{N}_2\text{O}/\text{O}_2$ mixtures as a rocket propellant, it would be more important to know the maximum amount (mass fraction, not mol fraction) of oxygen that can be dissolved in liquid N_2O at any temperature and pressure. These data are displayed in Figure 37.

Nitrox is composed of equilibrium or non-equilibrium mixtures of nitrous oxide and oxygen [172]. The primary advantages of this system over the pure oxidizers are: 1) self-pressurization capability, 2) high density and density impulse, 3) non-cryogenic operational temperatures, 4) higher I_{sp} performance compared with N_2O , 4) improved safety, 5) efficient gas-phase combustion, and 6) easier development of stable and efficient motors compared with liquid oxygen due to the exothermic decomposition of the N_2O molecule.

3.8.5 Solubility of Other Oxidizers and Contaminants in Liquid Nitrous Oxide

Liquid nitrous oxide is an excellent solvent and will dissolve water and form hydrates. The solubility of water in compressed nitrous oxide was measured over pressure ranges of 0.1–6.08 MPa (1–60) atm and temperatures ranging from 293 to 373 K (20 to 100 °C) [173]. Second cross virial coefficients representing deviations from ideality caused by gas/water pair interactions were more negative than those for water with ethane at all temperatures. For water with nitrous oxide, the anomalously large values of these coefficients were interpreted as indicating that a reversible hydration reaction occurs between nitrous oxide and water vapor in the gas phase

Supercritical N_2O , similarly to supercritical CO_2 , is an excellent solvent for a wide range of substances. So it should come as no surprise that CO_2 and N_2O are totally miscible with each other over the entire range of compositions in the liquid and supercritical range. Energy wise, there is no advantage in diluting N_2O with CO_2 , but safety and physical properties (freezing point) may improve.

Nitrous oxide and carbon dioxide have very similar physical properties. Both are excellent solvents in the supercritical state. Carbon dioxide is not a good rocket propellant oxidizer, we see it more as a combustion product than a rocket propellant oxidizer. In the liquid state, it is totally miscible with nitrous oxide. If there is any need to lower the combustion temperature of nitrous oxide bipropellant or hybrid rockets, or if there is a need to lower the freezing point and widen the liquidus range, one might consider adding just a few percent of carbon dioxide to nitrous oxide. The $\text{N}_2\text{O}/\text{CO}_2$ system has been investigated up to near the critical point because the critical properties of these two gases are very similar. The phase boundaries, orthobaric densities, and critical constants of five mixtures of carbon dioxide and nitrous oxide have been measured between 293 K and the critical point [42]. The same physical properties for the two pure gases have also been measured. The apparatus consisted of a calibrated thick-walled hard-glass pressure tube, fitted with an electromagnetic stirrer, for visual observation of the dew-points, boiling-points, and critical points, plus auxiliary equipment for precise temperature and pressure measurements. The system behaves

almost as an ideal solution with small positive deviations from Raoult's law, which can be interpreted satisfactorily by the theory of conformal solutions. The instruments and techniques used for the study of the $\text{N}_2\text{O}/\text{CO}_2$ system may be useful for the study of the solubility and phase behavior of solutions of other fuels in nitrous oxide.

The excess molar enthalpy, H_m^E , and excess molar volume, V_m^E , of the binary system $[x\text{CO}_2 + (1-x)\text{N}_2\text{O}]$ were measured in both the liquid and supercritical regions over the range 262.4–324.7 K at pressures up to 12.08 MPa [174]. The excess functions at 262.4 K were small, but in the critical region, very large H_m^E and V_m^E were measured. The Patel-Teja equation of state could reproduce all the main features of $H_m^E(x)$ and $V_m^E(x)$ and has been used to generate $H_m^E(p,x)$ and $V_m^E(p,x)$ surfaces at 312.5 K.

3.8.6 Solubility of Fuels in Liquid Nitrous Oxide

The kinetics of gas phase reactions of N_2O with CO have been studied extensively, usually as part of environmental studies of combustion products of energy conversion processes and also in dilution with inert gases [175–178]. This gas mixture may also be used in chemical lasers. Liquid N_2O may be miscible with liquid CO, but the safety properties of such a monopropellant blend would have to be examined before the process is scaled up.

The solubility of N_2O and CO_2 in ionic liquids can be quite different, such that the otherwise difficult to separate gases can be separated by selective absorption into ionic liquids in a countercurrent trickle flow reactor. Solutions of N_2O as the oxidizer in ionic liquids as fuels might be used as monopropellants. Mixtures of nitrous oxide and ethylene are already being evaluated as monopropellants.

The combination of premixed gaseous nitrous oxide and ammonia has been evaluated as a monopropellant for micropropulsion devices, and one version of this concept envisioned storing the two chemicals premixed in the liquid instead of the gaseous state. Insufficient data were available about the range of miscibility of liquid nitrous oxide and liquid ammonia over the entire range of mixture ratios. Experiments were started at the University of Washington in Seattle to fill this data gap but could not be completed because a Phase II STTR contract was not obtained.

In searching the literature, only incomplete information about the range of miscibility of liquid nitrous oxide and liquid ammonia could be found. In one case, a solution of 0.4-M nitrous oxide in liquid ammonia was subjected to electron nanosecond pulse bombardment at temperatures down to 198 K (–75°C) and the UV spectra of the amino free radical recorded [179]. The N_2O served as a scavenger for free electrons dissolved in liquid ammonia.

3.8.7 Solubility of Other Gases in Liquid Nitrous Oxide

When it is to be used as an oxidizer in a pressure-fed rocket system, liquid nitrous oxide does not need a pressurant gas like helium or nitrogen as some of the other oxidizers would. Nevertheless the solubility of pressurant gases in liquid nitrous oxide

has been measured. If a pressurant like helium is used to expel liquid nitrous oxide from a tank, one has more latitude in selecting the discharge rate from the tank without having to worry about inadvertently freezing the tank contents. But unless the gas and the liquid phase are separated by an impermeable diaphragm, some of the pressurant will dissolve in liquid nitrous oxide and reduce its performance and will change the flow rate if the saturated liquid is passing through cavitating venturi as a means of flow rate control. If the saturated liquid is pumped with a centrifugal pump, cavitation may occur at the tips of the rotor.

Liquid-vapor data for the helium-nitrous oxide system were determined at 195, 215, 235, 245, 255, 265, and 285 K at pressures up to 136 bars [180]. The data were analyzed for internal consistency using pseudo-Henry's law constants and enhancement factors. For instance, at 285 K and 136 bar, the liquid phase contained 4.18 mol-% He. At 265 K and 136 bar, the vapor phase contained 25.97 mol-% N₂O. Figure 38 shows the pseudo-Henry's law constant as a function of pressure. Henry's law constant is defined here as

$$H = \frac{P - P_1}{X_2}$$

The helium pseudo partial pressure is defined as $P - P_1$. The constant is nearly independent of pressure. Figure 39 shows the pseudo-Henry's law constant as a function of temperature based on data obtained at 20 and 120 bar. Data for both pressures fitted on a linear relationship.

One of the basic components of many propellant metering systems is a cavitating venturi. This device causes a rather sudden drop in the static liquid N₂O pressure, and there was concern that this sudden pressure drop would cause helium desorption from the liquid. If such desorption and two-phase flow occurred, the gaseous helium would tend to choke the flow of liquid N₂O through the venturi throat and, thereby, interfere with proper functioning of the metering system. Calculations indicated that significant choking would occur if equilibrium conditions prevailed. In order to determine the effect of helium on flow choking, flow tests were run using both saturated and unsaturated N₂O. It was found that the flow rate of the helium-saturated N₂O was 9 to 12% lower than that of the unsaturated liquid [181]. The flow of saturated N₂O through the venturi is neither equilibrium flow nor frozen flow but is rather something in between the two. Thus, there is some effect due to helium desorbing from the liquid N₂O, but the effect is much less than that predicted for equilibrium flow conditions.

Under an AFWL contract Rocketdyne conducted full-scale N₂O flow tests and measured flow rates with both turbine flow meters and cavitating venturi [92, 182]. The oxidizer flow rate to the combustor was controlled by a cavitating venturi located between the main valve and the primary injector. This was a 5-cm (2-in.) variable area unit in which the throat area was modulated by the position of a movable pintle. The venturi was calibrated with gaseous nitrogen to obtain a curve of effective throat area as a function of pintle position. In parallel, nitrous oxide flow rates in all these tests were

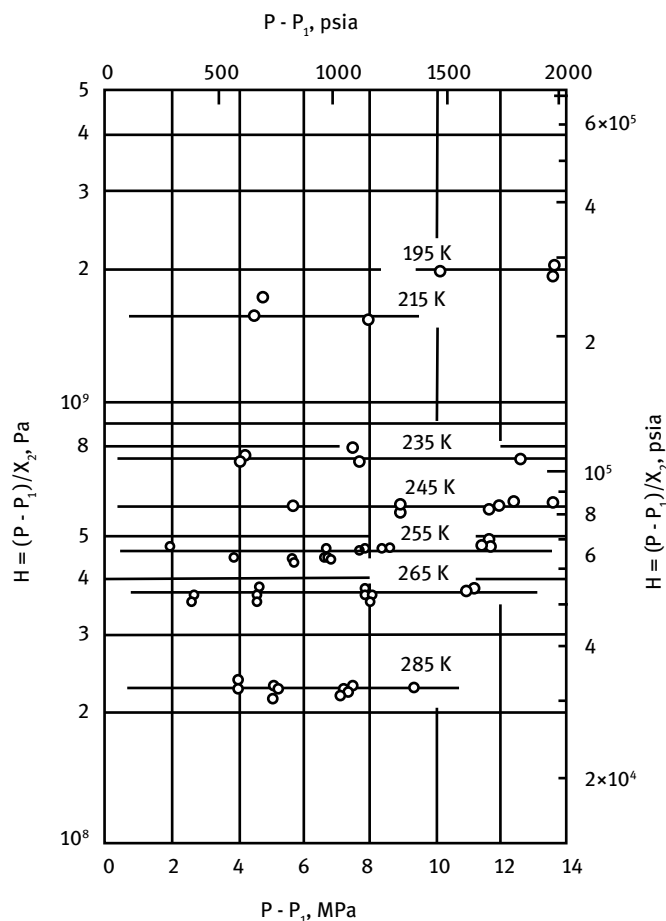


Figure 38: Pseudo-Henry's law coefficient of helium in liquid nitrous oxide as a function of pressure. (Reproduced and modified from [180].)

measured with turbine flowmeters. On the basis of the measured flow rates, the effective throat area of the cavitating venturi was calculated in each case. When plotting N_2O results together with the GN_2 calibration curve, all flows of neat N_2O fell on a line which was slightly displaced from the calibration curve. When the N_2O was (partially) saturated with helium, however, the effective throat area of the cavitating venturi was a function of the proportion of helium dissolved.

Another pressurant gas of interest for nitrous oxide is oxygen. Mixtures of liquid nitrous oxide and liquid oxygen ("Nytrox") have been proposed as oxidizers for rockets [172], see Section 3.8.4.

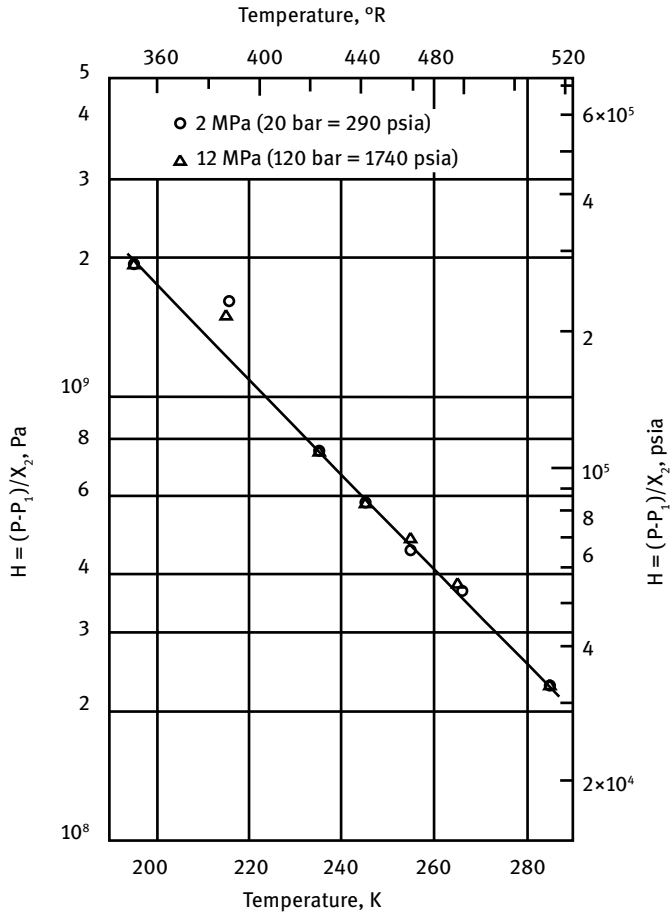
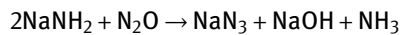


Figure 39: Pseudo-Henry's law coefficient of helium in liquid nitrous oxide as a function of temperature. (Reproduced and modified from [180].)

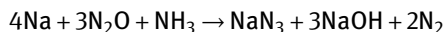
4 Chemical Properties of Nitrous Oxide

4.1 Reactions with Nitrous Oxide

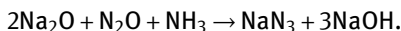
Nitrous oxide is not very reactive as an oxidizer and will react hypergolically only with very few fuels at room temperature. Reactions of industrial importance are the production of sodium azide by reaction of molten sodium amide with nitrous oxide:



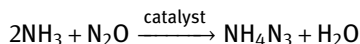
Sodium azide can also be formed in the reaction of N_2O either with metallic sodium dissolved in liquid ammonia



or with sodium oxide dissolved or suspended in liquid ammonia



The reaction of N_2O with ammonia over a $\text{Ni-Al}_2\text{O}_3$ catalyst can form ammonium azide, which is potentially explosive:



It has been speculated that oxidation of ammonia by nitrous oxide under carefully controlled (non-combustion, catalyst) conditions may even result in the formation of hydroxylamine. If premixed nitrous oxide and ammonia were to be used as a monopropellant, the above reactions would be very undesirable since they would detract from the storage stability of the premixed propellant.

Nitrous oxide containing 96% ^{15}N in the end position and analysis of the reaction products by mass spectrometry was used to determine in which combustion reactions with N_2O the oxygen is stripped from the end of the molecule, leaving the $\text{N}-\text{N}$ bond and the $^{15}\text{N}:^{14}\text{N}$ ratio intact, and in which reactions a complete rearrangement and equilibrium between the three possible dinitrogen isotopologues is achieved [183].

A good summary of the chemical reactions of all nitrogen oxides including nitrous oxide was published in 1972 [184]. The literature review by Leontev [1] contains a good summary of chemical reactions with nitrous oxide [1].

Nitrous oxide for non-anesthetic applications has to conform to Specification MIL-N-37996.

4.2 Conversion of Nitrous Oxide to Other Oxides of Nitrogen

The diagram in Chapter Nitrogen Oxides, Section 2.5 already illustrated that nitrogen oxides readily undergo conversions into each other, depending on the conditions. Oxidation of nitrous oxide in the stratosphere leads to nitric oxide [185].

4.3 Selective Oxidation Reactions with Nitrous Oxide as an Oxidizer

The decomposition of nitrous oxide leads to atomic oxygen as an intermediate, which is a very reactive species that can be used in the oxidative hydroxylation of aliphatic or aromatic hydrocarbons, leading to alcohols, ketones, or phenols. A large industrial plant for the production of 140000 tons of phenol using this process has been built

in Florida. However, attempts to convert methane to methanol by oxidation with N_2O have failed.

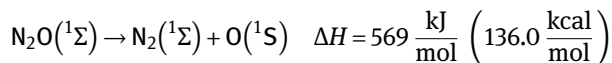
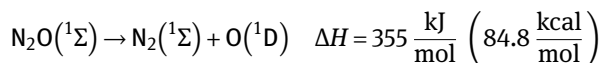
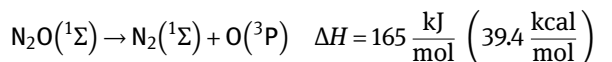
4.4 Decomposition, Thermal Stability, and Combustion of Nitrous Oxide

The decomposition of nitrous oxide as a monopropellant in rocket engines is discussed in detail in *Encyclopedia of Monopropellants*, in the chapter Nitrous Oxide Monopropellants. Here, we only discuss academic studies on N_2O decomposition that are not related to a specific application but support the development of N_2O monopropellant decomposition reactors and help explain the hazards caused by unexpected N_2O explosions.

Because nitrous oxide absorbs infrared radiation from the sun, similarly to carbon dioxide in the atmosphere, it acts as a “greenhouse gas” potentially contributing to global warming. It was estimated that the average residence time of nitrous oxide in the lower layers of the atmosphere is 120 years because of the lack of reactions or biological cycles that would lead to its consumption. Nitrous oxide gradually diffuses from the troposphere to the stratosphere where it eventually becomes photolyzed by UV from the sun. Until recently, large amounts of nitrous oxide were dumped with stack gases from industrial processes like nitric acid production, released as an unwanted byproduct of the industrial fossil fuel combustion processes, as an intermediate in air pollution, and as an industrial waste product during the production of nitric acid [186] and caprolactam or adipic acid [187] and cyclohexanone oxime (“Nylon”) production. It has been estimated that annually about 1.2 million tons of N_2O are emitted by the nitric acid industry, which is equivalent to the CO_2 emissions of 80 million passenger cars. The problem with nitrous oxide as an atmospheric pollutant is that there are very few natural mechanisms that will destroy nitrous oxide once it is released into the atmosphere (as opposed to carbon dioxide, which can be assimilated by plants and immobilized into the shells of crustaceans). The chemical industry has taken steps to minimize emissions of nitrous oxides by changing chemical processes and passing stack gases through N_2O decomposers before releasing them above the roof. Studying the decomposition N_2O as a monopropellant and looking for catalysts will direct one quickly to the large amount of literature dealing with catalytic decomposition of N_2O in industrial waste gases. However, these processes operate at much lower temperatures than a rocket engine, and most of the catalysts studied for waste gas cleanup are not suitable for use in a rocket engine. The catalytic decomposition of N_2O will be discussed in *Encyclopedia of Monopropellants*, chapter “Nitrous Oxide Monopropellants”. A partial discussion of the homogeneous decomposition of nitrous oxide in the gas phase is started here because homogeneous decomposition in the gas phase often precedes the decomposition of nitrous oxide before it has a chance to come in contact with a catalyst. The homogeneous decomposition rates are just so much slower than the catalyzed decomposition rates that they are often neglected when conducting experiments with active catalysts.

4.4.1 Kinetics of Nitrous Oxide Decomposition

Early work has shown that nitrogen atoms are not formed during the N_2O decomposition process, which indicates that the decomposition takes place via the break-up of the N—O bond. The following three reactions, each corresponding to a different electronic state for the atomic oxygen formed as an intermediate, are possible:



The measured activation energy for the nitrous oxide decomposition of approximately 243 kJ/mol (58 kcal/mol) rules out the last two reactions, which require significantly more energy. This indicates that the decomposition of nitrous oxide follows the non-adiabatic spin-forbidden elementary unimolecular reaction, which requires a change in the multiplicity, from the singlet ground state for the N_2O molecule to a triplet state in atomic oxygen, which is a spin-forbidden transition in quantum mechanics and may be one of the causes for the abnormally slow unimolecular reaction rate for N_2O decomposition. Due to its unique spin-forbidden nature and also the relatively simple structure of N_2O , the decomposition reaction has been the subject of many theoretical studies. In the recent literature, an extensive number of classical and quantum mechanical molecular dynamics simulations have been reported. The primary objective of these studies has been to gain more insight on the spin-forbidden unimolecular decomposition of the nitrous oxide molecule and other nitrogen oxides.

The experimental and theoretical absolute rates for the non-adiabatic, homogeneous decomposition of N_2O were shown to be in good agreement [188]. There are only a few other reactions involving singlet-triplet transitions of oxygen, which can be compared to the spin-forbidden N_2O decomposition. A convenient method of constructing potential functions for polyatomic molecules which fit the spectroscopic data, and which apply in a proper way for the various dissociation processes, was developed for the N_2O molecule as an example for the utility of this method.

For a first-order reaction of a homogeneous gas phase reaction, a plot of the reciprocal of the half-reaction time against pressure should be a line parallel to the pressure axis, while for a second-order reaction it should be a line inclined to the axis and passing through the origin. In a series of investigations, it has come to light that the form of this curve for nitrous oxide is really rather complex, and may be divided into the following parts: (a) an initial steep increase, starting from the origin, which between 50 and 100 mm Hg becomes shallower and passes into (b) an almost linear curve continuing up to several atmospheres of pressure when it gradually bends again passing into (c) an almost straight line of still smaller slope, which continues up to 20–30 atm, when it bends round and becomes nearly parallel to the pressure

axis, as one would expect for a reaction of the first order [189, 190]. Various interpretations have been suggested: **(1)** The twisted curve results from the superposition of three “quasi-unimolecular” reactions, each of the second order at low pressures and of the first order at higher pressures (typical of reactions in which activation is by collision and is followed by transformation of isolated molecules). The three components represent different activation modes with different transformation probabilities of the activated molecules. **(2)** The curve is not really composite in form, but represents a single quasi-unimolecular reaction, the transformation probability of the molecules being a continuous function of the excess energy they contain. Experimental data of the thermal decomposition of nitrous oxide at 1020 and 925 K (747 and 652°C) where the variation of reaction rate with pressure was expressed both in terms of the reciprocal half-reaction time and in terms of the initial rates showed that the two curves obtained were similar enough to show that previous conclusions based upon the half-time curve are proven correct. The mean value of the activation energy decreased at lower pressures, and the absolute magnitude of this energy agreed with most previous determinations, but not with those suggesting that the reaction is abnormally slow for certain quantum-mechanical reasons.

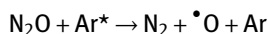
In a study of the role of nitric oxide in the decomposition of nitrous oxide it was found that although initial yields of nitric oxide were as high as 50–60%, the nitric oxide quickly inhibited its own formation [191].

The mechanism proposed by Lindars and Hinshelwood was later modified by considering the potential energy diagram of N_2O by proposing that the two intermediate triplet states suggested by them are the unstable $^3\Sigma$ and $^3\Pi$ states [192]. This hypothesis satisfactorily accounted for the changes in the first-order decomposition rate constant with pressure. The kinetics of the formation of nitric oxide as an intermediate needs additional explanation. The oxygen atoms formed by the primary dissociation of nitrous oxide will possess a considerable amount of kinetic energy, and it was suggested that, as a result, they will have a greater chance of reacting with another nitrous oxide molecule to give nitric oxide. This accounts for the effect of inert gases, surface area, and temperature on nitric oxide formation. The reaction of nitric oxide with oxygen atoms accounts for the way in which nitric oxide inhibits its further formation. The thermal decomposition of nitrous oxide via nitric oxide produces mainly nitrogen and oxygen.

On the basis of experimental data on the ignition temperatures of pure nitrous oxide flow with $p = 0.3\text{--}4.1$ MPa, and using the equation given by the ignition theory of Zeldovich, the reaction order and the Arrhenius parameters for the process of thermal decomposition of N_2O was calculated [193]. For $p > 0.7$ MPa, good agreement with the established values recommended in the literature was observed. Lower values of the effective activation energy were found for lower N_2O pressures. This may be due to the influence of a heterogeneous catalytic surface.

The thermal, homogenous dissociation of N_2O was measured in dilution with three different carrier gases in a laminar flow reactor in the temperature range

1000–1350 K and at atmospheric pressure in order to determine activation energy and third body efficiency of N_2 [194]. A rate constant for the reaction



of

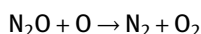
$$4.0 \times 10^{14} \exp\left(\frac{-28230}{T}\right) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

was recommended with an estimated uncertainty factor of 1.5 in the 1000–3000 K range. The third body efficiency for N_2 compared to Ar was determined to be 1.6, independent of temperature, while the collision efficiency of He apparently increased with temperature, from 2.3 at 1200 K to 4.5 at 2000 K. In terms of a pseudo first-order reaction, the data with N_2 as the carrier gas could be represented by the rate constant

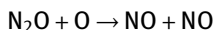
$$k = 4.2 \times 10^9 \exp\left(\frac{-27000}{T}\right) \text{ s}^{-1}$$

The uncertainties associated with the flow reactor technique have been analyzed, and flow reactor studies on N_2O dissociation were examined and compared with recent results. The thermal dissociation of N_2O compared to other decomposition mechanisms in fluidized bed combustion is important.

A detailed N/O kinetic mechanism has been developed and tested in comparison with experimental data for N_2O ignition, NO and NO_2 decomposition at high temperatures [195]. It consisted of 27 reactions among 11 species. A sensitivity analysis revealed which reactions are critical for the quality of the modeling in comparison to experimental results. The proper choice of the rate constants for these reactions can result in good agreement for the ignition delays in the pure N_2O and its mixtures with Ar, and decomposition rates of NO and NO_2 in static reactors and behind shock waves. The modeling also tested controversial rate constants for the key reactions

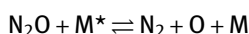


and



and demonstrated that the use of too low or too high values of the rate constants was incompatible with experimental data.

Nitrous oxide decomposition in the temperature range 1100 to 1600 K at atmospheric pressure was studied in a quartz flow reactor externally heated in an electrical furnace with mixtures of N_2O /Ar, N_2O /H₂O/Ar and N_2O /CO₂/Ar [196]. Based on these experiments and the modeling of a one-dimensional flow reactor, the kinetic parameters of the reaction



for Ar, H₂O and CO₂ as a third body M were determined. The relative efficiencies compared to Ar were found to be 3.0 for CO₂ and 10.0 for H₂O.

4.4.2 Quantum Mechanical Aspects of Nitrous Oxide Decomposition

A classical trajectory surface-hopping energy potential study of the effects of initial mode of excitation on the spin-forbidden predissociation of N₂O revealed a certain mode specificity [197]. Incomplete energy randomization together with significant variation in energies of the surface crossing points with molecular geometry can lead to changes in the accessibility of the dissociation channel and, hence, the rate of reaction when different modes are excited. The variations in the predissociation rate are most marked at relatively low energies. At higher energies, although energy randomization is still incomplete, there is less dispersion in the rate constants. This has been attributed to the fact that at high energies a larger percentage of the crossing points become accessible, and thus the directionality of the initial motion is less relevant to the rate. Finally, it was shown that in cases where the surface-hopping probability is low, the kinetics of spin-forbidden reactions will be characterized by unusually unfavorable entropies of activation. As a consequence, reactions involving a spin-state change can be expected to compete poorly with spin-allowed reactions at high temperatures (or energies); see also Reference [198].

The spin-forbidden predissociation reaction of the ground-state N₂O was studied by quantum dynamics *ab initio* calculations to obtain the potential energy surfaces of the singlet ground state of N₂O and three triplet states correlating with the asymptote N₂ + O(³P) and the spin-orbit coupling elements among them [199, 200]. The decay rate of individual singlet vibrational state to the ³A' state was estimated by applying the Fermi golden rule. For the ¹A' state, a total of 1692 vibrational eigenstates with even parity for the total angular momentum $J = 0$ were obtained, and time-dependent wave packet calculations on the triplet potential energy surfaces were performed to obtain the autocorrelation functions whose Fourier transforms should provide the decay rates. The resultant decay rates for 887 singlet vibrational states in the energy range $67.3 \leq E \leq 83.7$ kcal/mol were analyzed in terms of a random matrix/transition state theory. The analyses of calculated decay rate distributions indicated an incomplete energy randomization of the vibrational energy in the singlet state even near the singlet state dissociation threshold.

Molecular dynamics model calculations for the thermal decomposition of N₂O with an external magnetic field suggested that the increase of the rate constant by an external magnetic field could be explained by means of an increase of the interaction term, which is dependent on the angle of orientation [201]. The magnetic field would orient the molecules in a position more favorable to interact with partners. Lowering the onset temperature of exothermic decomposition on a catalyst by applying a magnetic field would facilitate the use of nitrous oxide as a monopropellant.

4.4.3 Flame Velocity of Gaseous Nitrous Oxide Decomposition

Decomposition flames of nitrous oxide in the absence of a fuel are discussed in *Encyclopedia of Monopropellants*, chapter “Nitrous Oxide Monopropellants”. The rate of propagation of N_2O decomposition flames in closed tubes (“flashback”) must be measured before designing rockets with N_2O . Similar measurements have been made for flames supported by premixed combustible gases with N_2O as the oxidizer. Essentially, at the very lean end of the range of O:F ratios studied, the flame is mostly an N_2O decomposition flame.

4.4.4 Autoignition Temperature of Nitrous Oxide in the Absence of Combustibles

The autoignition of nitrous oxide by simple heating in the absence of combustible materials or a spark or open-flame source of ignition was determined in steel tubes [92, 202]. Nitrous oxide autoignition tests were conducted by preheating a steel pipe to the desired temperature and then suddenly opening the inlet valve to permit high-pressure 5.52 MPa (800 psig) N_2O at rising pressure to flow into the test pipe until the pressures equalized, and the flow stopped. Two different supply systems were used. One was fed through a 12-mm (1/2-in.) diameter tube from a bank of five N_2O bottles to produce a relatively high pressurization rate, and the other was fed through a 6-mm (1/4-in.) diameter tube and pressure regulator to provide slower pressurization rates. No autoignitions were obtained in the 25-mm (1-in.) pipe. The data for the 50-mm (2-in.) diameter pipe showed a trend of decreasing pressurization rate with increasing pressure. At 505 K (450 °F) pipe preheat temperature, autoignition occurred at a pressurization rate of only 1.38 MPa/s (200 psi/s). This is extremely low compared to pressurization rates commonly used in pneumatic systems. Even at ambient temperature, N_2O ignition occurred at a rate of only 7.93 MPa/s (1150 psi/s). This is surprising because the compressed gas also loses heat to the wall of the pipe. It was estimated that autoignition occurred somewhat below 672 K (750 °F). A correlation was developed to express the quenching-controlled propagation limits in terms of pressure, temperature, and pipe size:

$$1.1 \times 10^9 = PT^{2.5} \frac{D^{-2}}{(D - 0.38)}$$

where P is the pressure in psia, T is the temperature in °R, and D is the internal diameter in inches. A comparison of autoignition temperature versus pressure limits is shown in Figure 40.

The data in Figure 40 show that pipe diameter, along with pressure and temperature, is a significant variable. The effect of pipe diameter indicates the important role of quenching in inhibiting the ignition and autodissociation reaction. As the pipe diameter decreases, the surface to volume ratio of the pipe increases. Thus, if decomposition in a small pipe is compared with that in a larger pipe, the surface to volume

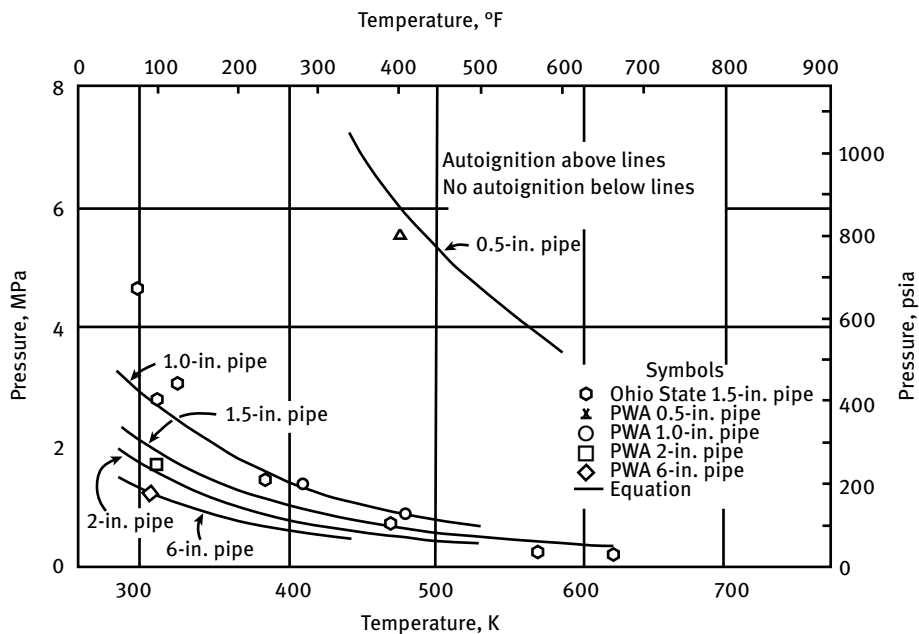


Figure 40: A comparison of autoignition temperature versus pressure limits of nitrous oxide autoignition. (Reproduced and modified from [92].)

Symbols legend: PWA [202] data; Ohio State [203] data

ratios indicate that a greater fraction of the heat released by the dissociation will be to the environment from the small pipe than from the large pipe. This heat loss tends to quench the reaction and, as a result, higher temperatures and pressures are required to initiate and sustain a decomposition reaction in a small tube

A theoretical model of gaseous nitrous oxide autoignition and an induction period as a function of pressure and reactor volume showed that for a large vessel under adiabatic (no heat loss) conditions, the predicted autoignition temperature is in the range 670–700 K [204] (Figure 41). Dilution with oxygen shifts the curves only very little to the right.

During the induction period, the reactions are slow, and the temperature slowly increases up to the overheating limit, where a runaway reaction takes place, often in an explosive manner (Figure 42).

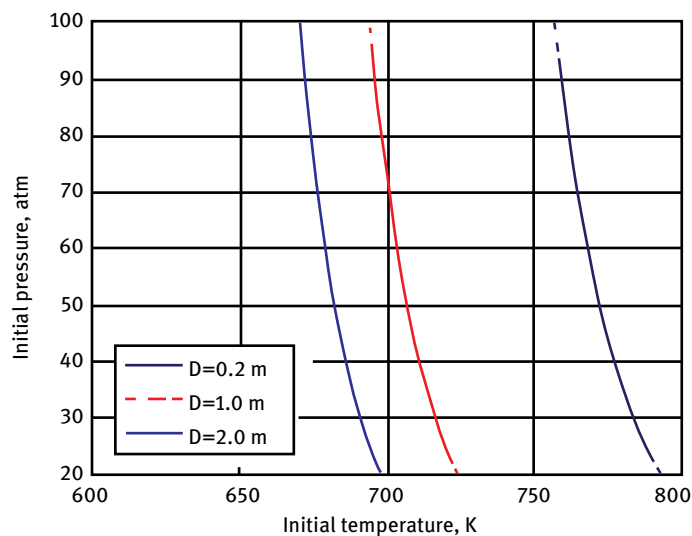


Figure 41: Nitrous oxide ignition boundary for cylindrical vessels with varying diameters. (Reproduced and modified from [204] with permission granted by Dr Arif Karabeyoglu 29 April, 2021.)

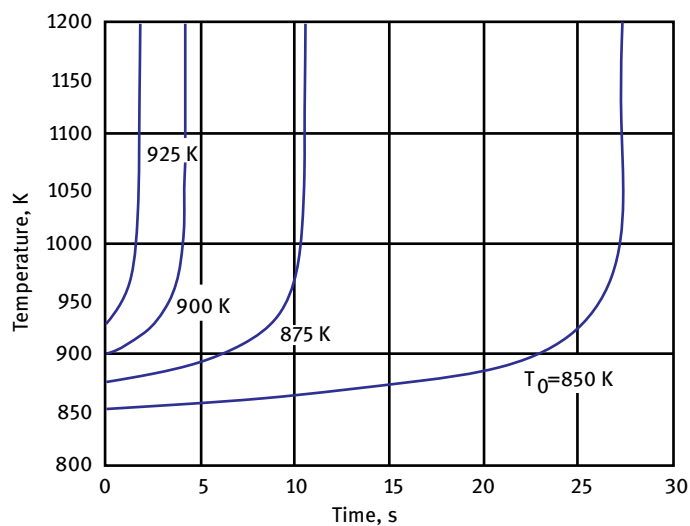


Figure 42: Nitrous oxide decomposition induction time as a function of initial temperature, adiabatic conditions. (Reproduced and modified from [204] with permission granted by Dr. Arif Karabeyoglu 29-Apr-2021.)

4.4.5 Explosive Decomposition of Nitrous Oxide in the Absence of Combustibles

The explosion hazards of nitrous oxide will be discussed in more detail in Section 9.2. Here, we only discuss some of the mechanisms that lead to a self-propagating reaction in the gas phase.

The initiation of explosions in gaseous nitrous oxide in different sized heavy-walled containers and with different sources of ignition was studied over the pressure range from 0.05 to 8 bar [205]. Generally, the pressure rise curve in a closed container was measured, but in a few cases, the reaction was filmed with a high-speed camera, and the reaction products were analyzed by gas chromatography (GC). The ratio of explosion peak pressure to initial pressure increased with pressure. Due to the relatively slow rate of decay of nitrous oxide, the type and location of the source of ignition and the size of the container had a pronounced effect on the rate of reaction and the fraction of gas decomposed. The required dilution with oxygen, nitrogen, or air as diluents required to prevent an explosive decomposition reaction was determined. For all three gases, a diluent concentration of 30 vol.-% was sufficient to prevent explosions. In a container with saturated liquid/gas conditions, the decay could no longer be initiated when the temperature was below 218 K (-55°C), and the vapor phase pressure was below 5.7 bar.

A stainless steel cylindrical bomb, 61 mm I. D. and 545 mm long, with five windows at equal intervals along the length of the bomb, was used to study the explosive limits in gaseous nitrous oxide [206]. The nitrous oxide was ignited by short-circuiting the current from a 220 V/12 V transformer across a 0.2–0.3-mm diameter copper wire, placed at one end of the bomb. The ignition limit was at 2.63 ± 0.08 bar, at an initial temperature of 290 K, when the bomb was placed vertically, for bottom ignition. This value was unaffected by an increase in ignition energy by a factor of 10 or by creating isobaric conditions, using a ballast vessel, filled with nitrogen. When ignition was made to occur at the top end of the vertically placed bomb, the value of the ignition limit increased to 11.1 bar (absolute). An experiment at high initial pressure of 50 bar resulted in the destruction of the heavy-walled apparatus. Testing the effect of nitrogen as a diluent it was found that 4.5 and 10% nitrogen diluent resulted in higher limit pressures of 3.19 and 5.57 bar, respectively, both at 290 K.

The explosive decomposition of nitrous oxide was studied in the temperature range 323 to 398 K, at initial total pressures up to 13.8 bar (gauge) [207]. The flanged vessel was cylindrical in shape with an internal volume of 2.522 L and an internal diameter of 4.5 inches (114.3 mm). It was constructed of stainless steel and designed to withstand dynamic pressures of up to 105 bar. Ignition was with a coiled electrically heated exploding nichrome wire providing 30 mJ. Stainless steel liners could be inserted to reduce the internal volume and diameter of the bomb. Different wire lengths and thicknesses were tested, and best results were obtained with a wire 1.4 in.-long 24 gauge thickness. In addition, the internal volume to surface area ratio of the pressure vessel was varied by the use of suitable liners. The flammability limits for pure nitrous oxide are shown in Figure 43. The ignition limit varied from

7.93 bar (gauge) at 298 K to 2.41 bar (gauge) at 473 K, on an exponential S-shaped curve. With the heavier liner that reduced the internal volume to 300 mL, only partial decomposition could be achieved. The use of nitrogen, as an inert diluent, to suppress the explosive decomposition of nitrous oxide was studied in the temperature range 323 to 398 K, at initial total pressures up to 13.8 bar (gauge). Nitrogen acted as an inert diluent in suppressing the explosive decomposition of nitrous oxide. The amount of nitrogen required to suppress the decomposition was a function of initial temperature and pressure. The effect of initial pressure on the burning velocity, calculated from the P-t record, and the effect of initial pressure on the amount of inert diluent required to suppress decomposition, indicated that the decomposition of nitrous oxide is a first-order reaction.

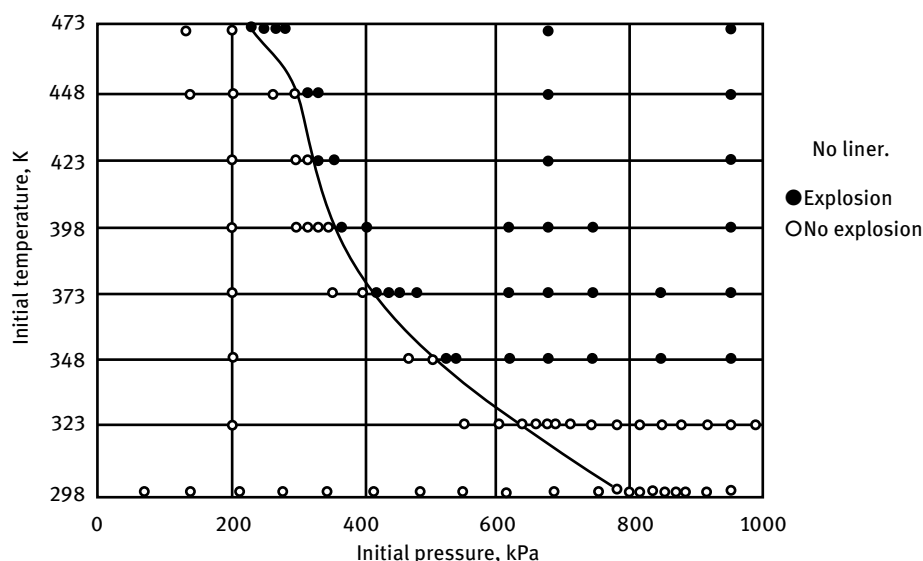


Figure 43: Explosion limit of nitrous oxide with exploding wire ignition. (Reproduced and modified from [207].)

4.5 Photolysis of Nitrous Oxide

Photolysis of nitrous oxide in the stratosphere under the action of unfiltered sunlight is the prime mechanism for the destruction of nitrous oxide and prevention of its buildup and becoming a greenhouse gas global warming problem. Consequently, the photolysis of nitrous oxide has been thoroughly investigated. Ultraviolet radiation not only decomposes nitrous oxide, but on irradiating a mixture of nitrogen and oxygen, some nitrous oxide is formed in reversal of the photolysis reaction.

In addition, the photolysis of nitrous oxide is a convenient source of atomic oxygen, which then can be used for other chemical reactions and kinetics studies. It is possible that laser photolysis of nitrous oxide in a rocket engine could be used for ignition of nitrous oxide or nitrous oxide/fuel mixtures, but if it is feasible, then the photolysis of nitrous oxide must be better understood to build a reliable laser ignition device.

The average quantum yields during the photolysis of nitrous oxide in a flow system at 1470, 1295, 1236, or 1165 Å with regard to decomposed nitrous oxide were found to be larger in the experiments using the longer wavelengths than in the experiments using the 1236 and 1165 Å radiation [208]. It was assumed that at 1295 Å the initial absorption of a light quantum leads to the production of nitrogen molecules and oxygen atoms. At the shorter wavelength, the initial absorption act probably proceeds in a dual manner where competitively both the splitting of nitrous oxide into nitrogen molecules and oxygen atoms and into nitrogen atoms and nitric oxide might occur at this wavelength.

Oxygen atoms in the singlet 1S state can be produced by the vacuum-UV photolysis of N_2O . and their emission can be observed at 5577 Å in the $^1S \rightarrow ^1D$ transition [209]. The stimulation of this emission by collision with added gases has been studied. The emission was found to be proportional to the pressure of the added gas. Xenon is the most efficient stimulator of the gases used, followed in order of decreasing efficiency by Kr, Ar, N_2 , H_2 , and He.

Photofragment ion imaging has been used to study the $O(^1D_2)$ atoms produced in the ultraviolet (~ 200 nm) photodissociation of nitrous oxide in a molecular beam [210]. The images of $O(^1D_2)$ revealed a speed-dependent angular distribution resulting from both variation in the spatial anisotropy of the recoil and alignment of the electronic angular momentum of the $O(^1D_2)$ fragment. The orbital alignment effects were revealed by a change in the images when different transitions of the O atom are employed in the resonance enhanced multi-photon ionization process.

Laser photolysis was proposed as an efficient method for removing N_2O in stack gases at atmospheric pressure and at room temperature without using any catalysts. N_2O diluted in N_2 or air was decomposed into N_2 , O_2 , and NO by using a 193-nm ArF excimer laser [211, 212]. The maximum conversion of N_2O in N_2O/N_2 or $N_2O/N_2/O_2$ mixtures was 93% at a laser power of 136 mJ, a repetition frequency of 5 Hz, and an irradiation time of 30 min. The formation ratios of $N_2:O_2:NO$ in N_2O/N_2 and $N_2O/N_2/O_2$ mixtures were 64 : 31 : 5.1% and 60 : 27 : 13%, respectively.

N_2O removal was investigated in N_2 or air using 172-nm Xe_2 excimer lamps (50 or 300 mW/cm²) without using any catalysts [213]. The residual amount of N_2O and the formation ratios of products were measured as functions of irradiation time, N_2O concentration, and O_2 concentration. N_2O (100 ppm in N_2) was completely converted to N_2 and O_2 without NO_x emission at atmospheric pressure after 30 min photoirradiation using a high-power Xe_2 excimer lamp (300 mW/cm²). The conversion of N_2O in air increased more than twofold by decreasing the total pressure from atmospheric pressure

to 20 kPa by suppressing the collisional quenching of $O(^1D)$ by N_2 and O_2 buffer gases. In a flow experiment with a total flow rate of 0.1–1 L/min., the conversion of N_2O/N_2 was only 6–18% due to the short residence time of N_2O in the photolysis chamber; see also [214, 215].

Photodissociation of nitrous oxide near 203 nm has been studied by a combination of a high-resolution slice ion imaging technique and resonance-enhanced multi-photon ionization spectroscopy by measuring the recoil velocity and angular distributions of N_2 fragments by ion images of the state-resolved photofragments to verify the effects of the stagnation pressure on the formation of N_2O clusters and their photodissociation in the UV [216]. Slice imaging is characterized by a delayed pulsed extraction of ions. The N_2 fragments were highly rotationally excited, and the $NN-O$ bond dissociation energy was determined to be 3.635 eV. In addition, photofragment images from the photodissociation of N_2O clusters at various stagnation pressures provided information on the affinity attraction of N_2O molecules in clusters.

Photolysis of N_2O in an argon matrix deposited on an IR-transparent window resulted in formation of N_2O_2 having the structural formula $O-O-N-N$, which has been named asymmetric dinitrogen dioxide [217]. The experiment was conducted under vacuum with a flowing gas pressure between 10^{-5} and 10^{-4} mm Hg. Argon was used as the non-reactive matrix. A gas stream of one part by volume N_2O and 400 parts by volume argon was directed to a cooled CaF_2 window maintained at a temperature between 8 and 20 K. The gas stream condensed to form a solid N_2O/Ar layer on the surface of the window. Oxygen atoms in the $[^1D]$ excited state were generated by photolysis of a portion of the condensed N_2O with UV radiation pulses of 15 ns duration at a repetition rate of one hertz, having an intensity of about 100 mJ at a wavelength of 193 nm using an excimer laser. A tunable IR source was directed through the window to a monochromator, and IR absorption spectra were monitored and recorded. An absorption peak at a frequency of about 1220 cm^{-1} , which falls within the region of the predicted $N-O$ stretch frequency for asym- N_2O_2 , was present only after irradiation.

4.5.1 Photocatalysis of Nitrous Oxide Decomposition

In addition to photolysis of N_2O in homogeneous reactions in the gas phase, photocatalytic decomposition of N_2O on illuminated catalytic surfaces has received a lot of attention as a possible method for destruction of N_2O in industrial waste gases. This seems to be a symbiotic combination of both photolysis and catalytic decomposition of nitrous oxide.

Photodecomposition of N_2O under irradiation with UV light ($\lambda < 300\text{ nm}$) at room temperature readily proceeds on the surfaces of transition metal oxide compounds applied to inert supports. Ions of different transition metals in zeolite matrices exhibit high catalytic activities.

An Ag(I)/ZSM-5 catalyst containing highly dispersed Ag ions on ZSM-5 exhibited much higher photocatalytic reactivity for the decomposition of N_2O than Ag(I)/Y formed on Y-zeolites, indicating that highly dispersed Ag ions play a significant role in the photocatalytic decomposition of N_2O [218, 219].

The photocatalytic decomposition of N_2O on highly dispersed distorted tetrahedrally coordinated Fe-oxide on ZSM-5 having low Si/Al ratios proceeded with a good linearity against the UV-irradiation time [220]. The photocatalytic efficiency decreased when the Si/Al ratio was increased; see also [221, 222].

4.6 Radiolysis of Nitrous Oxide

Radiolysis of nitrous oxide might be one way to synthesize higher oxides of nitrogen, which might be better oxidizers than N_2O . Radiolysis of nitrous oxide might also occur in nitrous oxide propellant tanks in outer space under the impact of cosmic radiation. Radiolysis of nitrous oxide in the upper stratosphere under the influence of cosmic radiation might be one loss mechanism that converts N_2O to dinitrogen and dioxygen or to other nitrogen oxides. So there are multiple reasons why radiolysis of nitrous oxide is being investigated here [223, 224]. Nitrous oxide acts as a hydrogen atom scavenger [225]. Nitrous oxide reacts with electrons rather than hydrogen atoms in liquid hydrocarbons. The radiolysis of pure liquid nitrous oxide and of nitrous oxide/cyclopentane solutions were investigated [226].

The radiolytic decomposition of nitrous oxide has been proposed as the basis of a dosimeter, where the amount of nitrogen formed is taken as a measure of radiation exposure. The system was developed using γ radiation from a ^{60}Co source. It was shown that the measured dose was independent of the cell diameter [227]. A Fricke dosimeter was used as the reference of the absorbed dose. The dose actually absorbed by the gas was calculated by the Bragg-Gray principle. The results obtained indicated that there is no significant dependence on the G-factor for N_2 on the cell diameter. The mean $G(\text{N}_2)$ of 11.4 ± 0.8 obtained during these experiments compared well with values reported by others.

The N_2O dosimeter was calibrated for 1-MeV electrons by ionization measurements [228]. The G-factors at 297 K (24 °C) and 106.6 kPa (800 mm Hg) were: $G_{\text{N}_2} = 10.0 \pm 0.2$, $G_{\text{O}_2} = 4.0 \pm 0.4$, $G_{\text{NO}} = 3.9 \pm 0.3$, and $G_{-\text{N}_2\text{O}} = 12.0 \pm 0.4$. All yields increased with increasing temperature. The ratio $G_{\text{NO}} : G_{\text{O}_2}$ increased from 1.0 at 297 K (24 °C) and 106.6 kPa (800 mm Hg) to greater than 2.0 above 423 K (150 °C). The pressure dependence for G_{N_2} and G_{NO} was consistent either with ultimate dissociative electron capture of all electrons and bimolecular deactivation of N_2O^* or with no significant electron capture and termolecular deactivation.

4.7 Decomposition of Nitrous Oxide in Electrical Discharges

4.7.1 Decomposition of Nitrous Oxide in a Corona Discharge

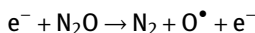
It has been attempted to remove N_2O from industrial waste gases by passing it through a corona discharge at high electric potentials. N_2O becomes easily ionized under those conditions and decomposes, sometimes forming ozone in the process. If ionized N_2O is passed over a catalyst, it may be possible to start the exothermic decomposition of N_2O in a monopropellant rocket without having to preheat the catalyst.

Measurements of the spatial growth of prebreakdown ionization currents in uniform electric fields in mixtures of nitrous oxide and oxygen showed that the ratio of effective primary ionization coefficient to the total gas number density decreased as the oxygen concentration in the mixture increased up to about 10% [229]. Measurements of the breakdown voltage of mixtures with oxygen concentrations up to about 10% showed that the dielectric strength of the mixtures increased above that of N_2O alone.

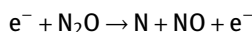
4.7.2 Decomposition of Nitrous Oxide in a Glow Discharge

The decomposition of nitrous oxide in a glow discharge would be of interest as a means of removal of nitrous oxide as a pollutant in stack gases or as the process taking place at the inlet of a mass spectrometer. It would also take place in the high atmosphere in an aurora.

A time-of-flight mass spectrometer has been used to examine the dissociation of nitrous oxide in a glow discharge, where the dissociation arose from direct electron impact reactions [230]:



and



The overall dissociation coefficient was $7.3 \times 10^{-17} \text{ cm}^2$ for 2.2 Torr N_2O ($E/p \sim 30 \text{ V cm}^{-1} \text{ Torr}^{-1}$) and increased by nearly an order of magnitude when the N_2O was mixed with argon. The discharge product NO altered the discharge conditions significantly and itself became considerably dissociated.

4.7.3 Decomposition of Nitrous Oxide in an Accelerated Electron Beam

Low-energy electron bombardment has been used to disaggregate N_2O clusters. Stronger energy beams will not only disaggregate the clusters but also decompose the N_2O molecule. Ozone and several oxides of nitrogen (NO_2 , N_2O_2 , N_2O_3 , N_2O_4 , and N_2O_5) were observed during the 1-keV electron beam irradiation of a solid N_2O ice sample formed at 25 K [231]. Such reactions may have important implications for the ice chemistry of outer solar system planets/satellites and interstellar ices. Electron

bombardment of nitrous oxide molecular beams can be used as a diagnostic tool to determine the degree of association of N_2O clusters.

The dissociation of N_2O into neutral metastable fragments by electron impact has been investigated for incident electron energies from threshold to 120 eV [232]. A number of dissociation channels that produced $\text{N}_2(^1\Pi_g)$ and $\text{O}(^5\text{S})$ metastable fragments were found. The kinetic energy spectra and excitation functions for both of these metastable species supported a mechanism for the production of $\text{N}_2(^1\Pi_g)$. It was noted that the relatively high kinetic energies of metastable intermediates produced in dissociative excitation may contribute to the heating of the upper atmosphere, particularly under auroral conditions.

Calculated and measured elastic and absorption cross sections using a crossed electron-beam/molecular-beam with electron beams in the intermediate energy range were compared, and the angular distribution of the scattered electrons was converted to absolute cross sections using a relative-flow technique, which showed good agreement between the measured results and theoretical calculations [233]; see also [234–237].

4.7.4 Decomposition of Nitrous Oxide in a Microwave Plasma

The decomposition of nitrous oxide in an electrodeless microwave plasma discharge reactor was examined as a method for the removal of nitrous oxide pollutants from industrial stack gases.

The decomposition of N_2O into N_2 , O_2 , and NO by an electrodeless microwave discharge in $\text{N}_2\text{O}/\text{He}$ or $\text{N}_2\text{O}/\text{Ar}$ mixtures was studied at various total pressures [238–241]. Although discharge could be maintained only in the low total-pressure range of 0.13–10 kPa (1–80 mm Hg) in $\text{N}_2\text{O}/\text{He}$ mixtures at N_2O and He flow rates of 25 and 2000 standard cm^3/min , respectively, stable microwave discharge could be maintained in the wider total-pressure range of 0.13–101 kPa (1–760 mm Hg) in $\text{N}_2\text{O}/\text{Ar}$ mixtures at N_2O and Ar flow rates of 25 and 1000 sccm, respectively, at a microwave power of 200 W. The decomposition efficiency of N_2O in $\text{N}_2\text{O}/\text{Ar}$ mixtures at 101 kPa (760 mm Hg) was measured as a function of the microwave power or the N_2O flow ratio at a relatively high N_2O concentration range of 9900–47600 ppm. Mass spectrometric and optical emission spectroscopic analysis helped to develop a hypothesis for the decomposition mechanism of N_2O under these conditions.

The operating pressure regime of microwave plasma discharges could be expanded by incorporation of microwave absorbers in the reactor. The decomposition of N_2O has been studied in a microwave-absorbent assisted discharge of N_2 at atmospheric pressure [242]. Although a discharge could not be maintained without using microwave absorbents, stable discharge could be maintained by using two types of rods of Zr or W microwave absorbents. The maximum conversion of N_2O was $\geq 97\%$ at a microwave power of 150–200 W and a distance of 10 mm between the rods.

4.8 Nitrous Oxide GDL, CW, and Chemical Lasers

A gas dynamic laser (GDL) is a laser based on differences in relaxation velocities of molecular vibrational states where the lasing medium gas has such properties that an energetically lower vibrational state relaxes faster than a higher vibrational state, and so a population inversion is achieved during expansion. Instead of CO_2 in a mixture with nitrogen or helium, N_2O can be used as the lasing medium [243].

Pulsed coherent emission was obtained from N_2O molecules in a $\text{N}_2\text{O} + \text{He} + \text{N}_2$ supersonic heated mixture emerging from a planar nozzle in a shock tube. The power and duration of the output pulses were a function of the concentration of N_2O , temperature, and pressure [244].

A tunable-diode laser operating in the $2120\text{--}2350\text{ cm}^{-1}$ wavenumber region was used to probe a conventional CW N_2O laser discharge [245]. Absorption lines in more than ten different vibrational bands were observed, enabling one to determine vibrational populations in all levels of concern to the dynamics of the $10\text{-}\mu\text{m}$ N_2O laser. The populations in the three normal modes of vibration of N_2O were found to follow Boltzmann distributions, with the ν_1 and ν_2 modes maintaining a common vibrational temperature under all discharge conditions. The factors limiting the small-signal $10\text{-}\mu\text{m}$ gain were investigated in detail, and it was found that electron deexcitation of the $00(0)1$ level is much more important than N_2O dissociation.

Similar to continuous wave (CW) CO_2 lasers, N_2O can also be used as a lasing medium in electrical discharge lasers. In addition, the exothermic decomposition of nitrous oxide of the reaction of N_2O and CO in a lasing cavity provides sufficient energy to use this as the propellant for a chemical laser.

A pulsed N_2O electron-beam-controlled laser with an optical cavity volume of $\sim 2\text{ L}$ was developed with a radiation energy of 8 J , specific output energy of $16\text{ J L}^{-1}\text{ atm}^{-1}$, and 9% efficiency, which was substantially higher than the performance values known for electric-discharge N_2O lasers [246–248]. The addition of CO to an $\text{N}_2\text{O}/\text{N}_2/\text{He}$ active mixture (or complete substitution of N_2 by CO) improved the energy characteristics of an electron-beam-controlled N_2O laser by more than an order of magnitude.

A simplified two-temperature model was developed for the vibrational energy levels of N_2O and N_2 molecules of an $\text{N}_2\text{O}\text{--}\text{N}_2\text{--He}$ GDL, and the governing equations for the unsteady flow of the gas mixture in a convergent-divergent contour nozzle were solved using a time-dependent numerical technique [249]. Final steady-state distributions were obtained for vibrational temperatures, population inversion, and the small-signal laser gain along the nozzle. It was demonstrated that for plenum temperatures lower than 1200 K , an N_2O GDL is more efficient than a CO_2 GDL under identical operating conditions.

In an effort to optimize the active mixture composition by varying the ratio of molecular (N_2 , CO) and monatomic (He , Ar , Xe) gases to N_2O on the energy characteristics of a pulsed electron-beam-controlled N_2O laser in a device having an optical

volume of ~ 10 L at a gas pressure of 0.25 atm, it was found that the laser output energies were ~ 80 J (a specific output energy of $\sim 30 \text{ J L}^{-1} \text{ atm}^{-1}$) for an active medium temperature $T = 20^\circ\text{C}$, and 106 J ($36 \text{ J L}^{-1} \text{ amagat}^{-1}$) for $T \approx -30^\circ\text{C}$ ($N = 0.3 \text{ amagat}$) [250]. An overall efficiency of $\sim 10\%$ was achieved.

In continuation of this development, an experimental and theoretical investigation was made of the small-signal gain in a pulsed electron-beam-controlled N_2O laser [251]. The gain was found to exceed $\sim 1 \text{ m}^{-1}$. A comparison of the experimental and calculated gain values was used as the basis for estimating the pumping efficiency of N_2O molecules in an electron-beam-controlled discharge and the relaxation constant of the upper active level. The lasing frequency of the N_2O laser was tunable in spectral ranges corresponding to vibrational-rotational transitions from R(46) to R(2) and from P(2) to P(46). The laser output energy, at its maximum in the distribution over the rotational numbers, was ~ 8 J.

4.9 Catalytic Decomposition of Nitrous Oxide

The catalytic decomposition of nitrous oxide is of substantial interest not only for its use as a rocket propellant but also for the abatement of nitrous oxide as a pollutant from combustion processes, industrial processes, and decomposition of organic matter in swamps.

It was decided to deal with the catalytic decomposition of nitrous oxide in *Encyclopedia of Monopropellants*, the chapter Nitrous Oxide Monopropellants. The homogeneous gas phase decomposition of nitrous oxide became a subsection to that chapter since we did not want to separate the two modes of decomposition.

Therefore, the chapter on catalytic decomposition of nitrous oxide was allowed to remain in *Encyclopedia of Monopropellants*. The current section contains all the other physical, chemical, and handling properties of nitrous oxide. The actual design of reactors for decomposing nitrous oxide for use in rocket engines will be discussed in *Encyclopedia of Monopropellants*, where it belongs.

4.10 Combustion Sustained by Nitrous Oxide as an Oxidizer

All publications dealing with combustion of solid fuels with nitrous oxide as an oxidizer may eventually be discussed in a planned future volume on hybrid propellants. All publications dealing with diffusion-flame combustion of gaseous or liquid fuels with nitrous oxide as an oxidizer will be discussed in a future volume on non-hypergolic bipropellants. Premixed mixtures of nitrous oxide with fuels, either in the liquid or gaseous state, usually intended to be used as monopropellants, are discussed in *Encyclopedia of Monopropellants*, following the use of pure nitrous oxide by itself as a monopropellant.

5 Toxicity of Nitrous Oxide

The main concern about the inadvertent inhalation of nitrous oxide is the narcotic effect that may render the accident victim unconscious. Nitrous oxide is heavier than air and may accumulate on the floor of a room.

Even if the inhalation hazard is under control, spills of liquid nitrous oxide leaking from an apparatus and spilled on unprotected skin can cause severe frost damage [252]. Exposure of the skin to nitrous oxide, a liquefied gas stored under pressure in a cylinder, can occur in anesthesiologists and in those involved in recreational misuse of the gas. A case was reported of a man who presented to the emergency department with frostbite on the face after sniffing nitrous oxide. Because of the numbness induced by the anesthetic, the victims do not feel the cold pain that would normally be a warning.

5.1 Inhalation Toxicity of Nitrous Oxide

Nitrous oxide acts as an analgesic at concentrations above 20 vol-% and as an anesthetic at concentrations above 70 vol-% in air. Because of the widespread use of nitrous oxide as an analgesic and anesthetic, the potential side effects of nitrous oxide inhalation have been thoroughly investigated. This affects not only patients that are exposed to this gas rarely in their lifetime but also operating room personnel who may breathe air that has been exhaled by patients undergoing medical treatment. See also Reference [253].

Nitrous oxide concentrations typically used for anesthetic purposes have cardiodepressive effects and can induce cardiac dysrhythmia.

The inhalation toxicity of nitrous oxide is described in the *Material Safety Data Sheet* of a nitrous oxide supplier as follows [254] (quoted verbatim):

Simple asphyxiant. May cause suffocation by displacing the oxygen in the air. Exposure to oxygen-deficient atmosphere (<19.5%) may cause dizziness, drowsiness, nausea, vomiting, excess salivation, diminished mental alertness, loss of consciousness and death. Exposure to atmospheres containing 8–10% or less oxygen will bring about unconsciousness without warning and so quickly that the individuals cannot help or protect themselves. Lack of sufficient oxygen may cause serious injury or death. Anesthetic effects may occur when mixed with oxygen at a ratio of 80% nitrous oxide to 20% oxygen. Laughter effects seem to occur after incipient asphyxia accompanied by the sudden return of oxygen. Nitrous oxide is a slight narcotic. Intentional misuse by deliberately concentrating and inhaling nitrous oxide may be harmful or fatal.

5.2 Toxic Action Mechanisms of Nitrous Oxide

The embryotoxic, teratogenic, neurologic, and hematotoxic activity of nitrous oxide is caused by irreversible oxidation of vitamin B₁₂. The lack of vitamin B₁₂ inhibits me-

thionine synthase, resulting in reduced deoxyribonucleic acid (DNA) synthesis and causes the myelotoxic, neurotoxic, and potentially reproductive toxic effects of N₂O [255, 256].

Neurological impairment from nitrous oxide exposure has been reported at concentrations of several hundred to several thousand ppm; however, decrements in human cognitive and psychomotor functions have been reported at much lower concentrations [257], also tremor [258]. Dentists exposed to nitrous oxide longer than 3000 h within the prior 10 years exhibited neurologic symptoms such as weakness, tingling, and numbness.

A neurological disorder developed after prolonged exposure to nitrous oxide in 15 patients, all but one of whom were dentists [259]. Thirteen patients had abused nitrous oxide to some extent for periods ranging from 3 months to several years, but two patients were exposed to nitrous oxide only professionally, by working in poorly ventilated surgeries. Symptoms included early sensory complaints, loss of balance, leg weakness, gait ataxia, impotence, and sphincter disturbances. Neurological examination showed sensorimotor polyneuropathy, often combined with signs of involvement of the posterior and lateral columns of the spinal cord. The effects can be prevented by folinic acid or methionine supplements in the diet. Nitrous oxide can lead to severe neurological deficits in patients with vitamin B₁₂ deficiency. Neurologic degeneration has been observed in vitamin B₁₂-deficient patients after N₂O exposure of only 1.5 to 3.5 h during routine surgery [260]. Nitrous oxide in anesthetic concentrations is teratogenic in rats, but in humans there is no unambiguous epidemiological evidence for an increase of fetal abnormalities following N₂O exposure during pregnancy, typically experienced by female dental assistants in poorly ventilated dentist's offices.

Nitrous oxide interacts with vitamin B₁₂, resulting in selective inhibition of methionine synthase, a key enzyme in methionine and folate metabolism. Thus, nitrous oxide may alter the one-carbon and methyl-group transfer most important for DNA, purine, and thymidylate synthesis. Detailed summaries of the toxicity of N₂O are published in [261–264].

The adoption by the American Conference of Governmental Industrial Hygienists of a Threshold Limit Value (TLV) of 50 ppm for an 8-h average exposure to nitrous oxide was in response to numerous publications in the 1980s that outlined the potential dangers of routinely inhaling N₂O. Although N₂O was for many years believed to have no toxicity other than that associated with its anesthetic action, bone marrow depression in patients administered N₂O for extended periods of time and neurological abnormalities in healthcare workers who inhaled N₂O repeatedly recreationally have disproved this notion. Retrospective surveys of dental and medical personnel have also linked occupational exposure to N₂O with a number of health problems and possible reproductive abnormalities. Nitrous oxide reacts with the reduced form of vitamin B₁₂, thereby inhibiting the action of methionine synthase, an enzyme that indirectly supports methylation reactions and nucleic acid synthesis. Many, if not all, of the non-anesthetic-related adverse effects of N₂O may be based on this reaction.

Animal and human studies indicated that the toxic effects of N_2O are concentration- and time-dependent. It was suggested that a time-weighted average of 100 ppm for an 8-h workday and/or a time-weighted average of 400 ppm per anesthetic administration would provide adequate protection of dental personnel and be achievable with existing pollution control methods [265]. It is difficult to extrapolate from animal tests to human health hazards on nitrous oxide [266].

5.3 Teratogenicity of Nitrous Oxide

In animal tests with pregnant Sprague-Dawley rats and concentrations of 50 vol-% N_2O , even single exposure during days of gestation between 8 and 10 d, the exposure caused malformations in offspring, and N_2O was classified as embryotoxic and teratogenic under those conditions [267–271]. A maximum of fetal deformations was observed in rats exposed on day 9 of the pregnancy, but no effects were observed with 75% N_2O exposure during days 11 to 15 or 16 to 20 of the pregnancy [272]. Concentrations of 35 vol-% or below were not embryo- or fetotoxic [273]. The no-effect level was established at 10 vol-% N_2O . Epidemiological studies of humans exposed to N_2O as operating room personnel have not identified any teratogenicity of N_2O in humans.

On the other hand, some MSDS caution as follows: “Reproductive toxicity has been observed in humans and animals following exposure to nitrous oxide in concentrations in excess of the TLV. Exposure to nitrous oxide alone resulted in a 50% increase in congenital abnormalities and a 100% increase in spontaneous abortion in female dental assistants compared to non-users of nitrous oxide.”

5.4 Fatal Accidents as the Result of Nitrous Oxide Inhalation

There have been numerous reports of fatal accidents due to the recreational substance abuse and inhalation of nitrous oxide to achieve a hallucinogenic “high” [274, 275]. In comparison to those frequent fatalities there are only few fatalities where the exposure was truly an industrial accident.

The abuse of nitrous oxide while on the job caused at least 11 deaths in 1984 to 1987, as found in investigations by the Occupational Safety and Health Administration and in reports to the Consumer Product Safety Commission [276]. The 11 deaths involved recreational inhalation of N_2O by young male employees from cylinders normally used for legitimate business purposes. In six cases, the victims worked in food serving establishments and inhaled N_2O that was used to power whipped cream dispensers. Moreover, there have been fatal errors in nitrous oxide (and lack of oxygen) delivery in the operating room, either by human error or equipment failure [277].

6 Environmental Impact of Nitrous Oxide

It has been estimated that among the greenhouse gases carbon dioxide, methane, and others, the contribution of nitrous oxide to the greenhouse effect is 6%. Depending on which source you believe, the heat-trapping greenhouse-effect power of nitrous oxide is variously reported as anywhere between 260 and 310% of that of carbon dioxide, and its half lifetime in the atmosphere is substantially longer than that of carbon dioxide since there are no known biological sinks for nitrous oxide.

A good summary of the role of nitrous oxide in the global nitrogen cycle is given in [278]. Nitrous oxide is an important trace component of the Earth's atmosphere with a 120-year atmospheric residence time. It exhibits a global warming potential 310 times that of CO_2 on a per molecule basis, and like CO_2 , its atmospheric concentration is increasing. Nitrous oxide is produced naturally as a byproduct of nitrification and denitrification. There are also several anthropogenic sources. The reactions known to yield N_2O must be identified before one can control the N_2O buildup in the atmosphere. Fundamental chemical kinetics and mechanisms that lead to its formation depend on research involving nitric acid, nitric oxide, and ammonium nitrate as N_2O precursors.

There are several books with information about nitrous oxide and climate change [279, 280]. Nitrous oxide is the third most important (in global warming terms) of the greenhouse gases, after carbon dioxide and methane. Although it only comprises only 320 parts per billion of the earth's atmosphere, it has a so-called global warming potential nearly 300 times greater than that of carbon dioxide. N_2O emissions are difficult to estimate because they are predominantly biogenic in origin. N_2O is formed in soils and oceans throughout the world, by the microbial processes of nitrification and denitrification that utilize the reactive nitrogen compounds ammonium and nitrate.

7 Materials' Compatibility with Nitrous Oxide

All materials that may come into contact with nitrous oxide need to be thoroughly cleaned. SpaceDev, the hybrid rocket motor supplier for Scaled Composites and its SpaceShipOne and SpaceShipTwo commercial spacecraft, and its predecessor AMROC have accumulated a vast amount of experience in handling nitrous oxide and selecting materials that are compatible with it [88]. That includes special methods for cleaning all components that come into contact with nitrous oxide prior to each use.

7.1 Metallic Materials of Construction

Stainless steel CRES-304 bomblets with 52 mL internal volume were filled with 25 mL of liquid N_2O and heated to 302.6 K (85 °F), which is just below the critical point for

30 d [202]. As blank reference samples, in addition to the six tests with impurities or metals in contact with N_2O in CRES-304 bomblets, one CRES-304 bomblet and one CRES-316 bomblet (both without any test impurity) were filled with N_2O and placed in the bath under the same test conditions. After 30 days at 302.6 K (85 °F), no pressure buildup was noted in any of the 8 compatibility containers containing Cu, Ni, Fe_2O_3 , Cr_2O_3 , FX 190 3-M Corp. leak test solution or CRES-304 wire mesh screen.

7.2 Non-metallic Materials of Construction

Impact tests of 19 materials immersed in liquid N_2O were conducted at the White Sands Test Facility by NASA in a pressurized test apparatus [281]. These tests consisted of placing 12-mm (1/2-in.) diameter specimens in a cup-like device, immersing the cup and specimen in liquid N_2O , and dropping a 9-kg (20-lb_m) 12-mm (1/2-in.) diameter ballast weight on the specimen. The energy density of the impactor at the area of impact was 762 N/m² (367.5 ft-lb_f/sq. in.). The results showed that there were no effects to the materials and no problems with N_2O ignition. The materials tested included metals, alloys, polymers, and grease.

Three materials were tested in a bladder materials evaluation program [282]. These were FEP Teflon, AF-E-332, and Arrowhead Rubber AP-2962. The tests consisted of immersing the specimens in liquid N_2O at room temperature for several days and then comparing the mechanical properties of specimens. It was found that the tensile properties and resistance to cyclic strain of both FEP Teflon and AF-E-332 were practically unaffected by exposure to liquid N_2O , but the properties of the Arrowhead Rubber degraded considerably. These tests eliminated Arrowhead Rubber as a possible bladder material.

Due to the good solvent properties and high rate of permeation of liquid N_2O , it is important to test polymeric seals intended to be used in N_2O systems for swelling in liquid N_2O .

8 Components for Nitrous Oxide Systems

Ignition of combustible materials will happen more readily in the presence of nitrous oxide. This is why the Department of Transportation (DOT) requires that cylinders containing nitrous oxide, meet the requirements listed in the Code of Federal Regulations (CFR-49) section 173.304 “Charging of cylinders with liquefied compressed gas” paragraph (a)(4)(ii). Each cylinder must be cleaned in compliance with the requirements of Federal Specification RR-C-901c § 3.7.2 and 3.8.2. Cleaning agents equivalent to those specified in RR-C-901c may be used; however, any cleaning agent must not be capable of reacting with oxygen or nitrous oxide [283]. The piped systems for the in-plant transfer and distribution of nitrous oxide shall be designed, installed, maintained,

and operated in accordance with Compressed Gas Association (CGA) Pamphlet G-8.1-1964 [284, 285]; as specified in Section 1910.6.

8.1 On-Site Storage Systems

The design of on-site storage tanks and distribution systems for nitrous oxide is described in [286].

8.2 Design of Self-Pressurizing Feed Systems

Most rockets in launch vehicles feed the propellants by the use of turbopumps, one for the oxidizer and one for the fuel. Satellites and space probes used pressure-fed feed systems where a pressurant gas, usually helium, pressurizes a propellant tank and expels the liquid into the rocket engine. Pressure-fed systems are very similar for bipropellant systems and monopropellant systems or for some hybrid systems. Most propellants that are pressure-fed do not have a very high vapor pressure of their own and depend on the pressurant gas to get moving. Nitrous oxide (and a few other propellants, such as propane) are an exception in this group of propellants in that they have sufficient vapor pressure to expel themselves from a propellant tank without the aid of a pressurant gas like helium. However, the moment liquid is withdrawn from the tank, and some of the liquid has to vaporize to maintain the pressure in the enlarging vapor space, the energy required for vaporization is withdrawn from the liquid and may cause it to freeze if no heat is supplied from the outside and if the fluid has a narrow liquidus range like nitrous oxide or carbon dioxide. This would be the case regardless of whether the nitrous oxide is used as an oxidizer in a bipropellant engine or a hybrid motor or used as a monopropellant.

Accurate modeling of propellant tank pressurization is an essential element of the prediction of rocket performance. A real fluid, quasi-phase-equilibrium thermodynamic propellant tank model that is applicable to a broad range of propellants including those that are highly volatile and/or cryogenic was developed and validated by comparison with the measured results of cold flow blow-down tests or a self-pressurizing nitrous oxide system [287, 288]. Data from one of the cold flow tests showed evidence of stratification within the oxidizer tank during the blowdown. Accurate modeling of the propellant evaporation rate is a crucial element in the prediction of the pressure history of the propellant expulsion process. With a change in the input parameters, this model can also be used for other volatile propellants.

Regardless of whether N_2O is to be used as working fluid for cold gas thrusters, electrothermal thrusters, as monopropellant, or as oxidizer in bipropellant or hybrid propulsion systems, one property that all applications take advantage of is the self-

pressurization of N_2O tanks, expelling liquid N_2O under its own vapor pressure, which eliminates the need for a separate tank pressurization system.

One of the advantages of nitrous oxide over storable propellants that require a helium pressurization system is that below certain propellant withdrawal rates, the tank is self-pressurizing. An instrumented experimental ground test system was built simulating a satellite to study the propellant-tank self-pressurization process of a sub-Newton-thrust-class N_2O monopropellant propulsion system [289]. Numerical simulation using a three-region lumped parameter model was conducted to simulate the same process. Simulation results under adiabatic wall conditions agreed well with the experimental data. Both experimental and simulation results showed that the heat compensation for the propellant tank heat balance is necessary during the propellant self-pressurization propellant withdrawal, in order to keep stability of the tank pressure. The initial filling factor (ullage), the volume of the tank, and the propellant flow rate influence the rate of propellant tank pressure decay; see also Reference [290].

A theoretical model was developed that predicted the pressure draining history of a self-pressurized N_2O oxidizer tank with helium as the pressurant to within $\pm 5\%$ of experiment [291]. Two models were produced, both assuming thermodynamic equilibrium states at every point in time throughout draining. The first model assumed that the P - V - T behavior of the nitrous oxide/helium mixture is ideal; the second model assumed that the mixture adheres to the non-ideal Peng-Robinson equation of state. Results from both models were compared to experimental data from pure nitrous oxide (no helium pressurization) draining tests [287]. The additional complexity introduced by a non-ideal equation of state was necessary due to the high pressures encountered in the tank during draining. It was found that despite the highly non-linear nature of the draining process, the liquid flow rate from the tank remained reasonably constant, which is a highly desirable characteristic of a rocket oxidizer delivery system.

An engineering model was developed to calculate the two-phase saturated fluid mass flow rate of self-pressurizing nitrous oxide [292, 293]. The model assumed adiabatic expansion for which, during propellant discharge from the tank, the current tank fluid entropy and the fluid entropy that has discharged through the feed system equate to the initial, predischARGE entropy of fluid in the tank. While flow of N_2O through a network of tubing cannot be accurately modeled using traditional ideal gas, compressible or incompressible flow assumptions, a more accurate mass flow rate one-dimensional analysis included both incompressible fluid and homogeneous equilibrium mass flow rate models. Mass flow calculations from the two models were independently weighted and summed to obtain a representative two-phase mass flow rate. The model excellently predicted mass flow rates as verified by comparison to experimental cold flow data. The experimental conditions resulting from the test apparatus setup produced fluid stratification and incomplete mixing effects that cannot yet

be modeled by the algorithm as developed. Therefore, the run tank and temperature drops as predicted by the model were significantly larger than measured. The results were compared to those obtained with CO_2 , which behaves very similarly to N_2O .

Hybrid rockets commonly use nitrous oxide as a self-pressurizing oxidizer, but no comprehensive models existed for predicting the performance of such a system. To aid in the development of such a model, an experimental apparatus with a transparent cylinder was designed that allowed for visual observation as well as pressure, temperature, and mass flow rate measurements [294]. Because the physical properties are very similar, carbon dioxide was used as a substitute for nitrous oxide, facilitating laboratory-scale testing. Initial results of tests with this system showed that there is significant boiling within the liquid and that the propellant is not maintained in thermodynamic equilibrium.

A self-pressurizing propellant like nitrous oxide has the potential to reduce propulsion system mass and complexity. In the case of nitrous oxide, the liquid propellant has a high vapor pressure that may be used to pressurize the liquid, allowing a traditional pressurization system to be eliminated entirely or significantly reduced in size. However, the expulsion dynamics of a self-pressurizing propellant tank must be accurately modeled for system performance to be predicted. To aid in the development of such a model, an experimental apparatus has been constructed with a transparent polycarbonate cylinder functioning as a propellant tank [295, 296]. This allowed for optical measurements to be made in addition to traditional pressure, temperature, and mass flow rate measurements. Carbon dioxide has been identified as an analog substitute for nitrous oxide, facilitating a significant reduction in the cost, negative environmental consequences, and hazards to personnel associated with this type of testing. Both the supercharge configuration and the mass flow rate strongly affect the dynamics of self-pressurizing propellants. In order to demonstrate carbon dioxide's validity as an analog ("stand-in") for nitrous oxide, side-by-side comparison tests with nitrous oxide and carbon dioxide have also been performed.

Subsequently, an improved system was constructed [297]. Several pressure transducers were added to record pressure in the ullage, at the base of the tank, and in the exit lines. Temperature sensors in these locations allowed the complete determination of the thermodynamic state. Fast response time thermocouples have been used to capture transient temperature changes. Significant amounts of boiling and condensation were observed, and transient bubble phenomena appeared to be responsible for some characteristics of the pressure history. By using a pressure vessel manufactured from cast acrylic as opposed to the previous extruded polycarbonate, the optical clarity has been greatly increased.

8.3 Propellant Tanks for Nitrous Oxide

The design of a lightweight pressurized oxidizer tank for a hybrid sounding rocket with a capacity of 20 kg of either nitrous oxide or hydrogen peroxide envisioned a tank made from graphite epoxy prepreg composite with unidirectional lamina designed for a burst pressure of 13 MPa (2000 psi) and had the shape of a cylinder with hemispherical ends [298]. The tank diameter would be 20.3 cm (8 in.), and the total length would be 1.52 m (5 ft.) This gave a total dry mass of 3.7 kg.

9 Safety Properties of Nitrous Oxide

The guidelines issued by Compressed Gas Association provide a reliable summary of precautions for the safe handling of nitrous oxide [299]. As part of the proposed use of N_2O as an oxidizer in a combustion process for an airborne laser weapon system, a number of potential problem areas were investigated by Air Force Weapons Laboratory (AFWL) or by other organizations under contract to AFWL [92]. Two of the programs investigated the decomposition characteristics of N_2O/CO mixtures. It was determined that the decomposition of gaseous N_2O is not difficult to initiate, but that it is also easily quenched. Tests with the N_2O/CO mixture revealed that this combination has significant explosive potential; however, it was difficult to initiate such an explosion. Another series of investigations addressed potential flow choking problems. The liquid N_2O in the system is pressurized by helium in the ullage of the tank and absorbed some of this He. With more than about 0.5 mol-% absorbed He, the effective throat area of a cavitating venturi used in the metering system was appreciably reduced. A second aspect of the flow studies concerned the possibility of N_2O solidification when it had to be dumped overboard under emergency airborne conditions. Tests confirmed the formation of N_2O snow when liquid N_2O was dumped into a vacuum chamber; however, no flow problems were encountered.

Additional information on the safe handling of nitrous oxide is provided in the Material Safety Data Sheets available from nitrous oxide manufacturers and distributors, for instance:

Refrigerated Liquid:

http://msds.lindeus.com/files/msds/WPS_LIND_067_NA_MSDS_FINAL_REV_9_2_10.pdf

Compressed Gas: [254]. Section 10. STABILITY AND REACTIVITY in the latter MSDS describes N_2O gas as “**Stability: Stable**”, a misleading description that we question, but a few lines down the MSDS is more specific:

Hazardous Decomposition Products

At elevated temperatures, nitrous oxide decomposes into nitrogen and oxygen, the rate of decomposition being appreciable at about 1112°F (600 °C). Nitrous oxide exposed to fire or other intense heat source may decompose violently.

The recommended maximum storage temperature for compressed gas cylinders filled with N_2O gas is 225 K ($52^\circ\text{C} = 125^\circ\text{F}$).

During an investigation of potentially catastrophic explosions propagated in condensed-phase nitric oxide NO (not N_2O) at temperatures near its normal boiling point, a control experiment, made in the same way using liquid N_2O instead of liquid NO at 85 K, showed no evidence of oxidation or explosion [300]. These explosion experiments were in a vertical CRES-304 stainless steel pipe, 52 mm internal diameter (I.D.), 4 mm wall thickness, and 1220 mm length. All samples were initiated by the detonation of an RDX booster charge.

A very thorough study of the explosion potential of nitrous oxide was conducted by several contractors under sponsorship of the US Air Force [202]. The test program was divided into three phases: **(1)** ignitability of gaseous N_2O , **(2)** ignitability of liquid N_2O , and **(3)** materials' compatibility of liquid N_2O . The results are discussed in other sections of this book.

The conditions under which the decomposition of gaseous nitrous oxide proceeds with explosive force were determined in closed vessels at room temperature and at initial pressures between 0.05 and 8 bar and with various methods of initiation [301]. The pressure profile in the vessels was measured, and, in some cases, the reaction was filmed with a high-speed camera in a windowed bomb. The decomposition products were analyzed by GC. In the high-pressure regime, the ratio of explosion pressure to initial pressure increased with increasing initial pressure. The rate of decomposition was relatively slow, and the type and location of the ignition source and the geometry and the size of the closed bomb had a substantial influence on the rate of reaction and the degree of N_2O decomposition. It was found that at least 30 vol.-% of a diluent gas (air, oxygen or nitrogen) was required to prevent an explosive decomposition. For a container containing both liquid and gaseous N_2O , the vapor phase was no longer detonable after the vapor pressure dropped to below 5.7 bar, which corresponds to a liquid temperature of 218.1 K (-55°C).

Besides avoiding all potential sources of ignition, there are other steps the designer can take to prevent or mitigate explosion hazards when operating at high pressures with gases capable of explosive decomposition such as nitrous oxide or acetylene [302].

In the wake of the accident at Scaled Composites at Mojave in August 2007, a thorough literature search and critical evaluation of available hazard property data for nitrous oxide was conducted [303]. Accounts of serious, large N_2O system accidents are mysterious since a technically satisfying explanation of how the incidents occurred seems lacking. The inadequacy of technical information for serious N_2O incidents indicated that safety practice understanding beyond current knowledge is needed. At a minimum, application of some standard safety practices used with high-pressure oxygen systems, but not specified for N_2O operations, may provide some safety improvements. The inadequacy of historical N_2O hazard study experiments was that they used too small volumes in their studies, and scaling criteria were ne-

glected. N_2O /organic material mixtures constitute special hazards. One of the several potential sources of ignition in any flowing, non-conductive fluid is the buildup of electrostatic charges and an electrostatic discharge spark ignition. The triboelectric effect is the generation of electrostatic charges when differing materials are separated or rubbed or flow over one another. With highly insulating materials and large surface areas, voltages can become quite large. Highly insulating materials might be those having an electrical resistance above $10^{10} \Omega/\text{cm}$. For instance, solid propellants having electric resistances above $10^{10} \Omega/\text{cm}$ can be sensitive to electrostatic ignitions, while solid propellants having electrical resistance below $10^{10} \Omega/\text{cm}$ are insensitive to fire ignition by ESD sparks. Solid propellants are often coated with graphite powder to make them conductive. Nitrous oxide is a material that has very high electrical resistance in both gas and liquid states. For comparison, as gas pressure is increased, ignition energies for initiation of fire with solid propellants can diminish dramatically. Threshold electrostatic discharge voltage for getting a solid propellant ignition between 1 atmosphere (0.10 MPa, 14.7 psi) and 40 atmospheres (4.1 MPa, 600 psi) can decrease by a factor of 30. Since the spark energy is proportional to voltage squared, the spark energy for propellant ignition at 40 atmosphere pressure was about one-thousandth $= (1/30)^2$ of that required for propellant ignition at 1 atmosphere pressure. Since N_2O vapor pressure at 293 K (20 °C) is about 5.2 MPa (50 atm = 750 psi), pressure conditions are fairly optimal for having ESD events occurring that might attain combustion ignitions with N_2O /fuel mixtures. The fuel in this instant might be gasket materials, lubricant contamination, or the composite fiber-reinforced tank wall.

A very thorough evaluation of hazards in using nitrous oxide as an oxidizer in hybrid propulsion systems and other industrial applications has been conducted with a model of N_2O decomposition events [58]. In order to underscore the importance of such calculations, that paper contains a list of nitrous oxide decomposition accidents compiled from literature sources. Consequently, the hazard analysis looked at three hazard scenarios in a rocket: **(1)** N_2O decomposition in the oxidizer tank, **(2)** N_2O decomposition in the feed system, and **(3)** uncontrolled decomposition in the combustion chamber. The primary objective of this paper was to evaluate and assess the hazards that exist in N_2O -based propulsion systems by using the fundamental understanding of the N_2O decomposition physics/chemistry. A secondary goal was to establish a list of practical recommendations for the safe use of nitrous oxide. The decomposition of nitrous oxide was also compared to that of another monopropellant, hydrogen peroxide. The reaction rate constant for H_2O_2 is almost six orders of magnitude larger than the rate constant for N_2O decomposition. Approximately half of this difference is attributed to the lower value of the reaction rate coefficient r_A (primarily due to the spin forbidden transition of N_2O), and the other half is due to the lower activation energy associated with the decomposition of H_2O_2 (203 kJ/mol = 48.5 kcal/mol versus 243 kJ/mol = 58 kcal/mol for N_2O).

Safety precautions recommended for use of nitrous oxide in hybrid rockets apply just as well to all other rocket uses of nitrous oxide [88].

9.1 Autoignition Temperature of Gaseous Nitrous Oxide

The temperature above which the decomposition of gaseous nitrous oxide becomes self-sustaining and potentially leads to explosions depends on the pressure of the gas, the dimensions of the reaction vessel, and the materials of the hot surfaces that the gas is in contact with.

The autoignition of gaseous nitrous oxide was already discussed in the chapter on thermal stability and decomposition of nitrous oxide, see Section 4.4.

Nitrous oxide ignited spontaneously during attempts to fill a heated high-pressure detonation tube to an initial pressure of 2.16 MPa (21.4 atm). The tube was at a temperature of 598 K (325 °C) [304]. The ignition of nitrous oxide flowing at 0.05 m/s over a heated 3-mm diameter metal rod was dependent on the chamber pressure and flow rate. Ignition was only possible at pressures above 0.3 MPa. The temperatures of ignition decreased with increasing pressure, as shown in Table 23. The rod was heated up at a rate of 25–30 K/s.

Table 23: Ignition temperature of nitrous oxide gas.

N ₂ O pressure, MPa	Ignition temperature, K	
	Flowing gas	Natural convection gas
0.3	1515 ± 15	
0.4	1473 ± 20	
0.5	1454 ± 10	
0.6	1406 ± 10	
0.7	1398 ± 15	
1.1	1359 ± 10	1308 ± 15
2.1	1309 ± 10	1278 ± 15
3.1	1292 ± 10	1273 ± 10
4.1	1280 ± 15	1238 ± 20

Data source: [304]

9.1.1 Ignitability and Detonability of Gaseous Nitrous Oxide

The detonability of gaseous nitrous oxide was investigated at initial temperatures from 296 to 483 K (23 to 210 °C = 533 to 870 R) and at initial pressures from 2.16 to 20.92 MPa (21.4 to 207.1 atm) in a high-pressure detonation tube (32 mm I. D. × 1.14 m = 1.25 in. I. D. × 45 in. in length) [304]. Ignition was provided by a pyrofuse Al/Pd alloy wire rapidly heated with a 24-V DC power supply. No true detonations developed during any of these experiments. At first, experiments were conducted with the gas initially at room temperature, while the initial pressures ranged from 3.53 to 6.28 MPa (35.0 to 62.2 atm). The maximum pressure observed at the tube end was only 1.15 to 1.64 times the initial pressure, whereas a detonation wave would have produced an impact pressure 25 times higher than the initial pressure. Some explosions,

however, were encountered. The maximum impact pressure was 3.66 times greater than the initial pressure as measured by a quartz crystal transducer. The time intervals of the reactions (from ignition to the maximum pressures) lasted from 1 to 4 s, which indicated that relatively slow reactions occurred. The results showed that nitrous oxide will decompose and burn deflagratively under the conditions employed. At certain higher initial pressures and temperatures, some explosions occurred.

Explosion and decomposition limits of gaseous nitrous oxide with and without diluent gases have been determined in a 117-mL cylindrical reaction chamber for pure nitrous oxide and mixtures consisting of (volume parts) $1\text{N}_2\text{O} + 0.25\text{air}$, $1\text{N}_2\text{O} + 0.88\text{N}_2$, and $1\text{N}_2\text{O} + 0.88\text{N}_2 + 0.50\text{air}$ in order to minimize the explosion risk if using such gas mixtures for aerodynamic tests in supersonic wind tunnels [203]. Two types of igniters were employed: (1) a 0.127-mm (0.005-in.) diameter copper wire was melted by applying 31 V DC to its terminals and (2) a 0.5-mm (0.020-in.) diameter platinum glow wire was heated with approximately 210 W AC. The explosion limit curve for nitrous oxide followed an exponential path for both igniters. Explosions could not be produced in the $\text{N}_2\text{O} + 0.25\text{air}$ mixture. However, slow reactions were observed when the mixture was preheated to between 593 and 887 K. No reactions could be initiated in the $1\text{N}_2\text{O} + 0.88\text{N}_2$ and $1\text{N}_2\text{O} + 0.88\text{N}_2 + 0.50\text{air}$ mixtures. Experiments with nitrous oxide were conducted at initial temperatures of 296, 348, 373, 423, 473, 523, 573, and 623 K with initial pressures ranging from 0.1 to 4.85 MPa (2 to 48 atm). The electric current melted the copper wire very quickly, thereby producing a concentrated heat source for ignition. The initial experiments were carried out at low pressures (2 atm) and at ambient temperature (296 K). In later experiments the temperature was maintained constant, while the pressure was elevated gradually from experiment to experiment until an explosion was obtained. For a given initial temperature, measurements were made up to pressures well within the explosion region to make sure that the explosion limit had actually been reached and exceeded. Then, the temperature was elevated, and the experiments were repeated. This procedure was continued up to a temperature of 623 K, which was the maximum temperature obtainable with the experimental equipment at that time. At 623 K, the explosion limit was at 0.2 MPa (2 atm). Although the explosion limit in Figure 44 was drawn as a sharp line, it is more likely a band of a given thickness. For the data in Figure 44, ignition was achieved by melting a 0.127-mm (0.005-in.) diameter copper wire with 31 V.

Similarly, in a second series of tests, the explosion limits of pure nitrous oxide ignited by a platinum glow wire were determined at various temperatures between 423 and 1035 K. In this temperature interval, a pressure range from 0.1 to 7.57 MPa (2–75 atm) was investigated. Experiments were performed in a heavy-walled stainless steel cylindrical reaction vessel. The volume of the reaction vessel was 117 mL. The graphic representation of the explosion boundary was not as clean as the one with

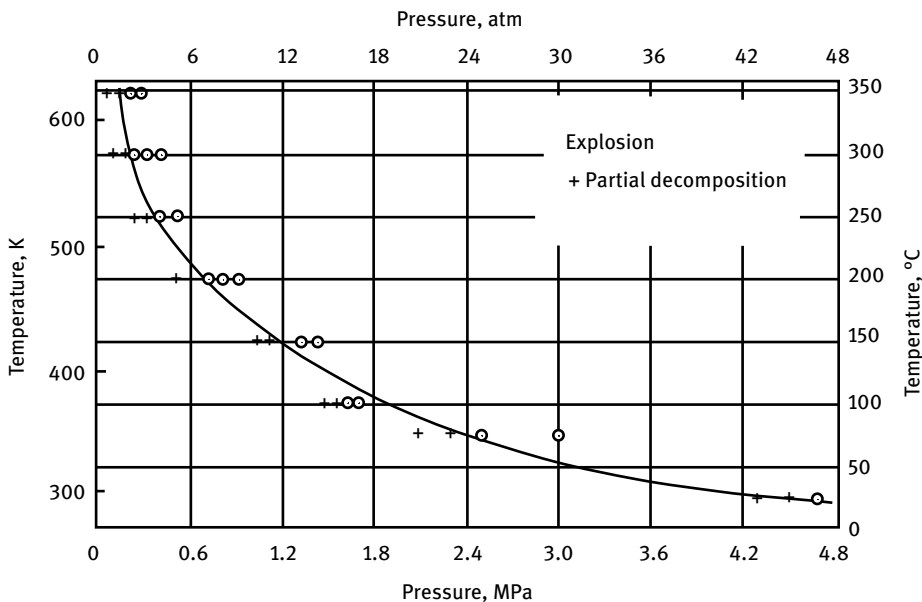


Figure 44: Explosion limits of gaseous nitrous oxide. (Reproduced and modified from [203].)

the exploding copper wire shown in Figure 44. There was a transition regime where only very slow and only partial decomposition was observed. The decomposition time, as obtained from pressure-time traces, was of the order of 0.2 to 0.4 s, which is very slow. After the reaction products had cooled off, the final pressure of the closed vessel exceeded the starting pressure by 30–45%. Dilution of nitrous oxide with helium retarded the spark ignition in a 15-cm (6-in.) diameter pipe under most of the conditions summarized in Table 24.

Table 24: Test conditions for spark ignition of gaseous N₂O/He mixtures.

Mol fraction N ₂ O	Mix total pressure		Pre-test temperature		Comments
MPa	psia	K	°F		
0.33	14.45	2100	297	75	No temperature or pressure rise
0.47	15.14	2200	297	75	No temperature or pressure rise
0.49	9.63	1400	296	74	No temperature or pressure rise
0.5	10.32	1500	300	80	No temperature or pressure rise
0.63	7.57	1100	296	74	No temperature or pressure rise
0.84	5.50	800	296	73	No temperature or pressure rise
0.93	4.75	690	294	70	Mixture ignited; chamber ruptured; flame propagation rate: 40 cm/s

Data source: [92]

Figure 9 on page 20 of an accident investigation report shows a graph of critical diameters of tubing for the propagation of nitrous oxide decomposition as a function of temperature and pressure [305]. It was not shown how the authors arrived at this illustration; see also [306, 307].

9.2 Shock Sensitivity and Detonability of Liquid Nitrous Oxide

Ignition and detonation tests of liquid N_2O were conducted in a steel pipe with a diameter of 50 mm (2in.) and length of 30 cm (12in.) [202]. To conduct a test, the pipe was cold-filled with liquid N_2O and warmed to the desired temperature. Two sets of ignition tests were conducted: electrical resistance heated wire ignition tests and explosive cap ignition tests. Only slight pressure and temperature increases were recorded when the electrical igniter was fired. The tests showed that any N_2O that may be vaporized and ignited by the exploding wire was immediately quenched by the surrounding liquid. The explosive cap ignition tests were essentially the same as the electrical ignition tests, except that the exploding wire was replaced with a standard No. 6 blasting cap. In all, eight tests were conducted, four using just plain water to provide a basis of pure hydraulic shock for comparison and four using liquid N_2O . Of the four tests using liquid N_2O , one bulged the tube slightly as in the first three water tests, and the other three ruptured the tubes. The three ruptured tubes were permanently stretched about 20% before rupture. If the liquid N_2O had fully detonated, the energy released would have been equivalent to almost 1 kg (2lb) of TNT. This quantity of detonating TNT would have broken the pipe into many small pieces of shrapnel. The difference in results between the N_2O tests and the water tests clearly showed that some N_2O decomposition occurred. The relatively small amount of damage, however, also showed that the reaction is either slow or quenched.

Using the same techniques as previously developed for detonability testing of nitric oxide (which was much more sensitive than nitrous oxide) the detonation characteristics of nitrous oxide as a solid and non-boiling liquid were examined at USBM [308]. Solid N_2O (136 K, 0.1 MPa) and non-boiling liquid N_2O (197 K, 0.4 MPa) confined in a 26.6-mm-ID by 3.38-mm-wall Schedule 40 steel pipe failed to initiate and detonate when shocked with a 50-g tetryl donor charge close-coupled to a 1.27-mm-thick steel attenuator foil that sealed the bottom of the container [309].

In one of the first systematic studies of nitrous oxide ignition by a local heat source leading to explosions in the gas phase the pressure had to be at least 1.6 atm [206]. Since nitrous oxide is used in practice at elevated pressures, the classification of nitrous oxide as a non-explosive gas based on atmospheric-pressure tests seems incorrect. In estimating the explosion hazard of nitrous oxide two important circumstances must be considered: its sensitivity to the presence of combustible contaminants (since it is an efficient oxidizer) and a sufficiently high temperature (309 K) in a liquid-filled tank with ullage space to raise the vapor pressure into the detonable regime.

9.3 Detonability of Nitrous Oxide/Fuel Mixtures

The detonability of nitrous oxide is enhanced, and it becomes more sensitive in the presence of combustibles, even trace amounts of combustibles like oil. On the other hand, mixtures of nitrous oxide with a wide range of fuels have been studied as monopropellants because nitrous oxide/fuel mixtures would give a higher Isp than nitrous oxide by itself. These premixed monopropellant mixtures will be discussed in *Encyclopedia of Monopropellants*. The detonability of liquid nitrous oxide/ethylene mixtures was investigated extensively. These mixtures have been evaluated as monopropellants.

The detonability of liquid nitrous oxide was tested as part of a program that primarily investigated the detonability of liquid nitrous oxide/carbon monoxide mixtures that were considered as a laser propellant [92]. In those experiments, the blast hazards of $\text{N}_2\text{O}/\text{CO}$ mixtures were examined by firing detonators in liquid $\text{N}_2\text{O}/\text{CO}$ mixtures, which were held in cylindrical containers with a diameter of 90 cm (3 ft.). The total liquid depth was approximately 30 cm (1 ft.), and explosion of the stoichiometric liquid mixture was attempted by means of either two blasting caps or a blasting cap and a squib. The results of six tests showed that while fires occurred in all cases, explosions only occurred in two cases, and both of these used dual blasting caps for ignition. A limited test program was conducted to obtain preliminary explosive yield data for the propellant combination of liquid carbon monoxide and liquid nitrous oxide, under conditions that simulate credible failure modes in a planned test facility [310]. During the course of the program ten tests were conducted using mixtures of these propellants in both liquid and gas phases. Propellant weights ranged from about 50 to 800 lbs. The results from the tests showed that the propellant combination has significant explosive potential, but that it is much more difficult to initiate an explosion in this combination than in the other liquid propellant combinations studied previously.

9.3.1 Adiabatic Compression Sensitivity of Nitrous Oxide

Adiabatic compression of N_2O gas into 51-mm (2-in.) tubes at about 283 K ($10^\circ\text{C} = 50^\circ\text{F}$) temperature would not start monopropellant decomposition at compression rates of 4.1 MPa/s (600 psi/s), but monopropellant decomposition would occur at higher gas compression rates near 6.9 MPa/s (1000 psi/s) [202]. In the 51-mm tubes, N_2O monopropellant decomposition was observed to quench as added cool N_2O gas was admitted to the reaction vessel. Decomposition reaction quenching was expected to be less likely as the container being pressurized became larger in diameter. The threshold adiabatic compression rate to initiate N_2O decomposition at 293 K (20°C) would be expected to attain a fixed minimum value once some critical vessel diameter was exceeded. That critical vessel diameter is unknown, but the diameter is likely to exceed the 51 mm diameter (2 in.) that was used during testing. The threshold minimum pressurization rate at 293 K (20°C) in a larger diameter would likely fall to a value less than the 6.9 MPa

(1000 psi/s) observed at the 51 mm (2 inch) diameter employed during these adiabatic compression tests [311].

Cavitation involves the rapid formation and collapse of vapor bubbles in flowing liquids. Cavitation in turbopumps and in propellant feed systems must be avoided if the fluid is potentially detonable, like nitrous oxide. A computer simulation of the liquid phase flow of nitrous oxide under high pressure was used to predict and avoid the cavitation in the feed system lines of rocket engines [312]. The method involved a substantially simplified 1-D description of the fluid motion with sufficiently accurate determination of cavitation risk where the feeding duct exhibits blunt variations of the cross area or steep turns and corners involving sensible static pressure variations of the fluid.

9.3.2 Boiling Liquid Expanding Vapor Explosion (BLEVE) of Liquid Nitrous Oxide

Even without a chemical reaction leading to the decomposition of nitrous oxide, the rupture of a pressurized tank containing liquid N_2O can cause substantial damage. Similar explosions can occur with more inert cryogenic liquids or condensed liquids under their own vapor pressure at room temperature such as CO_2 or LPG. These types of physical explosions are called **Boiling Liquid Expanding Vapor Explosion (BLEVE)**. The behavior of nitrous oxide liquid upon instantaneously relieving the pressure in a storage vessel with a burst diaphragm was observed and visually recorded through a window in the test vessel in a series of tests in a remote open-air test area, in an attempt to distinguish whether homogeneous nucleation of bubbles (the defining characteristic of a BLEVE) occurred at a specific test temperature between 250.9 and 271.5 K (−8.1 and +29.1 °F) [313, 314]. The question was also whether a physical explosion BLEVE can heat up the N_2O vapor sufficiently to initiate a chemical explosion. High-speed piezoelectric pressure transducers at the inside of the exhaust duct, above the burst disc, recorded a secondary pressure pulse that was believed to result from a rapid phase transition of the liquid nitrous oxide, releasing large quantities of N_2O vapor in a very short time interval. Close-up videos of the window showed that in all tests, nitrous oxide “ice” crystals were formed in the test vessel. Based upon the review of free-field high-speed pressure data, a BLEVE with the formation of a shock wave occurred when liquid nitrous oxide temperatures were 275 or 269.3 K (29 or 25 °F). A BLEVE was not evidenced when the liquid nitrous oxide temperatures were colder, at 256.2 K (+1.5 °F) and 250.9 K (−8.1 °F). The strength of the shock wave decreased as the liquid nitrous oxide temperature decreased. Even without a shock wave that may indicate a BLEVE event, a large volume of rapidly expanding gas was generated for all tests at all liquid nitrous oxide temperatures, between 250.9 and 271.5 K (−8.1 and +29.1 °F). The rapid phase change from liquid to vapor within 400 ms might have occurred via homogeneous bubble nucleation (characterizing a true BLEVE) or, alternatively, via heterogeneous nucleation promoted by nitrous oxide crystals. None of the rapid releases resulted in a chemical explosion.

9.3.3 Accident History of Nitrous Oxide

9.3.3.1 Explosion Accidents with Nitrous Oxide

A tank truck being loaded with subcooled liquid N_2O (relatively low pressure) exploded in Eindhoven, The Netherlands, on July 2, 2001. An accident investigation concluded that a not properly precooled centrifugal pump was running hot and started decomposition of the nitrous oxide vapor [315, 316]. Another theory believed that following the depletion of the liquid from the storage tank, the pump ran dry and overheated, thus igniting the vapor in the lines. The flame apparently flashed back into the tank, resulting in the rupture of the vessel. Gaseous nitrous oxide at >5.7 bar and in the presence of an ignition source can start a runaway reaction. Flashback into the tank car caused the tank to rupture. The remains of the accident are shown in Figures 45 and 46.



Figure 45: Post-accident scene of N_2O tank car explosion at Eindhoven, The Netherlands. (From [315].)

Early speculation about possible causes of the accident at Scaled Composites in California on July 26, 2007 suggested that the oxidizer tank of the propulsion system under development for Virgin Galactic's SpaceShipTwo suborbital rocket was the origin of the nitrous oxide explosion that killed three employees. The explosion occurred at the Rocky propulsion test site, which Scaled Composites rented from the Mojave Air and Space Port. One of the accident reports described the sequence of events as follows: "The workers had transferred the nitrous oxide from the [mobile conditioning system] into the propulsion equipment apparatus tank mounted on the test stand. The catastrophic explosion occurred about 3 s after the [cold nitrous oxide] flow began."

Information on nitrous oxide explosions during production and storage is not always very well documented. There is a report of an explosion of a gas bottle being filled



Figure 46: Remnants of N_2O tank car after tank car explosion at Eindhoven, The Netherlands. (From [315].)

with nitrous oxide gas in Berlin dating back to the year 1900 [317]. The gas bottle, presumably empty, heated up and exploded, which, in all likelihood, was caused by the presence of easily oxidizing organic contaminant compounds in it, but certainly not by N_2O decomposition.

A very detailed study sponsored by USAF in 1974 [202] made reference to “at least one instance of an unexpected and violent decomposition reaction” without revealing possibly classified details, but the incident(s) exposed the need for additional information defining the conditions under which N_2O can be decomposed and prompted an investigation into its safety and handling characteristics.

At about 1645 hours on Friday, July 6, 1973, a heated, pressurized tank of gaseous nitrous oxide exploded and burned on the B-8 test stand at Pratt & Whitney Aircraft at West Palm Beach, FL, where preparations were underway for testing an N_2O -CO laser combustor. Although there were no personal injuries, significant property damage occurred. A detailed description of the damage and test history was published [318]. The report contains numerous pictures of the damage, but unfortunately the pictures in the copy that could be downloaded from the internet were faded and could not be reproduced here. The pressure vessel holding the N_2O gas was made of 304 stainless steel, had walls that were 38 mm (1.5 in.) thick, and had four access openings. Both the supply line to the top and the run line from the bottom were connected to pressure relief valves set to open at 9.48 MPa gauge (1375 psig). The tank was reported to have been hydrostatically tested to its working pressure (12.4 MPa gauge at 294 K = 1800 psig at 70 °F) before the test. The tank and all components had been cleaned to

LOX standards. Four gas samples of N_2O from the run tank had been taken prior to the explosion, and the results of these analyses produced no evidence of decomposition while the gas was heated to 478 K (400 °F). Prior tests had used N_2O at 378 K (220 °F) and pressures up to 10.3 MPa gauge (1500 psig) without any undue events. The target conditions for this planned test were 478 K (400 °F) and 8.96 MPa gauge (1300 psig). In an effort to equilibrate temperatures in the run line prior to test, hot gas from the tank was admitted to a non-pressurized segment of the line. Approximately 5 s after the remotely operated valve signal light indicated an open position, system failure occurred. The 74-mm (3-in.) line at the top of the tank and both 3.1 mm (1/8 in.) threaded fittings holding pressure and temperature probes failed, resulting in large holes in the tank wall. Some damage occurred in the 51 mm (2 in.) run line: the Teflon seat of the valve disintegrated, and the stainless screen filter exhibited a few localized areas of ignition. The ball-bearing assembly of the flow meter was rendered inoperable due to complete burnout or disintegration of the bearing cage. The tank yielded about 5% in circumference, and the calculated pressure to achieve this yield was 41.4 MPa (6000 psig). It was postulated that opening a remotely operated valve allowed hot N_2O to suddenly pressurize the hot (413 K = 315 °F) ambient pressure nitrogen gas trapped in the run line between the valve and the laser reactor. Raising the pressure of this nitrogen isentropically to the tank pressure of 8.96 MPa gauge (1300 psig) would increase its temperature to 1366 K (2000 °F), well above the N_2O ignition temperature. The ignited N_2O could then burn back through the run line to the main tank and ignite the bulk of the mixture. There is another report of an explosion at a Puritan Bennett's (a medical gas supplier) manufacturing plant in Richmond, CA, in 1981 [319].

An explosion of a nitrous oxide trailer truck at an Airgas facility at Pensacola, Cantonment, Florida on August 8, 2016 resulted in one fatality and severe damage to the facility. It was determined that the explosion occurred due to overheating of the nitrous oxide pump during loading of the truck [305]. The feed to the Airgas nitrous oxide process was a by-product gas from a chemical manufacturing facility adjacent to the Airgas facility. This feed gas contained primarily nitrous oxide, nitrogen, oxygen, and carbon dioxide. At the time of the incident, Air Liquide owned and operated all five nitrous oxide manufacturing facilities in the United States and Canada. The Chemical Safety Board identified six previous major explosion incidents in the nitrous oxide industry that occurred before the explosion at Cantonment. Since 1973, the nitrous oxide industry has averaged one major explosion about every 7 years. These incidents killed 6 workers and injured 21 other people. Since 2001 these explosions have occurred more frequently, with an average of one explosion every 4 years during this timeframe.

9.3.3.2 Poisoning and Suffocation Accidents with Nitrous Oxide

The following information is lifted and quoted from CGA Fact Sheet and may require additional editing [320]. We quote verbatim:

Nitrous oxide fact sheet

What is nitrous oxide?

Nitrous oxide (N_2O) is a clear, colorless, oxidizing liquefied gas with a slightly sweet odor. The product is stable at room temperature. While classified by the US Department of Transportation (DOT) as a non-flammable gas, nitrous oxide will support combustion and can detonate at temperatures in excess of 650 °C (1202 °F). Contact your supplier to obtain a nitrous oxide Safety Data Sheet (SDS) for information on the safe handling and security of this product.

What are the principal applications of nitrous oxide?

Nitrous oxide finds beneficial use in a number of legitimate applications such as:

- Medical/dental anesthesia and analgesia
- Food processing propellant
- Semiconductor manufacturing
- Analytical chemistry
- Chemical manufacturing
- Auto racing engine injection

Nitrous oxide is blended with oxygen when used in anesthesia applications. Pure nitrous oxide will cause asphyxiation, resulting ultimately in respiratory arrest. Nitrous oxide in auto racing applications is denatured to deter inhalation. Nitrous oxide, used in food propellant applications, is typically supplied to commercial packagers of pressurized food dispensing containers.

Effects of nitrous oxide on the human body

Nitrous oxide's painkilling and numbing qualities begin to take effect when the gas is inhaled at concentrations of 10 percent. At increasingly higher concentrations, a sense of well-being, or "high," is experienced. A person experiencing a nitrous oxide high could:

- Have slurred speech
- Have difficulty in maintaining his or her balance or walking
- Be slow to respond to questions
- Be immune to any stimulus such as pain, loud noises, and speech
- Lapse into unconsciousness

Nitrous oxide that is inhaled accidentally over a long period of time at places of employment can lead to a vitamin B_{12} deficiency. When the level of vitamin B_{12} in the body is reduced, the red blood cell count is lowered, anemia results, and nerves degenerate. A vitamin B_{12} deficiency causes a person to have painful sensations in the arms or legs, have an unsteady walk or gait, become unbalanced and tend to fall over, feel or appear to be irritable, or even suffer intellectual deterioration.

What Are the Dangers?

Nitrous Oxide readily displaces air, causing asphyxiation. A person who is rendered unconscious by nitrous oxide is likely to stop breathing within a few seconds as a result of a depressed central nervous system, brain, brain stem, and spinal cord. Depression is caused by a combination of the effects of nitrous oxide and the lowered oxygen content that occurs as pure nitrous oxide displaces oxygen from the lungs with each succeeding inhalation of the gas; i.e., the person is asphyxiated.

Tragedy can occur very quickly. Long-term exposure (several minutes) is not necessary before death occurs. Sudden, prolonged exposure to high levels of nitrous oxide, or a series of inhala-

tions (without breathing clean air between inhalations) can result in death. The length of this action can be measured in seconds. Since the narcotic effect of nitrous oxide is very brief (several seconds) abusers tend to follow this repetitive action pattern.

If a person remains conscious and stops breathing the nitrous oxide, recovery (full consciousness and alertness) can occur within minutes. A person who loses consciousness, however, and continues to inhale a pure gas is most likely to die. Death usually occurs when abusers, in their attempt to achieve a higher state of euphoria, breathe pure nitrous oxide in a confined space, such as in a small room, inside an automobile or other vehicle cab, or by placing their head inside a plastic bag.

If death does not occur, the person who suffers from these symptoms may recover from all of them. The debilitating process is reversible, although some persons have experienced permanent loss of balance.

Abuse of nitrous oxide as an inhalant is on the rise, as is evidenced by the increased media attention to the subject. Its abuse has grown significantly at concert venues and on college campuses. Dealers will typically fill balloons with nitrous oxide and sell them. Police and other enforcement officials have found empty and/or discarded cylinders at the end of concerts. In some cases, dealers have removed required labels that identify cylinder contents and that provide information about safe use.

While most of the publicity regarding nitrous oxide abuse focuses on its occurrence at concerts, nitrous oxide abuse for recreational purposes is equally prevalent among individuals and small groups in settings far removed from the concert hall.

Theft of cylinders has made nitrous oxide available to people who are seeking the euphoric qualities of the gas, but who are unaware of the hazards of abusing nitrous oxide. People typically steal the cylinders from distributors or legitimate users or falsely represent themselves as legitimate users.

Guidelines to prevent nitrous oxide theft

CGA recommends the following guidelines for nitrous oxide sales and security. These guidelines are intended to help implement principles of product stewardship and to identify sufficiently responsible control measures that will minimize the theft of nitrous oxide and deter its abuse. These guidelines are established for the following groups:

PRODUCERS

Producers are anyone who produces nitrous oxide and then purifies, compresses, and liquefies this product for storage, shipment, and sale to a second party.

It is recommended that producers:

Establish a written sales policy that identifies legitimate applications for nitrous oxide, that may include but is not limited to medical, industrial, and food-based uses;

Restrict sale of nitrous oxide to those who can substantiate the legitimate use of nitrous oxide, as enumerated above;

Establish a written policy that clearly defines conditions for cash sales of nitrous oxide (e.g., all cash sales must be accompanied by a driver's license and a certified document that identifies the company or medical practice that will use the product);

Provide customers with a current SDS and any additional instructions for proper use and safe handling practices;

Provide this nitrous oxide fact sheet to customers;

Alert employees and customers to the dangers of nitrous oxide abuse.

Non-Bulk producers should keep an inventory of both full and empty cylinders and investigate any discrepancies.

Bulk producers (having large non-portable storage containers) should have a policy to investigate any tampering or vandalism of their bulk storage container.

COMMERCIAL CARRIERS

Commercial carriers are anyone who transports for hire nitrous oxide by road, rail, sea, or air.

It is recommended that commercial carriers:

Take appropriate steps to prevent the theft of nitrous oxide cylinders, both full and empty, since empty cylinders may contain residual product.

Keep cylinders in a secure area when on company premises.

Do not leave a delivery vehicle unattended without limiting access to nitrous oxide cylinders.

Keep an inventory of both full and empty cylinders and investigate any discrepancies.

Report any thefts promptly to the police and the shipper.

Alert employees to the dangers of nitrous oxide abuse and train them on the special security measures they should take to prevent its theft.

CONTAINER FILLERS OR DISTRIBUTORS

Container fillers and distributors are anyone who transfers nitrous oxide from a bulk vessel to cylinders, and anyone who sells nitrous oxide to medical, industrial, food, and other legitimate users.

It is recommended that container fillers or distributors:

Establish a written sales policy that identifies legitimate applications for nitrous oxide, that may include but is not limited to medical, industrial and food-based uses;

Restrict sale of nitrous oxide to those who can substantiate the legitimate use of nitrous oxide, as enumerated above;

Establish a written policy that clearly defines conditions for cash sales of nitrous oxide (e.g., all cash sales must be accompanied by a driver's license and a certified document that identifies the company or medical practice that will use the product);

Sell denatured (e.g., rendered unfit for human consumption) nitrous oxide for enhancing performance of internal combustion engines, so as to deter abuse;

Screen existing nitrous oxide accounts to assure that all are legitimate users of nitrous oxide;

Provide customers with a current SDS and any additional instructions for proper use and safe handling practices;

Provide this nitrous oxide fact sheet to customers;

Take the following steps to prevent the theft of nitrous oxide cylinders, both full and empty, since empty cylinders may also contain residual product:

Keep cylinders in a secure area when on company premises;

Do not leave a delivery vehicle unattended without limiting access to nitrous oxide cylinders;

Keep an inventory of both full and empty cylinders and investigate any discrepancies;

Report any thefts promptly to the police and the supplier;

Alert employees and customers to the dangers of nitrous oxide abuse and train them on the special security measures they should take to prevent its theft.

LEGITIMATE USERS

Legitimate users are anyone who can substantiate a medical, industrial, food, or other legitimate use for nitrous oxide.

It is recommended that legitimate users:

Minimize theft and indiscriminate use of nitrous oxide by storing containers and utilization equipment in a secured area subject to removal by authorized personnel only;

Keep an inventory of bulk product and or containers (both full and empty) and investigate any discrepancies;

Report any thefts promptly to the police and the shipper;

Use denatured (e.g., rendered unfit for human consumption) nitrous oxide, if required, for enhancing performance of internal combustion engines, so as to deter abuse;

Alert employees to the dangers of nitrous oxide abuse and train them on the special security measures they should take to prevent its theft;

Provide employees with a current SDS and any additional instructions for proper use and safe handling practices.

Contact your supplier to obtain a nitrous oxide Safety Data Sheet (SDS) for information on the safe handling and security of this product.”

Compressed Gas Association, 14501 George Carter Way, Suite 103, Chantilly VA 20151-2923; Phone: 703-788-2700; Fax: 703-961-1831; Email: cga@cganet.com

10 Handling of Nitrous Oxide

10.1 Disposal of Nitrous Oxide

Disposal methods for nitrous oxide depend on the concentration of N_2O and diluents present. We need to differentiate between disposal of process streams that contain $>90\%$ N_2O or disposal of combustion products or exhaled air in operating rooms that may contain only less than 1% N_2O .

10.1.1 Abatement and Destruction of Nitrous Oxide in Stack Gases

Nitrous oxide in combustion products and stack gases from industrial power plants is a contaminant that is more difficult to remove than NO_x . Nitrous oxide is a greenhouse gas that contributes to global warming. For this reason, methods are sought to remove N_2O from stack gases along with the more reactive $\text{NO}/\text{NO}_2/\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$ gases. Prior to the concern about greenhouse gases, a substantial effort was implemented to remove NO_x from stack gases, sometimes using ammonia, cyanuric acid, or urea as reductants in a so-called *selective non-catalytic reduction* process. While this process achieved the initial objective of NO_x reduction, it at the same time created a new problem by increasing the N_2O emissions. Thus, additional technology was sought to remove N_2O from stack gases. Undiluted nitrous oxide that is no longer needed or has become contaminated should not simply be vented to the atmosphere where it would aggravate the problem with global warming due to greenhouse gases. The gas can be fed to a flare torch and burned with natural gas or propane (and releasing CO_2 , which is not as bad as N_2O). Reburning with hydrogen, carbon monoxide, methane, or ethylene in a jet-stirred reactor has been studied as a means of N_2O destruction in stack gases [321].

Instead of consuming a valuable fuel like methane in the removal of nitrous oxide, it would be less energy intensive to pass the stack gases over a catalyst that decomposes the nitrous oxide into harmless nitrogen and oxygen. It turns out that catalysts

developed for industrial N_2O removal may also be useful as catalysts for rocket engines using N_2O as a monopropellant and vice versa.

Instead of simply thermally preheating the gases that have to be purified of N_2O one can pass them through an arc discharge. The presence of catalysts in this plasma-catalytic N_2O removal process greatly accelerated the rates of N_2O destruction [322]. A rotating arc discharge, combined with a catalytic bed, has been tested for nitrous oxide removal in oxygen-containing stack gases. It has been found that under conditions of a rotating arc, nitrous oxide in mixtures with oxygen or air not only decomposed to oxygen and nitrogen but was also oxidized to nitric oxide. The overall conversion of nitrous oxide, as well as the degree of N_2O oxidation to NO , were studied as a function of its initial concentration, flow rate, and discharge power. The overall N_2O conversion and degree of oxidation to NO decreased with increasing flow rate and initial N_2O concentration and increased with increasing discharge power. The degree of N_2O oxidation to NO varied within 20–37%. The overall conversion and degree of N_2O oxidation increased when granular dielectric materials (TiO_2 , SiO_2 , $\gamma\text{-Al}_2\text{O}_3$) were introduced into the reaction zone. The energy efficiency and the overall conversion of N_2O were still further increased due to catalytic effects of a number of metal oxides (CuO , NiO , MnO_2 , Fe_2O_3 , Co_3O_4 , ZrO_2) deposited on $\alpha\text{-Al}_2\text{O}_3$. The activity of the oxide catalysts decreased in the order: $\text{CuO} > \text{Fe}_2\text{O}_3 > \text{NiO} > \text{MnO}_2 > \text{Co}_3\text{O}_4 > \text{ZrO}_2$. It has been suggested that the combined plasma-catalytic processing may be an efficient way to reduce N_2O emissions.

The thermal (non-catalytic) decomposition of N_2O was studied in order to establish an industrial process for N_2O abatement in an adipic acid production plant. N_2O from an adipic acid plant was decomposed in a plug-flow reactor under atmospheric pressure at temperatures of less than 1500 K [323]. For a model simulating the conversion of N_2O and NO , it was assumed that the reaction was carried out in an adiabatic reactor incorporating a completely uniform mixing system. The results of the simulation indicated that N_2O at concentrations between 30 and 50 vol-% is spontaneously decomposed into N_2 , O_2 , and NO at a reaction temperature between 1273 and 1473 K by using its own heat of reaction.

10.1.2 Removal of Nitrous Oxide in the Air in Operating Rooms

The gas administered to patients for anesthesia may contain up to 70 vol.-% N_2O with the rest being oxygen. A majority (70%) of patients achieved ideal sedation with between 30 and 40% N_2O . The exhaled air from patients may contain up to 50 vol.-% N_2O . Because nitrous oxide is minimally metabolized in humans (with a rate of 0.004%), it retains its potency when exhaled into the room by the patient and can pose an intoxicating hazard to the attending clinic staff if the room is poorly ventilated. If the exhaled air diffuses into the ambient air in the operating room, and the room is not properly ventilated, N_2O concentrations can build up to a level where they begin to affect medical personnel attending to the patient. Methods have been sought to remove N_2O from the air in operating rooms [324, 325].

10.1.3 Disposal of High Concentrations of Nitrous Oxide

If liquid nitrous oxide intended to be used in a flight application in the Airborne Laser Laboratory is no longer needed, it has to be dumped overboard because the aircraft cannot land safely with the extra propellant mass on board, and a contingency plan for in-flight dumping of N_2O has to be developed. The problem is that the liquid may freeze as soon as it expands and clog the discharge orifices. The sudden accidental freezing of liquid N_2O during rapid discharge from an airborne tank would prevent the aircraft from dumping the unwanted propellant in order to reduce its touchdown mass. The freezing of flowing N_2O has been studied in several oxidizer dump tests [91, 92]. Analysis of the liquid dumping showed that solidification of the liquid N_2O might occur if the pressure in the line falls below 87 kPa (12.7 psia). Flow experiments were run with the liquid N_2O dumping into a large vacuum chamber that simulated the high-altitude environment during flight. In seven tests, 6–12 kg (12–24 lb_m) liquid N_2O were expelled either under its own vapor pressure or with helium pressurant 8.27 MPa (1200 psia) in the ullage space above the liquid. The flow rates were 1.45 to 3.6 kg/s (3.2 to 8 lb_m/s). The piping configuration used in the tests was identical to that of the airborne system. The tests showed that the pressure at the dump line exit remained above 87 kPa (12.7 psia) for all conditions tested; therefore, no solidification occurred in the lines. The N_2O transformed to snow after it exited from the dump line and entered the vacuum chamber.

11 Other Uses of Nitrous Oxide

Most books with the title “Nitrous Oxide” deal only with the medical use of nitrous oxide as an analgesic and anesthetic agent [326, 327]. The main uses for nitrous oxide are in medicine as an analgesic and anesthetic agent and in food chemistry as a pressurant and foaming agent for whipped cream in spray cans. It is preferred over other pressurants for food application because it is bacteriostatic (stops bacteria from growing) and leaves no taste or odor in the whipped cream. Nitrous oxide was used as a refrigerant in the past, but that use has been discontinued. Although it has a relatively high ozone depletion potential, it is still better than some of the halocarbons it was intended to replace for low-temperature refrigeration. ASHRAE, in a recent version of Standard 34.1 designates it as R744a or R744A. An extremely pure grade of nitrous oxide is used for etching semiconductors.

Nitrous oxide injection is used in “souped up” racing cars for increased performance [328]. Nitrous oxide for racing car use is denatured with an odorant to discourage inhalation. There are images on the internet of racing cars bursting in flames after being “souped up” by nitrous oxide injection.

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Noble Gas Fluorides

Until half a century ago, generations and generations of chemists were taught that gases in IUPAC Group 18 of the periodic table of elements will not enter into **any** chemical reactions. They were a class by themselves, they did not want to mingle with common elements, and therefore they were called “noble” gases. This changed in the 1960s, when in short succession fluorides, oxyfluorides, hydroxides, and oxides of xenon and krypton were synthesized, and those events opened new vistas on the nature of the chemical bond. Chapters in many chemistry textbooks had to be rewritten after this discovery. The section at hand contains only a short summary of literature references reflecting the excitement that prevailed among fluorine chemists in the 1960s when the first noble gas fluorides were discovered. Many more publications have appeared in the interim, but listing them all would fill an entire book by itself.

To date, noble gas compounds have been mostly a chemical curiosity and have not found industrial applications (except some noble-gas/fluorine mixtures in lasers). Most of the noble gas compounds are solids that cannot be used in liquid rocket engines. Although xenon is now used as a working fluid in electric rockets, the limited supply of the heavier noble gases will prevent the use of these compounds as chemical rocket propellants. We list them here only in the hope that one of these days the fluorides and oxides of the lighter noble gases, such as argon, neon, or even helium (!!), will be synthesized and tested as rocket propellants (as unlikely that seems to be possible at this time). Noble gas fluorides are listed here only because the study of noble gas fluorides has provided a better understanding of the chemical bond in all covalent fluorides, and that knowledge benefits the synthesis of other fluorides, which may be suitable as rocket propellants.

Along with noble gas fluorides, noble gas oxides and oxyfluorides have been synthesized. Noble gas oxyfluorides, ternary noble gas/oxygen/fluorine compounds, will be discussed in a separate, subsequent chapter of this book. If they could be made cheaply, they should also be evaluated as rocket propellants.

There are many summary publications on the chemistry of noble gas fluorides, and only a few are given here [1–7]. In addition to binary noble gas fluorides, there are also ternary noble gas compounds containing both oxygen and fluorine.

A historical (not up-to-date) summary of observed properties of some noble gas fluorides is given in Table 1.

1 Preparation of Noble Gas Fluorides

A substantial amount of high-energy activation is required to get noble gases to react with elemental fluorine. Methods used are high pressure combined with high temperature, glow discharge, UV photolysis, and laser irradiation.

Table 1: Historical summary of first properties of noble gas fluorides reported in the literature.

Compound name	Chemical formula	Properties	References
Krypton difluoride	KrF ₂	So far only seen spectroscopically, short-lived	[8]
Krypton tetrafluoride	KrF ₄	Colorless, clear crystals, vapor pressure somewhat higher than that of XeF ₄ , thermally less stable than XeF ₄ , sublimates at 233 to 243 K (–40 to –30 °C) in vacuum	[9, 10]
Xenon difluoride	XeF ₂	Colorless, clear crystals, heat of sublimation 51.5 ± 0.8 kJ/mol (12.3 ± 0.2 kcal/mol)	[11–16]
Xenon tetrafluoride	XeF ₄	Colorless, clear crystals, can be sublimed undecomposed in vacuum. Melting point above 373 K (100 °C), heat of sublimation 64.0 kJ/mol (15.3 ± 0.2 kcal/mol), Molar heat capacity $C_p = 188$ J mol ^{–1} °C ^{–1} (45 cal mol ^{–1} °C ^{–1}), Entropy $S_{298} = 360$ J mol ^{–1} °C ^{–1} (85.9 cal mol ^{–1} °C ^{–1})	[17–20]
Xenon oxyfluoride	XeOF ₂	Colorless crystals	[9]
Xenon hexafluoride	XeF ₆	Colorless crystals, melting point 319 K (46 °C), vapor pressure at 273 K = 0 °C: 1 kPa = 7.5 mm Hg, at 298 K = 25 °C: 4 kPa = 30 mm Hg, turns yellow at temperatures above 315 K = 42 °C in all physical states; Other sources gave the melting point as 322.63 ± 0.10 K, and the enthalpy of fusion as 5743 J/mol.	[21, 22]
Radon fluorides		Not yet identified for sure	

This table has not been updated and is included here only as part of a historical account of noble gas fluorides.

The photolysis by laser radiation (488 nm) of Kr, Xe, O₂, and UF₅ dissolved in liquid fluorine resulted in the formation of KrF₂, XeF₂, O₄F₂ or O₂F₂, and UF₆, respectively [23]. No reaction product was observed as the result of laser photolysis of liquid fluorine saturated with Ar, N₂, IF₅, RuF₅, or OsF₆.

1.1 Preparation of Xenon Fluorides

It appears that the walls of Monel pressure vessels in which the high-pressure synthesis of xenon fluorides is carried out have a distinct catalytic effect on the reaction [24]. The formation of xenon fluorides is not a homogeneous gas-phase reaction. The reactions are heterogeneous and occur for the most part on the fluorinated walls of the Monel reaction vessels. CoF₃ or NiF₂ also exhibited catalytic activity in fluorine-xenon reactions. See also [25–29].

1.2 Preparation of Krypton Fluorides

Krypton fluorides can be prepared using methods similar to those used for xenon fluorides [30, 31].

2 Physical Properties of Noble Gas Fluorides

The physical properties and molecular structures of noble gas fluorides have often been derived from optical or X-ray diffraction (XRD) measurements [32–41].

2.1 Thermodynamic Properties of Noble Gas Fluorides

Although noble gas fluorides are not likely to be used as rocket propellants, their thermodynamic properties have been summarized here just in case someone wants to run theoretical rocket performance calculations. Knowledge of thermodynamic properties also will help to predict the thermal stability of these compounds under different temperature and pressure conditions and will help optimize the conditions for the formation of these compounds during their synthesis from the elements [42, 43].

The standard entropy of formation of solid XeF_4 at 298 K was found to be $-407.95 \pm 0.17 \text{ J K}^{-1} \text{ mol}^{-1}$, and the standard Gibbs energy of formation at 298 K was $-145.48 \pm 0.88 \text{ kJ/mol}$ [44]. The corresponding quantities for gaseous XeF_4 at 298 K were $-250.97 \pm 0.40 \text{ J K}^{-1} \text{ mol}^{-1}$ and $-131.36 \pm 0.91 \text{ kJ/mol}$. The standard enthalpies of formation of the solid and of gaseous xenon tetrafluoride at 0 K were $-266.29 \pm 0.88 \text{ kJ/mol}$ and $-201.39 \pm 0.90 \text{ kJ/mol}$, respectively. The equilibrium constant for the formation of gaseous XeF_4 from the elements at various temperatures was tabulated and compared with experimental measurements.

The melting point of XeF_6 is $322.63 \pm 0.10 \text{ K}$, and the enthalpy of fusion is 5743 J/mol . The vapor pressure of the liquid between 323 and 350 K can be calculated by

$$\log P = -6170.88/T - 23.67815 \log T + 80.77778$$

where P is the vapor pressure in mm Hg and T is the temperature in kelvin. The high entropy of vaporization ($136.9 \text{ J K}^{-1} \cdot \text{mol}^{-1}$) at the boiling point (348.72 K) and the high and rapidly rising heat capacity of the liquid suggest that the liquid is associated [45]. Thermodynamic functions of the condensed phases were tabulated at various temperatures. At 298 K the values of C_p° , S° , $H^\circ - H0^\circ$, and $(G^\circ - H0^\circ)/T$ for solid XeF_6 were $171.59 \text{ J K}^{-1} \text{ mol}^{-1}$, $210.38 \text{ J K}^{-1} \text{ mol}^{-1}$, 30999 J/mol , and $-106.41 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. At 355 K the standard entropy S° was $255.5 \text{ J K}^{-1} \text{ mol}^{-1}$ for liquid XeF_6 and $402.6 \text{ J K}^{-1} \text{ mol}^{-1}$ for the gas.

2.2 Chemical Properties of Noble Gas Fluorides

2.2.1 Complex Salts with Noble Gas Fluorides

Reactions of xenon hexafluoride with tin(IV) fluoride [46], germanium tetrafluoride or silicon tetrafluoride, [47] and arsenic pentafluoride or phosphorus pentafluoride [48] result in the formation of complex salts of the XeF_5^+ cation.

The IR and Raman spectra of solid $\text{XeF}_5^+\text{BF}_4^-$ and $\text{XeF}_5^+\text{AsF}_6^-$ and their Raman and ^{19}F NMR spectra in HF solution were recorded [49]. The observed spectra were consistent with a square-pyramidal XeF_5^+ cation of symmetry C_{4v} .

Xenon tetrafluoride forms stable 1:1 adducts with $(\text{CH}_3)_4\text{NF}$, CsF, RbF, KF, and NaF [50]. These adducts are salts containing a planar pentagonal pentafluoroxenate(IV) XeF_5^- anion, as shown by XRD crystal structure determinations and IR, Raman, and NMR spectra.

Noble gas fluorine oxidizers of neon, krypton, argon, and xenon have been synthesized and characterized, and KrF^+ and XeF^+ cations have been made with neutral organic bases. Even Kr-N and Kr-O bonded molecules were synthesized and characterized and the hypervalent compound XeF_5^- was made [51–53]. See also [54].

3 Ternary Fluorides

By way of definition, we call binary fluorides those that contain only one type of atom that is different from fluorine. Examples are ClF_3 and NF_3 . We call ternary fluorides those compounds that contain two different atoms other than fluorine. Examples are XeOF_4 and XeO_2F_4 .

4 Noble Gas Oxyfluorides

Along with noble gas fluorides, the discovery of noble gas oxides and noble gas oxyfluorides has opened a new chapter of fluorine chemistry. Both are theoretically energetic rocket propellant oxidizers, but they are not practical because they are available only in limited quantities. It would be desirable to make similar compounds with argon, but that has not yet been accomplished.

4.1.1 Preparation of Noble Gas Oxyfluorides

Xenon oxide tetrafluoride, also known as xenon fluoride oxide, XeOF_4 , CAS RN [13774-85-1], can be prepared by partial hydrolysis of XeF_6 using either dynamic or static methods. In the static methods XeF_6 is reacted with either H_2O or SiO_2 . These reactions, particularly on a larger scale, are very hazardous and, unless great care is exercised, can result in violent explosions due to the localized accumulation of highly

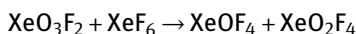
explosive XeO_3 . This hazard of the static methods can be diminished somewhat by the dynamic method of bleeding air saturated with water vapor into a circulating loop filled with XeF_6 vapor and monitoring the XeF_6 consumption by IR. The reaction of NaNO_3 with a slight excess of XeF_6 provides a convenient, one-step synthesis of XeOF_4 according to [55]



Alkali metal nitrates and NO_2 are useful reagents for the stepwise replacement of two fluorine atoms by one oxygen atom in xenon fluorides or oxyfluorides. Thus, the reaction of an excess of XeF_6 with CsNO_3 yields XeOF_4 , FNO_2 , and CsXeF_7 . The reaction of XeF_6 with CsNO_3 in excess gave CsXeOF_5 and FNO_2 , and after longer reaction times some CsXeO_2F is also formed. The reaction of CsNO_3 with an excess of XeOF_4 produced mostly FNO_2 and XeO_2F_2 but also CsF and CsXeOF_5 as byproducts [56, 57].

4.1.2 Physical Properties of Noble Gas Oxyfluorides

Xenon dioxide tetrafluoride, XeO_2F_4 , CAS RN [15195-51-4], was made by the reaction



and identified by mass spectroscopy [58]. It is the most volatile of the known xenon compounds and may therefore possess the symmetrical, non-polar, D_{4h} symmetry. XeO_3F_2 , which originally was made by the reaction of XeF_6 with Na_4XeO_6 , can be made in much better yield by the reaction of XeF_6 with XeO_4 . It is destroyed by more than brief contact with XeF_6 , being converted to XeOF_4 .

The microwave spectrum of XeOF_4 has been measured in the 20–40 GHz range [59, 60]. Transitions were observed for five naturally occurring isotopes of xenon in the ^{16}O species and for two of these isotopes in an ^{18}O -enriched sample. The data support a C_{4v} symmetry for this molecule.

4.1.3 Chemical Properties of Noble Gas Oxyfluorides

Xenon oxide tetrafluoride is a clear, colorless liquid freezing at 224.9 K (-48.2°C) [61]. Its electrical conductivity at 297 K (24°C) is $1.03 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$, and its dielectric constant is 24.8 at 297 K (24°C). It is miscible with anhydrous HF, but its conductivity is not enhanced in such a solution. The addition of CsF or RbF to XeOF_4 increased its conductivity markedly. Xenon oxide tetrafluoride formed a series of addition compounds with the heavier alkali fluorides. The following complexes have been isolated: $\text{CsF} \cdot \text{XeOF}_4$, $3\text{RbF} \cdot 2\text{XeOF}_4$, and $3\text{KF} \cdot \text{XeOF}_4$. Xenon oxide tetrafluoride reacted with SbF_6 to form a complex of composition $\text{XeOF}_4 \cdot 2\text{SbF}_6$. A reaction also occurred with AsF_5 at 195 K (-78°C), but the complex was unstable at room temperature.

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Oxygen

Introduction

Among the oxygen-containing oxidizers we count molecular dioxygen, O_2 , ozone O_3 (“trioxygen”), and also hydrogen peroxide, $H-O-O-H$, a compound that contains an oxygen-oxygen peroxide link. Of course, many other oxidizers contain oxygen but it is bound in some form or another to a non-oxygen central atom like nitrogen or chlorine. Beyond those oxygen compounds well known and thoroughly characterized, we need to look at other oxygen species that are either short-lived at room temperature or can be stabilized at low temperatures. Other poly-oxygen species are either purely speculative, exist only in the mind of some researchers or on paper and computer printouts, but nevertheless it would be tempting to evaluate them as rocket propellants. Some are predicted to exist only at very high pressures, pressures not typically encountered in a rocket engine. *Encyclopedia of Oxidizers*, chapter “Oxygen” and chapter “Ozone” discuss poly-oxygen species either in relation to dioxygen or to ozone.

1 Oxygen

Liquid oxygen, correctly named liquid dioxygen, CAS RN [7782-44-7], commonly abbreviated as LOX (from **L**iquid **O**Xygen), has been the most important rocket propellant oxidizer since the early days of rocketry. It has maintained this leading position for almost a century and in all probability will maintain this position in the future as well. The reason is the unlimited availability of oxygen, which is a constituent of atmospheric air on Earth. Atmospheric air on Earth contains 20.8 vol.-% oxygen, which can be readily separated from nitrogen and the other air constituents.

Oxygen is the most abundant element in the Universe after hydrogen and helium, and therefore it is expected to be present in the solid phase in giant gas planets and “icy” grain mantles of comets and interplanetary particles. Being able to find dioxygen (or oxygen in the form of water) on any extraterrestrial body that might be a destination for future space travel or even planetary colonization would be a great bonus to in-situ resource utilization (ISRU).

2 Production and Availability of Liquid Oxygen

Air separation and liquefaction technology is a mainstay of cryogenic engineering and does not have to be explained here in detail. Most air separation and liquefaction plants produce both liquid oxygen and liquid nitrogen and capture some argon and other noble gases as by-products. Other methods for preparation of oxygen are pressure-swing absorption (up to 90% O_2) and solid electrolyte oxygen separator

(SEOS) technology. An SEOS breadboard demonstration unit was capable of generating >99.9% oxygen at pressures up to 15.1 MPa (2200 psig) using electric power [1, 2]. The oxygen was stored in high pressure cylinders and analyzed per US MIL-PRF-27210. The SEOS method would be suitable for remote locations where cryogenic oxygen as breathing oxygen for military pilots is not available.

Logistics of liquid oxygen for rocket test and launch sites in remote areas require advance planning. Most of the medium-scale portable LOX production equipment is for breathing air for pilots in military airplanes based in remote airfields and not for rocket applications. There are pallet-mounted air separation and liquefaction plants that can be flown in by airplanes, assembled in a few hours, and can generate 360 kg LOX/h [3]. Other LOX generators can be mounted on a semitrailer for transportability [4]. Other generators that can be transported by road or rail have production capacities of 75 metric tons/day and take 5 h to come up to speed. Stationary installations can have capacities of up to 150 metric tons/day [5].

The Joule-Thomson coefficient determines how much a gas cools off or warms up as it expands through a restriction. For the Joule-Thomson effect to take place, the initial gas temperature must be below its inversion temperature. The inversion curve in a temperature-pressure diagram separates regions of positive and negative Joule-Thomson coefficients (Figure 1). The Joule-Thomson coefficient along this curve is

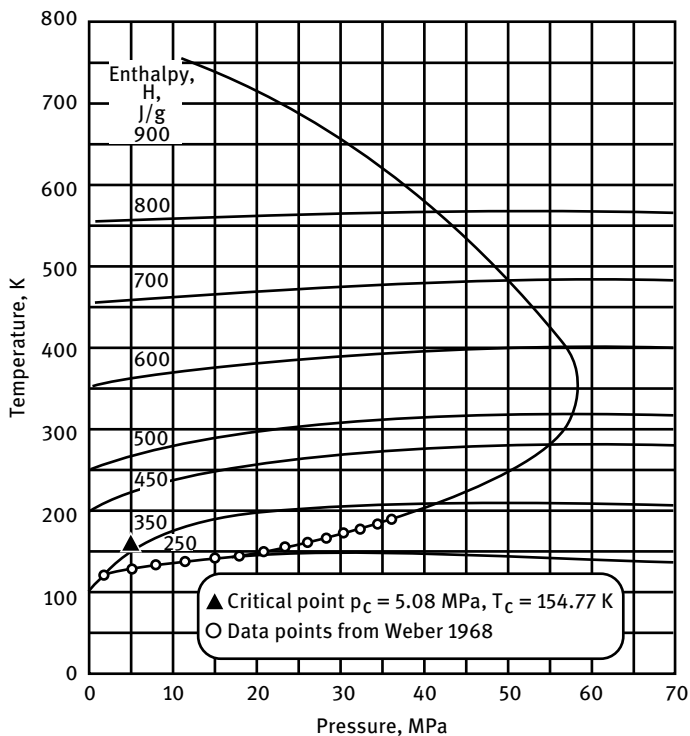


Figure 1: Joule-Thomson inversion curve for oxygen (reproduced and modified from [6])

zero. If the properties of various non-associated, non-polar gases are plotted in terms of their reduced pressure and reduced temperature (properties normalized by their critical point properties), they all share the same inversion curve [6]. There are two inversion temperatures for every pressure. The Joule-Thomson inversion point of oxygen is near 350 K at 58 MPa.

The basic oxygen liquefaction cycle is the Linde-Hampson cycle with variations and improved performance cycles. Alternative liquefaction cycles are the Claude and Collins cycles.

The ideal work required for liquefaction of oxygen beginning at 300 K and 101.3 kPa is 635.6 kJ/kg. The actual optimized theoretical energy requirement of a Linde-Hampson liquefaction cycle is 3804 kJ/kg. The energy consumption for production of one metric ton of LOX from air is approximately 920 kWh. Starting with pure oxygen gas instead of air will reduce the energy consumption to 173 kWh/Mg. Estimates dating back to 1973 for liquefaction work were 630 kWh_e/ton for liquid oxygen and 662 kWh_e/ton for liquid nitrogen, from a production facility that was about 25 and 29% Carnot efficient, respectively.

Liquid and gaseous oxygen is produced in an energy-intensive air separation process that also generates nitrogen. More than 65% of the cost of oxygen is attributable to energy costs [7]. Air separation plants can produce more than three times more nitrogen than oxygen, but present markets demand, at most, only 1.5 times more. Full utilization of liquid and gaseous nitrogen should be encouraged, so that the wasted separation energy is minimized. There are potential markets for nitrogen in production of ammonia for fertilizer.

The largest oxygen consumer (approx. 65% of total oxygen production as of 1979) is the steel industry [8]. If steel plants do not have their own liquid oxygen plant on site, they will often have the oxygen delivered by tank car in liquid form or by pipeline in gaseous form. Rocket technology, steel works and hospitals use a common liquid oxygen supply infrastructure.

The daily production of liquid oxygen in the world was estimated to be 70000 metric tons/day in the 1960s. The annual LOX consumption of the rocket industry peaked in 1966 at 600000 metric tons. This was the time when the F-1 engine and the SATURN-V stages underwent static testing. For a test duration of 150 s, a single F-1 engine would typically consume 500 metric tons of LOX (although some of this was due to evaporation losses during cooldown).

3 Physical Properties of Oxygen

Under normal conditions, oxygen (dioxygen, O₂, CAS RN [7782-44-7]) is a colorless and odorless gas that condenses at 90 K (−183 °C) to form a pale blue liquid. The faint blue tinge can also be observed in liquid air that has been sitting around for a while, allowing the lower boiling, more volatile nitrogen to evaporate first, leaving oxygen behind

and allowing some atmospheric oxygen to condense into the mixture. The molecular mass of dioxygen is 31.9988 g/mol (NIST Chem WebBook).

Physical properties of oxygen and other propellants can be calculated on-line with the reference fluid thermodynamic and transport properties (REFPROP) program developed by the National Institute of Standards and Technology (NIST) [9, 10].

In providing a summary of physical properties of oxygen in the following sections, no effort has been made to evaluate the reliability and accuracy of the data collected from various sources in the literature. The data are shown here in juxtaposition and where more than one source of data is available, the readers will have to decide for themselves which data set fits their application more closely. In many cases the physical properties data are shown in tabular and/or graphical format and, in addition, where possible expressed as polynomial functions of temperature and/or pressure that one can plug into a spreadsheet to generate a more detailed printout of physical properties in increments of one degree of temperature.

Additional data on the physical and thermodynamic properties data of oxygen in various physical states can be found in the references listed in Table 1 and several other tables further down in this chapter.

Table 1: Literature sources on the physical and thermodynamic properties of oxygen.

Topic	Authors	Year	References
Heats, free energies	Wagman	1945	[11]
Thermodynamic properties	Wooley	1948	[12]
Bibliography	Bernstein	1956	[13]
Cryogenic data book	Chelton and Mann	1956	[14]
Cryogenic data book	Chelton and Mann	1959	[15]
Thermodynamic and transport properties	Hilsenrath et al.	1960	[16]
Thermodynamic properties	Brewer	1961	[17]
Thermodynamic properties	Mullins, Ziegler, and Kirk	1962	[18]
Properties	George	1963	[19]
Thermodynamic properties	Mullins, Ziegler, and Kirk	1963	[20]
Pressurized gas systems	Illinois Inst. of Techn. Res. Inst.	1966	[21]
Thermophysical properties	Younglove	1982	[22]
Properties of condensed phase	Verkin, Ghojel, and Selover	1990	[23]
Thermochemical tables	Natl. Inst. of Standards and Technol.	1998	[24]

During the period 1998–1999, the Chemical Propulsion Information Agency (CPIA) released four versions of Cryogenics Information Retrieval System in CD form, including the National Bureau of Standards (NBS) Cryogenics Database, which had not been updated since the early 1980s and a wide range of other literature sources, eventually containing 133000 citations [25].

3.1 Freezing Point and Phase Transitions of Oxygen

3.1.1 Freezing Point of Liquid Oxygen

The parameters characterizing melting of oxygen at the triple point (anomalously low volume jump during melting, fusion entropy, and saturated vapor pressure) distinguish it (along with fluorine) from the simplest molecular systems. The assumption that the γ -O₂ chain structure is preserved in liquid oxygen in the form of a short-range order provides a satisfactory explanation for the observed anomalies. Freezing point data for liquid oxygen are summarized in Table 2.

Table 2: Freezing point and triple point of liquid oxygen.

Freezing point		Authors	Year	References
K	°C			
54.43	−218.71	Giauque and Johnston	1929	[26]
54.8	−218.35	NIST Chemistry WebBook		[27]
54.8	−218.35	Streng	1971	[28]
Triple point				
54.363 K at 1.125 mm Hg	−218.79	Brower and Thodos	1968	[29]
54.361 K at 146.33 kPa	−218.79	Stewart, Jacobsen, and Wagner	1991	[30]
54.36	−218.79	International Practical Temperature Scale	1968	[31]
54.359 ± 0.002 K at 0.001464 bar	−218.79	Weber	1977	[32]
54.363 K at 1.14 mm Hg	−218.79	Hoge	1950	[33]

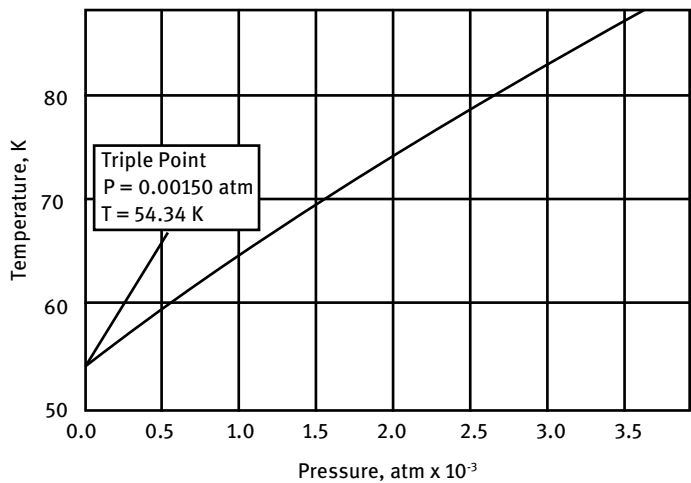


Figure 2: Melting point of solid oxygen as a function of pressure (reproduced and modified from [34])

Solid oxygen will melt at much higher temperatures than 54 K if it becomes pressurized to very high pressures in the order of thousands of atmospheres, as illustrated in Figure 2, based on reference [34].

3.1.2 Phase Transitions of Solid Oxygen

At low temperature and pressures near one atmosphere, three phases of solid oxygen are observed, α , β , and γ . The high temperature γ -phase is stable from the melting point (~ 55 K) down to 43.8 K, where it transforms to the β -phase and is not observed in matrices due to its high vapor pressure. The rhombohedral β -phase converts to the α phase at 23.880 K. The α -phase is monoclinic and the transition from β to α is driven by strain, induced through magnetic interactions with only a small heat of transition. The existence of $\alpha\delta$ phase has been suspected. Considerable experimental effort has gone into the investigation of the solid phase transition temperatures of oxygen because the transitions might be useful as secondary fixed points in thermometry [35]. The triple point of oxygen is the primary fixed point of the International Temperature Scale of 1990 and $\beta \rightarrow \gamma$ and $\alpha \rightarrow \beta$ phase transitions were recommended as secondary fixed points.

Oxygen occurs in at least three, possibly four solid modifications. The structure of α -oxygen was determined by XRD to be monoclinic. The structure of β -oxygen determined from electron diffraction data is rhombohedral. The structure of γ -oxygen was determined by XRD to be cubic. The structure of the δ -solid, if it is verified, is not known [36].

A quasi-harmonic lattice dynamics method coupled with a pattern recognition optimization scheme was used to determine the minimum energy structures and magnetic orientations of solid oxygen [37]. It was shown that the magnetic interaction is responsible for the stability of α O₂ with respect to β -O₂ at zero temperature and pressure. The calculated α O₂ lattice parameters, magnetic orientations, and sublimation energy were in good agreement with experimental data.

Phase transitions in solid oxygen at pressures up to 13 GPa at 298 K were studied by XRD [38, 39] and Raman spectroscopy [40].

Two important factors determine the mechanism and temperature of the $\alpha \rightarrow \beta$ phase transition in solid oxygen: the magnetoelastic coupling, which increases the temperature of the transition and the anti-ferromagnetic order in the β -phase, which stabilizes this phase at low temperatures, thus lowering the transition point [41]. It has been shown that the competition between magnetic and elastic forces leads to an instability of the crystal and, consequently, to the phase transition. The $\alpha \rightarrow \beta$ transition is a first-order reaction.

Solid oxygen is a unique crystalline material combining properties of a simple molecular solid and of a magnet [42]. Unlike ordinary magnets, the exchange interaction in solid oxygen acts on a background of weak van der Waals forces, providing a significant part of the total lattice energy. The magnetic and lattice properties in solid oxygen are very closely related and result in a very complex phase diagram and in nu-

merous anomalies of thermal, magnetic, and optical properties. Diamond anvil cell studies have extended the phase diagram of solid oxygen to the pressure range over 200 GPa and temperatures over 1000 K, thereby revealing an astonishing variety of phases. Pressure-induced changes in crystalline structures are accompanied by modifications of the optical properties. From a light blue transparent crystal, oxygen turns orange and then red at approximately 10 GPa. Upon further compression, the crystal gets darker and becomes nearly opaque to visible light at around 40 GPa. This color change, which is an evident example of how compression can perturb the electronic states of a simple molecule, is a peculiarity of solid oxygen and does not occur in any other diatomic molecular solids. At 96 GPa solid oxygen transforms to a metal retaining the diatomic molecular structure. At low temperatures of 0.6 K and 96 GPa metallic oxygen becomes superconducting. The enthalpy change during the $\alpha \rightarrow \beta$ transition taking place at 23.8 K has been measured by dozens of investigators and varies widely from 73 to 103 J/mol. The structural rearrangement at the $\beta \rightarrow \gamma$ transition at 43.8 K is so essential that the latent heat of transition (742 J/mol) is even larger than the heat of fusion of oxygen. The exact temperature of this transition, 43.7964 ± 0.0002 K, has been defined as a secondary fixed point of the International Temperature Scale of 1990 (ITS 90).

The various phases of solid oxygen have been identified with Greek letters ranging all the way from α to ϕ and beyond, some of which are only encountered at very high pressures up to 20 GPa [43].

The phase transition into β -O₂ occurs at $T = 17.75 \pm 0.2$ K [44]. It is first order with a calculated volume change $\Delta V = 0.06 \pm 0.10$ cm³/mol and is accompanied by a magnetic transition into a highly dynamic quasihelical state with a correlation length $l_c = 8 \pm 1$ Å at 18 K, that decreases rapidly with increasing temperature. The results indicated that O₂ behaves as a two-dimensional magnetic system.

Crystal structures of solid oxygen will be discussed in section “Crystal Structure of Solid Oxygen” further down in this chapter. Solid oxygen can serve as a matrix and stabilizer for solid ozone [45].

In situ high pressure-high temperature Raman measurements and optical observations of solid and fluid oxygen up to 1250 K between 8 and 25 GPa revealed the existence of a new molecular phase η and strikingly unusual behavior of the melting curve [46]. Three triple points were also identified in the P - T domain of the new phase.

Based on Raman scattering and infrared absorption at low temperatures results, a revised phase diagram of thermodynamically stable oxygen has been proposed [47]. In the revised phase diagram, the α phase existed up to temperatures of the β phase and up to a pressure of about 6 GPa, where a clear first-order transition to the δ phase occurred.

Solid oxygen might be encountered in a rocket by accident if the oxygen supply line runs through the liquid hydrogen tank or the two lines run parallel and too close to each other. This would be a very undesirable situation. It is possible that frozen oxygen exists on other gas giant planets in orbit around some distant stars. It is also

possible that frozen oxygen in those planets exists under extremely high pressures. Frozen oxygen under extremely high pressures is unlikely to be encountered in any type of rocket operation, but it is interesting to briefly mention the unusual behavior of frozen oxygen at extremely high pressures. Speculation and a bit of imagination could lead to the suggestion that compressing oxygen could irreversibly lead to new forms of super-oxygen denser and more powerful, but thermally more stable than ozone that could be used as a high-energy, readily available rocket propellant oxidizer. Unusual arrangements of oxygen atoms and dioxygen molecules under high pressures can lead to molecular structures of dioxygen dimers (O₂)₂, trimers (O₂)₃, and molecular oxygen tetramers (O₂)₄, all candidate rocket propellants. Frozen oxygen would be the first choice of oxidizers for cryogenic solid propellants. An inverse hybrid rocket engine firing a mixture of frozen oxygen and gaseous hydrogen was tested at the United States Air Force Phillips Laboratory with promising results.

Slush oxygen, that is a mixture of solid and liquid oxygen, has been considered as an alternate to liquid oxygen in rocket propulsion primarily because the density increases in going from liquid to mixtures of liquid and solid. In 2015, Space-X began flying subcooled oxygen in its Falcon launch vehicles. The higher density of subcooled liquid oxygen allowed them to load more oxidizer in the same size tank.

3.2 Boiling Point of Liquid Oxygen

Boiling point data for liquid oxygen are summarized in Table 3. The boiling point of oxygen was a reference point on the International Practical Temperature Scale.

Table 3: Boiling point of liquid oxygen.

Boiling point		Authors	Year	References
K	°C			
90.2	−182.9	NIST Chemistry WebBook		[27]
90.17	−182.97	Giauque and Johnston	1929	[26]
90.154	−183.006	Aston and Moessen	1953	[48]
90.188	−182.962	International Practical Temperature Scale	1968	[31]
90.2	−182.9	Streng	1971	[28]
90.188	−182.962	Stewart, Jacobsen, and Wagner	1991	[30]

3.3 Density and Partial Molar Volumes of Liquid Oxygen

3.3.1 Density of Liquid Oxygen at Atmospheric Pressure

Density data for solid and liquid oxygen are listed in Table 4.

Table 4: Density of solid and liquid oxygen.

State	Temperature		Density	Authors	Year	References
	K	°C				
Liquid	85	−188	1.1671	Baly and Donnan	1902	[49]
Liquid	77.6	−195.5	1.2019 ± 0.0009	Jenkins and Dipaolo	1956	[50]
Liquid	77.5	−195.6	1.204 ± 0.004	Emelyanova, Strakhov, and Lebedev	1961	[51]
γ-solid	54.3	−218.8	1.372			
α-solid	20.6	−252.5	1.4256			

The density of liquid oxygen for a wide range of pressures can be displayed graphically or printed out as a table by an on-line app on the NIST Chemistry WebBook Fluids web page [52]. A sample calculation for $p = 0.101, 1.01$ and 10.1 MPa and $55 < T < 90 \text{ K}$ is shown in Figure 3.

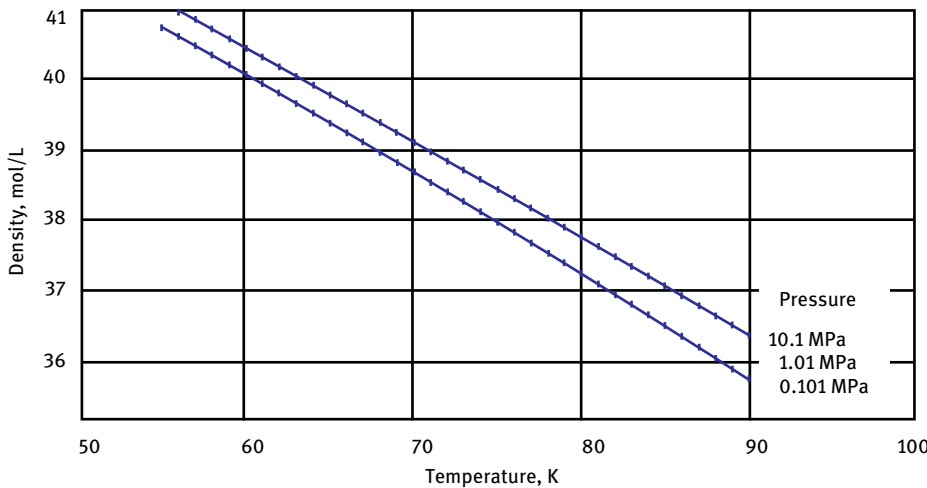


Figure 3: Density of liquid oxygen for $p = 0.101, 1.01,$ and 10.1 MPa (reproduced and modified from [52].)

For additional LOX density data see also [53–56]. The density of the liquid at the triple point is $24.492 \pm 0.02 \text{ cm}^3/\text{mol}$. The density data of liquid oxygen at atmospheric pressure measured by a pycnometric float/sinker method were fitted to a polynomial regression function of the form [57]:

$$\rho = a + bx + cx^2 + dx^3 + 6x^4 + fx^5$$

where ρ is the density in g/cm^3 , T is the temperature in kelvin, $x = (1 - T/T_c)$, and $T_c =$ critical temperature ($T_c = 154.77 \text{ K}$). The coefficients in this equation are: $a = 0.487609$, $b = -0.203117$, $c = 4.624474$, $d = -9.374911$, $e = 9.517905$, $f = -3.590726$.

The density of liquid oxygen at atmospheric pressure as a function of temperature can be expressed by the following simple equation:

$$\rho = 1.248874 - 0.00481(T - 68)$$

where ρ is the density in g/cm^3 and T is the temperature in kelvin. Data for the coefficient of thermal expansion of liquid oxygen at constant pressure are listed in Table 5.

Table 5: Coefficient of thermal expansion of liquid oxygen at constant pressure, α_p .

Temperature	$1/V (dV/dT)$
K	$1/^\circ\text{C}$
90.31	3.95×10^{-3}
77.35	3.81×10^{-3}
90.00	3.95×10^{-3}
80.00	3.84×10^{-3}
70.00	3.73×10^{-3}
65.00	3.68×10^{-3}

Data source: [58, 59]

3.3.2 Density of Liquid Oxygen at Elevated Pressure

The density of liquid oxygen increases at elevated pressures. Density of LOX at up to 148 atm = 14.9 MPa is listed in Table 6 and shown in Figure 4.

The density data in Table 6 and Figure 4 above can be expressed by the equation

$$\rho = A + BP$$

where ρ is the density in g/cm^3 and P is the pressure in atm. The factors A and B are dependent on temperature and can be calculated from the following equations:

$$A = 1.5656 - 4.896 \times 10^{-3}T + 2.136 \times 10^{-6}T^2$$

$$B = (-0.53327 + 0.02824T)10^{-4}$$

where A and B are dimensionless constants and T is the temperature in kelvin.

The measurements at pressures up to 150 kg/cm^2 reported in 1960 suggested a linear dependence of density (= specific weight) of liquid oxygen with pressure; however, more accurate measurements over a wider pressure range at pressures up to 850 kg/cm^2 showed a more complex dependence of $(\partial\rho/\partial P)_T$ with pressure, as shown in Table 7 and Figure 5.

Table 6: Density of liquid oxygen as a function of temperature and pressure.

Temperature		Pressure		Density
K	°C	MPa	atm	g/cm ³
64.66	-208.49	5.14	50.9	1.2642
64.66	-208.49	4.05	40.12	1.2633
64.66	-208.49	2.93	29.04	1.2621
64.66	-208.49	0.80	7.96	1.2608
64.66	-208.49	0.79	7.82	1.2591
74.77	-198.38	4.52	44.75	1.2180
74.77	-198.38	3.45	34.2	1.2168
80.18	-192.97	4.79	47.42	1.1958
80.18	-192.97	1.65	16.35	1.1899
80.18	-192.97	0.67	6.6	1.1883
85.41	-187.74	4.43	43.88	1.1717
85.41	-187.74	3.35	33.2	1.1697
85.41	-187.74	2.27	22.44	1.1680
85.41	-187.74	1.26	12.5	1.1662
90.29	-182.86	4.80	47.48	1.1498
90.29	-182.86	3.81	37.7	1.1483
90.29	-182.86	2.81	27.84	1.1462
90.29	-182.86	1.84	18.18	1.1444
90.29	-182.86	0.87	8.57	1.1424
90.29	-182.86	0.19	1.91	1.1413

Note: compressibility, raw uncorrected data

Data source: [58]

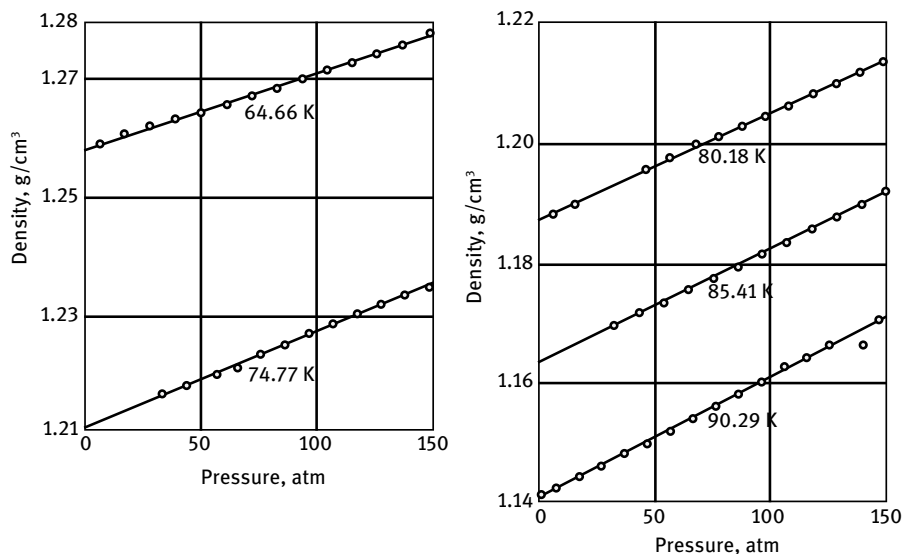
**Figure 4:** Density of liquid oxygen as a function of pressure (reprinted and modified from [58], with permission from © 1960 Elsevier; permission conveyed through RightsLink)

Table 7: Density of liquid oxygen as a function of temperature and elevated pressure.

Temperature		Pressure		Density
K	°C	MPa	atm	g/cm ³
90.26	−182.89	85.1	842.3	0.903
90.26	−182.89	65.5	648.3	0.8782
90.26	−182.89	50.1	496.2	0.8599
90.26	−182.89	37.9	375.2	0.8423
90.26	−182.89	28.3	279.9	0.8232
90.26	−182.89	20.1	199.1	0.8073
90.26	−182.89	13.2	131	0.7901
90.26	−182.89	0.0	0	0.7497
77.31	−195.84	58.0	574.2	0.903
77.31	−195.84	43.5	431	0.8882
77.31	−195.84	32.2	319.2	0.8705
77.31	−195.84	22.9	227.1	0.8558
77.31	−195.84	15.2	150.3	0.8419
77.31	−195.84	8.3	82	0.8274
77.31	−195.84	0.0	0	0.8079

Note: raw, uncorrected data

Data source: [60]

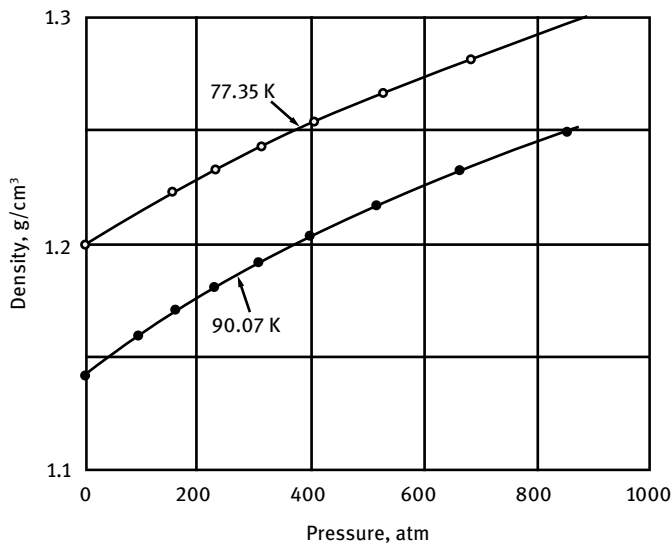


Figure 5: Density of liquid oxygen as a function of pressure up to 850 atm. (reprinted and modified from [60], with permission from © 1961 Elsevier; permission conveyed through RightsLink)

The data in Table 7 can be expressed by the following two equations:

$$\text{At } 90.26 \text{ K: } \rho = 0.7497 + 3.493 \times 10^{-4} \times P - 3.431 \times 10^{-7} \times P^2 + 0.01713 \times 10^{-8} \times P^3$$

$$\text{At } 77.31 \text{ K: } \rho = 0.8079 + 2.521 \times 10^{-4} \times P - 2.031 \times 10^{-7} \times P^2 + 0.007995 \times 10^{-8} \times P^3$$

where ρ is the density in g/cm^3 and P is the pressure in atm.

Some older data on the density of liquid oxygen as a function of temperature and pressure are shown in Figure 6.

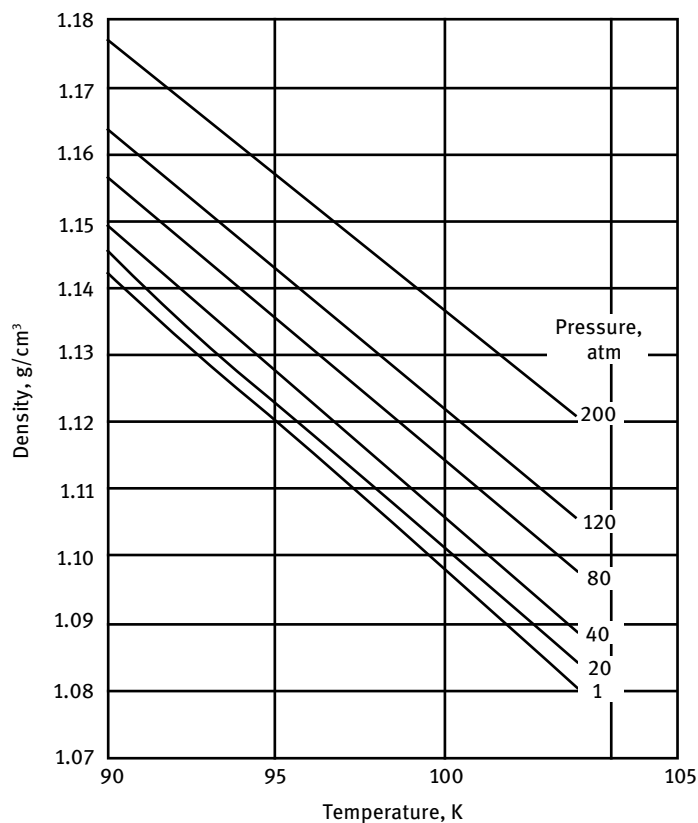


Figure 6: Density of liquid oxygen as a function of temperature and pressure (reproduced and modified from [55])

Note: pressure indicated as an auxiliary parameter next to each curve.

One of the older publications described a pressure-volume-temperature (PVT) equation that covers the range of temperatures 153–83 K and pressures $(78.5\text{--}196) \times 10^5 \text{ N/m}^2$ [61].

The following PVT measurements were carried out by weighing a sample of pure oxygen in a stainless-steel container and condensing it into a chamber of known volume [62]. Measurements of saturated liquid density of oxygen between 67.5 and 300 K for pressures up to 7.2 MPa were compared to data reported by 5 earlier investigators and fitted to the equation:

$$\frac{\rho}{\rho_c} = 1 + A\tau^{\frac{1}{3}} + B\tau^{\frac{2}{3}} + C\tau^{\frac{9}{3}}$$

where ρ is the molar density in mol/L, ρ_c is the critical density = 13.60 mol/L, $\tau = 1 - (T/T_c)$, T is the temperature in K, T_c is the critical temperature = 154.581 K, and the constants A through C are: A = -1.523779, B = 0.844538, C = 0.204933. Figure 7 illustrates density data calculated with this equation.

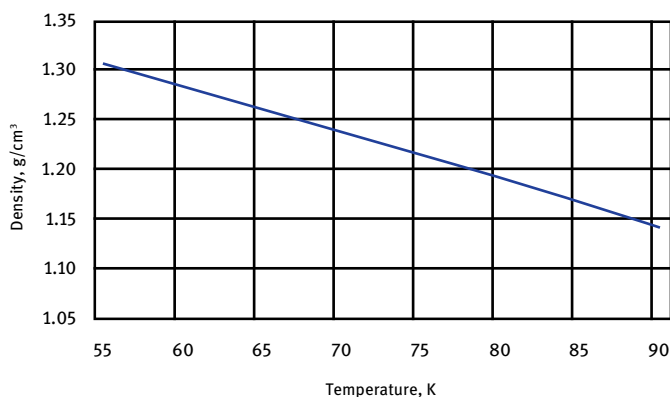


Figure 7: Density of liquid oxygen at atmospheric pressure (based on data from [62])

The density of the saturated vapor phase from 68 K to the critical temperature could be expressed by a more complex equation:

$$\ln\left(\frac{\rho}{\rho_c}\right) = A\tau^{\frac{1}{3}} + B\tau^{\frac{2}{3}} + C\tau^{\frac{3}{3}} + D\tau^{\frac{4}{3}} + E\tau^{\frac{5}{3}} + F\tau^{\frac{6}{3}} + G\tau^{\frac{19}{3}}$$

where ρ is the molar vapor density in mol/L, ρ_c is the critical density = 13.60 mol/L, $\tau = 1 - (T/T_c)$, T is the temperature in K, T_c is the critical temperature = 154.581 K, and the dimensionless constants A through G are: A = -1.306760, B = -5.514156, C = 21.220071, D = -67.611241, E = 93.883538, F = -57.568463, G = -39.328162.

The following form for an equation of state (EOS) for oxygen vapor follows the more traditional format with covolume and virial coefficients [63]:

$$\frac{P}{\rho RT} = 1 + B\rho + C\rho^2 + \dots$$

where P is the pressure and ρ is the density. The temperature dependence of the second and third virial coefficients is represented by the following functions:

$$B = f(T) = b_1 + b_2 T^{-0.25} + b_3 T^{-3.5} + b_4 T^{-4.5} + b_5 T^{-5.5} \quad (1)$$

$$C = f(T) = c_1 T^{-0.25} + c_2 T^{-6} + c_3 T^{-6.75} \quad (2)$$

where T is the temperature in kelvin, $B = f(T)$ is the covolume in L/mol, and $C = f(T)$ is the repulsive force constant in (L/mol)². The coefficients for Eqs. (1) and (2) are given below:

$$b_1 = 0.143389$$

$$b_2 = -0.629863$$

$$b_3 = -0.577814 \times 10^7$$

$$b_4 = 0.695858 \times 10^9$$

$$b_5 = -0.246023 \times 10^{11}$$

$$c_1 = 0.451336 \times 10^{-2}$$

$$c_2 = 0.987169 \times 10^{11}$$

$$c_3 = -0.364928 \times 10^{13}$$

These and PVT data from 22 different sources were critically reviewed and a small set of reliable data was selected to calculate density and compressibility data for LOX, resulting in a more accurate EOS [30].

A very accurate but also very complex equation of state for LOX is given by the equation [64]:

$$P = RT\rho_M + (A_1 + A_2T + A_3T^2) + (A_4 + A_5T + A_6T^2 + A_7T^3)\rho_M + (A_8 + A_9T + A_{10}T^2)\rho_M^2 + (A_{11} + A_{12}T)\rho_M^3$$

where P is the pressure in MPa, T is temperature in kelvin, ρ_M is molar density in mol/cm³, and R is the gas constant taken as 8.3147 J mol⁻¹ K⁻¹. The molecular mass

of oxygen is taken as 31.9988 g/mol. The constants have the following numerical values:

$$\begin{aligned}
 A_1 &= -1.641561252 \times 10^3 \text{ MPa}, \\
 A_2 &= 1.147287363 \times 10^1 \text{ MPa/K}, \\
 A_3 &= -1.893991658 \times 10^{-2} \text{ MPa/K}^2, \\
 A_4 &= 1.855069328 \times 10^5 \text{ J/mol}, \\
 A_5 &= -1.163758279 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1}, \\
 A_6 &= 1.470658133 \text{ J mol}^{-1} \text{ K}^{-2}, \\
 A_7 &= 5.082303291 \times 10^{-4} \text{ J mol}^{-1} \text{ K}^{-3}, \\
 A_8 &= -6.905607063 \times 10^6 \text{ (J/mol) (cm}^3\text{/mol)}, \\
 A_9 &= 3.696268789 \times 10^4 \text{ (J/mol K) (cm}^3\text{/mol)}, \\
 A_{10} &= -3.493447874 \times 10^1 \text{ (J mol}^{-1} \text{ K}^{-2}) \text{ (cm}^3\text{/mol)}, \\
 A_{11} &= 7.817570089 \times 10^7 \text{ (J/mol) (cm}^3\text{/mol)}^2, \\
 A_{12} &= -2.981428648 \times 10^5 \text{ (J mol}^{-1} \text{ K}^{-1}) \text{ (cm}^3\text{/mol)}^2
 \end{aligned}$$

Table 8 gives examples of density values calculated with this equation in comparison to densities calculated with another equation. These density data were later used to correlate dielectric constant measurements with density of liquid oxygen.

The density of LOX being loaded into a launch vehicle must be accurately known while the loading is in progress and until the engine ignites. The density can be calculated accurately if accurate temperature measurements are available [65]. The temperature readings can be fed to a microprocessor that adjusts the LOX temperature and density while the fueling is in progress.

The density of liquid oxygen was determined by a piezometric method at 93–153 K (–120 to –180 °C) and 20.26 MPa (200 atm) [66, 67]. The lowering of the density on changing the variables was determined by its outflow from the piezometer and the quantity was measured by its volume. The lower limit of pressure in this experiment was along the saturation curve. See also reference [68].

A cubic EOS was used to model the state of LOX in a rocket engine [69].

3.3.3 Density of Gaseous Oxygen at Elevated Pressure

The second virial coefficient for cold gaseous oxygen at the boiling point of liquid oxygen was derived from velocity of sound measurements [70].

The second and third virial coefficients of oxygen (and nitrogen) were calculated for a model pair potential considering the quantum corrections and non-additive components [71]. With this help a fourth virial coefficient was determined from the experimental data on p , ρ , and T . An empirical expression, the coefficients of which were found from an analysis of tabulated data on p , ρ , and T at pressures up to 100 MPa, was used for the fourth virial coefficient. Considering the fourth virial coefficient made it

Table 8: Density of liquid oxygen at elevated pressure.

Pressure MPa	Temperature K	Calculated density ^a g/cm ³	Calculated density g/cm ³
1.0009	91.3143	1.1374	1.1261
1.0004	80.9962	1.1873	1.1744
1.0009	76.0108	1.2106	1.1965
1.0008	71.1396	1.2330	1.2182
1.0006	66.3230	1.2547	1.2391
1.0000	61.4184	1.2766	1.2599
1.0002	55.3595	1.3033	1.2848
0.7500	91.2206	1.1373	1.1220
0.7501	80.9956	1.1869	1.1699
0.7502	75.9912	1.2103	1.1922
0.7501	71.1366	1.2326	1.2139
0.7505	66.3159	1.2544	1.2349
0.7501	61.4294	1.2763	1.2556
0.7502	55.3757	1.3029	1.2798
0.5009	91.1579	1.1370	1.1179
0.5000	80.9859	1.1865	1.1656
0.5001	75.9960	1.2099	1.1879
0.5001	71.1449	1.2322	1.2096
0.5003	66.3229	1.2541	1.2306
0.5001	61.4335	1.2759	1.2513
0.5003	55.3400	1.3028	1.2752
0.2508	91.1400	1.1365	1.1137
0.2504	80.9780	1.1861	1.1610
0.2502	75.9905	1.2095	1.1834
0.2501	71.1249	1.2319	1.2052
0.2501	66.3119	1.2538	1.2263
0.2502	61.4223	1.2757	1.2468
0.2502	55.3402	1.3025	1.2687

^aDensity calculated with equation above.

Data source: [64]

possible to more than double the size of the region of applicability of the EOS for both pure gases and mixtures. It turned out that the region of applicability of the expression obtained in many cases (helium, neon, nitrogen) appreciably exceeded 100 MPa, but this EOS has certain limitations.

3.3.4 Density of Solid Oxygen

The density of frozen O₂ at 16 K is $\rho = 1.54 \text{ g/cm}^3$ and the refractive index at 543 nm is 1.322 [72]. For solid oxygen, if it should accidentally freeze in a propellant line, it is important to know if it expands on freezing like water and ruptures the lines or if it continues to contract as it cools off [73]. There are small volume changes associated with the phase changes of solid oxygen.

Table 9: Measured and interpolated molar volumes and densities of solid oxygen.

Temperature K	Solid type	Molar volume cm ³ /mol	Density mol/cm ³	Density g/cm ³
4.2	α	20.75 ± 0.22	0.04819	1.542
18.75	α	20.75 ± 0.22	0.04819	1.542
20.0	α	20.75	0.04819	1.542
22.0	α	20.78	0.04812	1.540
23.880	α	20.82 ± 0.22	0.04803	1.537
23.880	β	20.95 ± 0.11	0.04773	1.527
24	β	20.95	0.04773	1.527
26	β	21.02	0.04757	1.522
28	β	21.08	0.04744	1.518
30	β	21.16	0.04726	1.512
32	β	21.24	0.04708	1.507
34	β	21.33	0.04688	1.500
36	β	21.42	0.04669	1.494
38	β	21.52	0.04647	1.487
40	β	21.63	0.04623	1.479
42	β	21.75	0.04598	1.471
43.801	β	21.87 ± 0.08	0.04572	1.463
43.801	γ	23.05 ± 0.06	0.04338	1.388
44	γ	23.06	0.04337	1.388
46	γ	23.18	0.04314	1.380
48	γ	23.30	0.04292	1.373
50	γ	23.43	0.04268	1.366
52	γ	23.55	0.04246	1.359
54	γ	23.67	0.04225	1.352
54.361	γ	23.69 ± 0.05	0.04221	1.351
54.361	Liquid	24.493 ± 0.02	0.04083	1.307

Data source: [36]

The density of the various phases of solid oxygen are summarized in Table 9 and illustrated in Figure 8.

3.4 Compressibility and Velocity of Sound of Liquid Oxygen

3.4.1 Compressibility of Liquid Oxygen

Data for the isothermal compressibility β_T and adiabatic compressibility β_S of liquid oxygen are listed in Table 10.

During pumping from the propellant tank, passage through the oxidizer pump and into the injector, the physical properties of LOX that are dependent on pressure will change slightly and will no longer be identical with the properties of LOX in the propellant tank. Calculations using the examples of LOX and RP-1 showed

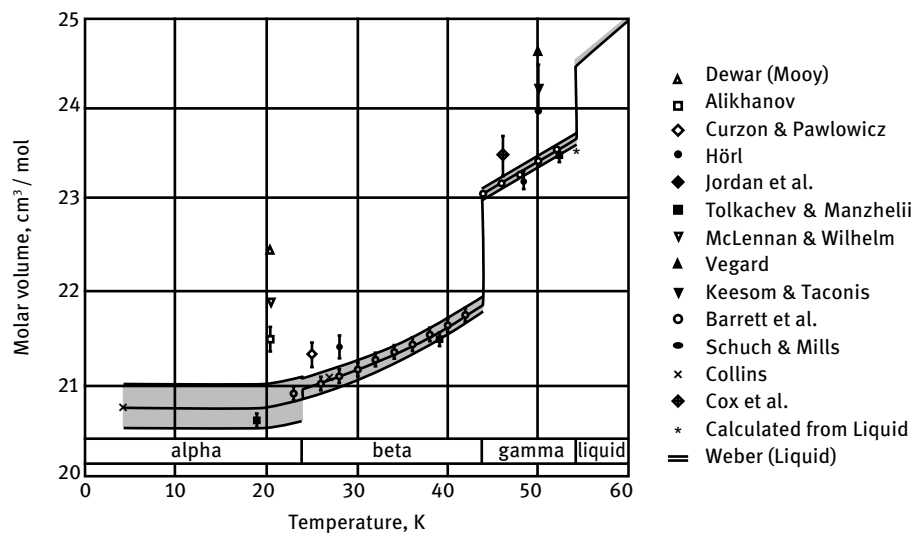


Figure 8: Molar volume of solid oxygen (republished and modified from [36], with permission of © 1978 American Institute of Physics; permission conveyed through Copyright Clearance Center Inc.)

Table 10: Isothermal compressibility β_T and adiabatic compressibility β_S of liquid oxygen.

Temperature K	β_T 1/atm	β_S cm ² /dyn	Density g/cm ³
90	1.90×10^{-4}	1.050×10^{-10}	1.142
85	1.71×10^{-4}	0.947×10^{-10}	1.167
80	1.53×10^{-4}	0.858×10^{-10}	1.191
75	1.37×10^{-4}	0.780×10^{-10}	1.215
70	1.22×10^{-4}	0.712×10^{-10}	1.239
65	1.06×10^{-4}	0.656×10^{-10}	1.263
60.5	0.93×10^{-4}	0.608×10^{-10}	1.282

Data source: [59, 74, 75]

that changes of density and temperature of LOX after adiabatic compression are not all that large but may have to be taken into consideration when designing a propellant feed system and injector orifices [76]. For instance, the temperature of LOX increased by 0.28 K for every 6.8 atm (100 psi) of pressure increase during adiabatic compression.

The adiabatic and isothermal compressibilities of LOX were calculated from thermodynamic data using two different methods [77]. As shown in Figure 9, the isothermal data obtained in this way agreed well with those measured by Chao [75] and Liepmann [78].

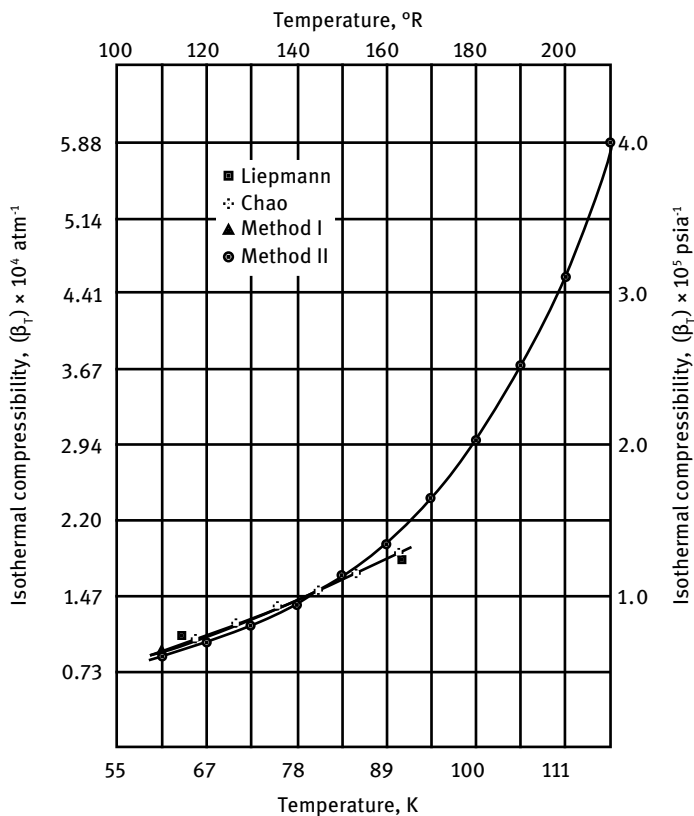


Figure 9: Isothermal compressibility of liquid oxygen (republished and modified from [77], with permission of © 1960 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

3.4.2 Velocity of Sound of Liquid Oxygen

Velocity of sound data of liquid oxygen are summarized in Table 11 and 12. The velocity of sound can be used to calculate the compressibility of liquid oxygen.

Figure 10 shows the velocity of sound in liquid oxygen at 539.6 kHz as a function of temperature [79]. Additional velocity of sound in liquid oxygen data are available also in comparison to liquid nitrogen [80] and for cold gaseous oxygen at the boiling point of liquid oxygen [70].

The velocity of sound in liquid oxygen as a function of temperature and pressure can be displayed graphically or printed out as a table by an on-line interactive application on the NIST Chemistry WebBook Fluids web site. An example for $p = 0.101, 1.01, \text{ and } 10.1 \text{ MPa}$ and $55 < T < 90$ is shown in Figure 11.

The transfer of LOX from a ground storage vessel to a flight tank and from a flight tank to a rocket engine generally requires the use of a pressurizing gas like helium or

Table 11: Velocity of sound in liquid oxygen.

Temperature		Velocity of sound, m/s	
K	°C ± 0.1°	at 7.5 MHz	at 1.537 MHz
89.5	−183.6	911 ± 4	—
89.4	−183.7	—	915 ± 9
87.3	−185.8	932 ± 4	928 ± 9
85.9	−187.2	945 ± 4	—
83.9	−189.2	954 ± 4	—
83.7	−189.4	—	962 ± 9
82.6	−190.5	975 ± 4	—
79.6	−193.5	1000 ± 5	—
77.5	−195.6	1021 ± 5	—
74.7	−198.4	—	1042 ± 10
73.9	−199.2	1043 ± 5	—
72.4	−200.7	—	1072 ± 10

Data source: [78]

Table 12: Velocity of sound in liquid oxygen.

Temperature		Velocity of sound
K	°C	m/s
77.4	−195.7	1007.27
90.3	−182.8	902.91

Data source: [58, 59]

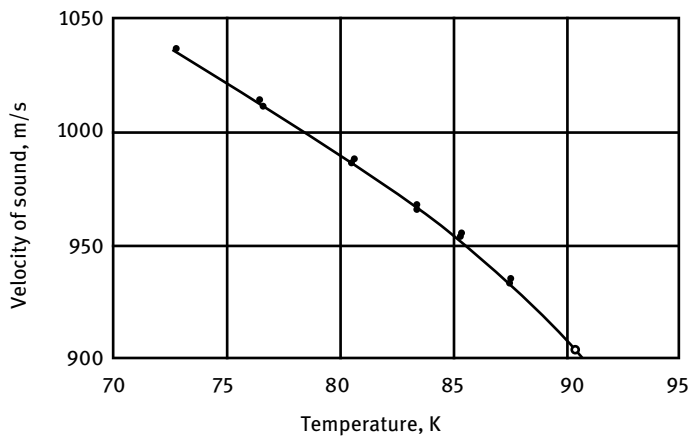


Figure 10: Velocity of sound in liquid oxygen at 539.6 kHz as a function of temperature (reprinted and modified from [79], with permission from © 1948 Elsevier; permission conveyed through RightsLink)

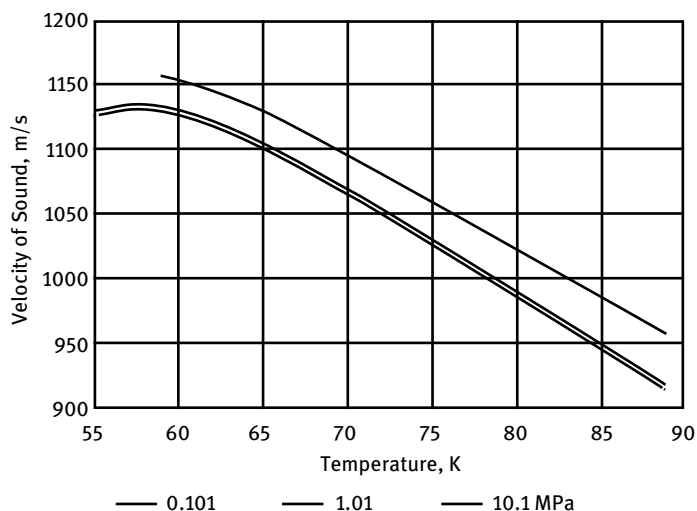


Figure 11: Velocity of sound in liquid oxygen for $p = 0.101, 1.01,$ and 10.1 MPa (based on data from [10])

nitrogen at pressures up to 20.6 MPa (3000 psi). If nitrogen instead of helium is used as the pressurant gas, the condensation of gaseous nitrogen into the cryogenic liquid, combined with high miscibility, results in contamination of the LOX, which has a deleterious effect on engine performance. It has been proposed to monitor the liquid oxygen/liquid nitrogen (LOX/LN₂) contamination through sound velocity measurements. Therefore, the sound velocity of LOX/LN₂ mixtures was measured under controlled conditions for later use in a practical LOX contamination monitor [81, 82]. The measurements, performed by the pulse-echo technique on several LOX/LN₂ compositions, revealed a slight deviation from a linear dependence of the sound velocity upon the mol fraction of LN₂. The results for pure LOX and pure LN₂ at 77.35 K (−195.8 °C) and 1 atm pressure were $1008.5 \pm 0.25\%$ m/s ($1009.05 \pm 0.25\%$ m/s) and $852.8 \pm 0.32\%$ m/s, respectively, and these results were compared to measurements reported in the literature. The relationship between sound velocity c and LN₂ content M is:

$$c = 1009.05 - 1.8275M + 0.0026507M^2$$

where c is the velocity of sound in m/s and M is the nitrogen concentration in mol-%. Measurement of sound velocity should prove an effective means for monitoring the contamination of LOX by LN₂.

Velocities of hypersonic (3–5 GHz) waves in liquid oxygen have been determined by thermal Brillouin scattering techniques [83]. The incident radiation ($\lambda = 5145 \text{ \AA}$) was obtained from a stabilized single-mode argon-ion laser, and the scattered radiation was analyzed at 90° with a piezoelectrically-scanned Fabry-Perot spectrometer. Mea-

surements covered the temperature range from the triple point (54.35 K) to the normal boiling point (90.18 K), and in this range the velocities were observed to decrease linearly with increasing temperature from 1193 to 909 m/s. These results were compared with ultrasonic (1.2 MHz) velocities as measured by van Itterbeek and van Dael at temperatures above 61 K, and no dispersion effects were evident at least up to 3.6 GHz. See also reference [84].

3.5 Vapor Pressure of Oxygen

3.5.1 Vapor Pressure of Liquid Oxygen

The vapor pressure of liquid oxygen is listed in Table 13.

Table 13: Vapor pressure of liquid oxygen.

Temperature K	Vapor pressure		
	mmHg	atm	psia
T_f 54.363	1.14	0.00150	0.022
T_b 90.190	760.0	1.0	14.696
T_c 154.780	38109	50.14	736.9
55	1.38	0.00182	0.027
60	5.44	0.00716	0.105
65	17.4	0.0229	0.34
70	46.8	0.0616	0.90
75	108.7	0.1430	2.10
80	225.3	0.2964	4.36
85	425.4	0.5597	8.23
90	745.0	0.9803	14.41
95	1223.3	1.6096	23.65
100	1905.0	2.5066	36.84
105	2838.2	3.7345	54.88
110	4072.9	5.3591	78.76
115	5661.6	7.4495	109.48
120	7658.6	10.077	148.09
125	10120	13.316	195.7
130	13102	17.239	253.4
135	16670	21.934	322.3
140	20892	27.489	404.0
145	25843	34.004	499.7
150	31631	41.620	611.6

Data source: [33]

The original vapor pressure equation for the temperature range between the triple point and the critical point as derived by Brower and Thodos [29] was:

$$\log P = 13.4275 - 469.150/T - 2.7391 \log T + 0.1155P/T^2$$

where P is the vapor pressure in mmHg and T is the temperature in kelvin. This is an unusual transcendental equation that includes the variable P on both sides of the equal sign. The equation should be solved so P is only on one side of the equal sign and T is only on the other side of the equal sign.

$$\log P - 0.1155P/T^2 = 13.4275 - 469.150/T - 2.7391 \log T$$

The average deviation of this equation is $\pm 0.43\%$. This is also called the Frost-Kalkwarf vapor pressure equation and was based on 259 data points.

The vapor pressure of liquid oxygen can be calculated from the Antoine equation

$$\log_{10}(P) = A - \left(\frac{B}{(T + C)} \right)$$

where P is the vapor pressure in bar and T is the temperature in kelvin [27]. The Antoine equation parameters are given in Table 14 for two different temperature ranges.

Table 14: Antoine equation parameters for vapor pressure of liquid oxygen.

Temperature range, K	A	B	C
54.36–100.16	3.85845	325.675	–5.667
54.36–154.33	3.9523	340.024	–4.144

Data source: [29] as cited by [27]

The vapor pressure of liquid oxygen as a function of temperature can be displayed graphically or printed out as a table by an on-line interactive app on the NIST Chemistry WebBook Fluids web site. An example for $55 < T < 120$ is shown in Figure 12.

Data compilations and evaluations by NIST [30] reference the data by Wagner, Ewers, and Penttermann [63, 85] as the most reliable source of vapor pressure and other data as of 1991:

$$\ln \pi = \left(\frac{T_c}{T} \right) \left(n_1 \tau + n_2 \tau^{\frac{3}{2}} + n_3 \tau^3 + n_4 \tau^7 + n_5 \tau^9 \right)$$

where π is the reduced pressure P/P_c , P is the vapor pressure in MPa, P_c is the critical pressure = 5.0430 MPa, T_c is the critical temperature = 154.581 K, T is the temperature

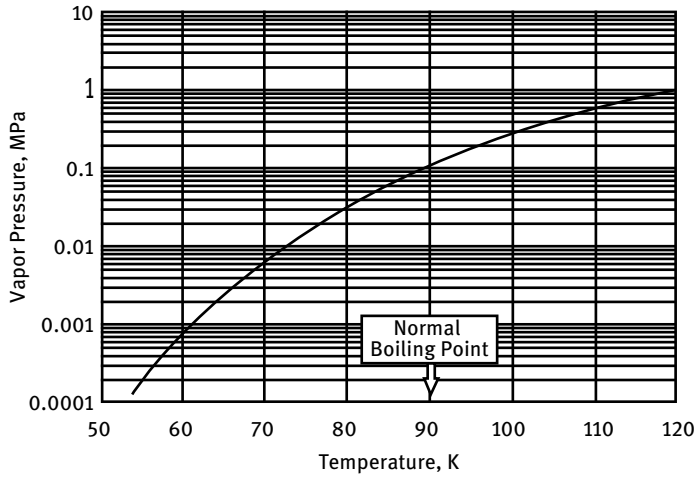


Figure 12: Vapor pressure of liquid oxygen (based on data from [52])

in kelvin, and $\tau = (T_c - T)/T_c$. The dimensionless coefficients n_1 through n_5 are as follows:

$$n_1 = -6.043938,$$

$$n_2 = 1.175627,$$

$$n_3 = -0.994086,$$

$$n_4 = -3.456781,$$

$$n_5 = 3.361499.$$

See also reference [86]. Alternatively, the following two equations can be used to calculate the vapor pressure of liquid oxygen between 66 and 90 K and between 90 and 110 K [87]:

$$\log p = 7.86224 - 408.740/T - 0.0049832 T \quad (66 \text{ K} < T < 90 \text{ K})$$

$$\log p = 6.92979 - 365.186/T \quad (90 \text{ K} < T < 110 \text{ K})$$

where p is the vapor pressure in mm Hg and T is the temperature in kelvin.

3.5.2 Vapor Pressure of Solid Oxygen

The vapor pressure of sublimation of solid oxygen is very small and difficult to measure, but it appears that it plays a role in the accumulation of oxygen on very cold extraterrestrial bodies where it would be a welcome resource for ISRU for future spacefarers.

It has been considered to store oxygen in the solid instead of the liquid form to minimize evaporation losses. In this case the vapor pressure of solid oxygen would determine the rate of loss of oxygen by sublimation [88–90].

Frozen oxygen would be a potential constituent of cryogenic solid propellants and therefore its physical properties must be known before such propellants can be formulated. Frozen oxygen is a constituent of slush oxygen. The transition of frozen oxygen to a metallic state at very high pressures changes its properties dramatically.

3.6 Viscosity of Oxygen

Instead of viscosity, sometimes the fluidity is given in its place. Fluidity is the reciprocal of viscosity. One must differentiate between dynamic (= absolute) viscosity and kinematic viscosity. The SI physical unit of *dynamic viscosity* is Pascal-second ($\text{Pa} \cdot \text{s}$), (equivalent to $(\text{N} \cdot \text{s})/\text{m}^2$, or $\text{kg m}^{-1} \cdot \text{s}^{-1}$). The cgs physical unit for dynamic viscosity is the *poise*, abbreviated as P or Ps, most often used as centipoise, abbreviated as cP or cPs. We prefer the abbreviation Ps because P is most often already used as the symbol for pressure.

$$1 \text{ P} = 1 \text{ Ps} = 0.1 \text{ Pa} \cdot \text{s}$$

$$1 \text{ cP} = 1 \text{ cPs} = 1 \text{ mPa} \cdot \text{s} = 0.001 \text{ Pa} \cdot \text{s}.$$

The SI unit of *kinematic viscosity* is m^2/s . The cgs physical unit for *kinematic viscosity* is the stokes, abbreviated as St. It is sometimes expressed in terms of centistokes (cSt).

$$1 \text{ St} = 1 \frac{\text{cm}^2}{\text{s}} = 10^{-4} \frac{\text{m}^2}{\text{s}}$$

$$1 \text{ cSt} = 1 \frac{\text{mm}^2}{\text{s}} = 10^{-6} \frac{\text{m}^2}{\text{s}}.$$

3.6.1 Viscosity of Gaseous Oxygen

Since dioxygen is a small diatomic molecule the temperature dependence of its viscosity in the dilute gas state or zero-density limit can be well represented by expressions derived from kinetic theory. The viscosity can be derived from an equation that contains the absolute temperature T , the molar mass M , Boltzmann constant k , Avogadro number N_A and the collision integral. Viscosity data for gaseous oxygen along the saturation line and for temperatures from 70 to 850 K and pressures up to 100 MPa calculated from that equation were included in a table (Table 3) of the following reference but are not shown here in full because it would take too much space [91]. An abbreviated version of Table 3 from Laesecke et al. [91] is shown in Table 15 that includes both viscosity and thermal conductivity data.

Table 15: Viscosity and thermal conductivity of oxygen along the saturation line.

Temperature K	Pressure MPa	Viscosity, liquid $\mu\text{Pa s}$	Viscosity, gas $\mu\text{Pa s}$	Thermal conduc- tivity, liquid $\text{mW m}^{-1} \text{K}^{-1}$	Thermal conduc- tivity, gas $\text{mW m}^{-1} \text{K}^{-1}$
70	0.006262	355.0	4.776	181.3	5.981
80	0.03012	248.4	5.661	167.2	7.105
90	0.09935	186.9	6.544	153.1	8.258
90.188	0.1013	186.0	6.561	152.8	8.280
100	0.2540	146.4	7.436	139.0	9.477
110	0.5434	117.4	8.359	124.8	10.82
120	1.022	94.96	9.355	110.3	12.41
130	1.749	76.58	10.52	95.44	14.44
140	2.788	60.25	12.10	79.48	17.41
150	4.219	43.13	15.23	60.11	23.16
154.581	5.043	24.91	24.91	37.47	37.47

Data source: [91]

The viscosity and thermal conductivity data in Table 15 for gases above the boiling liquid at the saturation pressure differ substantially from viscosity and thermal conductivity data for gases at atmospheric pressure, shown in other parts of this chapter.

3.6.2 Viscosity of Liquid Oxygen

The dynamic viscosity of liquid oxygen is summarized in Table 16.

The viscosity of liquid oxygen at atmospheric pressure in the range from 68 to 90 K is shown in Figure 13 where the open circles and the $\times$ symbols indicate van Itterbeek, Zink, and van Paemel [92] data and the other symbols indicate data from Rudenko and

Table 16: Dynamic viscosity of liquid oxygen η .

Temperature K	Dynamic viscosity η	
	$\mu\text{Pa s}$	Ps
68.70	379.3	379.3×10^{-5}
71.40	336.9	336.9×10^{-5}
74.00	311.2	311.2×10^{-5}
76.95	279.3	279.3×10^{-5}
80.66	248.1	248.1×10^{-5}
83.60	226.2	226.2×10^{-5}
86.73	208.5	208.5×10^{-5}
90.25	187.9	187.9×10^{-5}

Data source: Gmelin Handbook 1935

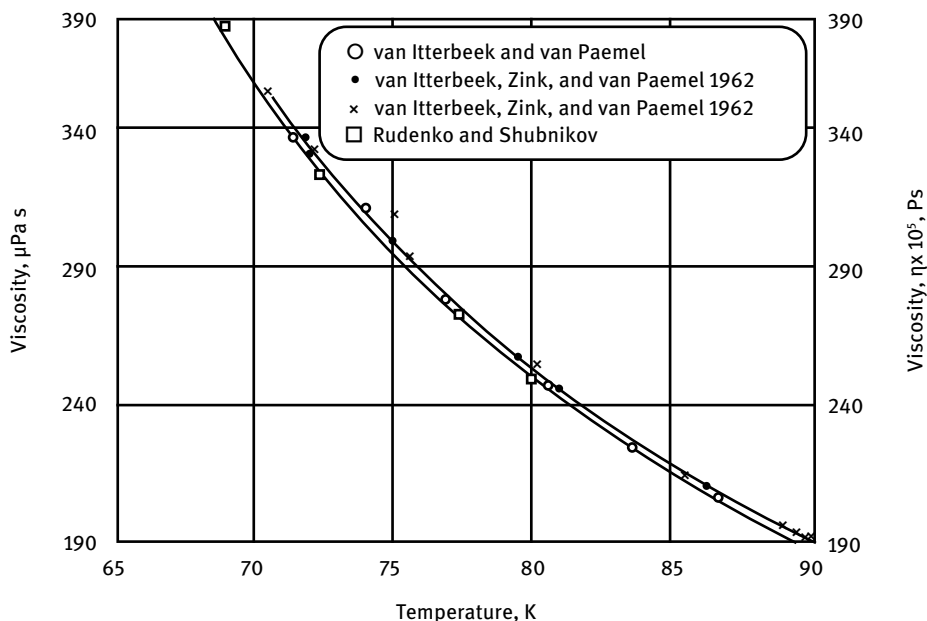


Figure 13: Viscosity of liquid oxygen (reprinted and modified from [92], with permission from © 1962 Elsevier; permission conveyed through RightsLink)

Shubnikov 1934 [93], but the authors failed to identify the units of measurement for η on the ordinate scale. We assume the units of the ordinate scale are Poise (1 Poise = 0.1 N s m^{-2}) multiplied times 10^5 , reference [92].

Viscosity of liquid oxygen was calculated from the residual viscosity expressed by a complicated equation that contained terms for reduced density and parameters derived from a set of critically evaluated literature data. Viscosity data for liquid oxygen from 70 to 154 K along the saturation line calculated from that equation are included in Table 15 (this is based on Table 3 as shown in reference [91]). A shortened version of that table is shown.

Equations for the viscosity and thermal conductivity of oxygen derived from several dozen of carefully evaluated literature references were developed and they were valid over all liquid and vapor states [94]. For instance, the viscosity of oxygen at 100 K for a liquid with a density of 35.0 mol/L was calculated as $172.136 \mu\text{Pa s}$ and the viscosity of oxygen at the critical point at 154.6 K with a density of 13.6 mol/L was calculated as $24.7898 \mu\text{Pa s}$.

The viscosity of liquid oxygen as a function of temperature can be displayed by an on-line interactive app on the NIST Chemistry WebBook Fluids web site. An example for saturated liquid/gas two-phase region and $55 < T < 120$ is shown in Figure 14.

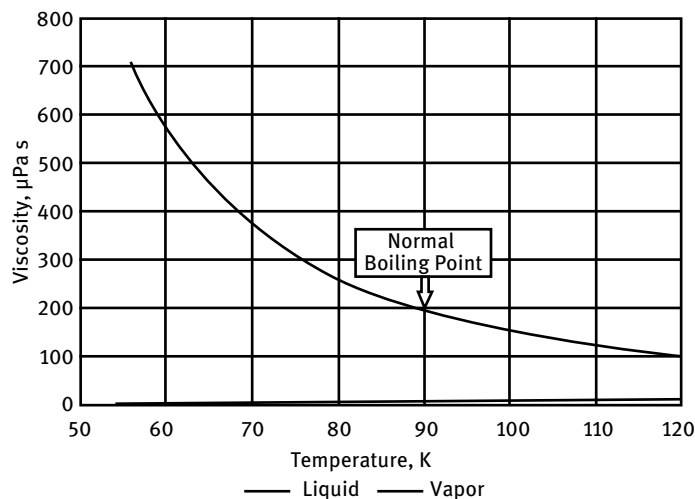


Figure 14: Dynamic viscosity of saturated liquid and gaseous oxygen (based on data from [52])

Absolute dynamic viscosity of subcooled liquid oxygen from 0.15 to 1.0 MPa and from 55.20 to 90.19 K was measured using a pressurized gravitational capillary (PGC) viscometer specifically designed for subcooled liquefied gases [95]. Measurements of the dependency of viscosity on pressure between 0.15 and 1 MPa showed that there is very little variation of viscosity with pressure in this range. Selected viscosity and density data are summarized in Table 17.

Table 17: Dynamic (=absolute) viscosity and density of subcooled liquid oxygen at different pressures.

Temperature K	Pressure kPa	Viscosity $\mu\text{Pa s}$	Density kg/m^3
55.000	152.3	799.3	1303.9
90.187	153.7	196.7	1140.7
54.991	309.0	809.7	1304.1
90.186	305.7	193.2	1141.4
55.984	508.6	816.2	1300.0
90.188	518.9	195.6	1140.7
54.998	810.6	814.9	1303.7
90.187	811.1	198.0	1140.7
55.000	1013.7	813.7	1303.7
85.001	1017.3	228.5	1166.3
90.187	1020.8	198.8	1140.7

Data source: [95]

The slope of the pressure curves $\partial\mu/\partial P$ decreased from 0.014 to 0.0044 ns as the temperature was increased from 55 to 90 K. The natural logarithm of viscosity as a function of reciprocal absolute temperature can be displayed as a straight line in an Arrhenius-type graph (Figure 15). Only the lowest pressure (0.15 MPa) data points are shown in this graph because they all overlap. See also [96, 97].

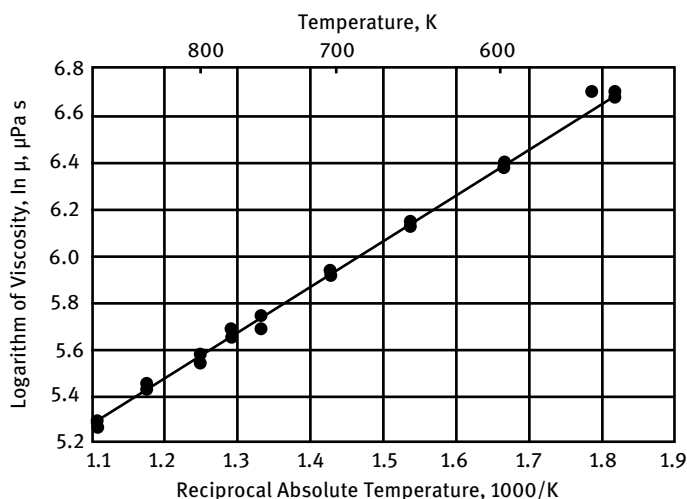


Figure 15: Absolute dynamic viscosity of subcooled liquid oxygen at 150 kPa (reprinted and modified from [95], with permission from © 2008 Elsevier; permission conveyed through RightsLink)

3.7 Surface Tension of Oxygen

The surface tension of liquid oxygen as listed in Table 18 is almost double that of liquid nitrogen ($\sigma_{\text{O}_2} = 16.51 \text{ dyn/cm}$ and $\sigma_{\text{N}_2} = 8.94 \text{ dyn/cm}$ at $T = 77 \text{ K}$, $\sigma_{\text{O}_2} = 16.25 \text{ dyn/cm}$, and $\sigma_{\text{N}_2} = 8.72 \text{ dyn/cm}$ at $T = 78 \text{ K}$).

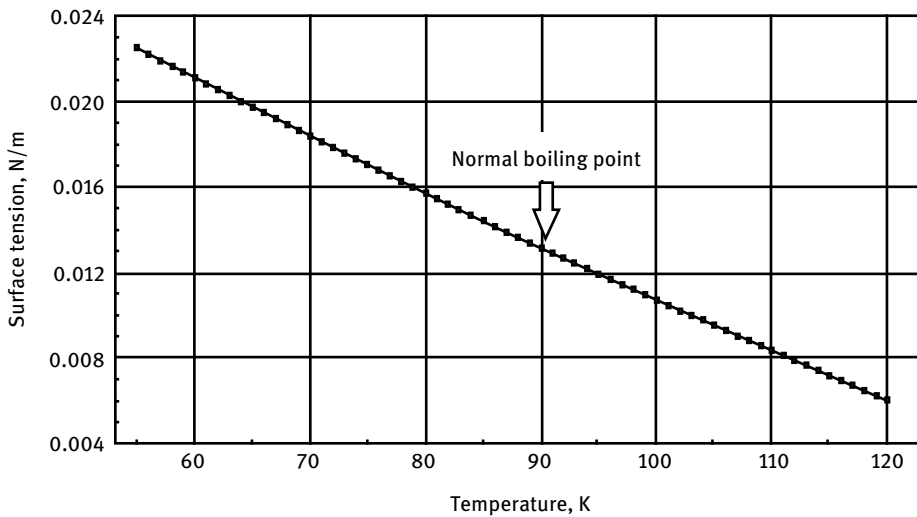
Conversion: $1 \text{ dyn/cm} = 10^{-3} \text{ N/m}$

The surface tension of liquid oxygen as a function of temperature can be displayed by an on-line interactive app on the NIST Chemistry WebBook Fluids web site [52]. An example for saturated liquid/gas two-phase region and $55 < T < 120$ is shown in Figure 16.

Using a capillary method and a split-type superconducting magnet, the surface tension of liquid oxygen has been measured in magnetic fields up to 5 T at 65.3 and 77.1 K [98]. It was found that the dependence of surface tension on magnetic field strength is so small that it cannot be the main cause of the shape deformation of the meniscus.

Table 18: Surface tension of liquid oxygen.

Temperature		Surface tension, σ	Authors	Year	References
°C	K	dyn/cm			
-182.7	90.5	13.2 ± 0.2	Jenkins and Dipaolo	1956	[50]
-203.2	70	18.3	Baly and Donnan	1902	[49]
-198.2	75	17.0	Baly and Donnan	1902	[49]
-193.2	80	15.7	Baly and Donnan	1902	[49]
-188.2	85	14.5	Baly and Donnan	1902	[49]
-183.2	95	13.2	Baly and Donnan	1902	[49]

**Figure 16:** Surface tension of saturated liquid oxygen (modified from [52])

The surface tension of oxygen at the liquid-vapor interface was calculated for the temperature range of 60–90 K using molecular dynamic simulations and could be reproduced within 1.0% error of experimental values for most of the temperatures studied, as summarized in Table 19 and illustrated in Figure 17.

The experimental data points are from reference [100], which in turn lists four older sources of surface tension data ranging from 1902 to 1970 [101–104].

The surface tension of LOX as a function of temperature can be calculated from

$$\sigma = 38.612652\tau^{1.228}$$

where σ is the surface tension in dyn/cm, $\tau = 1 - T/T_c$, T_c is the critical temperature in kelvin and T is the temperature in kelvin.

Table 19: Experimental and molecular dynamic theoretical results for surface tension of oxygen.

Temperature K	Surface tension	
	Experimental results $\sigma \times 10^2$, N/m	Molecular dynamics theoretical results $\sigma \times 10^2$, N/m
60	2.1122	2.1204
65	1.9759	1.9850
70	1.8414	1.8482
75	1.7086	1.6974
80	1.5777	1.5487
85	1.4489	1.4378
90	1.3221	1.2986

Source of data: [99]

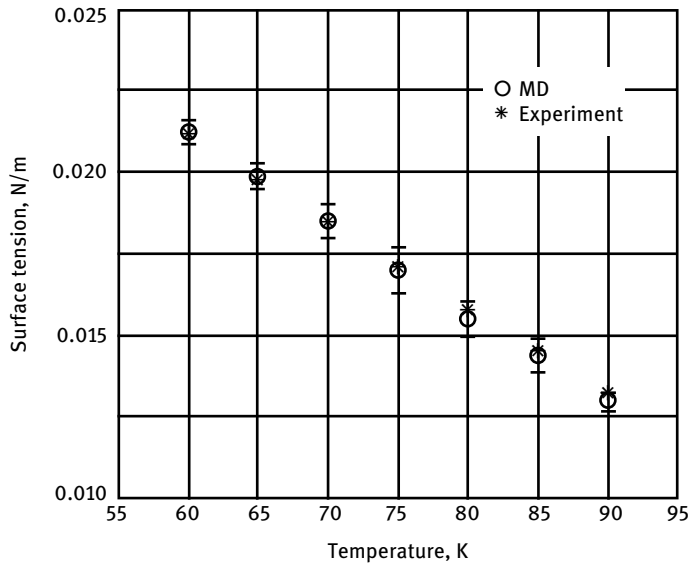


Figure 17: Surface tension of oxygen at the liquid-vapor interface (republished and modified from [99], with permission of © 2006 American Institute of Physics; permission conveyed through Copyright Clearance Center, Inc.)

Quite often LOX is pressurized with helium and a little helium will dissolve in LOX. The small amount of helium dissolved in LOX has not much of an effect on the surface tension of LOX [105, 106].

An older source [107] of surface tension of LOX gives the temperature dependence as a linear equation as:

$$\sigma = 36.64 - 0.262 T$$

where σ is the surface tension in $\text{N/m} \times 10^3$, and T is the temperature in kelvin. This function is illustrated in Figure 18 in comparison to experimental data from various sources. The purity of the oxygen, which was prepared by decomposition of potassium permanganate, was better than 99.9 mass %.

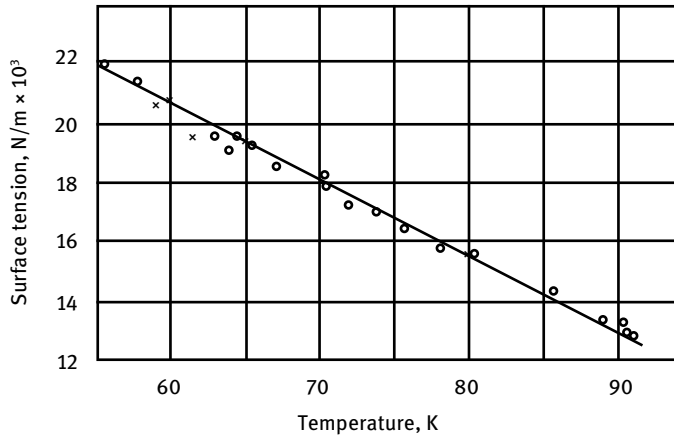


Figure 18: Surface tension of liquid oxygen (reproduced and modified from [107])

3.8 Thermal Conductivity of Oxygen

3.8.1 Thermal Conductivity of Gaseous Oxygen

Since dioxygen is a small diatomic molecule, the temperature dependence of its thermal conductivity in the dilute gas state or zero-density limit can be well represented by expressions derived from kinetic theory. The thermal conductivity can be derived from an equation that contains the absolute temperature T , the molar mass M , universal gas constant R , isochoric heat capacity, and the viscosity. There are substantially fewer reports on thermal conductivity of gaseous oxygen in the literature than there are publications on viscosity. Fourteen sets of original data from the literature were evaluated to obtain the coefficients for a very complicated thermal conductivity equation. Thermal conductivity data for gaseous oxygen along the saturation line and for temperatures from 70 to 850 K and pressures up to 100 MPa calculated from that equation were included a table (Table 3) of the following reference but are not shown here because it would take too much space [91].

A shortened version of that table was presented in the section “Viscosity of Gaseous Oxygen”.

The measured thermal conductivity of gaseous oxygen in Table 20 is given in several units and compared to numbers calculated from a curve-fit polynomial equation.

Table 20: Thermal conductivity of gaseous oxygen, measured and smoothed values.

T	Johnston and Grilly [108]		Yaws [109]		
	λ		from polynomial equation		
K	$\text{cal s}^{-1} \text{cm}^{-1} \text{K}^{-1} \times 10^5$	$\text{mW m}^{-1} \text{K}^{-1}$	$\mu\text{cal s}^{-1} \text{cm}^{-1} \text{K}^{-1}$	$\mu\text{W cm}^{-1} \text{K}^{-1}$	$\text{mW m}^{-1} \text{K}^{-1}$
80	1.701	7.12	17.70	74.0	7.40
90	1.930	8.08	19.93	83.4	8.34
100	2.159	9.03	22.15	92.7	9.27
110	2.387	9.99	24.35	101.9	10.19
120	2.614	10.94	26.53	111.0	11.10
130	2.840	11.88	28.70	120.1	12.01
140	3.064	12.82	30.85	129.1	12.91
150	3.287	13.75	32.99	138.0	13.80
160	3.508	14.68	35.11	146.9	14.69
170	3.728	15.60	37.21	155.7	15.57
180	3.946	16.51	39.30	164.4	16.44
190	4.162	17.41	41.37	173.1	17.31
200	4.375	18.31	43.43	181.7	18.17
210	4.584	19.18	45.47	190.3	19.03
220	4.790	20.04	47.50	198.7	19.87
230	4.993	20.89	49.51	207.2	20.72
240	5.194	21.73	51.51	215.5	21.55
250	5.392	22.56	53.49	223.8	22.38
260	5.586	23.37	55.46	232.1	23.21
270	5.780	24.18	57.42	240.2	24.02
273.1	5.839	24.43	58.02	242.8	24.28
280	5.970	24.98	59.36	248.4	24.84
290	6.139	25.69	61.29	256.4	25.64
298.1	6.314	26.42	62.84	262.9	26.29
300	6.350	26.57	63.20	264.4	26.44
310	6.547	27.39	65.10	272.4	27.24
320	6.748	28.23	66.99	280.3	28.03
330	6.954	29.10	68.86	288.1	28.81
340	7.164	29.97	70.72	295.9	29.59
350	7.378	30.87	72.56	303.6	30.36
360	7.594	31.77	74.40	311.3	31.13
370	7.812	32.69	76.22	318.9	31.89
380	8.033	33.61	78.03	326.5	32.65

Data source: [108]

The measured data from Johnston and Grilly [108] can be closely represented by a polynomial equation [109]:

$$\lambda = -0.7816 + 23.8 \times 10^{-2} \times T - 0.8939 \times 10^{-4} \times T^2 + 2.324 \times 10^{-8} \times T^3$$

where λ is the thermal conductivity in $\mu\text{cal s}^{-1} \text{cm}^{-1} \text{K}^{-1}$ and T is the absolute temperature in kelvin.

The thermal conductivity of liquid and gaseous oxygen was measured at temperatures between 80 and 200 K at pressures between 1 and 130 atm using a vertical coaxial cylinder method and the results were compared with those of other authors [110, 111]. The thermal conductivity of gaseous oxygen as a function of temperature and pressure is shown in Figure 19 and 20. The shape of a graph displaying the thermal conductivity as a function of temperature and pressure (Figure 20) is very similar to one displaying density as a function of temperature and pressure.

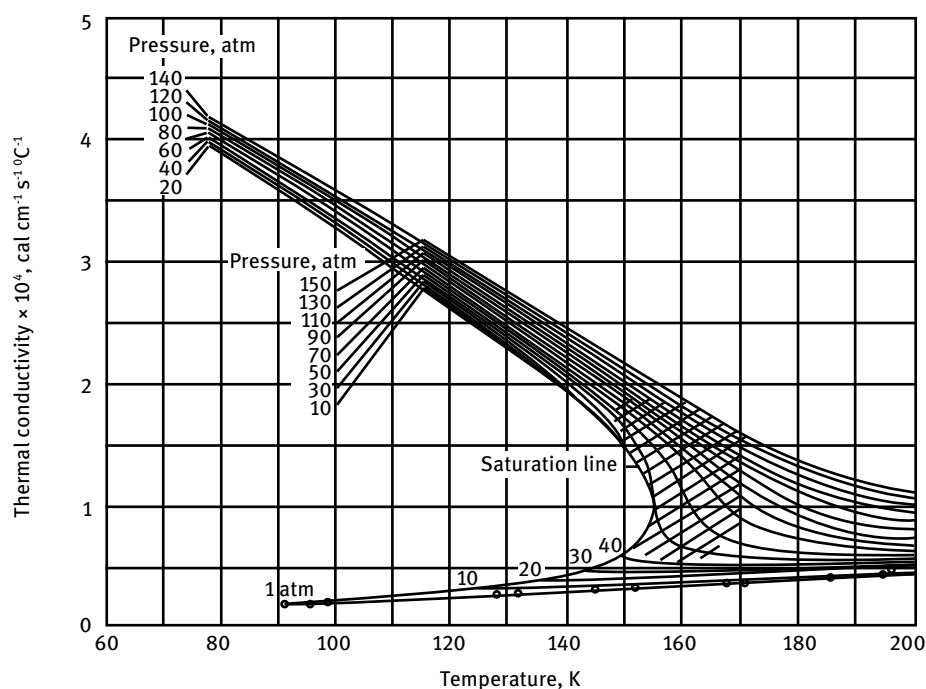


Figure 19: Thermal conductivity of saturated oxygen as a function of temperature and pressure (Reproduced and modified from [110], with permission granted by © 1955 IOP Publishing. All rights reserved.)

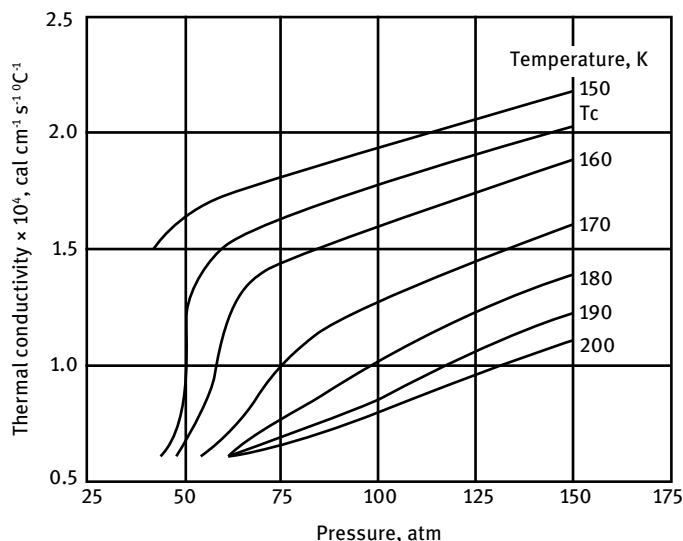


Figure 20: Thermal conductivity of gaseous oxygen as a function of pressure and temperature. (reproduced and modified from [110], with permission granted by © 1955 IOP Publishing. All rights reserved)

3.8.2 Thermal Conductivity of Liquid Oxygen

Investigators measuring the thermal conductivity of LOX and other cryogenic fluids have utilized thin layers of liquids and small temperature differences. One investigator designed an apparatus which used a liquid layer only 0.4 mm (0.0156 in.) thick and a temperature difference of 0.5 K (1 °F) and obtained fairly accurate data; however, it has been found that it becomes exceedingly difficult to accurately measure the temperature difference with very thin layers of liquids. Other investigators constructed an apparatus using a hot wire technique with a liquid layer of 5 mm thickness and temperature difference of the order of 1 °C or less. In order to minimize the effect of convection on thermal conductivity measurements on fluids near the critical region, it is necessary that the fluid film through which the heat is transported should be as thin as possible. Thus, the parallel plate method, or the coaxial cylinder method is to be preferred to the hot wire method. The thermal conductivity of liquid oxygen between 66.1 and 82.1 K (–207 and –191 °C) has been determined as described in reference [112]. In this method the liquid layer 1.2 cm thick was enclosed between two parallel copper disks, the heat flow being measured from the upper to the lower disk. The temperature difference was measured by differential thermoelements located in the liquid layer. The values of thermal conductivity of LOX between 93.5 and 91.1 K (–179.6 and –182 °C) have been calculated from the heat transfer data using Nusselt's equation and are given in Table 21. The points are fairly scattered as is usually the case with heat transfer data, but they compare favorably with the extrapolated data of Hammann [112] who mea-

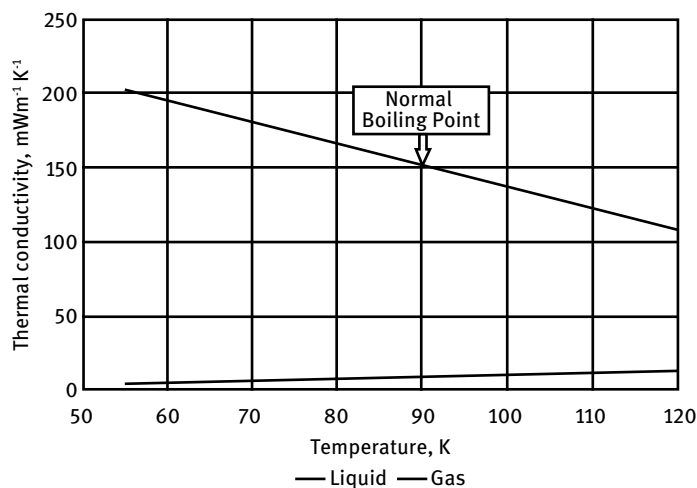
Table 21: Thermal conductivity of liquid oxygen.

Temperature		Coefficient of heat transfer		Thermal conductivity	
K	°C	$\text{W m}^{-2} \text{K}^{-1}$	$\text{cal } ^\circ\text{C}^{-1} \text{cm}^{-2} \text{s}^{-1}$	$\text{W m}^{-1} \text{K}^{-1}$	$\text{cal } ^\circ\text{C}^{-1} \text{cm}^{-1} \text{s}^{-1}$
77	-196			0.186	$4.44 \times 10^{-4} *$
91.1	-182.0	7942	1897×10^{-4}	0.224	5.36×10^{-4}
91.8	-181.3	5112	1221×10^{-4}	0.212	5.06×10^{-4}
92.1	-181.0	3961	946×10^{-4}	0.194	4.64×10^{-4}
92.4	-180.7	3952	944×10^{-4}	0.210	5.02×10^{-4}
93.3	-179.8	3856	921×10^{-4}	0.220	5.27×10^{-4}
93.5	-179.6	3768	900×10^{-4}	0.223	5.32×10^{-4}

Data source: [113], except * which is from [114] and [115].

sured at 73 K (-200°C) $\lambda = 4.98 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} ^\circ\text{C}^{-1}$. The mean value of the thermal conductivity between 95.5 and 91.1 K (-177.6 and -182°C) is $5.05 \times 10^{-4} \text{ cal s}^{-1} \text{ cm}^{-1} ^\circ\text{C}^{-1}$.

The thermal conductivity of liquid oxygen as a function of temperature can be displayed graphically or printed out as a table by an on-line interactive app on the NIST Chemistry WebBook Fluids web site. An example for thermal conductivity in the saturated liquid/gas two-phase region for $55 < T < 120$ is shown in Figure 21.

**Figure 21:** Thermal conductivity of saturated liquid oxygen (reproduced and modified from [52])

Equations for the thermal conductivity of oxygen derived from several dozen carefully evaluated literature references were developed and they were valid over all liquid and vapor states, and a simplified cross-over equation was used to model the behavior of the critical enhancement for thermal conductivity [94]. For instance, the thermal

conductivity of oxygen at 100 K for a liquid with a density of 35.0 mol/L was calculated as $146.044 \text{ mW m}^{-1} \text{ K}^{-1}$ and the viscosity of oxygen at the critical point at 154.6 K with a density of 13.6 mol/L was calculated as $377.476 \text{ mW m}^{-1} \text{ K}^{-1}$.

The thermal conductivity of liquid oxygen below 80 K and at pressures up to 1 MPa was measured using a horizontal, guarded, flat-plate calorimeter [116, 117]. Raw data are summarized in Table 22.

Table 22: Thermal conductivity of subcooled liquid oxygen.

Temperature, K	Pressure, MPa	λ , $\text{W m}^{-1} \text{ K}^{-1}$
55.9486	1.0002	0.19990
60.1572	1.0003	0.19472
65.5879	0.9998	0.18754
71.3274	0.9993	0.17966
75.6650	1.0022	0.17340
80.6776	1.0002	0.16640
55.9423	0.7500	0.19966
58.8036	0.7493	0.19616
70.7689	0.7496	0.18018
75.3548	0.7503	0.17357
80.6889	0.7498	0.16614
56.5024	0.5002	0.19880
60.1102	0.5002	0.19435
71.1511	0.5020	0.17942
75.1652	0.5003	0.17370
80.6849	0.5003	0.16587
55.4962	0.2503	0.19979
60.7846	0.2507	0.19325
71.1504	0.2498	0.17920
75.1497	0.2506	0.17345
80.5935	0.2504	0.16576

Data source: [117]

The thermal conductivity of subcooled liquid oxygen as a function of temperature and pressure is shown in Figure 22. In the range from 0.1 to 1 MPa, thermal conductivity of liquid oxygen is not very sensitive to pressure, and the curves virtually fall on top of each other.

Thermal conductivity data for liquid oxygen from 70 to 154 K along the saturation line calculated are included in Tables 3 and 5 of reference [91] shown in the section “Viscosity of Gaseous Oxygen”. See also [96, 97, 118].

The thermal conductivity of gaseous oxygen was investigated by a heated wire method at temperatures from 83 to 298 K (−190 to +25 °C) and at constant pressures of 100 and 60 atm [119, 120]. In this apparatus, heat was supplied by an electrically

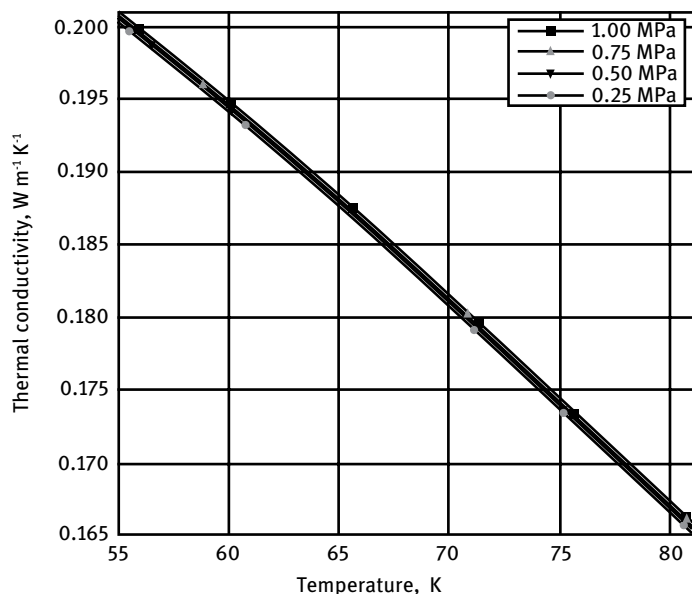


Figure 22: Thermal conductivity of liquid oxygen as a function of temperature and pressure (reprinted and modified from [117], with permission from © 2005 Elsevier; permission conveyed through RightsLink)

heated wire and flowed in a radial direction to the wall of a capillary across a gap of 0.21 mm. From a logarithmic correlation of the experimental results, two different equations were derived:

$$\lambda = \lambda_0 + 4.30 \times 10^{-8} \times \rho^{2.11}$$

for ρ greater than 825 kg/m³ and

$$\lambda = \lambda_0 + 1.246 \times 10^{-5} \times \rho^{1.24}$$

for ρ between 50 to 535 kg/m³, where λ and λ_0 are the coefficients of thermal conductivity of liquid and gaseous oxygen in kcal m⁻¹ h⁻¹ °C⁻¹, respectively, ρ is the specific gravity of oxygen in kg/m³. By means of these two formulas, the coefficients of thermal conductivity of oxygen can be calculated for pressures from 1 to 100 atm and temperatures from 73 to 313 K (−200 to +40 °C). See also reference [121].

The thermal conductivity of oxygen has been measured at temperatures from 77 to 310 K with pressures to 70 MPa and densities from 0 to 40 mol/L [122]. The measurements covered the physical states of the dilute gas, the dense gas, the region near critical, compressed liquid states, metastable liquid states at conditions just below saturation, and vapor states at temperatures below critical and pressures less than the vapor pressure. The results were analyzed in conventional terms to develop a mathematical

description of the thermal conductivity surface. The thermal conductivity surface was represented with an equation that was based in part on an existing correlation of the dilute gas. The new thermal conductivity surface revealed that the critical enhancement, or an anomalous increase in thermal conductivity, persisted to reduced temperatures that were quite high, approximately $2T_c$. Figure 5 of that publication attempts to illustrate the thermal conductivity as a function of density and temperature, but it is very difficult to extract specific data from that graph. The deviation in the curve for 159 K reveals the anomalies as the system goes through the critical point.

Equations for the transport properties in terms of pressure and temperature, so-called transport EOS, are useful design tools. The surfaces of transport properties and density as a function of pressure and temperature reveal similarities, which become even more evident when the residual transport property as a function of pressure and temperature is considered. Based on these similarities, a cubic transport EOS has been developed for the residual thermal conductivity of oxygen, which is only a little less accurate than the already established virial transport EOS for oxygen [123]. It is, however, much simpler and needs only a few parameters. The accuracy is still good enough for practical applications.

3.9 Heat Transfer Coefficient of Liquid Oxygen

When measuring the boiling heat transfer to liquid oxygen flowing in tubes in the range of nucleate and film boiling, it was observed that the coefficient of heat transfer was quite dependent on surface conditions, the type of metal and the diameter of the tubes [124, 125]. The results are illustrated in Figure 23.

The operating pressure of LOX rocket engines has been steadily increasing over the decades, gradually approaching critical point conditions. Therefore, heat transfer properties of LOX in the proximity of the critical point had to be measured [126, 127]. Table 23 contains a small portion of the data in the range of nucleate boiling.

A very thorough compilation and critical evaluation of heat transfer data in liquid oxygen (also containing some liquid hydrogen data) was published in reference [129]. This publication compared the data obtained by eight other sources in the regime of nucleate as well as film boiling. The experimental data were in good agreement with the equation proposed by Kutateladze [130].

Propellant evaporation is a criterion for rocket engine design and experimental performance evaluation and heat transfer rates have been measured with various propellant combinations and compared to model predictions [131, 132].

Bipropellant rocket engines are usually regeneratively cooled with the fuel instead of the oxidizer. Just in case design changes require an engine to be cooled with oxidizer (or with both oxidizer and fuel), the heat transfer coefficient at supercritical temperature conditions has been examined [133]. A bulk property Nusselt number was modi-

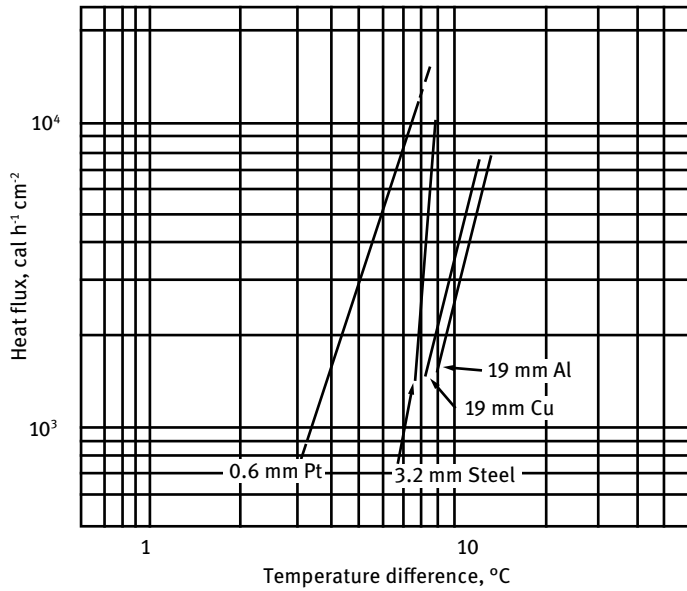


Figure 23: Heat transfer to flowing liquid oxygen in tubes in the range of nucleate boiling (reproduced and modified from [124])

Table 23: Heat transfer to LOX in the regime of nucleate boiling.

Pressure Atm	ΔT °C or K	λ $\text{W cm}^{-1} \text{ } ^\circ\text{C}^{-1}$	Q^*/A W cm^{-2}
0.225	9.83	1.47	14.5
1.004	8.93	2.50	22.4
2.02	8.73	3.68	32.2
4.07	7.11	5.16	36.7
7.93	6.12	7.06	43.2
15.47	4.58	10.9	50.1
25.65	7.54	5.87	44.3
32.01	6.96	5.69	39.6
40.84	6.18	3.60	22.2

Data source: [128]

fied by bulk-to-wall temperature property ratios to give the correlation equation. Heat transfer coefficient data were obtained using electrically heated steel tubes at supercritical pressure levels 6.2–34.4 MPa (900–5000 psia) and bulk temperatures ranging from subcritical to supercritical (105–278 K = 190–500 °R) with wall temperatures up to 1000 K (1800 °R).

The heat transfer in boiling liquid oxygen in the temperature range 79–120 K (–194 to –153 °C) at pressures of 0.025–1.08 MPa was experimentally investigated and an empirical dependence of the heat-transfer coefficient on thermal flux density and pressure was derived [134]. See also [135, 136].

3.10 Critical Constants of Liquid Oxygen

The critical constants of oxygen compiled from several literature sources are summarized in Table 24.

Table 24: Critical constants of oxygen.

Property	SI units	Other units	Authors	Year	References
$t_{\text{crit.}}$	154.58 K	–118.57 °C	Pentermann and Wagner	1978	[62]
	154.581 K	–118.569 °C	Wagner, Ewers, and Pentermann	1976	[85]
	154.33 K	–118.82 °C	Brower and Thodos	1968	[29]
	154.581 K	–118.569 °C	Stewart, Jacobsen, and Wagner	1991	[30]
	154.581 K	–118.569 °C	Weber	1977	[32]
	154.78 K	–118.37 °C	Hoge	1950	[33]
$P_{\text{crit.}}$	5.0197 MPa	49.7 atm	Pentermann and Wagner	1978	[62]
	5.043 MPa	50.43 bar	Wagner, Ewers, and Pentermann	1976	[85]
	5.043 MPa	50.43 bar	Stewart, Jacobsen, and Wagner	1991	[30]
	5.037 MPa	49.713 atm	Brower and Thodos	1968	[29]
	5.043 MPa	50.43 bar	Weber	1977	[32]
		50.14 atm	Hoge	1950	[33]
$\rho_{\text{crit.}}$	0.4299 g/cm ³	13.60 mol/L	Pentermann and Wagner	1978	[62]
		13.63 mol/L	Stewart, Jacobsen, and Wagner	1991	[30]
		0.01363 mol/cm ³	Weber	1977	[32]

3.11 Solubility, Miscibility, Solutions of Liquid Oxygen

3.11.1 Helium Dissolution

Henry's Law is used to describe the relationship between the concentration of a dissolved gas in a liquid with the pressure of the fluid and is usually expressed as:

$$c = f(P, T)$$

The solubility of helium pressurant gas in liquid oxygen is summarized in Table 25.

The solubility of helium in liquid oxygen, liquid hydrogen, and liquid methane was described by empirical correlations derived from published experimental data

Table 25: Solubility of helium pressurant gas in liquid oxygen.

Pressure		Liquid composition, mol-% helium.				
MPa	psia	143 K	128 K	113 K	93 K	77 K
1.72	250			0.27	0.14	0.04
3.45	500		0.86	0.74	0.33	0.14
5.17	750	1.80	1.59	1.13	0.53	0.20
6.89	1000	3.30	2.37	1.54	0.68	0.25
8.62	1250	4.61	3.14	1.95	0.83	0.32
10.3	1500	5.98	3.84	2.32	0.99	0.36
11.9	1750	7.26	4.46	2.67	1.14	0.43
13.8	2000	8.60	5.08	3.02	1.27	0.48

Data source: [137]

for the mol fraction of these pressurant gases in the liquid phase as a function of temperature and pressure [138]. The correlations were developed to yield accurate estimates of the mol fraction of the pressurant gas in cryogenic liquids at temperature and pressures of interest to rocket propulsion engineers. The helium solubility correlations were of the form

$$\chi = p^* \exp(a + bp^*)$$

where χ is the mol fraction solubility of the solute (helium) in the solvent liquid, p^* is a dimensionless pressure defined as $p^* = (P - P_0)/P_{\text{REF}}$, where P is the total pressure (from the pressurant gas and the vapor pressure of the liquid), P_0 is the saturated vapor pressure of the pure liquid solvent at temperature T , P_{REF} is a reference pressure defined as equal to 1 MPa, and a and b are empirically determined, temperature-dependent functions. For $b = 0$, the equation assumes the form of Henry's law. In a graph showing the mol fraction $\ln(\chi/p^*)$ as a function of pressure for 4 different temperatures between 67.5 and 113 K, the curves are linear and almost level, indicating minimum dependence of χ on pressure. A graph showing the mol fraction $\ln(\chi/p^*)$ as a function of temperature showed an almost linear increase of $\ln(\chi/p^*)$ with temperature. More specifically, the equation for the temperature dependence of χ based on empirical data becomes

$$\chi = p^* \exp(-13.82 + 0.0934 \times T/\text{K} - 0.00021 \times T^2/\text{K}^2)$$

where the terms in the parentheses need to be divided by kelvin and kelvin² to make them dimensionless. The helium mol fraction solubility in liquid oxygen is less than 0.3% in typical propulsion system applications, and the times to reach equilibrium are very long in the absence of active mixing. Considering as an example a tank at the normal boiling point temperature of liquid oxygen (90.2 K) and a total pressure of 1.72 MPa (250 psia, $p^* = 1.62$) the equilibrium mol fraction solubility is $x_{\text{He}} = 0.13 \pm 0.014\%$.

Even though the proposed operating conditions for higher pressure-fed engines are not likely to exceed 2.24 MPa (325 psia), there is still a significant amount of helium that can be dissolved into the liquid oxygen. While there are no data suggesting that the surface tension properties of the liquid oxygen will be significantly altered by this dissolved helium content, this remains to be verified. The solubility of helium in LOX is very low [139].

3.11.2 Solubility of Contaminants in LOX

Contaminants that are introduced from the air before it is liquefied and separated are carried over into the finished product and may eventually accumulate in the tank if the oxygen continues to boil off. The most abundant contaminant in ambient air is carbon dioxide. Frozen carbon dioxide in liquid oxygen might clog filters, valves, and injector orifices. Some contaminants may be introduced by venting LOX tanks to air and inadvertently allowing ambient air to enter the vessel. In addition to hydrocarbons introduced from the surrounding air, hydrocarbons may be produced from decomposition of the lubricants in the compressors that compress ambient air to later cool, expand and liquefy it. Accumulation of contaminants in LOX is a significant safety hazard and that is why the solubility of contaminants is described in some detail in this chapter. Mixtures of methane and LOX have been proposed as monopropellants (see *Encyclopedia of Monopropellants*), and therefore the miscibility of the two chemicals must be known. Mixtures of nitrous oxide and LOX have been proposed as oxidizers for bipropellants and hybrid propellants.

3.11.2.1 Solubility of Hydrocarbons in LOX

Infrared spectroscopy can be used to determine the concentrations and solubility of contaminants in LOX [140]. The solubilities of several potential contaminants are listed in Tables 26 through 29.

Table 26: Solubility of contaminants in LOX at 90 K.

Compound	Mol fraction $\times 10^6$
C ₂ H ₄	27500
C ₂ H ₂	5.4
<i>n</i> -C ₆ H ₁₄	5.7
C ₆ H ₆	0.01
(CH ₃) ₂ O	25
(C ₂ H ₅) ₂ O	4
(CH ₃) ₃ N	8.3
N ₂ O	140
CO ₂	4.3

Data source: [140]

Table 27: Solubility of solid hydrocarbons in liquid oxygen.

Hydrocarbon	Temperature, K	Solubility, log of the mol fraction
C ₂ H ₆	77.3	-1.784
C ₂ H ₆	80.0	-1.564
C ₂ H ₆	81.1	-1.526
C ₂ H ₆	85.3	-1.250
C ₂ H ₄	81.1	-2.350
C ₂ H ₄	82.3	-2.230
C ₂ H ₄	86.9	-1.939
C ₂ H ₄	87.6	-1.903
C ₂ H ₄	89.9	-1.870
C ₃ H ₆	83.0	-2.85
C ₃ H ₆	83.3	-2.64
C ₃ H ₆	86.8	-2.21
C ₃ H ₆	87.4	-2.18

Data source: [142].

The high solubility of ethylene is a real surprise [141]. Solubility data for ethane, ethylene, and propylene at lower temperatures (below 90 K) are listed in Table 27.

Liquid methane was found to form clear homogeneous solutions with LOX at 90 K (-183 °C) over the whole composition range from 0 to 100% oxygen [143]. The solutions were colorless on the methane-rich side and gradually approached the color of LOX on the oxygen-rich side. Cooling to the temperature of liquid nitrogen, 77 K, however, caused solid methane to separate in mixtures containing over 50 mass-% methane. Other investigators noted that the solubility of solid methane in LOX between 69 and 74 K (-204 and -199 °C) was limited. They found that at 74 K the saturation limit of methane in LOX was 49.35 mass-% CH₄. **Warning:** mixtures of LOX and methane are potentially **detonable**, see Section 11.8.1, Cap Sensitivity of Liquid Oxygen, and 11.9, Explosive Yield of Liquid Oxygen/Fuel Mixtures.

The mol fraction χ of methane in its saturated solutions in liquid nitrogen between 70 and 79 K and in liquid oxygen between 69 and 74 K can be expressed by the equations

$$\log \chi = 1.36576 - 120.48/T$$

for nitrogen and

$$\log \chi = 0.97986 - 85.822/T$$

for oxygen where T is the temperature in kelvin [144].

Measurements of the distribution of methane between the liquid and vapor phases of oxygen at very low concentrations of methane (~1000 ppm of CH₄) over the temperature range between 93 and 107 K were done under conditions where the

highest concentration of methane in any phase was far below the lower flammable and explosive limits for the system. Average values of the equilibrium distribution constants for methane in oxygen between 93 and 107 K were 2.8–3.35 [145].

Data for the solubility of solid acetylene and carbon dioxide in liquid oxygen and liquid nitrogen are listed in Table 28. Similar data were reported for solubility of ethylene and propylene in liquid nitrogen and liquid oxygen as shown in Table 29. See also reference [146].

Table 28: Solubility of solid acetylene and carbon dioxide in liquid oxygen and liquid nitrogen.

Contaminant	Solvent	Temperature, K	Concentration, mol fraction $\times 10^6$
Acetylene	Liquid oxygen	65.1	0.641
Acetylene	Liquid oxygen	78.9	2.04
Acetylene	Liquid oxygen	98.0	10.85
Acetylene	Liquid nitrogen	65.0	0.791
Acetylene	Liquid nitrogen	79.4	2.72
Acetylene	Liquid nitrogen	95.0	19.95
Carbon dioxide	Liquid oxygen	67.0	1.77
Carbon dioxide	Liquid oxygen	78.4	2.91
Carbon dioxide	Liquid oxygen	98	5.61
Carbon dioxide	Liquid nitrogen	67.0	2.21
Carbon dioxide	Liquid nitrogen	78.4	3.47
Carbon dioxide	Liquid nitrogen	98	7.26

Data source: [147].

Table 29: Solubility of solid ethylene and solid propylene in liquid oxygen and liquid nitrogen.

Contaminant	Solvent	Temperature, K	Concentration, mol fraction
Ethylene	Liquid oxygen	69	0.00065
Ethylene	Liquid oxygen	90.1	0.0142
Ethylene	Liquid oxygen	101	0.1743
Ethylene	Liquid nitrogen	69	0.00054
Ethylene	Liquid nitrogen	90.1	0.011
Propylene	Liquid oxygen	67	0.00202
Propylene	Liquid oxygen	80.6	0.0282
Propylene	Liquid oxygen	86.5	0.385
Propylene	Liquid nitrogen	67	0.0017
Propylene	Liquid nitrogen	83	0.072

Data source: [148].

The solubilities of solid C_2H_2 and CO_2 in liquid oxygen and liquid nitrogen and their mixtures at sea-level pressure and at temperatures from 77.4 to 90.0 K can be calculated by the linear relations

$$\log \chi = -(59.78/T) - 4.56494$$

for C_2H_2 and

$$\log \chi = -(141.18/T) - 3.77814$$

for CO_2 [149].

The solubilities of hydrocarbons in liquid oxygen and the phase behavior of hydrocarbon-oxygen systems have substantial theoretical and practical interest. Predicting solubilities of chemicals in liquid oxygen is difficult because of the non-ideal thermodynamic behavior of the liquid phase. The solubilities of hydrocarbons in liquid oxygen can also be predicted by computational methods based on statistical thermodynamics [150] or EOS, cell theory partition functions and fugacities [151, 141].

3.11.2.2 Solubility of Nitrous Oxide in LOX

The solubility of nitrous oxide in liquid oxygen at temperatures between 78 and 90 K has been determined by filtering of a sample of the saturated solution, evaporating it and analyzing it by pumping away the oxygen and trapping the nitrous oxide in liquid nitrogen [152]. The solubility can be satisfactorily expressed by the equation

$$\log \chi = 0.9954 - 435.8/T$$

where χ is the mol fraction of nitrous oxide in the saturated solution. The solubility is lower than would be expected for an ideal mixture and varies over the temperature range between 2.5×10^{-5} and 14.2×10^{-5} mol N_2O /mol O_2 . The liquefied “permanent” gases are not solvents in the usually accepted sense. In fact, the only substances which will dissolve in them to any extent are other gases of comparable volatility. Ambient air contains 0.3 ppm by volume nitrous oxide which might end up in liquid nitrogen or liquid oxygen from an air liquefaction and separation plant. Nitrous oxide and carbon dioxide are unwanted contaminants in LOX, precipitating and potentially clogging filters and orifices. The solubility of N_2O in LOX must be accurately known to prevent such problems. Solubility data (χ_{N_2O} = mol fraction in liquid phase) versus absolute temperature are plotted in Figure 24 together with literature data [153]. The solubility increases sharply once the temperature exceeds the normal boiling point of LOX. Similar measurements were made for the co-solubility of nitrous oxide and carbon dioxide in LOX. Other sources [140] give the solubility of N_2O in LOX at 90 K as 140×10^{-6} mol/mol.

Accumulations of carbon dioxide and nitrous oxide in liquid oxygen may cause fouling and blockage in heat exchangers and pipelines and it may eventually cause serious explosions, like the one that occurred in Bintulu, Malaysia, in 1997. The CO_2/N_2O co-solubility has been measured in liquid oxygen at 90 K [154].

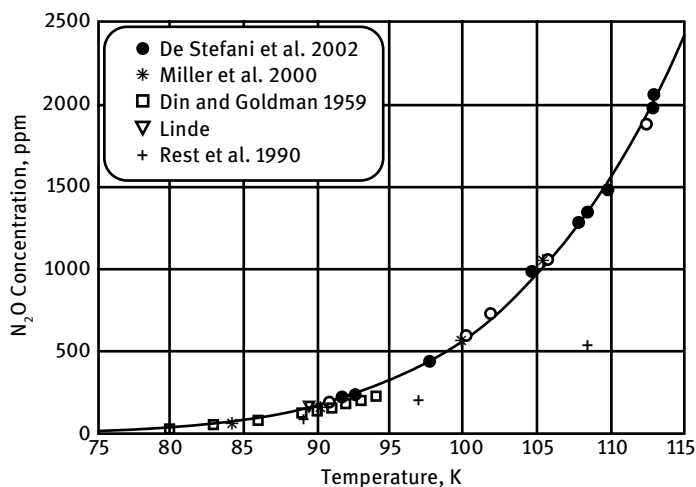


Figure 24: N₂O solubility in LOX under pressure (republished and modified from [153], with permission of © 2002 Elsevier Science Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

3.12 Thermodynamic Properties of Oxygen

With oxygen being a vital chemical and being known for a long time, there exists a plethora of thermodynamic data on oxygen in all physical states, including liquid oxygen which is of most interest as a rocket propellant. Unfortunately, the data do not always agree with each other, differences most likely caused by using different techniques to calibrate the equipment and the thermometers. Thermodynamic data on oxygen have been updated periodically as more accurate methods of measurement, supported by computational chemistry and modeling of the molecule, became available. The primary sources of thermodynamic data on oxygen are the JANAF tables [24] and the NIST Chemistry WebBook web site [27]. In addition, several publications provide tabulated data for heat capacity, enthalpy, and entropy of oxygen in all physical states [30, 155–160]. Because our main interest is in liquid oxygen, we have not included too many thermodynamic data on gaseous oxygen which are easy to find in the literature.

Continued developments in the design of rocket engines have resulted in the need for thermophysical properties data at higher and higher operating pressures. In an earlier interim report [161] NBS extrapolated data to 690 bar. In 1977 NBS presented new PVT measurements to 800 bar and derived thermodynamic properties from them [162]. Approximately 348 PVT data points were measured at 38 densities ranging from 15 to 41 mol/L (0.48–1.3 g/cm³) in the temperature range 58–300 K at pressures up to 800 bar. The reports include tables of the derived thermodynamic properties on iso-

bars up to 1000 bar, including density, internal energy, enthalpy, entropy, specific heats at constant volume and constant pressure, velocity of sound, and the property surface derivatives $(\partial P/\partial T)_\rho$ and $(\partial P/\partial \rho)_T$.

A review of the current status of mathematical models and correlations for the calculation of thermodynamic properties of cryogenic fluids included the thermodynamic properties of oxygen, nitrogen, and air [163]. There are now computer programs for thermodynamic properties of the fluids accessible on the Internet.

3.12.1 Heat Capacity of Oxygen

Giauque and Johnston in 1929 measured the specific heat of solid oxygen and discovered the existence of three phases, α , β , and γ . Transition temperature and latent heat are listed in Table 30. Table 31 gives a historical collection of the heat capacity of solid and liquid oxygen. Although these 1929 data that were already used in [164] are quite old, they were converted to S.I. units and kept only for comparison to more recent (and probably more accurate) data.

Table 30: Transition temperatures and latent heat of oxygen.

Transition point	Temperature, K	Latent heat, J/mol
Boiling point	90.17	6820
Triple point	54.36	442±2
$\beta - \gamma$	43.78	743±1
$\alpha - \beta$	23.89	0

Table 31: Heat capacity C_p of oxygen.

State	Temperature		Molar heat capacity		Heat capacity	
	°C	K	cal °C ⁻¹ mol ⁻¹	J K ⁻¹ mol ⁻¹	cal °C ⁻¹ g ⁻¹	J K ⁻¹ g ⁻¹
Solid	-260.2	13	1.1	4.602	0.034	0.144
Crystalline	-256.5	16.7	2.33	9.749	0.073	0.305
Solid	-254.7	18.5	2.79	11.673	0.087	0.365
Solid	-252.9	20.3	3.5	14.644	0.109	0.458
Solid	-251.3	21.9	4.2	17.573	0.131	0.549
Solid	-250.9	22.2	4.4	18.410	0.138	0.575
Solid	-248.1	25.1	5.42	22.677	0.169	0.709
Solid	-245.1	28.1	6.42	26.861	0.201	0.839
Solid	-239.8	33.4	7.73	32.342	0.242	1.011
Solid	-235.3	37.9	9.12	38.158	0.285	1.192
Solid	-230.9	42.3	10.73	44.894	0.335	1.403
Solid	-227.3	45.9	11.02	46.108	0.344	1.441
Solid	-221.5	51.7	11.03	46.150	0.345	1.442
Solid	-221	52.2	11.06	46.275	0.346	1.446

Table 31: (continued)

State	Temperature		Molar heat capacity		Heat capacity	
	°C	K	cal °C ⁻¹ mol ⁻¹	J K ⁻¹ mol ⁻¹	cal °C ⁻¹ g ⁻¹	J K ⁻¹ g ⁻¹
At the melting point		54.39 ± 0.05				
Liquid	-216.21	56.95	12.76	53.388	0.399	1.668
Liquid	-215.21	57.95	12.72	53.220	0.398	1.663
Liquid	-212.19	60.97	12.71	53.179	0.397	1.662
Liquid	-211.68	61.48	12.71	53.179	0.397	1.662
Liquid	-207.59	65.57	12.71	53.179	0.397	1.662
Liquid	-207.24	65.92	12.71	53.179	0.397	1.662
Liquid	-204.39	68.77	12.73	53.262	0.398	1.665
Liquid	-204.04	69.12	12.75	53.346	0.398	1.667
Liquid	-202.49	70.67	12.77	53.430	0.399	1.670
Liquid	-201.78	71.38	12.78	53.472	0.399	1.671
Liquid	-199.85	73.31	12.81	53.597	0.400	1.675
Liquid	-198.21	74.95	12.85	53.764	0.402	1.680
Liquid	-197.3	75.86	12.8	53.555	0.400	1.674
Liquid	-195.5	77.58	12.84	53.723	0.401	1.679
Liquid	-194.48	78.68	12.83	53.681	0.401	1.678
Liquid	-192.03	81.13	12.88	53.890	0.403	1.684
Liquid	-190.85	82.31	12.86	53.806	0.402	1.682
Liquid	-190.2	82.96	12.88	53.890	0.403	1.684
Liquid	-188.37	84.79	12.93	54.099	0.404	1.691
Liquid	-186.73	86.43	12.91	54.015	0.403	1.688
Liquid	-186.55	86.61	12.95	54.183	0.405	1.693
Liquid	-186.19	86.97	12.92	54.057	0.404	1.689
Liquid	-185.84	87.32	12.91	54.015	0.403	1.688
Liquid	-182.83	90.33	12.99	54.350	0.406	1.699
At the boiling point		90.33				
Gaseous	-223.16	50	6.963	29.133	0.218	0.910
Gaseous	-173.16	100	6.963	29.133	0.218	0.910
Gaseous	-73.16	200	6.962	29.129	0.218	0.910
Gaseous	25	298.16	7.017	29.359	0.219	0.918
Gaseous	773.16	500	7.429	31.083	0.232	0.971
Gaseous	1273	1000	8.335	34.874	0.260	1.090
Gaseous	1773	1500	8.739	36.564	0.273	1.143
Gaseous	2273	2000	9.024	37.756	0.282	1.180
Gaseous	2773	2500	9.305	38.932	0.291	1.217
Gaseous	3273	3000	9.518	39.823	0.297	1.245
Gaseous	3773	3500	9.711	40.631	0.303	1.270
Gaseous	4273	4000	9.879	41.334	0.309	1.292

Data source: [26]

The heat capacity of LOX along the saturation line as a function of temperature goes through a minimum near the freezing point, probably due to beginning association of O_2 molecules (Figure 25).

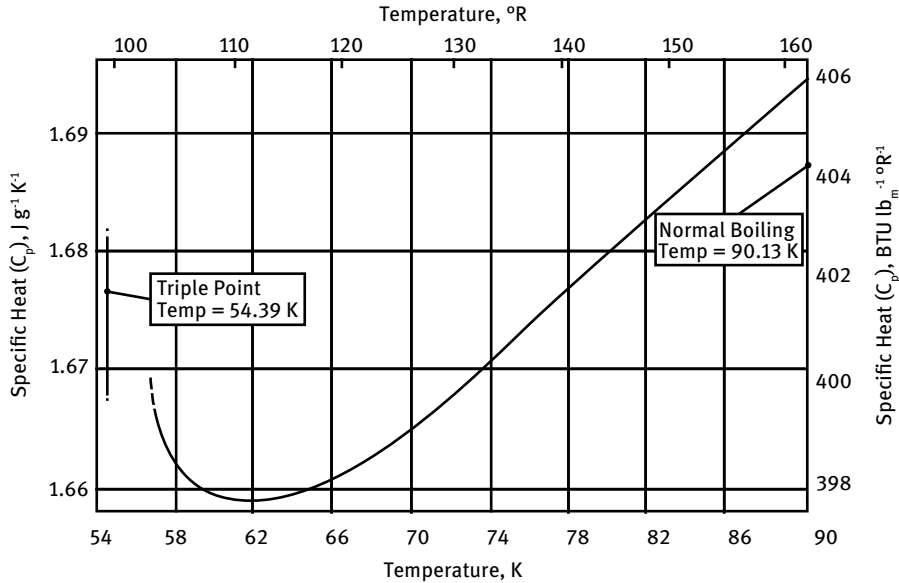


Figure 25: Heat capacity of liquid oxygen (reproduced and modified from [34])

An analytical description of the heat capacity of liquid oxygen as a function of temperature along the saturation boundary $C_v = f(T)$ is required for many engineering computations. Using a reduced temperature formulation,

$$\chi = (T_c - T)/(T_c - T_t)$$

where T_c and T_t are critical point and triple point temperatures, respectively, it can be shown that a plot of $C_v \chi^{1/2}$ versus T is a straight line, except for a small deviation as the temperature approaches the critical point, Figure 26 [165].

The isochoric molar heat capacity of liquid oxygen along the saturation line (“co-existence path in a two-phase system”) can be described by the following more complicated equation:

$$C_v = [A + B\chi + C(1 - r\chi)^n] / \chi^{1/2}$$

where C_v is the molar heat capacity in $J mol^{-1} K^{-1}$, $\chi = (T_c - T)/(T_c - T_t)$ where T_c and T_t are critical point and triplepoint temperatures, respectively, r is defined as $(T_c - T_t)/T_c$, and the exponent n is selected as $n = 12$. The constants A , B and C are:

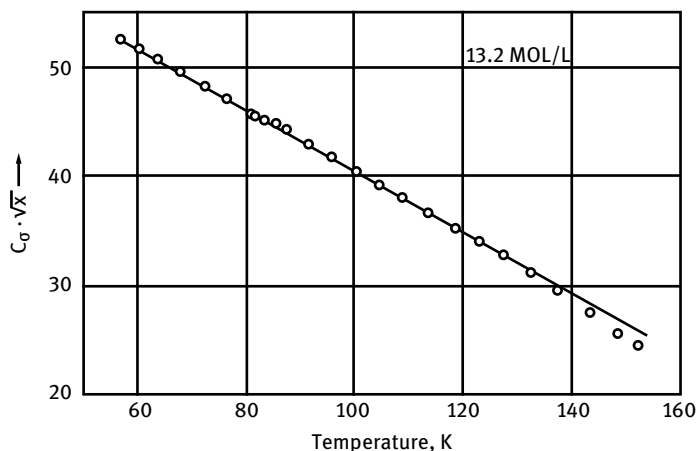


Figure 26: Heat capacity of saturated liquid oxygen (reproduced and modified from [165])

$A = 25.60277$, $B = 27.71001$, $C = -2.48274$. Using this equation, the molar heat capacity of liquid oxygen just above the melting point is $53.313 \text{ J mol}^{-1} \text{ K}^{-1}$ and at the boiling point it is $54.142 \text{ J mol}^{-1} \text{ K}^{-1}$. Integrating this equation for a temperature change between the triple point and the normal boiling point gives an enthalpy change of 1918.98 J/mol .

In expanding the temperature regime beyond the critical point pressure (50.140 atm at 154.77 K) to pressures of 350 atm at 300 K, additional heat capacity measurements were made in a range of physical conditions that is rarely encountered during storage of liquid oxygen but may well be encountered in a rocket engine for a very short time. Experimental specific heats at constant volume for oxygen in single phase domains were reported from the triple point to 300 K at pressures to 350 atmospheres [166]. A very complicated empirical equation with seven constants was used to describe specific heat over the entire domain of PT coordinates with an experimental accuracy of 1–2%. Values for the terminal slopes of PVT isochors at the coexistence boundary, $(\partial P/\partial T)_v$, were then derived for the liquid. One wonders why the authors did not publish the results in the format of a simple polynomial equation to the fourth or fifth degree that would be a lot easier to use.

Measurements of the heat capacity of solid oxygen in the temperature range from 1.3 K to about 71 K with particular attention to the behavior at very low temperatures, and in the neighborhood of the $\alpha \rightarrow \beta$ transition at about 23.89 K, led to the assumption that near 0 K each molecule moves as a single mass point with the passage of lattice waves, and the effective Debye temperature at 0 K was extrapolated to be $104 \pm 2 \text{ K}$ [167]. As the temperature rose above 10 K, the specific heat rose more rapidly than a reasonable Debye model would predict, suggesting the appearance of additional

degrees of freedom, which are thought to be the superposition of a librational motion of the molecules superimposed on the longitudinal and transverse lattice waves controlling the motion of a molecule's center of mass. The specific heat showed a very sharp high “spike” at the $\alpha \rightarrow \beta$ transition, but there was no evidence for a latent heat associated with this transition. See also [168, 169].

3.12.2 Heat of Formation of Liquid Oxygen

By definition, the standard enthalpy of formation $(\Delta H)_{298}^f$ of gaseous oxygen at 298 K and 101 kPa is 0.00 kJ/mol. Once gaseous oxygen is liquefied, heat of condensation is removed and the enthalpy of formation of liquid oxygen becomes a negative number. Enthalpies of formation of liquid oxygen reported by different sources are listed in Table 32.

Table 32: Enthalpy of formation of liquid oxygen at normal boiling point.

Authors	Year	Enthalpy of formation			References
		kJ/mol	kcal/mol	cal/g	
Callery Booklet		-12.887	-3.08	-96.2	
NASA CEA THERMO.INP	04/1995	-12.979	-3.102	-97	[170]
NWC NEWPEP	2007	-12.987	-3.104	-97	

Molecular mass: 31.9988 g/mol

It is strange that so many aerospace thermodynamic data summaries and rocket propellant books do not include LOX at its normal boiling point at 90 K = -183 °C. Kit and Evered [171, 172] on page 183 had a completely wrong number (126.9 BTU/lb = 90.5 cal/mol). The number should be negative! Siegel and Schieler (1964) [173] lists four pages of rocket propellant physical properties but neglects to include LOX. Barrere et al. (1960) [174] shows only gaseous oxygen at 298 K, where the enthalpy of formation is zero by definition and everyone should know that. NIST Chemistry WebBook [27] does not contain the enthalpy of formation of LOX.

3.12.3 Heat of Fusion of Solid Oxygen

The heat of fusion of solid oxygen is difficult to determine experimentally because of the preceding phase changes in solid oxygen. The heat of transition of some of the phase changes may even be more than the heat of fusion. The somewhat poorer agreement for solid oxygen may be due to some characteristics in its behavior in that liquid oxygen becomes viscous close to its freezing point and readily supercools to a glass interfused with crystals of the solid modification stable just below the melting point.

A few heat of fusion data of solid oxygen are summarized in Table 33, but may not be very accurate.

Table 33: Heat of fusion of solid oxygen.

Heat of fusion			Authors	Year	References
J/mol	kcal/mol	cal/g			
444.7	0.1063 ± 0.0003	3.322	Giauque and Johnston	1929	[26]
444.5	0.10624	3.32	Kit and Evered	1960	[171]

Molecular mass: 31.9988 g/mol

3.12.4 Heat of Evaporation of Liquid Oxygen

Heat of evaporation data of liquid oxygen from various sources are summarized in Table 34.

Table 34: Heat of evaporation of liquid oxygen at normal boiling point.

Heat of evaporation			Authors	Year	References
kJ/mol	kcal/mol	cal/g			
6.815 ± 0.0067	1.6288 ± 0.0016	50.9 ± 0.05	Giauque and Johnston	1929	[26]
6.815	1.6288	50.9	Kit and Evered	1960	[171]
6.825	1.631	50.98	Furukawa and McCoskey	1953	[175]

Table 35 is a summary of heat of evaporation of liquid oxygen at various temperatures (at the saturation pressure for each of these temperatures). The number for the heat of evaporation at the normal boiling point was interpolated. Another compilation of measured, calculated and literature data on the heat of evaporation of liquid oxygen at different temperatures is presented in Table 36. Figure 27 illustrates the decreasing heat of evaporation of liquid oxygen between the normal freezing point and normal boiling point as a function of temperature.

Table 35: Heat of evaporation of liquid oxygen

Temperature K	Heat of evaporation	
	J/g	J/mol
68.4065	231.71	7414.7
68.4122	231.99	7423.7
68.4146	231.73	7415.4
68.40	—	7418.2
76.0053	225.98	7231.4
76.0181	225.84	7226.9
76.0241	225.78	7225.0
76.00	—	7228.2
84.1392	218.87	7003.8
84.10	—	7004.9
81.2870	212.29	6793.3
90.190	213.27*	6824.8*
91.2870	212.14	6788.5
91.30	—	6790.4

* interpolated

Data source: [175]

Table 36: Heat of evaporation of liquid oxygen.

Temperature K	Heat of evaporation, calculated, J/mol			Experimental	Literature
	ΔH	$T\Delta S$	Clapeyron equation	Giauque and Johnston [26]	[175]
54.359	7761	7759	7730		
60	7624	7623	7624		
68.4	7417	7415	7423		7418
70	7377	7375	7382		
76	7222	7219	7224		7228
80	7114	7111	7114		
84.1	6998	6996	6996		7005
90.188	6814	6812	6810	6815±7	6825
100	6477	6474	6470		
110	6062	6061	6052		
120	5550	5549	5538		
130	4896	4897	4887		
140	4004	4005	4005		
150	2547	2547	2537		
154	1169	1169	1160		

Data source: [176]

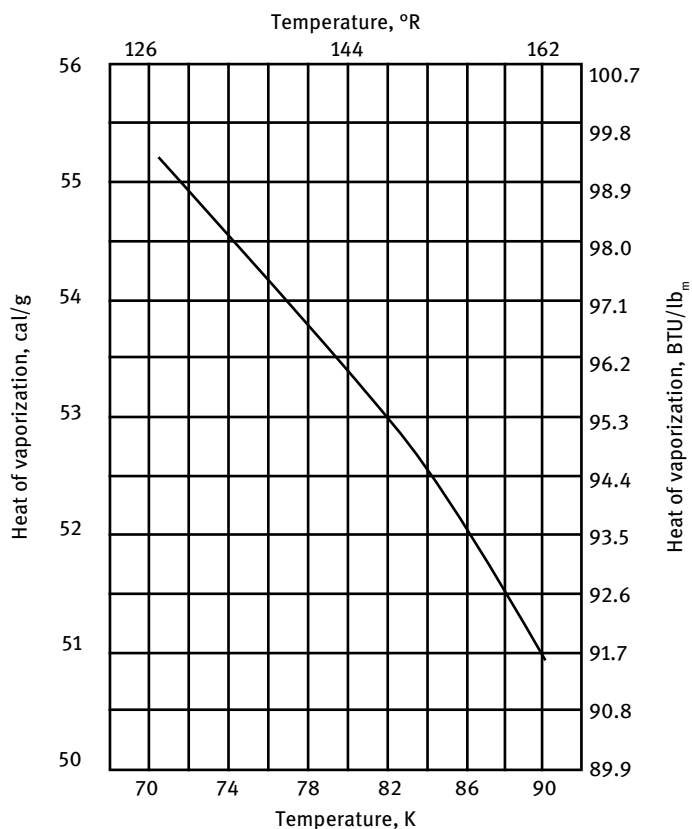


Figure 27: Heat of evaporation of liquid oxygen (reproduced and modified from [34])

3.13 Molecular Properties, Structure, Dipole Moment, Molecular Orbital Calculations of Oxygen

3.13.1 Structure of the Dioxygen Molecule

The distance of two oxygen atoms in dioxygen in the ground state triplet dioxygen is $1.21 \text{ \AA}$. The bond energy is 498 kJ/mol . The dissociation energy in the formation of atomic oxygen is equal to twice the heat of formation of atomic oxygen from molecular oxygen, $249.18 \pm 0.10 \text{ kJ/g-atom}$ at 298 K .

3.13.2 Structure of Polyoxygen Molecules

There is much interest in polyoxygen molecules O_n with $n \leq 3$, allotropes of dioxygen, as they may occur in the ozone layer of the atmosphere, in frozen or high-pressure oxygen and as short-lived intermediates in the decomposition of ozone. Here we are examining the potential for any of these molecules to be stabilized and used as a rocket

propellant. One may argue that if it is not even possible to use O_3 as a rocket propellant, how much more difficult would it be to use O_8 as a rocket propellant! Nevertheless, we need to look at O_8 and its unique properties from the standpoint of a rocket propellant chemist.

In discussing polyoxygen molecules, one must differentiate between molecules with true covalent bonds or those with loose van der Waals adducts. UV and electron beam irradiation of solid O_2 revealed a series of IR features near the valence anti-symmetric vibration band of O_3 which were frequently interpreted as the formation of unusual O_n allotropes in the forms of weak complexes or covalently bound molecules. The structure, relative energies, and vibrational frequencies of various forms of O_n ($n=1-6$) in the singlet, triplet, and, in some cases, quintet states were studied using computational chemistry [177]. The results of calculations demonstrated the existence of stable highly symmetric structures O_4 ($D3h$), O_4 ($D2d$), and O_6 ($D3d$) as well as the intermolecular complexes $O_2...O_2$, $O_2...O_3$, and $O_3...O_3$ in different conformations. For the ozone dimer, a new conformer was found which is more stable than the structure known to date.

3.13.3 Structure of Trioxygen Molecules

Trioxygen, ozone, and the several potential isomeric structures this compound may assume, are discussed in detail in *Encyclopedia of Oxidizers*, chapter “Ozone”.

3.13.4 Structure of Tetraoxygen Molecules

Most of the literature on tetraoxygen deals with the dimer of dioxygen, $(O_2)_2$. The question is if another tetraoxygen O_4 exists that is bound with covalent bonds instead of a loose van der Waals association or a collision pair of two dioxygen molecules.

3.13.5 Structure of Polyoxygen Molecules

Oxygen clusters O_8 have been observed in the ϵ -phase of solid oxygen which may be a tetramer of dioxygen $(O_2)_4$. As the pressure of oxygen at room temperature was increased to and above 10 GPa, it underwent a dramatic phase transition to a different allotrope. Its volume decreased significantly, and it changed color from blue to deep red [40]. Based on its IR absorption spectrum, researchers assumed in 1999 that this phase consists of O_4 molecules in a crystal lattice. Later it was shown by XRD that this stable phase known as ϵ oxygen or red oxygen is in fact octaoxygen, O_8 (Figure 28). No one had predicted the structure theoretically: a rhomboid O_8 cluster consisting of four O_2 molecules.

At very high pressures, solid oxygen changes from an insulating to a metallic state; at very low temperatures, it even transforms to a superconducting state. Six distinct crystallographic phases are unambiguously established. Of these, the ϵ phase of solid oxygen is particularly intriguing: it exhibited a dark red color, very strong IR absorp-

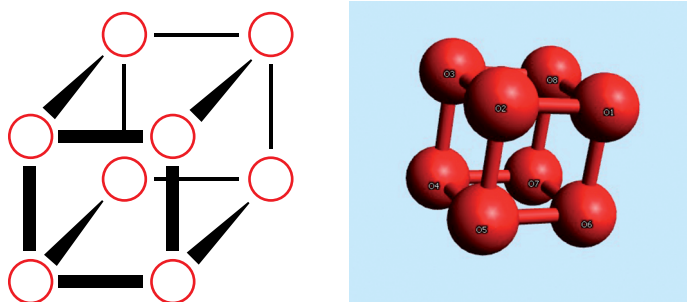


Figure 28: Molecular structure of octaoxygen.

tion, and magnetic properties. It was also stable over a very large pressure domain and has been the subject of numerous XRD, spectroscopic, and theoretical studies. But although ϵ -oxygen has been shown to have a monoclinic $C2/m$ symmetry and its IR absorption behavior attributed to the association of oxygen molecules into larger units, its exact structure remained unknown. ϵ -oxygen was then characterized by the association of four O_2 molecules into a rhombohedral box-shaped molecular unit, held together by what are probably weak chemical bonds. This structure was consistent with existing spectroscopic data and was further validated by the observation of a predicted Raman stretching mode [178, 179]. The cube-shaped molecular unit O_8 , or $(O_2)_4$, exhibits strong bonds in the diatomic units but much weaker $\pi^*-\pi^*$ bonds between them [180]. It was shown that the intracluster O_2 interaction is consistent with a donation-acceptor bond rather than the spin-pairing of two open-shell molecules [181]. Structural changes eventually lead to a structural transition at 96 GPa, as observed experimentally.

Multiconfigurational *ab initio* calculations were used to obtain a characterization of the ground singlet state of $(O_2)_4$, which is compatible with the non-magnetic character of the ϵ phase [182]. It was shown that $(O_2)_4$ is a van der Waals-like cluster where exchange interactions preferentially stabilize the singlet state. Oxygen exhibits an unusual O_8 cluster in its high-pressure solid phase. In addition, the dissociation of molecular oxygen into a polymeric spiral chain O_4 structure (space group $I4_1/acd$, θ - O_4) above 1.92 TPa pressure was predicted based on computations [183]. The θ - O_4 phase was predicted to have a similar structure as the high-pressure phase III of sulfur. Stabilization of θ - O_4 turns oxygen from a superconductor into an insulator by opening a wide band gap.

At large distances, the four triplet O_2 molecules are arranged in a way consistent with an anti-ferromagnetic structure, whereas at short distances, a significant spin redistribution is driven by the exchange process and it leads to a null magnetic moment per molecule [184]. Such behavior can be related with the magnetic evolution of solid oxygen across the $\delta \rightarrow \epsilon$ phase transition. Additional calculations of $(O_2)_4$ excited

states supported the conclusion that the relative stabilization and magnetic features of the ground singlet state are due to the onset of new intermolecular bonds, and not to an exclusive modification of the electron cloud within the O_2 molecules.

3.13.6 Crystal Structure of Solid Oxygen

Solid oxygen can exist in at least three different phases, depending on temperature and pressure (see section “Phase transitions of Solid Oxygen” on melting points and phase changes). The crystal structure of α oxygen (monoclinic, $C2m$, two molecules per cell) is consistent with O_2 molecules in contact along two rows in the (001) plane, and along two rows lying a plane that is 80.5° from (001) [185]. Contact is defined as the touching of the contours at the 0.002 level of electron density of the contoured electron density maps for O_2 . Twinning, with a twinning shear of 19° in the [90] direction on the (001) plane, should be easy; both twins and stacking faults are likely to be common and produce features in the XRD patterns. The β - O_2 phase can be seen as closely related to the α phase: if the (001) planes shear into an ABCABC... sequence and the configuration in the (001) plane is hexagonalized, the β -type structure is obtained. In this structure, if the O—O bonds are tipped about 75° to the threefold axis and precess around it, there will be contacting molecules in three directions normal to the threefold axis and along the triad axis of the rhombohedral cell. Calculated densities of the α and β phases are different at the transition temperature and the transformation is of first order.

Crystal structures and phase transitions in solid oxygen at pressures up to 13 GPa at 298 K were studied by XRD [186, 187] and Raman spectroscopy [40]. The crystal structure of the α -phase of oxygen that exists at temperatures below 23.89 K is monoclinic of space group $C2/m$. The dense packing of molecules of oxygen in this structure and the nature of the transformation from the α - to the β -phase (rhombohedral, space group $R\bar{3}m$) at 23.89 °K led investigators to conclude that there is an increase in the molar volume of solid oxygen of about 0.1 cm^3 per mol (about 0.5%) accompanying the $\alpha \rightarrow \beta$ transition and it was suggested on the basis of this volume change that the transition is of first order. The unit cell of frozen γ -oxygen is cubic, its space group is $Pm\bar{3}n$, and it has a lattice dimension of $a = 6.83\text{ \AA}$. The unit cell contains eight oxygen molecules. Oxygen molecules located at the center and corner of the cube can rotate freely, and each oxygen in the face of the cube can rotate in the plane perpendicular to the face. The crystal structure of β -oxygen is rhombohedral with a space group of $R\bar{3}m$. Its corresponding hexagonal cell has the dimensions $a = 3.307$, $c = 11.250\text{ \AA}$, and contains three oxygen molecules with their axis parallel to the hexagonal axis. The crystal structure of α -oxygen is monoclinic with $a = 5.403$, $b = 3.429$, $c = 5.086\text{ \AA}$, $\beta = 132.53^\circ$, unit cell volume = $69.44\text{ \AA}^3$, calculated density 1.530 g/cm^3 . The cell contains two molecules centered at the lattice points 000 and $\frac{1}{2}\frac{1}{2}0$, which are symmetry centers. The nearest center-to-center distances between molecules is $3.20\text{ \AA}$ and the O—O bond axis was found to be perpendicular to the a - b plane. Crystal structures did

not indicate the presence of any O_4 molecules (postulated to exist in solid oxygen, based on other observations) [188].

3.14 Optical, Electrical, and Magnetic Properties of Liquid Oxygen

3.14.1 Absorption, Emission, and Fluorescence Spectra of Liquid Oxygen

Dioxygen O_2 is the second most abundant constituent in the earth's atmosphere and vital for life on earth. The dissociation, predissociation, and band system of molecular oxygen play an important role in the aurora, airglow, and nightglow in the upper atmosphere. It is the photolysis of oxygen in the upper atmosphere that forms the ozone layer and protects life on Earth from the sterilizing UV radiation from the sun. In addition to neutral O_2 , atomic oxygen and oxygen ions like O_2^+ or O_2^- and to a lesser extent O_2^{2+} populate the ionosphere. All these are important constituents of stellar atmospheres (including that of the sun) and possibly of exoplanetary atmospheres. Even at the orbital height of satellites circling around the earth, high above the upper limits of the atmosphere, the small concentration of atomic oxygen is the most destructive species and is responsible for the degradation of elastomers, plastic coatings, paints, and solar cells in satellites.

In laboratory studies with air-filled instruments below 2000 Å, spectrographs must be evacuated because of the strong absorption of light by O_2 . This range of the spectrum is therefore called the vacuum-UV.

Photoionization cross-section measurements of oxygen are an important part of atmospheric studies. Photolysis of liquid or solid oxygen is one method to prepare ozone and other polyoxygens in the laboratory. This reaction may also occur on the cold surface of outer planets and their icy moons. Liquid oxygen and liquid ozone have been photolyzed in a search for more energetic polyatomic polyoxygen species (O_4 , O_6 , O_8) that can be stabilized at low temperatures and possibly used as rocket propellants. Atomic oxygen formed by photolysis of dioxygen is a prime reactant in atmospheric pollution studies in the oxidation of hydrocarbon vapors and formation of NO_x .

The energy levels the O_2 molecule assumes as it absorbs or emits radiation are usually designated by capitalized Greek letters, such as Δ , Π or Σ . There are several hundred publications on the spectra of dioxygen and its ionization and dissociation products, and we cannot possibly reference all of those here. Most of those publications relate to processes in the upper atmosphere. There are several good summaries that are a good starting point if one wants to study spectra of oxygen [189]. Figure 2 on page 520 of that publication shows the potential energy curves for O_2 , O_2^+ , and O_2^- and illustrates the complexity of electronic, rotational, and vibrational states and the transitions between them, each of those creating a set of absorption bands in the spectrum.

3.14.1.1 Infrared Absorption Spectra of Liquid Oxygen

Although O_2 is electrically non-polar, and the O—O bond should be IR inactive, it has a permanent magnetic moment associated with the aligned spins of two unpaired electrons. Consequently, magnetic dipole (resonance) transitions are allowed between the spin multiplet components of the ground state of O_2 , i.e., components with the same value of N , but different values of J .

Absorption intensities in the 0-0 and 1-0 bands of the infrared and the 0-0 band of the red band systems of oxygen gas were measured in the range 50–150 atm at 298 K (25 °C) [190]. The integrated absorption coefficient of each band was expressed as a power series in ρO_2 , the Amagat density of oxygen. The coefficient of the linear term $A\rho O_2$ is a measure of the intrinsic (magnetic dipole) absorption of the O_2 molecule; it was much greater in the red than in the infrared system. The quadratic term, $B\rho O_2^2$, gives the induced absorption in O_2 - O_2 collision pairs; B was about ten times greater in the infrared than in the red system.

The IR spectra of industrial grade liquid oxygen and liquid nitrogen were measured in the range 3500–1200 cm^{-1} and the absorption bands were interpreted [191]. All contaminant bands except the one at 3015 cm^{-1} assigned to methane disappeared when the liquid oxygen was treated with dried silica gel. The bands at 1286, 2219, 2458, and 2560 cm^{-1} were close to known absorption bands of nitrous oxide, N_2O . The bands at 2862, 2873, 2935, and 2962 cm^{-1} most likely belonged to hydrocarbon impurities in the LOX. The last three are close to known bands for ethane C_2H_6 . The correctness of these assignments was verified by doping a sample of LOX with N_2O or C_2H_6 and re-analyzing the sample. In the industrial grade LOX no absorption was seen in the range 3150–3350 cm^{-1} where one would expect the C—H stretching band of acetylene, a frequently observed and dangerous contaminant of LOX. A LOX sample doped with a known amount of acetylene showed a peak at 3272 cm^{-1} where it was expected.

The spectrum of solid α -oxygen deposited at 15 or 20 K consists of a sharp absorption centered at 1549 cm^{-1} (half-width $\sim 4\text{ cm}^{-1}$) and a more intense, broad absorption (half-width $\sim 45\text{ cm}^{-1}$) with well-defined peaks at 1591 and 1617 cm^{-1} as shown in reference [192]. Warming through the $\alpha \rightarrow \beta$ phase transition (at 24 K) caused the broad band to become more diffuse. Recooling restored the low-temperature spectrum and showed that the $\alpha \rightarrow \beta$ transition is rapid and reversible. None of the spectra, including those of isotopic mixtures, suggested the presence of O_4 molecules.

The prominent feature of the spectrum of crystalline α -oxygen is a temperature-dependent absorption near 27 cm^{-1} , which appears to be an anti-ferromagnetic resonance mode, the first such collective excitation to be observed in a molecular solid [193].

The IR spectrum of gaseous oxygen was examined from 1480 to 1800 cm^{-1} at temperatures between 77 and 300 K at path lengths to 200 m [194]. At all temperatures a broad structureless band was observed, which was attributed to induced absorption by colliding pairs of oxygen molecules; however, near 90 K a doublet feature appeared on top of the broad absorption which exhibited a quadratic pressure dependence and

which was assigned to a bound state oxygen dimer (O_2)₂. The energy of formation of (O_2)₂, as determined from the temperature dependence of the doublet, was $\Delta E_f = -530$ cal/mol. Part of the IR absorption of oxygen is induced by intermolecular forces [195]. A summary of infrared spectroscopy in liquefied gases with 151 references is provided in [196].

The IR absorption spectra of molecular solid oxygen O_2 have been studied at pressures up to 92 GPa at room temperature to examine the structure of the ϵ phase [197]. The IR-active vibron fundamental around 1500 cm^{-1} consisted of at least 4 absorption bands and their frequencies showed a turnover at 25 GPa with increasing pressure and then monotonically increased to 87 GPa after an initial decrease. The significant increase in the frequencies of the IR-active and Raman-active vibrons suggested a strengthening of the O—O intramolecular bond with pressure.

3.14.1.2 Raman Scattering Spectra of Liquid Oxygen

The vibrational Raman effect has been observed in both liquid and gaseous oxygen. Rotational Raman spectra have been observed only in the gas.

The pure rotational and rotation-vibrational Raman spectrum of oxygen gas at 1 atmosphere pressure has been photographed under high dispersion in the first order of a 15000 lines/in., 21-foot concave grating [198]. The molecular constants were in good agreement with those obtained from the study of the electronic spectrum.

The Raman spectrum of gaseous oxygen at 3 atm was recorded with sufficient resolution and Rayleigh-line rejection to observe the fine structure caused by the multiplicity of the rotational levels of the $^3\Sigma_g^-$ ground state of oxygen [199]. Figure 29 shows the Raman spectrum of oxygen obtained at an absolute pressure of 3 atm. It was shown that all features of the observed spectrum came from expected transitions between well-known energy levels.

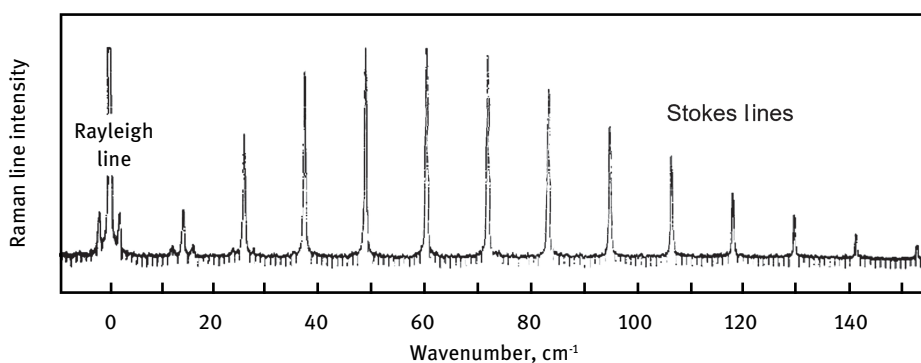


Figure 29: The rotational Raman spectrum of gaseous oxygen at 3 atm (reprinted and modified from [199], with permission from © 1969 Elsevier; permission conveyed through RightsLink)

Using Ar^+ 4880 excitation, the rotational spectrum of gaseous oxygen has been obtained with enough signal-to-noise ratio that measurements of intensities of the spin satellites of the S (3) and S (5) lines were possible [200]. The agreement with calculated results was excellent. The fundamental vibrational band was measured with the Q branch lines resolved and with an intensity sufficient to see spin structure.

High-resolution (0.002 cm^{-1}) stimulated Raman spectroscopy has been applied to the study of both normal and satellite Q branches of the fundamental vibrational band of molecular gaseous oxygen [201]. Using a pulsed molecular free-expansion jet to adiabatically cool the oxygen sample, satellite Q branches at 1554 and 1558 cm^{-1} that arise due to the splitting of the $^3\Sigma_g$ ground state by spin-spin and spin-rotation interactions were completely resolved for the first time.

The SS and OO branches of the fundamental vibrational band of molecular oxygen in its electronic ground state have been resolved for the first time in Raman spectroscopy [202]. The spectra have been observed at room temperature and low pressure with a stimulated Raman scattering (SRS) spectrometer using a multipass cell. From these accurate Raman data combined with microwave data, it was possible to calculate improved values of the vibrational, rotational, spin-spin, and spin-rotation interaction constants in the $\nu=1$ vibrational state. In addition, Raman Q branches of the first and second hot bands have been recorded, allowing the determination of a set of molecular parameters for the $\nu=2$ and $\nu=3$ states, useful for future coherent anti-Stokes Raman spectroscopy (CARS) diagnostics in combustion studies.

Lattice dynamical calculations for the bulk α , β , and γ phases of solid O_2 in harmonic approximation were made from the observed Raman spectra in frozen oxygen [203]. The observed Raman lines for $\alpha\text{-O}_2$ at 43 and 79 cm^{-1} , which are both known to exhibit isotope shifts, were tentatively assigned to an accidentally degenerate line and a two-phonon band, respectively. Some discrepancies between predicted and measured spectra still must be resolved.

Detailed Raman investigations on gaseous, liquid, and solid oxygen in its α , β , and γ phases led to observation of some new features in the spectra, such as a temperature-dependent splitting of the vibrational line in $\gamma\text{-O}_2$ and a vibron-phonon combination in $\alpha\text{-O}_2$ and $\beta\text{-O}_2$ [204]. The influence of temperature on the librational line width was explained in terms of the anharmonic interaction. These data gave new information about the assignment of some of the vibration modes.

See also reference [205].

3.14.1.3 Ultraviolet Absorption Spectra of Liquid Oxygen

The photodissociation continuum of oxygen extends from 1750 to 1300 Å . The peak absorption coefficient is at about 1420 Å . The UV absorption and photodissociation of oxygen is essential for maintaining the ozone layer in the upper atmosphere and for protecting life on earth from the intense UV radiation of the sun. Consequently, the UV spectra of oxygen have been thoroughly investigated and there exist several hundred publications on this topic and an equal number on the UV spectra of ozone. On

top of that, several dozen publications reported on spectra measured with isotope-labeled oxygen. Only an incomplete random sample of oxygen UV spectra publications is referenced here. UV photolysis of oxygen is of interest for the laser initiation of oxygen/hydrogen rocket engines. The atmospheric absorption due to oxygen, ozone, and moisture very much limits the amount of astronomy that can be done from the surface of the earth. Therefore, satellites equipped with telescopes and UV spectrographs had to be sent into orbit above the atmosphere to study light from other celestial bodies (stars, planets, comets) in the UV range. The various UV absorption bands of oxygen are named after spectroscopists that first observed them:

- The Rydberg series describe the energy levels associated with almost removing an electron from the ionic core.
- Schumann-Runge bands between 176 and 192.6 nm
- Herzberg bands between 240 and 260 nm

Absorption coefficients of oxygen were measured between 300 and 1300 Å using a grazing incidence vacuum spectrograph together with a line emission light source [206]. The coefficients near 1300 Å were less than $k = 10 \text{ cm}^{-1}$. The bands in the region between 1300 and 1000 Å showed strong absorption. No strong continuous absorption was found in the region between 1300 and 740 Å. The continuous absorption of oxygen below 740 Å was interpreted as composed of the ionization continua of several Rydberg series converging to the excited states of the molecular ion of oxygen. The continuum had a broad maximum with k -values of about 700 cm^{-1} between 400 and 600 Å and, in contrast to nitrogen, still showed a large absorption of $k = 530 \text{ cm}^{-1}$ at 303 Å.

Absorption cross-sections for oxygen in the region 1850–2500 Å have been measured at different pressures, revealing a variation with pressure, probably due to the formation of $(\text{O}_2)_2$ or O_4 [207]. The values obtained by extrapolation to zero pressure varied from $15 \times 10^{-24} \text{ cm}^2$ at 1900 Å to $3 \times 10^{-24} \text{ cm}^2$ at 2300 Å. The absorption, which was about one million times weaker than that of the Schumann-Runge (S-R) system is the Herzberg continuum corresponding to a forbidden transition. The absorption cross-sections for this continuum have been calculated for different values of the internuclear distance r_e ; those for $r_e = 1.50 \text{ Å}$ agreed best with the experimental results. The calculation indicated that the maximum value of the absorption is $15 \times 10^{-24} \text{ cm}^2$ at 1870 Å. The dissociation of oxygen in the upper part of the earth's atmosphere, above 80 km, is predominantly due to absorption in the S-R continuum (1850–1350 Å), which is important in relation to the formation of the ozone layer. At wavelengths near 2100 Å the Herzberg continuum absorbs more of the sun's radiation than does the ozone continuum. Most of this absorption takes place below 25 km. The f -value of the Herzberg continuum is 3.5×10^{-5} .

The ultraviolet absorption spectra of oxygen over the wavelength range from 1750 to 2900 Å have been observed in liquid and solid media at low temperature [208]. By freez-

ing slowly from the liquid phase, samples of crystalline argon and nitrogen were prepared with added amounts of oxygen ranging between 0.01 and 10%. The Schumann-Runge bands of oxygen ($B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-, 1750\text{--}2000\text{ \AA}$) were observed in solid and liquid mixtures of oxygen in argon or nitrogen at concentrations less than 5%, over the temperature range 60–90 K. The bands were broad, with half-intensity width of $150\text{--}550\text{ cm}^{-1}$ and showed no structure. At concentrations of oxygen above 5% the Herzberg bands of oxygen ($A^3\Sigma_u^- \leftarrow X^3\Sigma_g^-, 2400\text{--}3000\text{ \AA}$) were observed in the region $2400\text{--}3000\text{ \AA}$. These bands were also broad ($200\text{--}600\text{ cm}^{-1}$) and showed some partially resolved structures. No differences were observed for changes either in temperature or matrix material.

Photodissociation processes in molecular oxygen occurring in the wavelength range $500\text{--}900\text{ \AA}$ ($14\text{--}25\text{ eV}$) were investigated through observation of the resulting atomic fluorescence radiation [209]. The dispersed radiation from a continuous light source was used to excite the gas, and the resulting fluorescence radiation was observed in the ultraviolet and infrared regions. For incident wavelengths between $750\text{ and }850\text{ \AA}$ ($14.6\text{--}16.5\text{ eV}$) the electronic state from which the $1302\text{--}1306\text{ \AA}$ resonance lines are produced, was populated by predissociation. At higher energies, between $650\text{ and }770\text{ \AA}$ ($16.1\text{--}19.1\text{ eV}$), a photodissociation process occurred which produced the $1302\text{--}1306\text{ \AA}$ lines.

Discrete and diffuse absorption bands in the region $80000\text{--}100000\text{ cm}^{-1}$ were only partly assigned and may belong to various Rydberg series converging to the first ionization potential [210]. The onset of the ionization continuum was observed at $1027.6\text{ \AA}$ (97314 cm^{-1}) by photoionization mass spectrometry. Relative photoionization efficiency curves were determined to produce O_2^+ , O^+ , and O^- from molecular oxygen in the wavelength region of the helium continuum. The photoionization efficiency curve for O_2^+ throughout most of the region from $1030\text{--}580\text{ \AA}$ showed a rotationless autoionization structure, which was broadened due to predissociation and/or autoionization.

The Schumann-Runge absorption bands of O_2 in the wavelength region $175\text{--}205\text{ nm}$ were measured at high resolution with a 6.65-m vacuum spectrograph and presented in the form of an atlas showing detailed rotational line assignments containing the bands, tables of wave numbers measured for rotationally assigned principal branch lines belonging to the bands and tables of measured wave numbers of lines in the region near the dissociation limit where many unassigned lines exist [211]. The resolution of the spectra is such that $1\text{--}2\text{ nm}$ is spread over the width of a printed page and three sections fill one page of the report. See also: [212–214].

3.14.1.4 Visible Range Absorption Spectra of Liquid Oxygen

In the visible absorption spectrum of liquid oxygen peaks are located at $630, 578, 534, 478, 446, 380, 362, \text{ and } 344\text{ nm}$ [215] (Figure 30). The most intense peaks are in the yellow to red spectral region ($630\text{ and }578\text{ nm}$, respectively) and are responsible for the blue color of LOX.

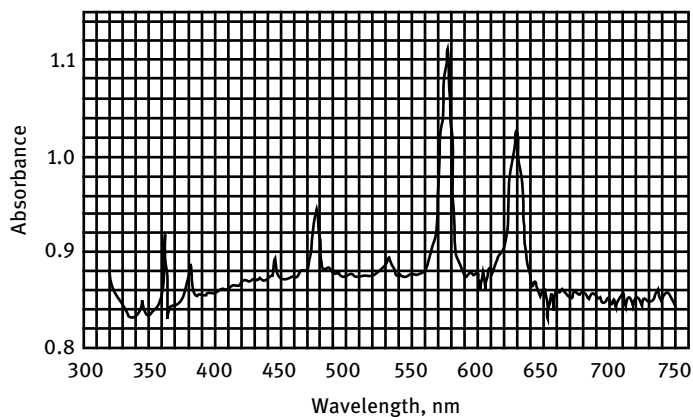


Figure 30: Absorption spectrum of liquid oxygen in the visible range (reprinted and modified from [215], with permission from © 2002 American Chemical Society; permission conveyed through RightsLink)

The absorption spectrum of LOX in the visible range (Figure 31) was used to select the wavelengths for a dual wavelength analysis system, one at the absorption maximum and another away from it [216]. This allows continuous on-line measurement of contaminants (see Section 4.1.2.2, Spectroscopic Methods for Analyses in Liquid Oxygen).

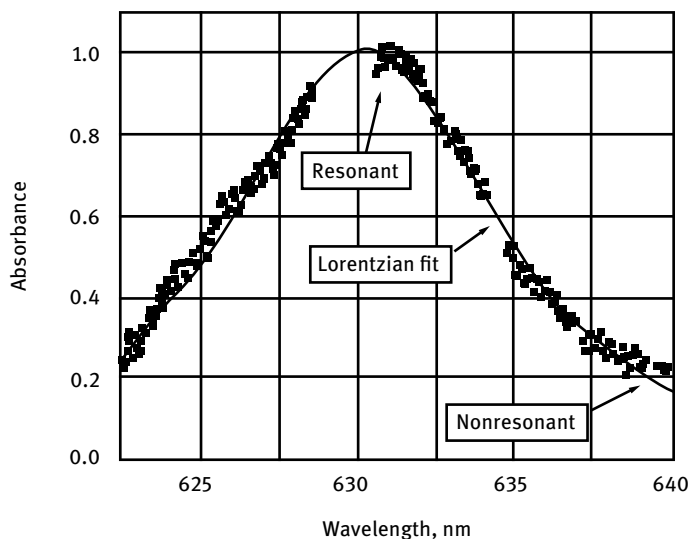


Figure 31: Absorption spectrum of liquid oxygen in the visible range (reproduced and modified from [216], with permission granted by © 2005 The Optical Society).

Legend: measurements: pure LOX, Cell path length = 20 mm

3.14.1.5 Index of Refraction of Liquid Oxygen

Index of refraction data for liquid oxygen at four different wavelengths are listed in Table 37.

Table 37: Index of refraction of liquid oxygen.

Temperature			Wavelength	Refractive index
K	°C	°F	Å	
64.9	−208.2	−342.8	4358	1.2518
73.5	−199.6	−327.3	4358	1.2446
79.7	−193.4	−316.1	4358	1.2382
85.5	−187.6	−305.9	4358	1.2328
90.2	−182.9	−297.2	4358	1.2277
64.9	−208.2	−342.8	5461	1.2483
73.7	−199.4	−326.9	5461	1.2401
80.4	−192.7	−314.9	5461	1.2345
85.5	−187.6	−305.7	5461	1.2295
90.2	−182.9	−297.2	5461	1.2243
65.6	−207.5	−341.5	6939	1.2441
73.7	−199.4	−326.9	6939	1.2382
79.7	−193.4	−316.1	6939	1.233
87.4	−185.7	−302.3	6939	1.2258
90.4	−182.7	−297.2	6939	1.2226
90.3	−182.8	−297	5893	1.2222

Data source: [217], as referenced in [171]

3.15 Microwave Absorption Spectra of Oxygen

Radio astronomy from the surface of the earth is very much limited to a few narrow windows outside the microwave absorption of oxygen, ozone, moisture and the ionosphere. Microwave emission and absorption provides the opportunity to remotely probe our own atmosphere of earth from the outside and those of other planets using microwaves in the search for livable, oxygen-bearing extraterrestrial planets [218]. Microwave-induced plasmas in flowing oxygen, a rich source of atomic oxygen and ozone, have been tested for the detoxification of environmental pollutants. Microwave absorption spectra of oxygen and oxygen-derived species have been extensively studied by atmospheric chemistry scientists and there exists a plethora of publications on this topic. Only a few randomly selected references on microwave spectra of oxygen are discussed in this section of this book. Some may be useful for analytical purposes.

Microwave attenuation and resonant eigenmode frequency determination of microwaves reflected and forming standing waves in a metal tank can be used for propellant gauging in LOX propellant tanks, also in low-g environments [219, 220].

The absorption of radiation emitted by atmospheric oxygen in earth's sky at decimeter wavelengths ($2.71 \text{ GHz} = 6 \text{ K}$) passing through a plastic tank filled with liquid oxygen with a receiving antenna at its bottom was compared to absorption of the same tank filled with liquid nitrogen [221]. The absolute absorption factor of liquid oxygen was $\tan \delta = 7.4 \times 10^{-4}$.

The theory of the fine structure of O_2 spectra was supported by high-resolution microwave spectra, which gave the rotational constant as $B_0 = 43102 \pm 5 \text{ MHz}$ for $^{16}\text{O}^{16}\text{O}$ [222]. There is evidence for the effect of higher order terms, such as centrifugal distortion on the magnetic interaction constants.

Ten microwave absorption frequencies of the oxygen molecule in the 60-kHz region have been measured with an accuracy of about 10 kHz [223]. The result was interpreted by successfully refining the existing quantum theory. Comparing the resultant value of the rotational constant B_0 with the value obtained in UV spectra, the velocity of light was calculated to be $299773 \pm 12 \text{ km/s}$.

The theory of the rotational spectrum of the oxygen molecule was revised by correcting the calculation of the effects of centrifugal distortion of the spinning molecule [224]. Precise measurements of the center frequencies of 8 of the predicted absorption lines were made and combined with measurement of 12 lines made elsewhere to obtain the values of 7 parameters appearing in the theory. See also: [225–227].

3.16 Electrical Conductivity of Liquid Oxygen

Liquid oxygen at its normal boiling point and atmospheric pressure is a dielectric and does not conduct electricity. Under very high pressures, such as those possibly encountered in the core of gaseous planets, at high atomic concentrations, the probability of electrons tunneling from one atom to another becomes very high, the negative ions degenerate into the conductivity band, and conduction is associated with transport of these quasi-free electrons. A fourfold increase in density was attained in oxygen in the course of multiple shock-wave impact. The pressure attained a value of 190 GPa and the temperature did not exceed 7000 K. With an increase in pressure from 30 to 100 GPa, the electrical conductivity sharply increased by almost six orders of magnitude and demonstrated a very weak dependence on pressure or density on a further increase in pressure. As in the case of hydrogen, the temperature dependence of electrical conductivity in the transition region is of an activation energy type. The high pressures required to convert liquid oxygen to a conductive state can be created by single shock compression, by shock reverberation or in a diamond anvil cell.

The electrical conductivity of single shock-compressed liquid oxygen has been measured in the dynamic pressure range 18–43 GPa (180–430 kbar) [228]. The data indicated that liquid oxygen partially dissociates and formed a two-component conductive fluid.

Electrical conductivities of fluid oxygen were measured between 30 and 80 GPa at a few thousand kelvin. These conditions were achieved with a reverberating shock wave technique [229]. The measured conductivities were several orders of magnitude lower than measured previously on the single shock Hugoniot because of lower temperatures achieved under shock reverberation. Extrapolation of these data suggested that the minimum metallic conductivity of a metal will be reached near 100 GPa.

3.17 Dielectric Constant of Liquid Oxygen

The dielectric coefficient can be determined from the ratio of the capacitance of a three-terminal, flat plate or concentric tube capacitor when it is filled with liquid oxygen to that when the capacitor is in vacuum at the same temperature. One of the earliest numbers thus determined for liquid oxygen was 1.491 at 91 K (−182°C) [230].

The dielectric constant of liquid oxygen at 90 K and 1 kHz was 1.46 ± 0.01 [231].

In a study that measured the dielectric constants of oxygen, ozone, and oxygen/ozone mixtures, the dielectric constant of pure liquid oxygen at its normal boiling point (90 K) was found to be $1.46 \pm 0.01\%$ [232]. The dielectric constant of saturated liquid oxygen ranged from 1.22 near the critical point to 1.57 near the triple point [233, 234]. The uncertainty in these measurements was $\pm 0.01\%$.

The dielectric constants of compressed gaseous and liquid oxygen were measured on 10 isotherms at temperatures between 100 and 300 K and on the saturated liquid boundary at temperatures between 55 and 154 K [235]. Densities ranged from 0.06 to 1.30 g/cm^3 at pressures up to 33 MPa.

Until 2005, dielectric coefficients of liquid oxygen had only been measured either along the liquid/vapor saturation curve [234] or above 100 K for compressed fluid [235]. Additional dielectric coefficients were measured below 95 K and for pressures up to 1 MPa and are illustrated in Figure 32 [64]. Other sources [236] list the dielectric constant of LOX as 1.483 at 90.2 K and 1.507 at 84.9 K.

Figure 33 is based on one of the few data sets that clearly show the distinct deviation of the dielectric constant from linearity as the temperature of the liquid oxygen approaches the freezing point.

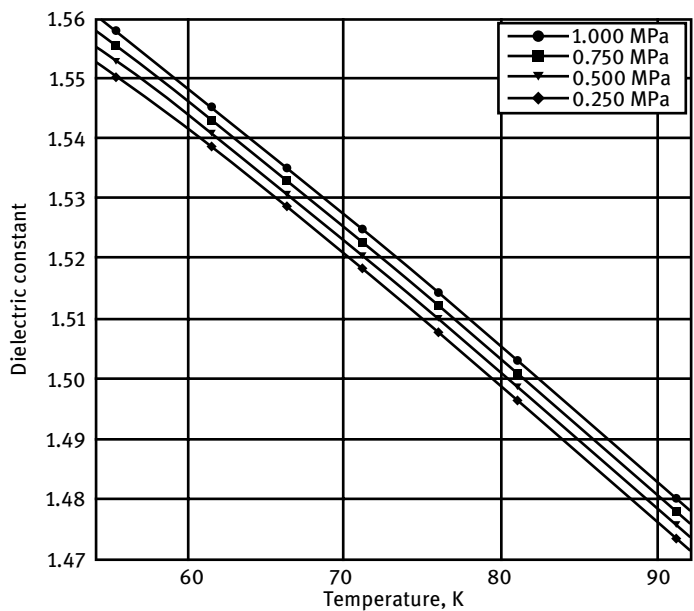


Figure 32: Dielectric constant of liquid oxygen (reprinted and modified from [64], with permission from © 2005 Elsevier; permission conveyed through RightsLink)

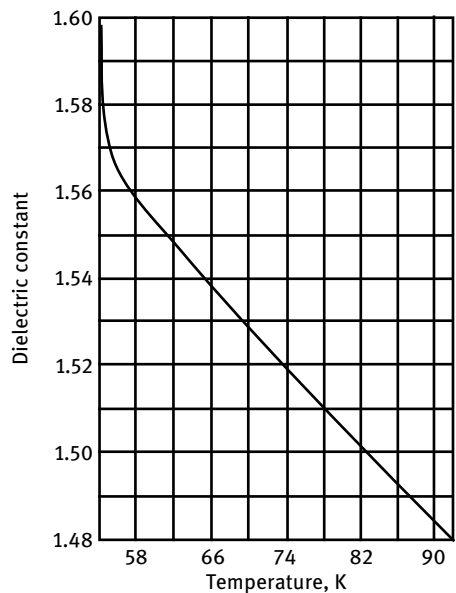


Figure 33: Dielectric constant of liquid oxygen (reproduced and modified from [34])

3.18 Magnetic Properties of Liquid Oxygen

Dioxygen O_2 is one of the few paramagnetic molecules with an even number of electrons. The ground state has a permanent magnetic moment due to unpaired spins. Oxygen is one of the few molecules that possesses a paramagnetism in the gas phase. The paramagnetism property is used to continuously measure the oxygen content of gases in flow-through on-line instrumentation, which is extremely important in administering anesthesia in hospital operating rooms. The paramagnetism of liquid oxygen can also be used to push or attract floating liquid oxygen droplets in a zero-g propellant tank and collect them at the tank outlet.

Oxygen has a triplet ground state and it becomes a magnetic liquid below 90.2 K. The magnetic characteristics can be related to the blue color of oxygen. The absorption mechanism, magnetostriction and pair correlation in the liquid were investigated through magneto-optical measurements in high magnetic fields [237].

The magnetic susceptibility (χ) of liquid oxygen is described as a function of absolute temperature (T) by the equation

$$\chi = \frac{1.01}{T}$$

where χ is the magnetic susceptibility in emu/mol and T is the temperature in kelvin. At 300 K, for example, it indicates considerably large paramagnetic susceptibility of 3.33×10^{-3} emu/mol.

It is expected from the Curie law that at low temperature magnetic susceptibility would become larger, but solid oxygen indicates extremely small susceptibility. The susceptibility of pure oxygen decreased abruptly at the melting point, again decreased sharply around 33 K and was almost constant below 33 K. At the transition point from γ to β phase, the susceptibility decreased sharply to one third. In β phase, it diminished gradually with the temperature to the next transition point from β to α phase, where it decreased abruptly once again to one half. This could be due to association of O_2 to form $(O_2)_2$ (which is diamagnetic) or to anti-ferromagnetism. There must be some interaction among oxygen molecules which reduces paramagnetism in the solid state. Many investigations have been made measuring absorption spectra, magnetic measurement, X-ray, and neutron diffraction of solid oxygen. These investigations have revealed anti-ferromagnetic interaction in solid oxygen.

The magnetic susceptibility of liquid oxygen at 90 K was measured as 2.6×10^{-4} cgs-units [238] and that of the solid at 54 K was 3.1×10^{-4} cgs-units.

Magnetic susceptibilities of single-crystal γ - O_2 and preferentially oriented polycrystalline samples of β - O_2 and α - O_2 have been measured [239]. The susceptibility of paramagnetic γ - O_2 was isotropic. The susceptibility of β - O_2 exhibited very little anisotropy but had an unusual temperature dependence which was probably due to the behavior of the lattice constants, modulation of in-plane and out-of-plane exchange interactions, and short-range order. The susceptibility of anti-ferromagnetic

α -O₂ was anisotropic, and data from five differently oriented samples were analyzed in terms of principal anti-ferromagnetic susceptibilities. This provided additional information on the crystal structure of solid oxygen phases, supplementing earlier XRD data. See also [240–243].

The shape of the liquid-vapor interface in a capillary partially filled with liquid oxygen deforms under the influence of strong magnetic fields [244, 245]. There seemed to be a relationship between the deformation of the gas-liquid interface and the square of the applied magnetic field strength in a range of 0–2 Tesla. The shape of the meniscus in a capillary tube changed from an ellipsoid into a sharp-pointed form with an increase in the field strength [246].

The extension of liquid oxygen meniscus in magnetic fields has been measured in various fields up to 5 Tesla at temperatures of 65.3 and 77.1 K [247]. It was found that the deformation of the meniscus can be determined by the balance between the magnetic normal stress and capillary pressure, which act in opposite directions at the interface.

Optical absorption spectra of solid oxygen α -phase and liquid oxygen were measured in high magnetic fields over 100 Tesla [248]. Absorption that typically originates from bimolecular transitions was observed. The spectra strongly reflected the local magnetic interaction between two oxygen molecules. The shape of the absorption spectrum of α -oxygen changed dramatically with increasing magnetic field strength, even though the absorption intensity of liquid oxygen simply declined. This difference could not be explained by the local magnetic interaction alone, and it was speculated that field-induced lattice distortion plays an important role in the solid oxygen α -phase and its visible light absorption. See also reference [188].

4 Chemical Properties of Liquid Oxygen

Oxygen is the archetype of all oxidizers. It is a stronger oxidizer than air. The increased oxidative power of oxygen in comparison to air is often demonstrated by inserting a glowing wood stick ember into a glass vessel containing oxygen, causing it to inflame instantly. Oxygen is non-toxic and sustains breathing and assimilation. Oxygen is chemically stable and can be stored indefinitely.

4.1 Assay Analysis and Quality Control

In the old days the oxygen content of grab samples of gas mixtures like air was determined in an Orsat apparatus with an alkaline solution of pyrogallol, which actively absorbed oxygen as it became oxidized to hydroxylated benzotropolone, purpurogallin. Nowadays such an apparatus can only be found in a museum, but the author remembers operating one of those apparatuses in his younger years.

Modern instruments are now available which continuously measure the oxygen content of gases and provide an instant readout and, if necessary, trigger an alarm if the oxygen content in air drops down to dangerous levels. One of the unique properties of oxygen, its paramagnetism in comparison to non-paramagnetic nitrogen or noble gases, can be used as the measurement principle in modern oxygen analyzer instruments.

4.1.1 Propellant Specifications for Liquid Oxygen

Liquid oxygen for use as a rocket propellant should meet all quality control purity requirements of the propellant specifications issued by the US military services or NASA. Type I is gaseous oxygen and type II is liquid oxygen. The grades of oxygen are as follows: grade A contains 99.6% O₂, grade B, reduced standard contains 99.5% O₂ and special grade F is 99.990% pure, for fuel cell and breathing oxygen. Requirements established in MIL-P-25508H (99.5 mass-% O₂) are summarized in Table 38 and 39 [249]. The two grades are for LOX in the as-delivered state and in the condition in which it might have been loaded into the Space Shuttle.

Table 38: Specification requirements of liquid oxygen.

Characteristic	Procured/delivered	Delivered (NASA Shuttle only)
Specification:	MIL-PRF-25508H, Type II,	Grade A SE-S-0073, Table 6.3-2
Purity	99.6% by vol. (min.)	99.2% by vol. (min.)
Alkynes as acetylene	0.25 ppm by mass (max.) for type II only	1.55 ppm by mass (max.)
Total hydrocarbon content (as methane)	50 ppm by vol. (max.)	75.0 ppm by vol. (max.)
Moisture	3 ppm by vol. (max.)	26.3 ppm by vol. (max.)
Particulate	1.0 mg/L (max.) or “continuous service”	N/A

The MIL-PRF states in 4.4.1 and 4.4.2 that analytical assay “Methods shall be selected from CGA G-4.3 except for grade F” and “Methods for analyzing impurities shall be selected from those of CGA G-4.3”. CGA G-4.3 is Commodity Specification for Oxygen G-4.3 Ed: 6 09/26/07, Commodity Specification for Oxygen, 11 pp., <http://www.cganet.com/publications.php>, http://www.cganet.com/customer/publication_detail.aspx?id=G-4.3.

Although the CGA web site writes “Any CGA publication incorporated by reference in US Federal Regulations after 1 January 2013 will be made available in a **free**, ready format online”, CGA G-4.3 is not available for free.

Table 39: Specification grade limits for oxygenper MIL-PRF-25508H (Oct 2011).

Grade	A	B	F	Test method
Purity, percent by volume, min	99.6	99.5	99.990	4.4.1
Impurities, ppm by volume, max	4000	5000	100	4.4.1
Total hydrocarbons as methane	50	67.7	20	4.4.2
Water	3	26.3	3	4.4.2
Methane	Note a	Note a	16	4.4.2
Ethane	Note a	Note a	2	4.4.2
Propane and higher hydrocarbons as propane	Note a	Note a	1	4.4.2
Nitrous oxide	Note a	Note a	1	4.4.2
Halogenated hydrocarbons	Note a	Note a	1	4.4.2
Carbon monoxide and carbon dioxide	Note a	Note a	1	4.4.2
Other (N, Ar, Kr, etc.)	Note a	Note a	75	4.4.2
Odor	Note a	Note a	None	4.4.2
Particulate ^b , mg/L, max	1.0	1.0	1.0	4.4.3

Note a: No limit established for this grade.

Note b: A filter with no more than a 10 µm nominal and 40 µm absolute rating shall be installed between the manufacturer's plant system and the manifold used to fill the gas or liquid containers for delivery.

4.1.2 Common Contaminants in Liquid Oxygen

The following compounds are found as common contaminants in liquid oxygen: nitrogen (as the result of inefficient separation in air liquefaction), water, and carbon dioxide (also carried over from the starting air). All volatile contaminants can be analyzed by gas chromatography (see section "Analytical Methods for Determination of Contaminants"). Some of the more worrisome organic contaminants may accumulate in the evaporation residues in a liquid oxygen tank or Dewar flask and form potentially explosive mixtures [250].

Experimental results indicated that a maximum safe level of hydrocarbons (e.g., hexadecane) film contamination is 100 mg per square foot [251, 252].

Mixtures of LOX and organic compounds can have friction and impact sensitivity properties similar to that of much-feared nitroglycerin [253]. One of the organics particularly worrisome is acetylene, which sometimes forms unwittingly as a product of pyrolysis of lubricating oils in hot parts of an air compressor and condenses along with the oxygen. Liquid acetylene is soluble in liquid oxygen up to 4 ppm by weight.

Comparing the solubilities of various aliphatic saturated hydrocarbons in liquid oxygen, it was noted that the solubility decreases with increasing chain length, as reported in [254]. Paraffinic hydrocarbons, such as n-decane and those typically used in lubricants, dissolve in liquid oxygen at only 1 ppm. The lower alkanes (C₁–C₄) in LOX can be detected by gas chromatography (see section "Analytical Methods for Determination of Contaminants") [255]. Liquid oxygen that has been stored in large storage containers for a long time and has been topped off many times to compensate for evap-

oration losses may slowly accumulate acetylene in its contents. If the incoming LOX contains 0.5 ppm acetylene, and the average evaporation loss is 0.4%/day, the detonable concentration will not be reached before 3 years of operation. In most cases, the turnover in a tank is faster than this period of time. The problem depends not on the size of the storage facility, but rather on boil-off losses. The 3-year safety period assumes a heat-leak loss of 0.4%/day. There are two ways to extend the period of safe operation: The first method prevents acetylene build-up by purifying the LOX introduced into the storage tank during the topping up operation. Each addition should be passed through a 6.3-kg (14-lb) silica-gel bed at a flow rate of 0.73 L/s (700 gph = 11.7 gpm), thereby eliminating acetylene and ethylene from the added liquid oxygen. The second method uses small quantities of the strong oxidizer fluorine. It was suggested that less than 0.5% of fluorine added to the LOX entering the tank would preferentially react with acetylene, and form inert soluble fluorocarbons [256]. An unusual method for removal and destruction of organic contaminants would be the addition of a small percentage (0.5 mass-%) fluorine, but that may open up a Pandora's box when it comes to subsequent corrosion problems.

It is recommended to pass the incoming LOX through an absorption column packed with silica gel which absorbs organic contaminants [257].

Carbon dioxide and water ice do not dissolve in LOX. They float about as crystals which in the worst case may clog tank outlets, filters, pumps, and injector orifices. For transfer of LOX, a filter is often inserted into the transfer lines to retain particulate contaminants (see also Figure 38).

Ambient air contains 0.3 ppm by volume nitrous oxide and 400 ppm (and rising) carbon dioxide which might end up in liquid nitrogen or liquid oxygen from an air liquefaction and separation plant. Nitrous oxide and carbon dioxide are unwanted contaminants in LOX, precipitating and potentially clogging filters and orifices. The solubility of N_2O or CO_2 in LOX must be accurately known to prevent such problems. Solubility data for N_2O or CO_2 in LOX are available in the literature [153]. The solubility of N_2O (see Figure 33, 34, and 35 in *Encyclopedia of Oxidizers*, chapter "Nitrous Oxide") or CO_2 in LOX increases sharply once the temperature exceeds the normal boiling point of LOX.

Mixtures of methane with LOX cooled to the temperature of liquid nitrogen form two liquid phases with a limited mutual solubility. Ethane also forms two liquid phases with oxygen, and in this case the mutual solubility is less than with methane and oxygen. Acetylene, carbon dioxide, and nitrous oxide are solid and virtually non-volatile at liquid oxygen temperature, and their solubilities in liquid oxygen are very small. See Tables 26 through 29.

4.1.2.1 Analytical Methods for Determination of Contaminants

Foreign materials in liquid oxygen normally come from the atmosphere and from contamination introduced during LOX production. The series "Advances in Cryogenic Engineering" contains numerous references to analytical methods for the assay and

analysis of contaminants in LOX, including [258, 259]. Other methods are described in the literature, for instance a fast method for determination of carbon dioxide in LOX [260].

4.1.2.2 Spectroscopic Methods for Analyses in Liquid Oxygen

Organic contaminants in LOX can be detected and identified using IR spectroscopic methods [261] or by gas chromatographic methods [262]. In combination with adsorptive preconcentration and 10–15 min. sampling time, hydrocarbon concentrations down to 0.01 vol.-ppm in the evolved gas can be detected.

The absorption spectrum of LOX (Figure 31 shown in an earlier section of this chapter) was used to select the wavelengths for a dual-wavelength analysis system, one at the absorption maximum and another away from it [216]. The resonant beam at 631 nm from a 35 mW laser and a non-resonant beam at 639 nm from a 5 mW laser were multiplexed and focused into a fiberoptic system and aimed into a Dewar with stair-step mirrors at the bottom to create different path lengths. The magnitude of each component beam was modulated out of phase from each other at 500 kHz and the amplitudes of modulation were balanced so that they were equal after passing through the test section at maximum attenuation. When the two components oscillated at equal magnitude, the resultant multiplexed beam maintained a constant intensity. Any lack of attenuation made the resonant beam stronger than the non-resonant beam, thus causing the intensity of the multiplexed beam to oscillate an amount equal to the difference. The detected signal was fed to a dual-phase lock-in amplifier, which directly provided the magnitude of oscillation (i.e., the difference in absorption) and the amount of contaminant in the oxygen.

Optical fiber sensors have advantages over conventional sensors, such as remote sensing, multiplexing and multi-point distributed sensing immunity toward electromagnetic interference. Laser Raman spectroscopy has been known for years as a relatively simple analytical method for identification of molecules in gases, liquids, and solids. By measuring the frequency and intensity of light inelastically scattered from the sample, LOX and LN_2 can be qualitatively and quantitatively characterized. Combining the two technologies, a Raman scattering optical fiber sensor was developed for instantly detecting and monitoring the purity of LOX in the oxidizer feed line during ground testing of rocket engines [263–266]. The Raman peak intensity ratios with different excitation light sources for LN_2 and LOX with varied weight ratios (LN_2/LOX) were measured (Figure 34). The system response time of this miniaturized sensor for LN_2/LOX measurement was in the range of a few seconds. Two frequency-doubled 532 nm cw Nd:YAG lasers and a diode laser operating at 670 nm were used as the excitation source. The 532 nm laser apparatus could measure a LN_2 percentage as low as 1% N_2 in a sample mixture. The diode laser had a poor signal-to-noise ratio and background problem.

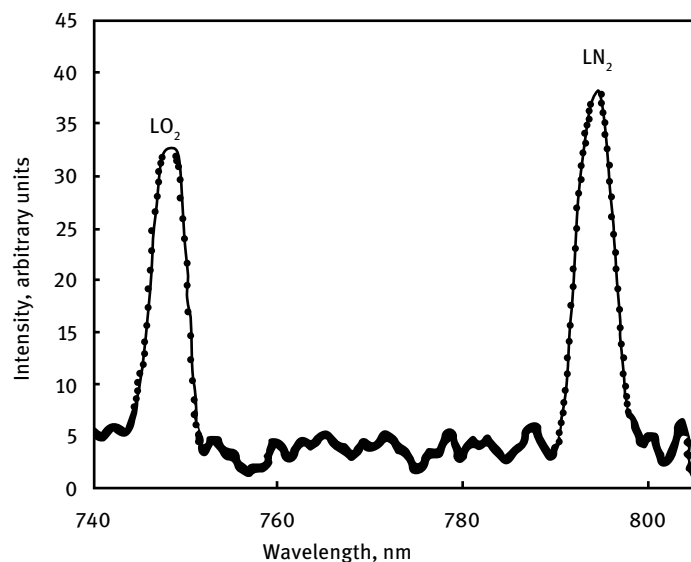


Figure 34: Raman spectrum for 60% LN₂ and 40% LOX with a 670-nm diode laser; background-subtracted spectrum (reprinted from [264] with permission granted by © 2007 The Optical Society)

4.2 Thermal Stability, Dissociation, and Radiation Stability of Oxygen

4.2.1 Dissociation of Oxygen

The dissociation energy D^0 for the ground state of O₂ is $41260 \pm 15 \text{ cm}^{-1}$. This value was determined from spectroscopic observations.

4.2.2 Photolysis and Radiolysis of Oxygen

Under the influence of energetic radiation (UV, cosmic radiation, X-rays, γ -rays) oxygen in either gaseous, liquid or solid state dissociates and may recombine to form ozone. This is the process that takes place in the upper layers of Earth's atmosphere and results in the formation of the beneficial ozone layer. Ozone has been detected in the vicinity of icy moons orbiting Jupiter and Saturn. In the presence of water, the radiolysis of oxygen may form hydrogen peroxide. Such processes are likely to occur on the surface of icy moons of the outer planets [267]. It is known that ozone formation occurs on icy moons in the course of millennia, but it is not known if oxygen storage in orbital propellant depots or future extraterrestrial bases would result in formation of detectable amounts of ozone as the result of cosmic radiation. The γ -irradiation of liquid or solid oxygen is one method of producing ozone [268, 269].

Liquid oxygen can serve as the lasing medium for pumped lasers, emitting photons with a wavelength of 1580 nm after being excited to different excited states with

a dye laser with wavelengths of 581, 634 or 764 nm [270]. The small signal gain was 0.23, 0.3 or 0.076 cm^{-1} , respectively. The small signal gain (pumped by photons of 634 nm) was significantly higher than that of common solid-state lasers and chemical lasers.

5 Materials Compatibility with Liquid Oxygen

This book is basically a chemistry book and not a book on cryogenic system design. Properties of materials listed here are primarily examined for potential chemical reactivity. Mechanical properties due to low temperatures are only dealt with in passing. There are many better sources for cryogenic system design information out there on the bookshelves and in on-line databases than this book can offer. The change in mechanical properties due to lowered temperatures is the same regardless of which cryogenic propellant or even an inert refrigerant like liquid nitrogen, liquid argon or liquid helium the material comes in contact with. We are not dealing with mechanical properties at low temperatures.

5.1 Materials for Construction of Liquid Oxygen Systems

Liquid oxygen is not as corrosive as any of the storable oxidizers used for rocket propulsion, but at the cryogenic temperatures encountered with LOX, many materials of construction become embrittled and lose their elasticity. Due to the increased fire hazard, only non-combustible materials of construction may be used for handling of liquid or gaseous oxygen.

There are many sources of information on the selection of materials (metallic and non-metallic materials) for operation at cryogenic temperatures, foremost of all the Cryogenic Material Properties Database [271]. This database is a critical evaluation of existing experimental measurements on the properties of engineering materials at cryogenic temperatures. Equations are given for the recommended property value as a function of temperature. Since the book at hand is mostly a chemistry book and not a materials science book, these sources are offered just as references recommended for further study, but the technical details cannot be provided in this book. Those mechanical considerations in the selection of cryocapable materials are essentially the same for LOX, LN_2 , LNG or LH_2 .

In the selection of materials of construction for operation in liquid oxygen, the ignition hazard is unique in comparison to the other cryogenic propellants. Special test methods were developed to measure the ignition hazard under carefully controlled and reproducible conditions. The following sections are subdivided by metallic and non-metallic materials, preceded by a section discussing test operations where both types of materials were tested. Here is a random selection of sources of information on compatibility of materials of construction for use in LOX systems.

The literature on high pressure oxygen compatibility has been surveyed and compatibility data, such as mechanical impact sensitivity, pneumatic impact sensitivity, ignition temperature and flash and fire point for pressures above 200 bar (2×10^7 Pa) were compiled [272, 273].

5.2 Impact Sensitivity of Materials for Construction of Liquid Oxygen Systems

This section deals with impact sensitivity of all types of materials for construction of LOX systems, both metallic and non-metallic materials were tested using the same apparatus.

Many materials will ignite or explode when in contact with gaseous oxygen (GOX) or liquid oxygen (LOX) if subjected to stimuli such as a mechanical impact, shearing surfaces, adiabatic compression (pneumatic impact), or an electrical discharge in the form of a spark. Such materials must therefore be characterized as to compatibility with LOX or GOX to define the degree of hazard with their use. Generally, materials are more sensitive in GOX than in LOX and impact sensitivity is known to increase with increasing pressure. Thus, the evaluation of the sensitivity of materials in GOX is required to supplement LOX impact test data. A test program was initiated to evaluate materials being used or considered for use in oxygen systems at NASA Kennedy Space Center (KSC) [274]. The ambient pressure LOX testing phase of this program was performed at KSC, the pressurized LOX testing at Marshall Space Flight Center (MSFC), the GOX mechanical impact testing at MSFC and White Sands Test Facility (WSTF), and the flash and fire point and pneumatic impact testing at WSTF. Twelve materials were evaluated for reactivity in liquid oxygen, pressurized LOX, and high-pressure GOX. These included an aluminum alloy (6061-T6), a polytetrafluoroethylene, four filled polytetrafluoroethylenes, a polyimide, a polychlorotrifluoroethylene, two fluoroelastomers, a perfluoro ether base grease (Perfluoroalkyl Ether Lubricant Krytox[®] 240AC), and a nylon polymer. The nylon 6/6 was the only material which reacted under the ambient pressure LOX mechanical impact test conditions. Viton PLV 5010B was found to be reactive in both thicknesses with threshold pressures of 6.8 MPa (1000 psia) and 3.4 MPa (500 psia) under the conditions of the high-pressure LOX mechanical impact tests. Reactions were observed with Viton PLV 5010B and Vespel SP-21 at 6.8 MPa (1000 psia) and 3.4 MPa (500 psia) in the high-pressure GOX mechanical impact tests. The WSTF tests indicated a higher reactivity for the filled polytetrafluoroethylenes than for the unfilled resin. A statistical study of the reproducibility of the test results indicated that the major source of variability is due to the go/no go nature of the test method and that variations due to sampling and testing operations were not significant [275].

Impact sensitivity tests described in [276], mechanical impact for materials in ambient pressure LOX (Test 13A) and mechanical impact for materials in variable pressure GOX and LOX (Test 13B), pages 42–44 are patterned after the American Society for Testing and Materials (ASTM) method D 2512-82, Compatibility of Materials with Liquid Oxygen (Impact Sensitivity Threshold and Pass-Fail Techniques).

In addition to impact tests in accordance with ASTM D 2512-95 where a test specimen immersed in LOX is impacted by a hammer, an ignition test also called calorimetric bomb test according to French standard NF 29-763 is often performed. In this test, the temperature of ignition of a material heated slowly to 823 K (550 °C) under a pressure of 120 bar, is determined. Results obtained with both standardized test methods on polymeric materials, e.g. polychlorinated tetrafluoroethylene (PCTFE), polyimide, polyamide-imide, armalon, and metallic materials (nickel alloys) obtained at the University of Liège in Belgium cryogenic test facilities were presented in comparison to results obtained with a new adiabatic compression test [277]. Because rocket engines are being designed to operate at higher and higher pressures, accidental ignition by adiabatic compression is becoming an increasing concern. For this test a piece of material is submitted almost instantaneously to a high oxygen pressure which can be as high as 100 MPa while the temperature of the medium can reach ~2300 K (~2000 °C). Adiabatic compression test results were compared to ignition tests with conventional test methods [278].

5.3 Metals for Construction of Liquid Oxygen Systems

Many materials are compatible with LOX under static conditions; however, when they are used in rocket systems where dynamic shear or shock producing conditions are ever present, a severe hazard of ignition or explosion exists, and the choice of materials becomes quite limited.

Iron and most iron alloys (with the exception of the austenitic 18-8 series of Ni-Cr stainless steels) will readily become brittle at 90 K (–183 °C) and are not suitable for LOX systems. Besides the stainless steels of the 300 series the following metals can also be used and are listed here in order of increasing embrittlement at cryogenic temperatures: pure soft nickel, Monel, Inconel, copper, aluminum, annealed brass. Titanium and titanium alloys which are preferred tankage materials for many other rocket propellants can be used for LOX only with additional precautions due to their tendency to ignite in oxygen when scraped, sheared or punctured [279, 280].

The selection of metals for oxygen service is described in ASTM F.94.92 “Standard Guide for Evaluating Metals for Oxygen Service”, “ASTM G94” “Guide for evaluating metals for oxygen service”, and the test used for ranking candidate metals is ASTM G.124-95 “Standard Test Method for Determining the Combustion Behavior of Metallic Materials in Oxygen-Enriched Atmospheres”. The accidental ignition in valves and pipeline networks is often caused by particle contamination and cannot be reproduced in clean systems. A particle impact test will be able to differentiate candidate metals under more realistic conditions than clean metals only found in a laboratory, but not in real life.

A comparison of different rankings concluded that stainless steel and aluminum bronze with 9–11% Al are equivalent choices for certain oxygen valves [281].

5.3.1 Impact Sensitivity of Metals for Construction of Liquid Oxygen Systems

Since the first observation of a violent LOX/Ti reaction in early 1959, the compatibility of titanium and its alloys with LOX has received considerable attention. Initially, laboratory investigations were primarily limited to impact studies utilizing the Army Ballistic Missile Agency (ABMA) impact tester or modifications thereof. Later the US Air Force initiated programs to determine the mechanism of the reaction.

Projectile impact tests with tanks made from various materials of construction and filled with LOX have shown that impact of projectiles with only 14–28 m kp = 137–275 N m of kinetic energy can initiate even more destructive titanium metal combustion reactions. Hypervelocity impact tests with N_2O_4 in titanium, aluminum, steel, or fiberglass-reinforced plastic tanks did not result in explosions, whereas titanium tanks filled with LOX combusted with a fireball [282].

Of all the metals studied, titanium exhibited the greatest sensitivity to impact when immersed in LOX [283–292]. This friction sensitivity is like that of one of the worst materials when it comes to friction sensitivity in oxygen (or even in air): zirconium. Titanium sensitivity in contact with LOX approached that of many organic materials such as greases and oils. Reactivity was observed in liquid oxygen and mixtures of liquid oxygen and liquid nitrogen at 26.7 N m (20 ft lb) until the LOX concentration was reduced to below 30%. Titanium can be partially protected from reactivity in LOX under impact by certain protective coatings, provided the coatings are not broken. Some protection is given by electroless copper and nickel, and to a lesser extent by Teflon and a fluoride-phosphate coating. Protection is also obtained by nitriding, which adds a protective film to the surface, and by annealing which increases the thickness of the oxide film. Titanium exhibited no great reactivity in LOX when deformed by compression, by exposure of a fresh surface by machining or rupture, or by exposure of bulk titanium to high-pressure or high-velocity LOX. In gaseous oxygen, titanium was highly reactive when a freshly formed surface was exposed at even moderate pressure.

Reaction Motors, Inc. reported what they called threshold values for titanium in LOX. The threshold value is the highest impact level at which no reactions occurred out of 20 tries. Data are as summarized in Table 40.

These data indicated that the harder (aged) Ti-13V-11Cr-3Al is more sensitive than its softer counterpart, and more reactive than Ti-6Al-4V and Ti-75A.

Table 40: LOX/metal impact sensitivity.

Material	LOX impact sensitivity threshold, ft lb/in. ²
Unalloyed titanium	78
Ti-6Al-4V	78
Ti-25Zr	78
Ti-13V-11Cr-Al (solution treated)	122
Ti-13V-11Cr-3Al (aged 72 h at 627–755 K (670–900 °F))	67

Data source: as listed in [280]

Aluminum tanks filled with LOX can be ignited only by more energetic impacts, such as those encountered during the impact of meteorites in outer space. Magnesium is somewhat more easily ignited than aluminum. The reactivity of titanium in LOX can be reduced slightly by applying protective coatings. Addition of LN_2 to LOX reduces the shock and friction sensitivity of metals in LOX only after relatively large percentages of LN_2 have been added [293, 294]. Twelve materials known to be impact sensitive in 100% LOX at 10 kg m were tested in LOX/ LN_2 mixtures with incrementally increased LN_2 content until 20 consecutive tests no longer resulted in an ignition. With most materials, relatively large LN_2 additions (20–50% LN_2) were needed to reduce reaction frequencies or increase the threshold energy levels. Even highly sensitive materials did not react in 20 LOX/80 LN_2 (= liquid air), but only a slight increase in oxygen content made them reactive.

In 1959, Aerojet-General designed a test to simulate actual conditions of LOX flow through a stainless-steel loop containing a 2.5-foot section of 3/16-inch-wall, 2.5-inch ID titanium-75A tubing [295, 296]. The intent was to impact the titanium section by a drop-weight method. Before the system was completely instrumented and while the system was unattended, a reaction took place that destroyed part of the system, some burning of both titanium and stainless steel occurring. The cause of this reaction could not be established, because of the many variables; however, LOX was flowing at the time, and the pressure of the system was approximately 4.8 MPa (700 psi).

When designing an apparatus for impact testing of materials in an oxygen atmosphere at pressures from 82.7 MPa (12000 psi) to 172 MPa (25000 psi), one had to make sure that the ignition of a sample under test would not propagate to the adjacent apparatus that is confining the test atmosphere and is meant to be used more than once [297]. An existing impact tester system was evaluated for potentially extending the test conditions from 69 MPa (10000 psi) to 82.7 MPa (12000 psi) and beyond. Although the structural integrity of the impact test cell and the compressor were sufficient for operation at 82.7 MPa (12000 psi), studies revealed possible material incompatibility at that pressure and above. It was recommended that if a component should be replaced for 82.7 MPa (12000 psi) operation, the replacement should meet the final objectives of testing at 172 MPa (25000 psi). Recommended changes in the system included: use of Monel 400 for pressures above 82.7 MPa (12000 psi), use of bellows to replace the seal in the impact tester and use of a sapphire window attached to a fiber optic for event sensing.

Al-Li alloys 8090-T3, 2090-T81, and Al alloy 2219 (tempers T851, T37) were tested for compatibility with liquid oxygen using pressurized mechanical impact apparatuses at two NASA laboratories [298–300]. In addition, WSTF conducted open-cup mechanical impact and promoted combustion tests on all alloys. Reactions occurred in some specimens of all alloys during pressurized mechanical impact tests at MSFC, but there were no reactions during similar tests at WSTF.

A wide range of composition and temper variants of Al/Li alloys were fabricated and subjected to an enhanced LOX impact test [301]. In addition, each of the five alloys

were evaluated using a promoted combustion test to determine the threshold pressure and a close correlation was found between mechanical properties and LOX impact reaction frequency as defined by visual observation. Scanning electron microscopy was used to examine tested specimens. In the promoted combustion test, Al/Li alloys displayed a tenfold increase in threshold pressure compared with conventional aluminum alloys.

The series “Advances in Cryogenic Engineering” contains numerous papers dealing with the selection of materials of construction for the design of cryogenic servicing systems. This includes papers on aluminum alloys [302–304].

The German Federal Institute for Material Research and Testing (Bundesanstalt für Materialforschung und -prüfung – BAM) has developed an apparatus for testing the impact reactivity of materials in liquid oxygen under carefully controlled conditions [305] (Figure 35).

The mass of the impact weight can be varied but is normally 76.5 kg. The drop height can be varied but is normally less than or equal to 1 m. Under these conditions, the maximum impact energy is 750 N m.

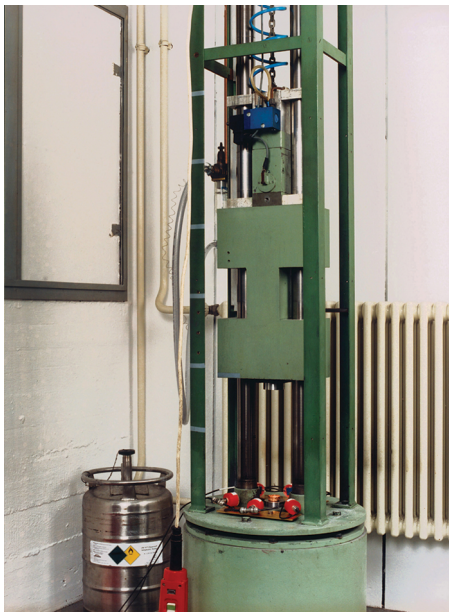


Figure 35: BAM apparatus for determination of reactivity (drop weight impact sensitivity) of materials immersed in liquid oxygen (photo courtesy of BAM; reproduced with permission from BAM)

5.3.2 Friction Sensitivity of Materials in Liquid Oxygen

Metal-to-metal friction in rotating machinery may expose fresh surfaces to oxygen that may ignite. Frictional heating in oxygen equipment has been a frequent cause of oxygen accidents.

Friction and wear studies were conducted with four material combinations run submerged in liquid oxygen to determine their potential as dynamic seal components for fluorine turbopump applications [306].

5.4 Non-metallic Materials for Construction of Liquid Oxygen Systems

While the selection of metallic materials in the construction of liquid oxygen systems requires a thorough understanding of the potential hazards involved, this is even more important when selecting non-metallic (organic polymer) materials for use with liquid oxygen. Most non-metallic materials are organic materials based on hydrocarbon skeletons and as such are readily combustible in oxygen [307, 308]. In an effort to develop non-combustible non-metallic materials for oxygen service, as many C—H bonds in those conventional polymers as possible have been replaced by C—F bonds to render the material less combustible but maintain the elastic properties.

The cryogenic properties of polymer materials have received much attention with new developments and more extreme requirements in space, superconducting, electronic, and defense technologies. Polymer materials developed for these applications are mainly employed as electrical insulators, thermal insulators, sealants, and matrix materials for fiber-reinforced composites used in cryogenic environments [309]. The requirements are extremely high and complicated for polymer materials in these unique applications. The polymer materials need to possess good mechanical and physical properties at cryogenic temperatures, such as liquid helium (4.2 K), liquid hydrogen (20 K), and liquid oxygen (90 K) to meet the high requirements of the cryogenic applications. A good summary of the cryogenic mechanical and physical properties of polymer materials is given in reference [310]. This includes cryogenic shear strength, impact strength, and fracture toughness as well as cryogenic thermal, creep, sliding, and dielectric properties of polymers.

Rocket engine and rocket aircraft manufacturers observed that when some organic materials came into intimate contact with liquid oxygen, they became prone to detonation when subjected to impact or friction stimuli. When liquid oxygen was accidentally spilled on asphalt and inadvertently stepped on, the asphalt would often explode. Leather gaskets immersed in liquid oxygen and subjected to surge impact detonated with disastrous effects [311].

5.4.1 Impact Sensitivity of Organic Polymer Materials in Contact with Liquid Oxygen

The standard liquid oxygen impact test method has been modified to include a grit sensitizing agent, silicon carbide, with the test specimen [312]. The silicon carbide increased the sensitivity of the material to impact, increased the frequency of reaction, increased the intensity of the reaction, and decreased the energy required to initiate a reaction. Test data were obtained for polyethylene, Nylon 66, Kel F-81, PCTFE, and

Viton FR58/90. The surface roughness of the striker pin, the presence of silicon carbide and sample thickness were evaluated in these tests.

Foam insulation on the outside of liquid hydrogen or liquid nitrogen tanks that is not perfectly sealed and is breathing (“cryopumping”) ambient air may become soaked with liquid oxygen and constitutes an explosion hazard [313].

5.5 Lubricants for Liquid Oxygen Systems

Tribology, from the Greek word *tribos* meaning rubbing, is the science of friction, lubrication, and wear. In an oxygen environment, friction can lead to ignition, so it is important that gliding surfaces be properly lubricated; however, if the wrong lubricant is selected, that could make the situation worse rather than better. Common lubricants such as those based on hydrocarbons and intended for automotive and jet engines may not be used for LOX service, because they are somewhat soluble in LOX and can form explosive mixtures that can be initiated by shock or friction [314–316]. There are perfluorinated oligomers (oils) and polymers (gaskets) that can be used for LOX service. One of the brand names is Fluorolube®; however, some of the perfluorinated oils are reactive with magnesium or aluminum alloys and should not come into contact with these metals in the presence of oxygen. There are a few solid lubricants, such as graphite or molybdenum disulfide (brand names Molykote®, Rocol Oxylube®) that can provide lubrication of threads or slow moving shafts.

In view of the large number (more than 100) of lubricants advertised for LOX service it is difficult to identify the best lubricant for a given application and it would be best to test its performance and safety under conditions of the actual application. The situation in the early 1960s was confusing [317] and it has not improved much since.

Most hydrocarbons in contact with liquid oxygen constitute a potential explosive situation. The only organic oils, greases, waxes, and plastics which appear to be compatible with liquid oxygen are polymers which are entirely fluorinated, or which are entirely chlorinated or fluorinated with the mol ratio of fluorine being at least three times that of chlorine [318]. An investigation of the reactivity (impact sensitivity) of launch vehicle materials with liquid oxygen included samples of fluorosilicone grease [319]. A generally accepted lubricant for LOX service is Krytox® 240AC made by DuPont. See also [320, 321].

5.6 Gaskets for Liquid Oxygen Systems

Latex rubber, neoprene, butyl rubber, polyvinyl chloride or polyethylene gaskets are not suitable for LOX service because they become rock hard at low temperatures and may ignite on impact or under friction. Teflon® and Kel-F® gaskets are chemically compatible with LOX but will also lose their elastic seal qualities at low temperatures.

Unfilled Teflon gaskets will cold flow under compression and would have to be periodically retightened. The gasket industry has attempted to use glass-fiber or glass powder filled Teflon to reduce the tendency to cold flow. Some gaskets use multi-layer laminated construction of Teflon alternating with fiberglass reinforcements [322]. Other gaskets were developed specifically for use in the SATURN-V launch vehicle [323]. See also [324–328]. Some silicone rubbers and some polyurethanes maintain their elasticity down to very low temperatures, but there is concern about chemical reactivity (ignition, explosion) when impacted or subjected to friction [329].

When designing gaskets for cryogenic service, the difference in thermal contraction (or expansion) of gaskets and surrounding parts must be taken into consideration, regardless of the type of gasket and metal involved. If the coefficient of thermal expansion is mismatched, the gasket may buckle or shrink, causing leakage and/or permanent deformation. If the reader gets the impression this is a difficult task to find the right material for liquid oxygen cryogenic service, the problem is even worse when selecting materials for liquid hydrogen service where the temperatures are 50 K cooler and the temperature swings between ambient temperature and operating temperature are even wider; however, experience gained in designing cryogenic liquid oxygen systems benefits the design of liquid hydrogen systems and vice versa. Extending the cryogenic range, designers for liquid helium systems face similar problems.

In a summary of design and materials selection for cryogenic gaskets it was explained that various demountable, low-temperature static seals can be made from rectangular-sectioned gaskets of Teflon or Kel-F, or of soft metal, or with plastic sealing surfaces, but gaskets require heavy flanges for compression [330]. O-rings of rubber, Viton, and neoprene have been used successfully down to 20 K with high initial loading designs. Hollow, metallic O-rings can be used, but they are hard and require smooth surface finishes, >16 rms (root mean square). Solid O-rings of soft metals (e.g., indium, lead, copper, and aluminum) can seal to $10^{-5} \text{ atm cm}^3 \text{ s}^{-1}$ (linear in.)⁻¹ leak rates. Pressure-actuated seals of C, U, V, or W configuration are said to be superior to all others for cryogenic space systems. They use lightweight flanges and will follow flange deflections, but they are expensive, and small leak paths can develop, but they have proved reliable in the field. Temperature-activated seals (favorable thermal contraction relationships) also show promise but have not been extensively used.

Viton[®] B, a Du Pont terpolymer of vinylidene fluoride, hexafluoropropylene, and a small amount of tetrafluoroethylene, is only one of several fluoroelastomers used in some oxygen systems. The effect of formulation components and the addition of fire retardants on the impact sensitivity of Viton B fluoroelastomer in liquid oxygen was studied with the objective of developing a procedure for reliably reducing this sensitivity [331]. Component evaluation showed that almost all the standard formulation agents will sensitize the Viton stock either singly or in combination. Cure and post-cure treatments usually reduced the sensitivity of a given formulation, but no formulated Viton was as insensitive as the pure Viton B stock. Coating formulated Viton with a thin layer of pure Viton gave some indication of reduced sensitivity. See also reference [332].

Static seals are relatively easy to design when compared to rotary, dynamic seals on valve stems and pump shafts for service with cryogenic fluids [333].

Ten polymeric materials including ethylene propylene diene monomer (EPDM), Nylon 6,6, Buna-N, and other materials marketed as TFE-Teflon[®] (PTFE), Kel-F[®] 81 (PCTFE), Vespel[®] SP-21, Viton[®] A, Viton[®] A-500, Fluorel[®], and Neoprene[®] were evaluated for their oxygen compatibility [334]. The properties examined included autoignition temperature (AIT), heat of combustion, and LOX mechanical impact sensitivity. A high-pressure autoignition test rig was used for a detailed study on the materials' autoignition behavior. This high-pressure vessel is capable of measuring the AIT of a material at temperatures up to 723 K (450 °C) and at oxygen pressures (prior to a thermal excursion) up to 34.5 MPa (5000 psig). Fluorinated polymers including TFE[®], Kel-F[®] 81, Viton[®] A, Viton[®] A-500, and Fluorel[®] exhibited good oxygen compatibility. Specifically, they possessed relatively high autoignition temperatures and reasonably low heat of combustion values. Among them, TFE[®] possessed the best property by showing the highest autoignition temperature (723 K = 450 °C), lowest heat of combustion (6347 J/g = 1517 cal/g), and low LOX impact sensitivity. Vespel[®] SP-21 (15% graphite-filled polyimide) exhibited an autoignition temperature higher than fluorinated elastomers like Fluorel[®] and Viton[®] A, but lower than Kel-F[®] 81 or TFE[®]. The variation of oxygen pressure, ranging from 12.4 to 34.5 MPa (1800–5000 psig), was found to exert little influence on the autoignition temperature of the polymers. See also reference [335].

5.7 Non-metallic Tank Liners and Composite Overwraps for Liquid Oxygen Systems

Use of glass-fiber filament-wound material for applications in structures exposed to a cryogenic environment has been of interest to cryogenic engineers for quite some time. Pressure vessels for containing liquid hydrogen and for containing high-pressure gases when immersed in liquid hydrogen have been of specific interest. Most composite overwrapped tanks have a thin, flexible metallic liner to separate the contents (liquid rocket propellant, pressurant gas) from the overwrap and to reduce leakage. For expendable systems that require only a single service cycle, it has been considered to use composite overwrapped tanks with an organic polymer liner.

An early assessment of structural properties of glass-fiber filament-wound cryogenic pressure vessels pointed out the difficulties in designing and operating such vessels at low temperatures and over wide temperature swings [336, 337].

The thermal conductivity of composite overwrapped tanks and lines is less than that of metallic tanks and lines. The requirement for cryogenic propellants, such as liquid oxygen or liquid hydrogen, in current and proposed booster rockets and space vehicles, has focused attention on the determination of properties of materials at extreme subzero temperatures. The need for thermal design data at cryogenic temperatures arises mostly from two fundamental requirements: **(1)** storage and containment

of high-energy cryogenics and (2) direct exposure of space systems to the cryogenic conditions of a space environment [338].

5.8 Adhesives for Liquid Oxygen Systems

Because most organic materials become very brittle at cryogenic temperatures and lose their adhesiveness, it is very difficult to find adhesives that maintain their strength and tackiness at low temperatures. Adhesives were developed based on fluorinated polyurethanes [339–343]. Polyethers were prepared from hexafluorobenzene and hexafluoropentandiol. Polyurethanes were prepared based on perfluoropropylene oxide and tetrafluoro-*m*-phenylene diisocyanate.

In a different approach to the synthesis of oxygen-resistant fluoropolymers, copolymers of fluorinated vinyl ethers with 1,1-difluoroethene gave excellent elastomeric polymers with glass transition temperatures between 272 and 266 K (–1 and –7 °C), with a potential of forming vulcanizable polymers [344–346].

Kel-F adhesives were developed for bonding Kapton[®] foils to make positive expulsion bladders for liquid oxygen [347].

5.9 Ceramic Materials for Liquid Oxygen Systems

Despite their brittleness and lack of elasticity, ceramic materials find applications in LOX systems where combustible metals or polymers cannot be used. Some hydrostatic bearings in pumps are made from silicon carbide which withstands LOX without ignition under conditions (friction, sliding contact) where other materials would ignite [348, 349]. Tribological tests were made on a pin-on-disc apparatus using LOX as the working environment. The measurement of friction and wear allowed a comparison between different kinds of SiC ceramic matrix composites and 440C steel materials.

6 Toxicity of Liquid Oxygen

6.1 Inhalation Toxicity

Oxygen in mixtures with nitrogen is non-toxic, since these are the normal constituents of air. It is only after the oxygen content deviates from the nominal 20% that problems due to oxygen toxicity may be encountered.

Oxygen is essential to human life, but the products of its metabolism are potentially harmful to lung tissue. Manifestation of these harmful effects follows a sequence of pathological changes involving cellular proliferation, exudation, and interstitial fibrosis [350, 351]. Changes in the alveolar capillary membrane give rise to altered

metabolic pathways in the lungs which can have a subsequent effect on aspects of care directly related to physiotherapy. For example, a progressive dose-related deterioration in pulmonary antibacterial mechanisms has been demonstrated, suggesting a progressive deterioration in host resistance to inhaled bacteria with prolonged exposure to high oxygen tension. This supports the clinical impression that prolonged oxygen therapy increases susceptibility of the lungs to infection. The biochemical basis of oxygen toxicity is increased production of highly reactive, partially reduced metabolites of oxygen, including hydrogen peroxide and free radicals, by cells in hyperoxia [352]. Enzymatic intracellular defense mechanisms exist which protect cells from the toxic effects of oxygen free radicals. The physiologic manifestations of oxygen toxicity include decreases in vital capacity, diffusing capacity, and lung compliance. No effective pharmacologic means exist for lessening pulmonary oxygen toxicity in humans.

All tissues of the body can be injured by sufficiently high oxygen concentrations, but the lungs are directly exposed to the highest partial pressure of inspired oxygen. The precise concentration of oxygen that is toxic to the lungs probably depends on many variables in the exposed person, including age, nutrition, endocrine status, and previous exposure to oxygen or other oxidants. Hyperbaric oxygen accelerates the effects of oxygen toxicity and damages the central nervous system [353].

During tanking operations with oxygen at a test site or on the launch pad in the open air, the inhalation toxicity danger to personnel is usually low because the exposures are short, the cold oxygen creeps along the floor, and there is always some convection to mix oxygen with ambient air.

6.2 Frostbite Hazard

The frostbite hazard with LOX is the same as with any cryogenic fluid, for instance liquid nitrogen. It is dangerous to touch cold pipelines with a bare hand, in particular if the hand is moist because it may freeze to the cold pipe and would be difficult to remove.

Small frostbitten spots on the skin can be bathed in tepid water to alleviate the cold pain. Larger frostbitten areas or limbs may be thawed only slowly, and the patient must be immediately taken to the emergency room for treatment by a physician.

7 Handling, Transportation, Storage, Transfer, and Disposal Equipment for Liquid Oxygen

Additional information on the safe handling of LOX can be found in references [354, 355]. There are many more publications that describe the hazards of handling cryogenic oxygen and teach recommended practices for the safe handling of liquid oxygen than can be listed here. Just a few examples are shown here as a starting point

for further research: [356–360], Chap. 11 in [361], also for breathing oxygen in military aircraft [362, 363].

7.1 Storage of Liquid Oxygen

Aside from the precautions common in the handling of all cryogenic liquefied gases, the handling of liquid oxygen is relatively simple and only few additional precautions must be added to those already taken for other cryogenic liquids. Logistics must be carefully planned to take into consideration the evaporation losses during storage and transfer of LOX. The boil-off is usually simply vented to the atmosphere, but one must prevent the intrusion of ambient air, best prevented by venting through a pressure relief valve or a check valve [364]. Unlike the storage of liquid fluorine, actively cooled, zero-venting storage of LOX in a bath of liquid nitrogen is not required.

7.1.1 Storage and Transport Vessels for Liquid Oxygen

A wide range of storage and transport vessels for LOX are commercially available. All have double-wall construction to reduce heat conduction into the stored medium. The interspace between the two walls is either evacuated (like a Dewar flask) or filled with an insulating material and then evacuated. Flight-qualified rocket tanks will use a different construction since double-walled tanks would be too heavy and since usually only short hold times during countdown prior to launch are required.

7.1.1.1 Tank Cars for Liquid Oxygen Transport

Large liquid oxygen tanker cars are now in use to transport LOX from manufacturing plants to points of end use (Figure 36).



Figure 36: Liquid oxygen transport tank car. (Copyright: Linde GmbH, Pullach, Germany)



Figure 37: LOX tank cars delivering LOX through a portable filter. (Reproduced from [359] with permission from AIAA)

A typical liquid oxygen transfer operation from a transport truck to a stationary storage tank is shown in Figure 37, including the in-line filter for the removal of particulates and organic contaminants.

7.1.1.2 Stationary Tanks for Liquid Oxygen Storage

Table 41 gives an overview over evaporation loss rates for LOX tanks of various sizes with different types of insulation.

Table 41: Evaporation loss rates for LOX tanks of various sizes with different types of insulation.

Container	Net contents, kg	Type of insulation	Boil-off losses, %/day	
			Small containers	Large containers
Tanker truck	2300–8500	30–40 cm Sil-O-Gel at atmospheric pressure	10–11%	7–8%
Rail car	28000–37000	Same, but evacuated down to 0.1 mm Hg	2%	1,5%
Stationary tank farm	4500–910000	30–90 cm Sil-O-Gel at atmospheric pressure	8%	1%
Stationary tank farm	9100–53000	30–40 cm Sil-O-Gel evacuated down to 0.1 mm Hg	0.4–0.5%	0.3–0.4%

Data source: [365]

In the cryogenic industry there are LOX storage vessels in use holding up to 1500 metric tons of LOX. NASA has two LOX storage tanks at LC-39A and LC-39B with 850000 gallon capacity each at KSC that once served the SATURN-V and the Space Shuttle propellant needs and now serve the FALCON and SLS launch vehicle needs (Figure 38). In addition to the historical insulation methods shown in Table 41, there is the multi-layer superinsulation that was first used mostly for liquid hydrogen tanks but is now just as frequently used for LOX tanks. The advantages of superinsulation are lighter weight, more flexible application and lower evaporation losses; however, superinsulation is more expensive than simply evacuated double-walled tanks or powder insulation and is therefore used mostly for flight tanks. New cryogenic storage tanks use glass bubble insulation that is more effective than perlite powder.



Figure 38: Liquid oxygen ground storage tank at LC39B launch site at NASA KSC. (Photo courtesy of NASA)

LOX should be stored only in well-ventilated areas, otherwise the entire area would be exposed to increased fire hazard and more likely to burn in case of accidental ignition.

If cryogenic liquids are stored in very clean containers with smoothly polished walls, it is possible to encounter boiling delays like superheating of water in a microwave oven. Boiling delay may be encountered if the polished walls are heated suddenly or if the pressure is suddenly reduced [366]. The subsequent sudden pressure rise may rupture the tank if the vents are not properly sized. It is best to avoid boiling delays altogether by attaching porous nucleating devices (“boiling stones”) to the bottoms of the tanks or by steadily bubbling a slow stream of gaseous oxygen through the liquid.

When liquid oxygen is vented and flashed in outer space, the liquid may freeze due to the sudden loss of heat of evaporation and sublimation. The vent valves must be designed such that frozen oxygen cannot clog the vent passage [367].

7.1.2 Storage of Oxygen in the Form of Solid Oxygen

The use of solid oxygen for storage and supply systems in space applications was studied both analytically and experimentally [88]. The analysis indicated that the use of solid oxygen could provide substantially longer storage times over that obtainable with subcritical liquid and supercritical oxygen. Oxygen transport from the vacuum storage condition of solid oxygen to a condition suitable for breathing or propulsion was demonstrated experimentally by two methods, vapor transport using cryosorption pumps and solid transport by mechanically moving the solid through a pressure lock. A preliminary analysis of the transport methods indicated that the mechanical system would be the most suitable.

7.1.3 Stratification of Cryogenic Liquids

A model was developed for a stationary, non-draining, and non-forced recirculating tank containing a cryogenic fluid (LOX or LH₂) [368]. A natural convection boundary layer develops along the tank wall and transports warm fluid and less dense fluid to the top layers of the liquid in the tank. Interaction between the boundary layer flow and the previously stratified fluid depends on temperature differentials and tank geometry. The liquid and its vapor are thermodynamically coupled by allowing mass and heat transfer at the liquid-vapor interface. The model predictions matched well with experimental data in cylindrical, vertical tanks.

All cryogenic liquids tend to stratification when stored under quiescent conditions in a gravity environment in the absence of convection currents or if the upper half of the tank receives more heat than the lower half of the tank. If the upper layer is warmer (and less dense) than the lower layer, the vapor pressure in the system is above the equilibrium value [369, 370]. If a stratified tank is suddenly agitated, the vapor pressure in the ullage may collapse because colder propellant is now at the interface between the liquid and the vapor phase. The physical properties of the contents of the tank that are measured and fed to the central control computer will vary depending on the level where the sensors are installed and may give erroneous messages. For stationary installations, stratification can be avoided by attaching the support structure, which is an undesirable, but inevitable heat leakage path, at the bottom instead of the sides of a stationary tank. Convection currents in the tank will maintain the contents in a well-mixed condition. For flight tanks and rockets sitting on the launch pad during countdown, active recirculation methods will be required. The propellant can be circulated through an external loop that at the same time may contain a heat exchanger to chill the propellant, or cold helium gas can be bubbled through the tank. In a low-gravity environment, the contents of a cryogenic tank need to be stirred by jet mixing [371–373].

A numerical investigation was performed on the fluid motion inside a rocket tank with natural circulation precooling loop based on computational fluid dynamic (CFD) techniques [374]. The results showed that convection heat transfer was dominant in

the bulk above the return inlet position and the heat conduction took place chiefly below the position. The axial thermal stratification was produced in the main region of the tank, the radial stratification appeared only at the bottom and the lowest temperature region moved towards the opposite bottom header region away from the side wall near the return position.

Such a model can handle both axial thermal stratification and radial stratification which appeared in the bottom of the tank, and the lowest temperature region moved towards the right of the bottom header. A clockwise vortex was formed in the liquid phase and the velocity vortex in the bottom area of the tank changed from clockwise to anti-clockwise due to the transformation of flow field [375, 376].

The return flow location of the circulation loop plays an important part in the fluid temperature and density distribution in an oxygen tank. The 3-D distributions of temperature and velocity fields were created by computational fluid dynamics (CFD), and the effect of the return flow location on thermal stratification was analyzed [377]. It was found that a return location 2m above the bottom header is optimal, where the volume and depth of subcooled liquid oxygen in tank have maximum values.

Thermal stratification in a rocket LOX tank with a natural circulation precooling loop was numerically analyzed under different return inlet locations and influx angles [378]. It was found that the heat convection was dominant in the bulk above the return inlet location and that the heat conduction became primary below the location. The axial thermal stratification existed in the whole range of the tank, and the radial stratification appeared mainly in the bottom. The stratifications were influenced by the selection of the return inlet location and influx angle, and the optimal values of the return inlet location were at $H/L = 0.3$ and an influx angle of 30° .

The rate of self-pressurization is related to the level of pre-pressurization that existed at the moment when the tank was locked up [379]. The pressurization performance and temperature distribution in a cryogenic LOX tank was examined using a CFD model with both the vapor-liquid interface phase change and external forced convection heat exchange considered. The results showed that during the ground prelaunch holding period, intense nucleate boiling initially appears in the cryogenic tank, then the boiling intensity becomes weaker, and finally, it tends to be stable. With the high temperature gas oxygen injecting into the tank, tank pressure fluctuates among the setting pressure limits. The ullage is condensed during the whole pre-pressurization phase. Influenced by heat transferring from the ullage and the external heat leakage, the thermally stratified top layer becomes thicker with time.

7.1.4 LOX Flight Tanks

The Saturn I first stage, the S-I, was conceived in 1958 to provide early capability for large payloads in preparation for Apollo. Existing hardware was used wherever possible. The decision to arrange the engines and tanks in clusters allowed the use of

equipment developed in the Army's ballistic missile program. Thus, the uprated S-IB stage had eight 1.78-m (70-in.) diameter tanks (from the Redstone missile) surrounding a single 2.67-m (105-in.) diameter tank (from the Jupiter missile). The center tank and four of the outboard tanks were used for LOX and the other four outboard tanks were used for the RP-1 fuel. All the tanks were approximately 18.2 m (60 ft.) long, and both the LOX and the fuel tanks were interconnected at the top and at the bottom. It was important to accurately know the density of the oxidizer in order to load the correct amounts of propellants [54].

One of the most impressive LOX tanks was the LOX tank in the external tank (ET) of the NASA Space Transportation System Space Shuttle. The LOX tank was an aluminum monocoque structure composed of a fusion-welded assembly of preformed, chem-milled gores, panels, machined fittings and ring chords. It operated in a pressure range of 138–152 kPa gauge (20–22 psig). The tank contained anti-slosh and anti-vortex provisions to minimize liquid residuals and to dampen fluid motion. The tank fed into a 43-cm (17-in.) diameter feed line (Figure 39) that conveyed the LOX through the intertank, then outside the ET to the aft right hand ET/orbiter disconnect umbilical that permitted LOX to flow at approximately 1262 kg/s (2787 lb_m/s) with the Space Shuttle Main Engines (SSMEs) operating at 104% power. The LOX tank's double-wedge nose cone reduced drag and heating, contained the vehicle's ascent air data system and



Figure 39: Workers raise the liquid oxygen feedline for the 17-inch quick disconnect toward orbiter Discovery for installation. Photo: NASA

served as a lightning rod. The LOX tank volume was 550 m^3 (19563 cu. ft.) It was 8.4 m (27.6 ft.) in diameter, 15 m (49 ft.) long and weighed 5436 kg (12000 lb) empty.

Most flight vehicles do not carry insulation around their LOX tanks in order to save weight. In the early days of rocketry (A4, VIKING), a temporary, removable jacket was placed around the rocket in order to reduce evaporation losses during countdown. The jacket was then removed just prior to the launch. In most cases nowadays the LOX is topped off through an umbilical line continuously during the countdown until the tank is locked up and allowed to self-pressurize just before launch.

The frost layer that builds up during the countdown substantially reduces the rate of heat transfer and evaporation losses [380–383].

Figure 40 shows a cross-section through the LOX-air interface at the surface of an uninsulated tank wall. For simplicity, it is assumed that the temperature on either surface of the metal wall is the same, since the conductivity of the metal is much higher than that of the ice or fluids on either side. T_1 is the ambient air temperature and T_2 is the LOX temperature. The heat flux can be calculated from:

$$\frac{dQ}{dA} = k \frac{T_1 - T_2}{\Delta X}$$

The rate of heat transfer through an uninsulated aluminum tank wall from the moment it is filled with LOX gradually decreases because the frost layer has some insulating quality (Figure 41). The frost layer thickness eventually remains constant after a certain time.

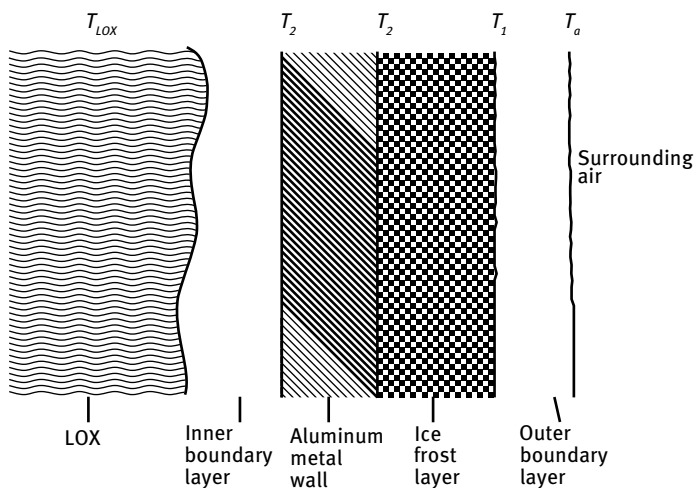


Figure 40: Cross-section through the frost-coated wall of a cryogenic liquid container.

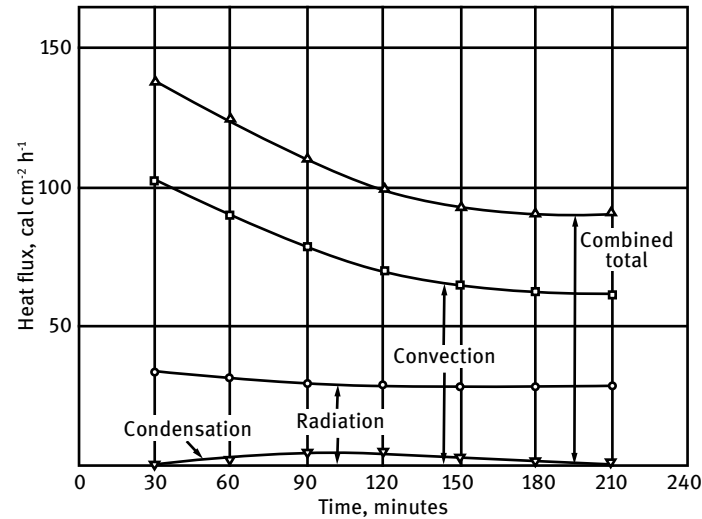


Figure 41: Time profile of heat transfer to an aluminum tank containing LOX (reproduced and modified from [380], with permission from © 1961 Springer Nature; permission conveyed through Copyright Clearance Center Inc.)

The magnitude of the heat transfer constant k is determined by components of convection, radiation, and condensation. The rate of formation of the frost layer depends on the relative humidity of ambient air. In a very dry desert climate, the frost layer may form much slower than at a launch site on the coastline where humidity is often close to saturation.

The frost layer that builds during the countdown usually flakes off during launch. Florida is a high-humidity climate and frost layers build up on cryogenic tanks very quickly. Chunks of ice breaking off from the external tank of the Space Shuttle damaged the leading edge of the wing of the Space Shuttle Columbia and caused a disaster and the loss of seven astronauts on re-entry into the atmosphere.

Aerodynamic heating during flight through the lower atmosphere increases the heat transfer into the cryogenic fluid tank. This is very pronounced in upper stages, where the heat input during maximum aerodynamic load increases by more than 3%. This is one of the reasons that many expendable launch vehicles (ATLAS-AGENA, THOR-DELTA, VANGUARD) used storable instead of cryogenic propellants in the upper stages. ATLAS-CENTAUR was the first cryogenic upper stage in the United States.

7.1.5 Storage of LOX in a Zero-g Environment

In the future, cryogenic propellants will have to be stored in orbital propellant depots where propellant is transferred to large, potentially reusable propulsion units. Experiments have been conducted to study the rate of heat transfer under zero-g conditions. Models have been developed to describe the thermal behavior of fluids in a low-gravity field [384]. One option is to store cryogenics in the supercritical state, as it was done in the LOX and LH₂ tanks for the fuel cells on the Apollo service module.

The chapter on liquid hydrogen in *Encyclopedia of Liquid Fuels*, chapter “Hydrogen”, contains a more detailed description of cryogenic propellant storage in orbital propellant depots.

7.1.5.1 Surface Tension PMDs for LOX Withdrawal in a Zero-g Environment

When transferring propellants in space, it is most efficient to transfer single phase liquid from a propellant tank to an engine. Gas bubble ingestion causes a multiplicity of problems. In earth’s gravity field or under acceleration, propellant transfer and draining a tank is simple; however, in low or zero gravity, withdrawing single phase fluid becomes a challenge.

One of the few cryogenic upper stages with multi-start capability is the Centaur upper stage and its derivative, the ATLAS V upper stage. Usually, a set of small thrusters is fired to allow the propellants in the main tanks to settle before the engine(s) is (are) restarted in orbit. As an alternative to the propellant settling maneuver, cryogenic surface tension tanks have been considered, also for orbital propellant depots [385–387].

A variety of **Propellant Management Devices** (PMD) are used to ensure single phase flow. These are routinely used for storable propellants but for cryogenic oxygen different design considerations must be applied. One type of PMD, a **Liquid Acquisition Device** (LAD) takes advantage of capillary flow and surface tension to acquire liquid. Testing with LOX at elevated pressures (and thus temperatures, maximum pressure 1724 kPa and maximum temperature 122 K) as part of NASA’s continuing cryogenic LAD development program evaluated LAD performance for LOX stored in higher pressure vessels that may be used in propellant systems using pressure-fed instead of pump-fed engines [388]. Test data showed a significant drop in LAD bubble point values at higher liquid temperatures, consistent with lower liquid surface tension at those temperatures. Test data also indicated that there are no first order effects of helium solubility in LOX on surface tension of LOX and LAD bubble point prediction. The geometry of the wire mesh pore and the fluid surface tension determine the bubble point of the screen. A high bubble point (fine screen mesh) is desirable to ensure single phase (liquid) fluid delivery and good wicking of liquid into the screen pores. Fine mesh screens, however, tend to generate a large pressure loss during outflow through the screen. The total pressure loss in the system must be less than the bubble point pressure to prevent vapor ingestion into a LAD channel.

7.1.5.2 Positive Expulsion Bladders for LOX Expulsion in a Zero-g Environment

It is very difficult to find elastomers for positive expulsion bladders that remain flexible at liquid oxygen temperatures and do not burst in flames when flexed in liquid oxygen.

Bladders made from Mylar[®] or Kapton[®] depend on adhesives that maintain their flexibility and adhesive bonding strength when exposed to low temperatures [389].

Expulsion bladders for LOX were fabricated from several different materials and evaluated by functional testing [390]. A total of 39 samples, representing several different materials in various thicknesses, were tested for LOX compatibility at 97 N m (72.3 ft-lb_f) of impact energy in accordance with MSFC-SPEC-106A. In general, only fluorocarbon and chlorofluorocarbon polymers, such as Teflon, Kel-F, Armalon, and Aclar, were acceptable. Mylar possesses excellent mechanical properties at LOX temperature. Therefore, attempts were made to desensitize this material to impact in LOX by use of insensitive metallic surface coatings, but without success. Results indicated that materials considered chemically compatible with LOX generally were not suited for fabrication of expulsion bladders because of their poor mechanical properties at low temperatures. Complex expulsion bladders involving reinforced films and predetermined fold patterns performed slightly better than simple unreinforced films.

7.1.6 Storage of Oxygen in the Supercritical State

In the supercritical state the boundary between liquid and gaseous phase disappears and the entire tank contents assume a uniform state. Oxygen required in a spacecraft for operation of fuel cells or as breathing oxygen can be stored in the supercritical instead of the liquid state. This mode of storage is used mostly for auxiliary systems in a crewed or uninhabited spacecraft and not for rocket propulsion systems but should be included here in case future small thrusters depend on a steady source of oxygen. If oxygen was stored in a spacecraft tank in the liquid state, it would be difficult to withdraw only GOX or only LOX since in a zero-g environment the phase boundary is wandering all over the tank. Surface tension propellant management systems are used mostly for storable and not for cryogenic propellants in a zero-g environment. Heat transfer to supercritical oxygen is independent of the gravity environment in which the tank is kept [391]. There are no convection currents.

The supercritical oxygen tank in the Apollo 13 Command and Service Module exploded and almost stranded the astronauts in outer space because a thermostat switch was stuck in the closed position and the tank overheated.

Oxygen is rarely stored on the ground in a supercritical state. It can be done but it does not offer any advantages over cryogenic liquid storage [392, 393].

7.1.7 Storage of Oxygen in Slush State and Densified State

If oxygen must be stored for some time before it is to be used, one might subcool it and allow some of it to freeze. During the storage time, any heat absorbed through the insulation would then go into latent heat of melting instead of latent heat of evapora-

tion and boil-off losses. Even cooling oxygen to just above the freezing point instead of actually freezing it has benefits of increased density and delayed boil-off.

Future orbital lunar and interplanetary space flights require long-term storage of cryogenics for life support, power from fuel cells and propulsion. Successful accomplishment of these missions could be enabled by optimization of high-performance insulation and other system conditions, such as initial cryogenic state (e.g., subcooled or slush) [394].

A large-scale LOX propellant densification system rated for 750 L/min. (200 gpm) and sized for the X-33 LOX propellant tank was designed, fabricated and tested at NASA Glenn Research Center (GRC) [395]. Objectives of the test program were validation of LOX production unit hardware and characterization of densifier performance at design and transient conditions. An initial series of simulated LOX densifier screening and check-out tests was done using densified liquid nitrogen instead of LOX. A second series of tests collected performance data during LOX densifier test operations with LOX as the densified product fluid. LOX X-33 tanking operations and load tests with the 75.6 m³ (20000 gallons) structural test article showed that thermal stratification occurs inside a flight-weight launch vehicle propellant tank unless a closed loop recirculation of LOX flows through the densifier and then back into the tank. Finally, in excess of 75.6 m³ (20000 gallons) of densified LOX at 66.6 K (120°R) was produced with the propellant densification unit during the demonstration program, an achievement that had never been done in the realm of large-scale cryogenic tests. Similar densification tests were planned for hydrogen to fly in the same reusable launch vehicle. While the oxygen densification unit had a capacity of 13.6 kg/s (30 lb/s) LOX, the LH2 densification unit was designed to process 3.6 kg/s (8 lb/s) of liquid hydrogen [396, 397].

The second phase of testing involved a series of closed-loop recirculation tests within a propellant test tank [398]. This testing used the densification unit in conjunction with the propellant test tank to simulate the recirculation and densification processes. For the recirculation tests the test tank was outfitted with a siphon outlet at the top of the tank and horizontal splash plates at the two fill points. A liquid level capacitance probe used to control the propellant liquid level and a series of silicon diode temperature sensors used to measure the thermal stratification were also installed in the tank. An analytical model of the in-tank densification process depended on the understanding of the effects of buoyancy-driven thermal stratification in complex-shaped tanks related to the recirculation of propellants and ambient heating. The results from the recirculation tests have confirmed the mathematical model.

7.1.8 Liquid Oxygen Property Changes During Pressurization

An analytic thermal model for pressurization and cryogenic propellant conditions during all mission phases of any liquid rocket propellant tank has been developed and validated [399]. The model assumed the propellant tanks to be divided into

five nodes and implemented an empirical correlation for liquid stratification if desired. The five nodes included a tank wall node exposed to ullage gas, an ullage gas node, a saturated propellant vapor node at the liquid-vapor interface, a liquid node, and a tank wall node exposed to liquid. Mass transfer at the liquid-vapor interface is included in the form of evaporation, bulk boiling of liquid propellant, and condensation given the appropriate conditions for each but pressurant gas dissolution was not included. Model predictions were validated by comparison with various Saturn-V era test data and reasonably successful against more recent LH2 tank self-pressurization ground test data.

The transient thermal behavior in the cryogenic oxidizer tank of a launch vehicle was theoretically investigated for the pressurization process by gaseous helium injection followed by a readiness countdown hold just prior to launch [400]. A numerical model was developed using the transient mass and energy conservation of oxygen/helium mixtures both in the ullage and in the liquid. At the liquid-gas interface, various modes of heat and mass transfer were considered, including liquid evaporation and helium absorption. Increasing the pressurization level affects tank pressure, ullage gas temperature and evaporation of liquid oxygen. As for helium absorption into the liquid, its mass is negligibly small, and it should not be a concern in design and operation of the oxidizer tank.

Ground experiments of LOX tank pressurization with high-temperature helium exceeding 600 K as the pressurant gas, and radial diffuser and anti-cone diffuser, respectively, at the tank inlet were performed and the pressurant gas requirements, axial and radial temperature distributions, and energy distributions inside the propellant tank were obtained and analyzed [401]. The tank pressure was controlled within a specified range and a stable discharging liquid flow rate was achieved. For the radial diffuser case, the injected gas impacted directly on the tank inner wall, where gas-wall heat transfer resulted in about 59% of the total input energy absorbed by the tank wall. For the pressurization case with anti-cone diffuser, the direct impact of high-temperature gas flowing towards the liquid surface resulted in a greater percentage of energy transferred to the liquid propellant, where the percentage reached up to 38%. Both of the two cases showed that the portion of energy left in the ullage in relation to the total input energy was quite small, only about 22–24%. This may indicate that a more efficient diffuser could be developed to improve the pressurization efficiency.

7.2 Transportation of LOX

Liquid oxygen is transported all over the country in a fleet of tank cars and railroad cars especially equipped for storage and transport of LOX. Several industrial gas (liquefied gas) companies have contributed to the widespread use of LOX in a variety of applications ranging from hospitals and home-bound patients with respiratory diseases to expendable and reusable space launch vehicles. These companies include

US companies such as Union Carbide (formerly Linde, USA) [402], Air Products [403] and more recently Praxair, now part of Linde US. As of 1960, Union Carbide alone had already built more than 450 trucks in more than 15 distinctly different styles with capacity ranging from 1700 to 12700 m³ (60000 cu. ft. to 450000 cu. ft). There has been a steady improvement of insulation, insulation casing, suspension, and ratio of payload to gross load.

Tank cars and railroad cars hold anywhere between 1700 and 12700 m³ of LOX. In order to minimize the sloshing of the liquid contents, which could change the center of gravity and cause vehicles to tip over, the tanks are compartmented by baffles. The valves are well insulated and located in the inside of the insulating layer, such that LOX cannot splash into passages that are extending to the warm outside world. Valve stems and pipe connections are made of metals with low thermal conductivity in order to minimize boil-off. The double-wall interspace is usually filled with porous powders and evacuated, like stationary storage tanks.

7.2.1 Logistics of Cryogenic Fluids

The logistics of cryogenic liquids, regardless of whether it deals with LOX or liquid hydrogen, require careful planning to make sure that the amount of propellant needed for a given launch application is available on the day when the launch is scheduled (and eventually postponed due to bad weather). Variables entering the equation include the boil-off of the various storage tanks, the size of the transport and supply vessels, and to a limited extent even atmospheric conditions [404]. It would be a waste of resources to store more LOX than is required to satisfy the demand [405, 406]. In the case of poor planning, as much as seven times the amount of LOX needed for a static test or a launch might be needed (wasted) for a given job.

If the distance between the LOX plant and the test or launch site is less than 10 km (7 miles), it may be more economical to install a pipeline rather than depend on a fleet of tank cars [407]. The question to be considered here is: is it necessary to transport the liquid in batches in transport containers, or can it be pumped over relatively long distances through pipelines? In the considerations of long transfer lines there are two areas which must be investigated: The feasibility of cooling down the systems and the feasibility of transferring the liquids after the line has been cooled. An accurate analysis of the cooling down transient problem is a difficult task, but one must also study the steady-state problems:

- Are equipment and techniques now available for long distance transfer of liquefied gases?
- Are the losses occurring in long distance transfers tolerable?

In the future, bases on the moon or on Mars will have to work on their own logistics using a slightly different set of parameters to keep a fleet of spaceships supplied with liquid oxygen and other propellants.

8 Flow Control Components and Instrumentation for LOX Systems

Selection criteria for components and instrumentation for LOX systems depend on the application. They are different if the application is for static testing of rocket engines on the ground, for ground service equipment at launch sites, or for the airborne (spaceborne) rocket-propelled vehicle itself. A lot of experience has been gained since the first pioneering LOX experiments of Goddard, von Braun and the likes. There is now a substantial industry of component suppliers specializing in components for cryogenic service in general and LOX in particular.

8.1 Valves

In the early days of rocketry valves were the most trouble-prone components of static test stands and flight vehicles. This has changed with the amount of experience gained as the space age matured. Now valves for LOX service are offered as off-the-shelf items and listed in on-line catalogs of component supply companies.

But even with the best valve available, improper installation can still cause problems. On the ground in stationary installations and on tank cars, problems often are caused if the valve stem and handle or actuator are covered with ice that impedes the motion of the valve stem or plunger [383]. The design of valves attempts to minimize the heat leakage into the valve (and the frosting of the exposed parts) by making the valve stems and housings from a material with poor thermal conductivity. If the valve is in an enclosure, it would help to reduce the access of ambient moisture by purging the enclosure with dry air or dry nitrogen. But even with dry air, some condensation might be observed that is due to condensing carbon dioxide. Carbon dioxide condensation is not a problem and can be easily wiped off.

A series of fires in medical oxygen tank valves in 1996/1997 caused a recall of 8000 oxygen cylinders due to incompatible valve seat materials containing polychlorotrifluoroethylene [408]. The ignitions occurred when the valve was opened for the first time after the tanks had been filled.

8.2 Quick Disconnect Couplings

Connecting a storage tank to a supply trailer or a launch vehicle requires flexible, yet leak-tight connections that can be made and unmade without a tool kit. Early models of quick disconnects for LOX are described in [409, 410]. More recent developments can be found in the catalogs of cryogenic equipment supply companies. A very large quick disconnect coupling is shown in Figure 39.

8.3 Liquid Level Indicators

The filling level of LOX tanks cannot be measured by conventional methods such as sight glasses or floats. For large stationary installations, strain gauges may be attached to the support structure to obtain a rough indication of the load in the tank. In most cases multiple sensors of the physical state of LOX vs. GOX will be arranged in an array to provide an incremental level indication.

Propellant loading of a missile or a space launch vehicle must be precisely controlled so that neither fuel nor oxidizer will be prematurely exhausted, resulting in loss of range because the remaining other component is carried as ballast. To satisfy the stringent loading accuracy requirements one must determine the true content of a tank containing LOX or liquid hydrogen.

The contents of a non-transparent tank can be measured by absorption of gamma radiation from radioisotopes. LOX would absorb more radiation than GOX; however, if the tank is covered with a crust of ice, the gamma ray absorption of ice would give false results.

Liquid level gauges based on measurement of the dielectric constant in a laddered capacitance circuit are widely used, also in cryogenic tanks that supply breathing oxygen to military aircraft [411].

One of the less accurate, but quite fundamental methods is simply measuring the hydrostatic pressure at the bottom of a vertical stationary LOX tank.

One of the more popular gauges for measuring liquid level is the differential pressure gauge frequently known as the Delta-P system. This device is adequate for many simple applications but has deficiencies where a gauge is required to provide information for a complex control system requiring extremely high accuracies and fast responses. Ultrasonic gaging is more accurate and widely applicable to cryogenic and non-cryogenic fluids [412]. The reflection of ultrasound either looking down at the liquid surface or looking up from the liquid at the bottom and measurement of the time of travel will allow one to determine the location of the phase boundary.

Another simple method is a resistance measurement of a hot wire immersed in the fluid. Its heat loss and resistance in liquid would be higher than in gas [413]. Special care must be taken not to heat the wire to the point where it might ignite in an oxygen atmosphere.

Some of these liquid level gauges are suitable only for stationary installations. Liquid level gauges for flight tanks must meet more stringent requirements. A liquid level gauge in the SATURN-V booster was based on a capacitance measurement [414]. Data from both oxidizer and fuel liquid level gauges were fed to a computer which was capable of adjusting the mixture ratio toward the end of the burn such that all propellant was consumed, and no puddles of unused propellant sloshing around would cause the vehicle to go unstable.

An optical fiber-based liquid level detection system for applications in cryogenic environment consisted of a multiplexed array of point liquid probes [415]. Two dif-

ferent designs of the probe were fabricated and tested. The multiplexing of multiple liquid probes using an optical time domain reflectometer (OTDR) device was successfully demonstrated.

Other liquid level gauges measure the difference in the thermal diffusivity in the vicinity of a hot wire [413]. The difference is mostly due to the difference in heat capacity of the two states of fluids: The heat capacity of oxygen at the normal boiling point are $1.699 \text{ J g}^{-1} \text{ K}^{-1}$ for the liquid and $0.910 \text{ J g}^{-1} \text{ K}^{-1}$ for the gas, with a gas:liquid ratio of 1:1.87, giving a more distinct reading than hydrogen, where the liquid:gas ratio of heat capacities is only 1:1.26.

Most of the instrumentation intended for density measurement of cryogenic liquids can also be used for liquid level sensing [416]. This includes dielectric constant/capacitance, resonant cavity, nuclear radiation attenuation, acoustic reflection, and forced harmonic oscillation.

Radio frequency sensors can be used for measurement of the quantity of liquid propellants in tanks of space vehicles both on earth (during their fueling) and in low gravity and zero gravity conditions during space flight [417].

Other liquid level gaging systems are described in references [418, 419], and [420].

A sensor consisting of a vertical linear array of 140 highly sensitive optical fiber refractometric transducers with a measurement range of 1.6 m with a resolution of up to 5 mm can be used for measuring the level of any cryogenic liquid such as LOX or liquid hydrogen [421].

8.4 Flow Meters

Flow meters for LOX can be either turbine flow meters or differential pressure gauges [422]. An integrating flow meter was required for dispensing LOX from tankers. A considerable number of positive displacement metering principles are in existence, but they are mainly developed for water meters. The rotary or oscillating piston meter is simple to manufacture because metering chamber and metering pistons are easily machined. A summary of information on flow meters for LOX service is given in [423].

One of the problems associated with the use of cryogenic fuels and oxidizers in rocket engine testing is that of accurately determining propellant flow rates, thereby providing essential information for the prediction of thrust and specific impulse. While many diversified approaches have been investigated for the measurement of propellant flow rates ranging from the now familiar turbine-type flow meter to the more exotic magnetic and ultrasonic-type flow meters, all of these systems have a common problem, i.e., even though a highly accurate flow meter may be developed, the limiting factor is the overall system accuracy including the error in calibrating the flow meter. High flow rate, open-loop type flow meter test stands have been widely used in calibration of flow measuring devices with non-cryogenic fluids; however, the calibration of flow meters using cryogenic fluids which are subjected to rapid boil-off

precludes the use of a system which is open to ambient conditions. In addition, cryogenic fluids inherently exhibit significant density changes as the temperature of the fluid varies. Inasmuch as most cryogenic systems are maintained under a pressure sufficient to insure subcooling of the liquid, the temperature-density variation could occur without cavitation but still present unique problems in determining the flow rate. Calibration of these flow meters can be achieved within ± 0.17 mass-% or ± 0.28 vol.-% by the method described in reference [424].

If a flow meter is calibrated at room temperature with water prior to calibrating it with LOX or LN_2 , it may be difficult to extrapolate from the water-room temperature calibration to the cryogenic fluid calibration [425, 426]

8.5 Pressure Gauges and Pressure Transducers

Pressure transducers for cryogenic service must have the capability to compensate for changes in temperature. The calibration of many pressure (load) sensing elements drifts substantially as soon as the temperature changes [427]. A summary of pressure measuring instrumentation for LOX service is given in reference [428]. All transducer types of pressure transducers, such as strain gauge, capacitance, potentiometric, or piezoelectric, were included and their uses with gaseous or liquid oxygen were reviewed.

8.6 Temperature Probes

Cryogenic temperatures are usually measured accurately with resistance thermometers. Early in the development planning for liquid hydrogen-oxygen rocket engines, it became apparent that routine high accuracy temperature measurements in the cryogenic ranges of liquid hydrogen and liquid oxygen would be necessary. Although these measurements had been accomplished in research laboratories, "ruggedized" sensors and associated equipment suitable for continued use in outdoor test stands had to be developed. A ruggedized system was developed that will, with individual calibration, provide measurement accuracy of $\pm 0.1^\circ\text{F}$ [429].

9 Transfer and Pumping of LOX

The transfer of LOX between stationary tanks, between transport tanks and stationary tanks, or from ground service tanks to flight vehicles must usually be completed with a minimum of time and a minimum of evaporation losses during transfer. Because it involves moving parts (pump shafts, valve stems), friction must be avoided since it has been the cause of several LOX transfer accidents. When filling flight tanks on

a launch pad, one describes the entire operation as “fueling a rocket”, but one hesitates to use the word “fueling” when actually the oxidizer is described. We prefer the more general, less specific term “tanking” which would cover either oxidizer or fuel without any chance of confusion.

LOX can be transferred by pressurizing a tank or with pumps. Of course, if the geographic arrangement allows this, it could also be gravity fed from a tank on a high ridge or on a high tower like a water tower. Even if pumps are used, the supply tank is often pressurized somewhat to maintain a net positive suction head and prevent cavitation in the inlet section of the pump.

Regardless of which method of transfer is used, under no circumstances may liquid oxygen be trapped in a section of tubing or hose between two closed valves if the transfer line is not jacketed with liquid nitrogen (which is rarely done). The stagnant LOX would warm up and the pressure would increase by thermal expansion of the liquid and/or increasing vapor pressure to beyond the pressure rating of the equipment. If LOX is allowed to achieve room temperature in a constant volume vessel, the pressure would increase to $247 \text{ MPa} = 2440 \text{ atm}$. Only few vessels can withstand such a pressure. Transfer systems will typically be designed such that each section carries its own sets of pressure gauges and pressure relief valves.

9.1 Pressurized Transfer

Gas-pressurization is a simple and commonly used method for feeding propellants into rocket combustion chambers. Nitrogen and helium are often used for pressurizing liquid oxygen. Ideally, the pressurizing gas should neither dissolve in the propellants nor condense in the tanks; helium is preferred on both counts. Nitrogen is considerably cheaper than helium and is widely used, especially with systems operated at earth surface ambient temperatures; however, for use at the low temperatures required with liquid oxygen, nitrogen is far less attractive than helium. At these low temperatures and at the pressures of interest, the nitrogen can dissolve in the oxygen to the extent that the propellant is seriously diluted. The dilution may vary from negligible amounts to equilibrium concentrations, depending on the elapsed time between pressurizing the tank and discharging its contents and on the rate at which equilibrium is attained. Therefore, both the equilibrium state of the oxygen-nitrogen system and the rate of solution are factors that must be considered when studying the feasibility of using nitrogen as a pressurizing gas.

When a tank containing a cryogenic liquid is pressurized with a pressurant gas, the pressurant gas slowly diffuses into the liquid from the liquid/vapor interface. In the absence of any mixing mechanism (such as convection or stirring), the diffusion of the solute molecule *A* into the solvent liquid *B* is governed by a diffusion equation. For a tank with a simple flat liquid/vapor interface, the problem can be considered one-dimensional. Imposing initial conditions of no solute in the liquid initially, and

an equilibrium concentration of solute c_0 at the interface for all times $t > 0$, the concentration of solute A in B at later times can be calculated.

Because LOX tanks are typically not designed to withstand excessively high pressures, pressurized transfer must be performed with a number of precautions to prevent inadvertent overpressurization of the supply tank. This will limit the flow rate at which propellant transfer can be achieved. For higher flow rates, pumps will be required. It makes a big difference if the pressurization of a cryogenic tank is done only to provide sufficient net positive suction head at the pump inlet to prevent cavitation, or (in the absence of pumps) the pressurant gas does the work of expelling the fluid from the tank (often against the substantial back pressure of propellants reacting in the combustion chamber).

LOX can be transferred under its own vapor pressure if the rate of heat conduction into the tank is known and if one has enough time to wait for the vapor pressure to overcome the hydrostatic pressure required to lift the liquid above the top of the tank. If one does not have the time to wait and transfer must be achieved at short notice (as in the old days when LOX-propelled ICBMs were on alert all the time and had to be fueled at a moment's notice), compressed helium or hot oxygen gas can be used to pressurize the tank. In many cases it may be more economical to use compressed nitrogen instead of compressed helium for LOX transfer, at least for ground operations. In these cases, one must take into consideration that some of the pressurization gas will dissolve in LOX and dilute it [430].

Depending on the amount of turbulence in the vapor space and at the liquid/vapor interface, the rate of nitrogen condensation may be tolerable. A small cryogenic transfer system was constructed and tested with LOX and LN_2 [431]. Transfer pressures were varied between 441 kPa and 3.2 MPa (50 and 450 psig). The test tanks were immersed in a vented tank of LN_2 so that LOX could be transferred in a sub-cooled thermodynamic state. Tests were carried out in which (1) an empty tank was pressurized, and the pressure was then held for 1 min, (2) a tank full of liquid was pressurized and liquid transferred to a receiver tank within 1 min. Gas requirements and tank temperatures and pressures were measured in each test. Estimates of the condensed gas and the residual cold gas were made from material balance calculations. In one run, LOX was pressurized and transferred with N_2 gas. Samples of LOX were taken in the receiver tank and analyzed for inert gas contamination. No contamination of the transferred LOX was noted. An analytical model was proposed for calculating the rate of heat transfer to the walls and liquid. The heat transfer estimation was combined with an equivalent mass concept derived from thermodynamics to yield estimated values of gas consumption. The calculated values of pressurization gas requirements for all runs were within $\pm 15\%$ of experimental values. Similar expulsion tests were performed with LN_2 as a substitute for LOX [432].

One of the first operational ICBMs with LOX was the ATLAS-I. The tanking ("fueling") system used compressed oxygen instead of compressed nitrogen to prevent dilution of LOX by inert pressurant gas [433]. Nitrogen dilution of LOX should be limited to

below 0.5 mass-% to minimize performance losses and changes in physical properties of the oxidizer [434, 435]. If helium is used as a pressurant gas for LOX, only very little helium dissolves in LOX [139].

In designing a main tank pressurization system, direct impingement of the gas jet on the cryogenic liquid surface is avoided. If the warm pressurant gas is slowly diffused into the head space (ullage) without turbulence, it will stratify which in this case is desirable because it will require less gas to achieve complete pressurization. The amount of pressurant gas will vary from one event to the next. The gas consumption depends on the filling status, the heat capacity of the tank wall, the heat capacity of the pressurant gas, the feed pressure, and the vapor pressure and heat of evaporation of the cryogenic liquid being pressurized. Equations have been developed that can be used to predict pressurant gas requirements [436]. See also [437–443].

If enough pressurant gas is available, it can be precooled to achieve more reproducible pressurization sequences.

9.1.1 Propellant Dilution Due to Pressurant Gas Condensation

If LOX is transferred by pressurization of the source tank with helium, it must be taken into consideration that some of the pressurization gas will dissolve in LOX and dilute it [444].

A method for determining the composition and phases existing within a propellant tank when LOX is pressurized with N_2 gas assumed that the pressurizing gas flows adiabatically from the pressurization gas tank and that an equilibrium state exists in the oxygen-nitrogen system [445]. Enthalpy-concentration plots for the oxygen-nitrogen mixtures at constant pressures from 0.698 to 4.14 MPa (100–600 psia) were provided to quantify the dilution. Both the equilibrium considerations and a small amount of experimental testing led some investigators to conclude that gaseous N_2 is unsuited for pressurizing liquid-oxygen systems. A 42-L (1.5 cu. ft.) cylindrical tank the size of a H-cylinder was filled with LOX and pressurized with nitrogen at 3.1 and 6.2 MPa (450 and 900 psia) and allowed to stand for 6 or 10 min. After withdrawing about half of the contents, the oxygen concentration dropped from 100 to 70% O_2 , indicating that significant dilution had taken place in the top layer of the tank. See also [446].

The penetration of gaseous N_2 into LOX at a pressure of 1.03 MPa (150 psia) was determined by monitoring the composition of the evaporating liquid in a nitrogen analyzer [447]. For pressurization times of about 1 h, the penetration depth varied between 0.06 and 0.45 mm (0.0024 and 0.018 in.) at an evaporation rate of about 1 gallon/day. In a quiescent tank where evaporation losses are taken from the surface, the contaminated surface partially cleans itself of condensed nitrogen.

The penetration of pressurizing gaseous nitrogen (GN_2) into LOX was investigated experimentally by measuring the extent of LN_2 build-up at the LOX interface as a function of GN_2 pressure [448]. Then an adaptation of the differential flash

evaporation technique was used to determine the binary diffusivity of the LOX-LN₂ system at a temperature of 90.2 K. The measured value D equals $0.000086 \text{ cm}^2/\text{s}$, which together with two prior measurements at lower temperatures revealed an excellent fit to the Arrhenius equation, yielding a pre-exponential factor $D_0 = 0.0452 \text{ cm}^2/\text{s}$ and an activation enthalpy H of 1.08 kcal/mol . At a pressure of 11.7 MPa (1700 psi) and holding time of 15 min , the depth of penetration of LN₂ into LOX (to a 1% contamination level) was found to be 0.9 cm .

9.2 LOX Pumps

The cryogenic equipment industry has developed LOX pumps for many applications and flow rates [449].

The selection of ignition-resistant and burn-resistant materials is a major factor in the design of 75000-rpm turbopumps, which can deliver 2.7 kg/s (6 lb/s) of liquid oxygen at 34 MPa (5000 psig). The potential operational hazards of rubbing friction and the impact of foreign particles at high velocity were investigated experimentally for a wide range of candidate materials including nickel, copper, Monel, CRES-316, Hastelloy-X, Invar-36, and silicon carbide [450]. Test parameters included oxygen pressures up to 34 MPa (5000 psig) and temperatures up to 700 K (800°F). The applicability of these materials to oxygen pump design was ranked by comparing the experimental results among themselves and an analytically determined parameter, called the burn factor. Nickel and copper demonstrated superior resistance to ignition and burn in the friction rubbing and particle impact tests relative to Monel, stainless steel, and nickel-iron base superalloys.

The best way to prevent contamination of pumped LOX by leakage from the turbine housing along the pump shaft is to operate the turbine on the same chemical as is being pumped as a liquid on the other end of the shaft: oxygen. A LOX pump turned by 477 K (860°R) hot oxygen driven turbine was designed for a 16.5-kN (3750-lbf) thrust dual expander cycle rocket engine [451]. This turbopump, which required no interpropellant seals or seal cavity purges was driven by a 116-kW (156-HP) single stage turbine. The pump was made of Monel, which has a low ignition potential in oxygen and delivered 2.18 L/s (34.7 gal/min) LOX at 32.1 MPa (4655 psia) at a shaft speed of 75000 rpm .

Various trade organizations have issued standards for design and installation of stationary LOX pumps [452].

9.3 Chillardown Losses During LOX Transfer

When transferring LOX between transport and storage tanks or between launch site storage tanks and flight vehicles, a substantial amount of LOX is lost by evaporation until all the conduits, valves, pumps, and receiving tanks are chilled to LOX temper-

ature [453]. These boil-off losses can be reduced if LOX is chilled to below the boiling point prior to the transfer operation. This requires additional energy and additional equipment and one will have to conduct a trade-off study from case to case to see if the potential LOX savings will justify the additional expense [454].

The transient behavior of a small-scale cryogenic transfer line was investigated during chilldown to cryogenic temperatures [455]. The vacuum-jacketed apparatus consisted of a vertical tube followed by a near-horizontal tube. The tube diameter was 1 cm and the overall length was 4.4 m. The apparatus was equipped with view ports in the near-horizontal section to allow visual observation of the flow patterns. Wall temperatures were measured at various locations along the length of the transfer line. Each test was conducted at a constant liquid volumetric flow rate at the transfer line inlet until saturation temperatures were obtained throughout the system. Liquid flow rate was varied by more than two orders of magnitude and resulted in chilldown times ranging from a few minutes to several hours. An optimum flow rate exists that minimizes liquid consumption during the chilldown process. At higher flow rates, there is insufficient time for heat transfer from the liquid to the wall and inefficiencies result from the greater amount of incompletely vaporized liquid passing through the system. At lower flow rates, chilldown time and total ambient heat leak into the system increase, which raises liquid consumption.

Evaporative losses during transfer can be calculated theoretically if the heat capacity and the mass of the receiving tank are known. For instance, if a 2300-L aluminum tank weighing 136 kg is to be filled with LOX, only 4% of the total mass of LOX is lost [456]. If LOX is prechilled to 80 K, one will not only avoid LOX losses during transfer, but a 2300-L tank in a launch vehicle which may have evaporation losses of up to 3%/h will not lose any oxygen for the next 80 min, while the vapor pressure in the tank comes up to atmospheric pressure. There are other reasons why one will want to prechill LOX prior to transferring it. Flow rate measurements in turbine flowmeters are inaccurate (excessively high) if the liquid is boiling and a two-phase mixture of liquids and bubbles keeps the turbine spinning. Even though the merits of cryogenic fluid metering are well known, the means of accurately doing this are not so well established. Flow measurement is useful in those applications that involve gases or liquids in processes which either produce or use cryogenic fluids. The measurement of cryogenic fluid flow is a difficult task. To a large part this is due to the very nature of the fluids being measured. Cryogenic fluids generally exist as saturated fluids. Pipe runs are generally short. Differential pressure measurement associated with head-type meters is often difficult. Because of the extremely low temperatures involved, thermal effects are significant. Pressure drop through a flowmeter must be kept low to avoid superheating the fluid. Cryogenic fluids provide little or no lubrication for meter bearings [457]. If the liquid is below its boiling point, more accurate flow rate measurements are possible. The effective density of boiling LOX is much lower than that of non-boiling LOX and this must be taken into consideration if filling a flight vehicle by volume instead of mass [458–460].

Instead of chilling LOX by recirculating it through an externally cooled heat exchanger, it can be cooled by bubbling very cold helium gas directly through the liquid [461].

Sub-cooling of cryogenic propellant by helium injection is one of the most effective methods for suppressing bulk boiling and keeping sub-cooled LOX during the countdown prior to rocket launch. Since the injected helium is pure, the difference in the partial pressure of the oxygen in the helium bubble and the vapor pressure of the LOX causes diffusional mass transfer of oxygen into the helium gas. This diffusion process (or boiling process) results in a cooling effect caused by the absorption of evaporation heat from the surrounding LOX. An analytical model for the helium injection system was developed that described the bubbling system using finite-rate heat transfer and instantaneous mass transfer concepts [462]. With this simplified approach, the effect of helium injection into LOX system under several circumstances could be studied. Experimental results along with simulations of single bubbles rising in LOX are reported with various helium injection flow rates, helium temperatures and injection methods. The injected helium does not have to be pre-cooled below the oxygen temperature. Some oxygen is lost with the helium that becomes saturated with oxygen. See also reference [463].

The full rate of transfer of LOX between tanks can be achieved only after the entire conduit has cooled to the temperature of LOX. If LOX was too rapidly splashed in conduit sections, it might cause sudden pressure spikes. The industry has developed sensors which indicate the proper cooling status of pipeline sections before throttling up to full flow rates [464].

Similar to the calculations for predicting the cooling time for a receiving vessel (discussed earlier), the cooling time required for a pipeline section can be calculated analytically [465]. The type of flow when the fluid emerging at the end of the pipeline is only a mist of droplets instead of a bubble-free liquid is called "*mist flow*". In some instances, not only one but even two or more rocket stages may have to be filled with LOX at the same time and cooldown time is critical for the mission [466].

Cooldown losses of LOX can be avoided altogether if the transfer line is jacketed with an outer shell filled with liquid nitrogen; however, such an elaborate plumbing set-up is rarely used. Instead of lining the entire length of the pipeline with LN_2 , it is sometimes more practical to pass the LOX through a heat exchanger immersed in a tank with LN_2 to cool LOX from 90 to 77 K prior to entering the long transfer line and thus reduce the boil-off during transfer.

An uninsulated 10.2-cm (4-in.) diameter pipeline may absorb $455 \text{ kcal h}^{-1} \text{ m}^{-1}$. After it is covered with a frost layer 4 mm thick, the heat conduction is reduced to $261 \text{ kcal h}^{-1} \text{ m}^{-1}$. A foam rubber lining reduces heat conduction to 17 to $143 \text{ kcal h}^{-1} \text{ m}^{-1}$, depending on the quality of the material and the thickness of the lining. A vacuum jacket or a powder-filled vacuum jacket would reduce the heat losses to 2.3 to $2.7 \text{ kcal h}^{-1} \text{ m}^{-1}$ [467].

A typical LOX tanking system, one which was developed for launching ATLAS ICBMs within the very short advance warning time, is described in [433], but is now only of historical interest. At the time when this system was designed, there were no LOX pumps available with the necessary capacity. The state of technology at that time was a pump with a capacity of 1900 L min^{-1} . The required rate of transfer was 19000 L min^{-1} and would have required the simultaneous use of 10 of these pumps. Thus, the designers chose pressurized transfer. The oxygen pressurant was stored at 160 atm gauge and reduced to 6.8 atm gauge (100 psig) before pressurizing the 106 m^3 capacity LOX tank. This tank was well insulated and had boil-off losses of only 0.25%/day. The feed pressure was 6.8 atm gauge (100 psig) and the pressure drop was less than 3.4 atm (50 psid). The flow rate of 19000 L was achieved only after all components had cooled to the temperature of LOX. The main duct was made from stainless steel, had a diameter of 30.4 cm (12 in.) and a wall thickness of 3.6 mm. It was not insulated with foam because during the short time of operation, the heat capacity of the insulating material would have caused higher evaporation losses than those caused by frost build-up and convection to the environment. The filter that was intended to retain ice crystals and other particulate matter was rated at $40 \mu\text{m}$.

In addition to the main duct, which was used to fill the LOX tank to only 90–95% of its capacity, a smaller line was used for topping off the tank and maintaining its LOX level during the countdown and extended high alert time. LOX used for topping off was precooled by passing it through a bath of LN_2 to allow more accurate metering (without bubbles) and maintain the filling level in the missile to within $\pm 0.5\%$ of the intended value.

Most of the stationary rocket engine development and performance tests use pressurized propellant feed systems for reasons of economy and expediency. Because of the need for obtaining accurate flow records, many pressurized cryogenic LOX systems are placed in LN_2 baths. If both the propellant tank and flow lines are covered by such a bath, more precise knowledge of the cryogenic fluid density is obtained and a two-phase flow through orifices or flow meters is eliminated. The density of LOX can vary by 1% for a temperature change of 1.3 K (2.3°F), and the uncertainty due to two-phase flow through an orifice cannot now be estimated [468].

In the meantime, LOX pump development has made significant progress and now pumps are available from cryogenic supply houses. Two of the pumps together can handle a flow rate of 22700 L/min [469].

Various components (valves, filters, flow meters) will cause pressure drop in the transfer line. Pressure drop during transfer of LOX and other cryogenic fluids can be calculated using the method described in reference [470].

9.4 Net Positive Suction Head in LOX Tanks

In a flight vehicle, the pressure in the LOX tank and the **Net Positive Suction Head** (NPSH) at the pump inlet must be maintained despite diminishing hydrostatic head throughout the flight of the stage in order to prevent cavitation. In many cases, it would require an excessive amount of compressed helium or compressed oxygen to maintain pressure in the increasing ullage space. In the SATURN-V S-IC booster stage some of the LOX was diverted through a heat exchanger/vaporizer and warm gas was used to pressurize the tank during flight [471, 472].

9.5 Transfer Lines and Piping

Transfer lines and piping are used either outside the flight vehicle on the ground or inside the flight vehicle. In the case of the Space Shuttle, transfer lines were used between different parts of the vehicle. If inside the flight vehicle, lightweight design is a requirement. For cryogenic service, the transfer lines may be insulated to reduce heat losses or if in use for only a short time, may be exposed to the atmosphere without external insulation. Design considerations for cryogenic transfer lines and stationary piping are different from the design for conveyance systems for room temperature liquids [473].

During cooldown, the worst problem happens if the top of a partially filled pipeline where the gas flows cools down at a different rate from the bottom of the pipeline where the liquid flows. Temperature differences cause the pipeline to bow and may tear it apart. In conventional piping systems, enough uniform thermal cool-down flexibility is obtainable by the use of expansion loops. Uniform thermal cool-down occurs when the pipe is full of liquid and the entire pipeline has cooled to liquid temperature. In the case of rocket fueling systems employing cryogenic transfer lines, space and weight limitations may preclude the use of expansion loops or bellows for achieving flexibility. In addition, this uninsulated thin-walled transfer piping is subject to temperature gradients of a scale not usually encountered in process piping systems and because of these temperature gradients the phenomenon of pipeline bowing occurs [474]. Bowing is the tendency of the centerline of the pipe to be deformed into an arc.

A numerical simulation for the steady flow and precooling and filling process of liquid hydrogen/LOX feed lines by using a method of CFD and numerical heat transmission included two aspects: **(1)** For compressibility of liquid hydrogen/LOX, the SIMPLE method has been used to calculate 2-D steady state transport, and a finite difference method has been adopted to simulate 1-D heat transmission of the high vacuum multi-layer adiabatic structure [475]. Flow field, temperature field and heat transmission have been calculated and analyzed in order to optimize existing propellant lines and reduce the loss of low temperature propellants. **(2)** Using a fluid dynamics

model of 1-D homogeneous equilibrium state and heat transfer model covering main heat transfer work conditions in a precooling process, considering compressibility of low temperature propellants, a pipe flow formula was calculated by a finite volume method and 1-D non-steady state heat conduction formula of the internal pipe wall. The precooling process of the test-bed system of a rocket engine was calculated, simulated and experimental results were analyzed, and the results provided support that the engine system could be improved.

9.6 Geysering in Vertical Lines

In a 1-g environment on the ground, if LOX remains standing in vertical sections of transfer lines, it will slowly warm up. Lower sections of the LOX volume will boil later due to the hydrostatic pressure of the liquid above it; however, once the stratification is disturbed and the layers with different temperatures become mixed, an effect called “geysering” causes sudden pressure rises and slugs of liquid to be ejected from the pipeline. This is like the periodic eruptions of hot springs in geothermally active areas. For a cryogenic fluid storage and transfer system, geysering must be avoided to prevent pressure surges and unpredictable flow rates, making accurate fluid metering impossible [476, 477]. In a flight vehicle tank, geysering can have catastrophic consequences. The LOX intake duct of the oxidizer pump might momentarily contain mixtures of liquid and gas which leads to cavitation in the suction area of the pump. The LOX tank of the SATURN-V S-IC stage used a steady flow of helium gas bubbled through and injected at the bottom of the tank to recirculate the LOX and prevent stratification and geysering [478].

Geysering can occur with all cryogenic fluids, but for rocket applications it is most frequently observed with LOX and LH_2 .

9.7 Zero-g Cryogenic Propellant Transfer for Retanking in Orbit

It is difficult enough to achieve refueling of satellites and space stations in orbit with storable, non-cryogenic propellants. This technology required more than 50 years of development before the first robotic demonstration propellant transfers in orbit were achieved. Transfer of cryogenic propellants in orbit has not yet been demonstrated but will be required for future space missions and orbital propellant depots [479, 480]. Cryogenic fluid transfer would allow the reuse of vehicles already in orbit, thus reducing launch lift mass, and extend the range of missions. Orbital tanking (fueling) stations, propellant depots, are still a thing of the future. While storable propellants can be transferred under zero-g conditions between diaphragm or bladder tanks, no such tanks exist for cryogenic propellants because most diaphragm or bladder materials are brittle at cryogenic temperatures.

There was also the plan to scavenge unused cryogenic propellants from Space Shuttle external tanks in orbit before those near-empty tanks were sent to a destructive re-entry. Such scavenging would depend on complete mastering the techniques of cryogenic propellant transfer under zero-g conditions; however, in practice, the tanks were usually jettisoned before the Space Transportation System (STS, Space Shuttle) orbiter reached orbital speeds.

10 Cleaning of LOX Equipment

Equipment intended to be filled with LOX must be carefully cleaned to prevent accidental ignition and particulate contamination. Similar cleaning specifications apply to both GOX and LOX equipment.

One section in an ASTM Manual describes cleaning requirements for LOX equipment [481]. The oxygen system cleaning specifications drawn from 23 industrial and government sources were compared along with cleaning processes employed for meeting these specifications and recommended post-cleaning inspection procedures for establishing the cleanliness achieved [482].

11 Hazards in Handling of LOX

Air Force Manual (AFMAN) 20-203V2, Chemical Rocket/Propellant Hazards (formerly designated as Air Force Manual (AFM) 161-30) contains a chapter on handling of LOX. NASA and ASTM have issued a series of LOX safety manuals [483–488].

11.1 Protective Clothing and Tools

Personnel handling propellants in the vicinity of LOX operations should wear protective suits, face mask or safety goggles, and gloves. Protective clothing for personnel handling propellants should protect against frostbite if LOX is accidentally spilled on the clothing. In addition, such clothing must be made of flameproof materials that will not burst into flames when accidentally ignited.

All components for LOX service must be thoroughly degreased. Even the skin grease from a fingerprint may be enough to initiate combustion or explosions. There are special lubricants (greases and oils) approved for LOX service (see section “Lubricants for Liquid Oxygen Systems”).

All tools for service in LOX installations should be spark-proof. Electrical service components (switches, circuit breakers) should be spark-proof. All tanks and transport containers should be grounded to prevent build-up of static electricity.

11.2 Firefighting

Fires that are sustained by LOX or evaporating oxygen are very difficult to extinguish. One must attempt to shut off the supply of oxygen as the first measure of defense. Only after the supply of oxygen has been shut off, can fires be brought under control using conventional methods of firefighting. The firefighting strategy depends on the proximity of the fire to adjacent fuel tanks at a launch site. If it involves only a building and no fuel tanks, one will allow the crew to get closer than if a fuel tank is exposed to the fire and must be cooled to prevent it getting involved in the disaster. If the temperature is high enough to involve structural metals (aluminum, iron), the combustion temperature will be extremely high and the fire becomes even more difficult to extinguish because molten aluminum and iron will react chemically with water, evolving hydrogen gas. The devastation caused by a fire in a tank farm is illustrated in Figure 42. This fire started from an unidentified cause in a pipe section between the storage tank and the tanker truck being filled with LOX and propagated rapidly through the entire facility, destroying several tank cars and trucks.



Figure 42: Destruction in a LOX transfer facility caused by a LOX-sustained fire (reproduced from [359] with permission from AIAA)

11.3 Liquid Oxygen Spills

If LOX and liquid fuels have leaked at the same time, forming a mixture of oxygen and frozen fuels, this mixture constitutes an extreme explosive hazard. It can be initiated by sparks, flame, impact or friction. In such a case all potential sources of ignition must be removed, and it is best to wait from a safe distance until all LOX has evaporated. If the leaked fuel is water soluble (ethanol, hydrazine, unsymmetrical dimethylhydrazine, UDMH), one can then dilute the puddle with enough water to bring the concentration below the flash point.

The evaporation rates of LOX spilled onto the ground surface were measured in laboratory tests [489]. To simulate the ground, concrete, dry sand, and wet sand layers were used in a vacuum-insulated transparent cylindrical glass vessel. Based on the temperature variations within the layer and detailed observation through the side of the vessel, the heat transfer modes controlling the evaporation phenomenon were revealed. When a wet sand layer was used, the LOX did not soak into the layer, because the frozen layer of water between the liquid and the sand layer acted as a barrier. When a concrete layer was used, the liquid vaporized above the layer. In these cases, the evaporation rates were inversely proportional to the square root of the time, except in the early stage just after the start of evaporation. This relationship could be predicted by a simple calculation of heat conduction within the layer. When a dry sand layer was used, LOX was observed to vaporize while constantly soaking into and rolling up the upper layer of the sand pit. In this case, the evaporation rate was determined simply by the velocity of liquid penetration downward through the sand layer.

11.4 Gelled Cryogenic Liquid Oxygen Mixtures

Gelled propellants have been tested typically only for storable propellants. It would be much more difficult to find suitable gelling agents for cryogenic propellants. One may want to gel LOX in order to suspend finely divided additive particles to enhance the performance or to make it hypergolic with other fuels; however, many of those mixtures with combustible gelling agents may be more useful as explosives instead of rocket propellants.

11.5 Explosive and Fire Hazards of Liquid Oxygen

In the wake of two gaseous oxygen supported fires, one on 27 January 1967 in the Apollo-1 capsule during ground rehearsals and one in an animal research facility, each with multiple fatalities, NASA expanded the fire safety testing for all materials, non-metallic and metallic, in oxygen-enriched atmospheres and developed standardized test methods to evaluate the acceptability of materials for future spacecraft. In addi-

tion, numerous accidents in hospitals where oxygen-breathing patients caught on fire have heightened the awareness of oxygen-sustained fire hazards.

Although most of these test methods were designed for testing materials in GOX, some can be adapted for tests in LOX and some have the capability to test both.

All oxygen systems on the ground should be designed and operated in accordance with ASTM Standards for Fire Hazards in Oxygen Systems [490] and ASTM Manual MNL36-2ND [481]. This heavily revised new edition provides a practical set of guidelines for safe oxygen system design, storage, handling, and usage. This manual begins with an overview of the basic oxygen safety guidelines, followed by a description of oxygen system ignition mechanisms and materials information related to flammability, ignition, and combustion. Next, the process for performing an oxygen compatibility assessment is described, followed by design principles, which are fundamental to the safe use of oxygen. Cleaning for oxygen service is the next topic, followed by various operational issues, such as storage facility design, transportation and transfer, equipment hazards, and emergency procedures. See also [484–487].

An *Acceptability Index* AI has been defined as

$$AI = (OI)^2 \frac{T}{C}$$

where AI is the acceptability index in arbitrary units, OI is the oxygen index, the lowest oxygen volume-% concentration in nitrogen which will sustain equilibrium (upward?) combustion of the material, T is the autoignition temperature in 100% O_2 and C is the heat of combustion at 20 atm in pure oxygen. The AI is a means for comparing different candidate materials [491].

The industry is well-advised to maintain a complete and up to date record of accidents with LOX to eliminate incompatible materials, share lessons learned, and develop safe handling practices [492].

11.6 Accidental Ignition in Oxygen

There are many types of stimuli that can lead to accidental ignition of materials in GOX or LOX. Cleanliness and elimination of contaminants is imperative with all oxygen systems. Accidental ignition in the Apollo space capsule in an oxygen atmosphere led to the death of three astronauts.

The ignition of non-metallic materials by electric arc and mechanical impact and by a resonant process involving repeated shock waves has been demonstrated and ignitions due to the rapid rupture of metal films and diaphragms were reviewed [493]. Burning rate studies of three non-metallic materials in oxygen-enriched environments were measured. Combustion under zero gravity was compared to combustion under 1-g gravity.

11.6.1 Metal Combustion in Oxygen

Starting in 1982, the ASTM Committee G-4 on Compatibility and Sensitivity of Materials in Oxygen-Enriched Atmospheres has organized a series of conferences and published a series of conference proceedings with constitute a rich source of information on combustion of metals and other materials in oxygen. References leading to a few of the conference proceedings are listed here: [494–499]. The ASTM Committee G-4 on Compatibility and Sensitivity of Materials in Oxygen-Enriched Atmospheres has issued a standard test method for compatibility of materials with LOX (impact sensitivity threshold and pass-fail techniques) [500] which has gone through several revisions during the past 30 years [501]. This method uses a modified Army Ballistic Missile Agency (ABMA) type impact tester. According to this test method, 20 separate samples of the material submerged in LOX are subjected to 98 J (72 ft · lb_f) impact energy delivered through a 12.7-mm (1/2-in.) diameter contact. More than one indication of sensitivity is cause for immediate rejection. A single explosion, flash, or other indication of sensitivity during the initial series of 20 tests requires that an additional 40 samples be tested without incident to ensure acceptability of the material. The threshold values are determined by this test method at ambient pressure. The sensitivity of materials to mechanical impact is known to increase with increasing pressure. Since most LOX systems operate at pressures above ambient conditions, some consideration should be given to increased sensitivity and reactivity of materials at higher pressure when selecting materials for use in pressurized system.

In many accidents a less compatible polymer was the source of ignition which then spread to adjacent metals. Excellent summaries on combustion of metals in oxygen-enriched atmospheres were published in [502–504]. “*Promoted ignition-combustion*” is a term which has been used to describe a situation where a substance with poor oxygen compatibility ignites and supports the combustion of a more combustion-resistant adjacent material [505]. This can happen in GOX or in LOX in contact with aluminum, carbon steel, stainless steels, or titanium alloys.

The conditions for ignition of compact specimens and foils made of iron, nickel, copper, and stainless steel in oxygen under pressures of 0.1–70 MPa were studied and modeled with the use of modified equations and dimensionless parameters of the heat theory of ignition of metal particles. Calculation results were compared with experimental data [506]. See also [507–509].

11.6.1.1 Aluminum Combustion in Oxygen

The use of aluminum alloys as a structural material for oxygen equipment has made it necessary to examine the conditions of combustion propagation in relation to the geometry of the part, the oxygen pressure, and the thermophysical parameters of the alloy [510]. It was experimentally established that the burning rates of aluminum wire 1 and 2 mm in diameter in pure oxygen increased with an increase in oxygen pressure in accordance with the equation $u \sim p^{0.5}$ in the pressure intervals $0.05 < p < 1.6$ MPa and $3.2 < p < 10.0$ MPa; however, in the intervals $1.6 < p < 3.2$ MPa and $p > 0.05$ MPa the

burning rates decreased as the pressure rose. In order to establish the dependence of the burning rate u on the oxygen pressure p and the specimen diameter d , cylindrical specimens of the aluminum alloys AMts (Mn 1.0–1.6%) and AMg-6 (Mg 5.8–6.8%, Mn 0.5–0.8%, Soviet standard GOST 4784-65) 300 mm long and 2–6 mm in diameter were tested in a constant-pressure bomb in the absence of an external oxygen flow. The initial temperature of the pure oxygen was 18 °C. The specimens were ignited at one end by an ignition coil. The time taken by the combustion zone to travel a length of 120 mm along the specimen was measured and recorded by means of a memory tube oscillograph.

Aluminum alloys are widely used in the construction of equipment found in rocket propulsion applications. The promoted-ignition combustion behavior of aluminum alloy 5183 was studied in oxygen-nitrogen gas mixtures over the pressure range of 0.1–20.8 MPa with oxygen purities ranging from 40 to 99.7% using 3-mm diameter rods (Figure 43) [502]. For comparison, utilizing the same test method and specimen size, the promoted ignition-combustion resistance of a commercially pure titanium alloy and Nb-55Ti titanium alloy was studied in oxygen-nitrogen mixtures with oxygen purities ranging from 30 to 80% oxygen at pressures up to 1.5 MPa.

The promoted ignition, flame spreading and combustion phenomena of aluminum tubing filled with LOX, surrounded by a shell of GOX, were systematically

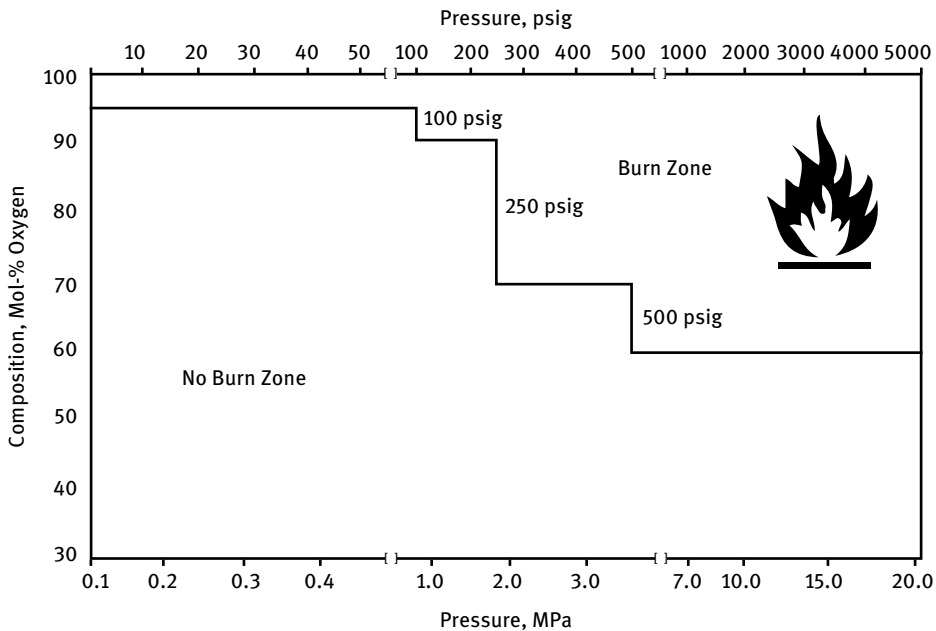


Figure 43: Flammability boundaries between burn and no burn zones for aluminum alloy 5183 (reprinted with permission from *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Seventh Volume*, © 1995 ASTM International)

observed and recorded with over 70 promoted combustion tests [511, 512]. The aluminum 3003 tube samples used were 30.48 cm long and 3.175 mm outer diameter. Two different wall thicknesses (0.254 and 0.356 mm) were used for comparison testing. Parameters studied included the tube and shell side pressures, LOX and GOX purities, tube sample wall thickness and the igniter location. Results from high-speed cinematography indicated that under certain operating conditions, a transition from a “normal” (much slower) burning mode to an extremely rapid and violent burning mode can occur. The “violent energy release,” or VER burning mode, is characterized by extremely high flame spreading rates (1–2 orders of magnitude faster than the flame propagation rate in a pure GOX environment), a high luminosity flame zone, and a very rapid rate of heat release. The rapid onset of transition to VER and the striking transformation between normal and VER burning modes can be seen on some of the high-speed photographs taken. It is believed that the onset of transition to VER is triggered by a high rate of convective mass flux of oxygen to the reaction zone, caused by the density change from liquid to gas phase of oxygen. The high tube-side oxygen flow velocity lowers the diffusion resistance of oxygen to the reaction zone and atomizes the molten aluminum near the reaction region, removing oxide accumulations and exposing fresh aluminum to direct chemical attack. This process then results in greatly enhanced homogeneous and heterogeneous reaction rates. The burning rate of 0.356 mm wall thickness Al-3003 tubing in gaseous oxygen at 27.57 MPa was 279 mm/s [513, 514]. Contaminants will facilitate ignition of aluminum in LOX [515]. The results of impact sensitivity tests depend on the type of striker pin used. See also reference: [516].

11.6.1.2 Steel Combustion in Oxygen

Steel will burn in GOX under certain conditions [517]. The experiments were carried out using cylindrical metal samples with a diameter of 3 mm made of SVO8A wire (a low-carbon steel with a carbon content of less than 0.1%) and SVO4Kh19N9 (Cr 19%, Ni 9%, C < 0.04%), as well as turned samples of 2Kh13 (Cr 13%, C 0.2–0.3%). The apparatus permitted setting up flow velocities up to 1.5 m/s. Ignition of the samples, oriented horizontally, was carried out from one end using an ignition coil. The direction of the oxygen flow was concurrent with the direction of propagation of the combustion. The initial temperature of the oxygen was equal to 291 K (18 °C). The experimental results are presented in Figure 44 for two different steels.

As is evident from Figure 44, the limiting pressure at which the combustion propagated over the sample, p_p decreased sharply even at small flow velocities U , and in the region $U = 0.08\text{--}0.2\text{ m/s}$ can be described by the relationship $p_p = 0.8U^{-1}$ (p_p in atm and U in m/s). At $U > 0.1\text{ m/s}$, there are substantial deviations from this dependence. With $U < 0.03\text{ m/s}$, i.e., at flow rates comparable to the rates of propagation of the combustion, the values of p_p practically do not change and at $U = 0$ are equal to 28 atm. At $U > 0.03\text{ m/s}$, the rates of propagation of the combustion rise. The rates of propagation of combustion along an SVO8A wire with $pU < 2.2$ obey the dependence

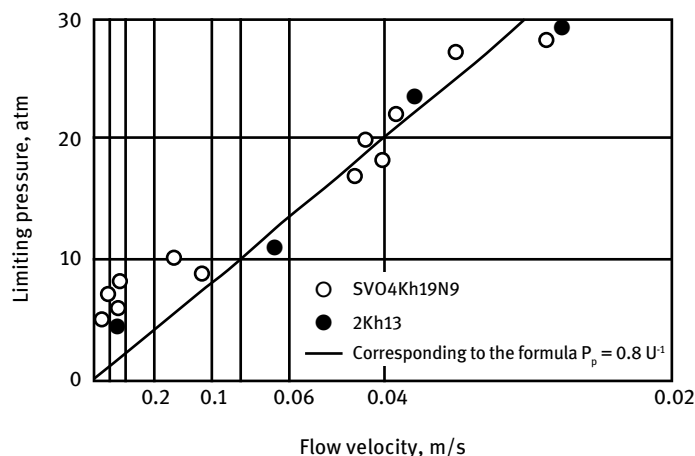


Figure 44: Combustible range of steel in gaseous oxygen (republished and modified from [517], with permission of © 1972 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

$U = 0.61 \times 10^{-2} (Up)^{0.5}$, while, at $pU > 2.2$, there are deviations from this dependence and with $U < 0.03$ m/s, U may take on values lower than in the absence of a flow.

It was shown that cylindrical iron and carbon steel specimens of diameters 1.5 and 3 mm ignited in oxygen at the moment the oxide film lost its protective properties, supposedly, as a result of melting of its main component (FeO) at 1644 K [518]. The ignition temperature did not depend on the oxygen pressure (in the range 0.2–20 MPa). The ignition was preceded by substantial (about 100 K) self-heating of a specimen owing to the heat released upon oxidation of the metal. A carbon-steel foil ignited in oxygen (0.14–0.6 MPa) according to the Semenov-Frank-Kamenetskii mechanism at an initial surface temperature not lower than 1233 K.

11.6.1.3 Titanium Combustion in Oxygen

Titanium alloys are preferred materials of construction in certain environments where severe corrosion is of concern and where lightweight tanks would improve the mass ratio of the rocket or satellite; however, there are known instances where they have proven to be incompatible with oxidizers, such as LOX, GOX, red fuming nitric acid (RFNA), and “red” dinitrogen tetroxide. Recent developments in titanium alloys have been oriented towards improvement of their ignition resistance in oxygen-enriched environments for specific applications.

Titanium can be quite reactive in oxygen environments. Besides being widely used in storable rocket propellant tanks, titanium is a preferred material of construction for numerous chemical process industry applications where corrosion resistance in hostile environments is required. Hazardous waste disposal via supercritical wet

oxidation and pressure oxidation processes used in gold mining are examples for the use of high-pressure titanium-clad reactors. It was reported that by alloying titanium with niobium, the pyrophoricity can be reduced to give a larger safety margin for autoclaves used in the chemical industry.

Titanium and its alloys are widely used in aerospace industry where the metal's low density, high-specific strength, and corrosion resistance properties are required. Titanium and its alloys are used in jet engines, airframes, and in oxidizing sulfuric acid environments present in sulfide pressure-leaching operations (pressure oxidation autoclave.). Titanium has been considered for use in oxygen-enriched environments, such as space suit applications; however, like most metals and alloys, titanium will burn in oxygen-enriched environments.

Early work conducted in 1960–1961 under a USAF contract demonstrated that titanium would be consumed by violent reactions when a freshly formed titanium surface was exposed to oxygen [286, 519]. The freshly formed surface was formed by pulling tensile specimens in the presence of oxygen. Reactivity was demonstrated in a temperature range from -190°F to room temperature. One pulled sample of pure titanium did not react at 515 kPa (60 psig) but did react at 620 kPa (75 psig) in the room temperature tests in 100% oxygen. This data demonstrated that this ignition test approach is much less severe than the promoted ignition combustion technique used in later investigations in which the sample was preheated by resistance heating and the sample tip temperature was raised to the melting point.

It was reported that titanium reacted not only in a 50% oxygen/50% carbon dioxide mixture at a temperature of 1033 K (1400°F), under 2.06 MPa (285 psig) pressure, but also in 100% carbon dioxide where a reaction occurred at 1700 K (2600°F) at 2.06 MPa (285 psig) [520]. Tubular test sections of stainless steel, cobalt, and nickel alloys, besides aluminum, copper, and titanium were resistance heated in controlled atmospheres of oxygen, carbon dioxide and an equal mixture of these gases. Motion picture coverage showed the manner in which the tubes heated and failed. Stainless steel and cobalt alloys ignited within the melting point range of each material. Nickel alloys did not ignite until the melting point was reached.

Testing commercially pure titanium at low pressures (0.14 MPa) and at 70% gaseous oxygen resulted in complete combustion of the test samples [502]. Testing at 60 and 50% O_2 identified the pressure thresholds at which combustion occurred as 0.17 and 0.27 MPa, respectively (Figure 45). At 40%, combustion did not occur at 0.79 MPa but did occur at 1.48 MPa. Finally, at 30% oxygen purity, the samples did not burn even at a pressure of 1.48 MPa. Figure 45 shows a summary of the promoted ignition-combustion data for titanium alloy Nb-55Ti. At oxygen purities in excess of 60%, this alloy is flammable at pressures down to the limit of the flow test apparatus although slightly less than the commercially pure titanium alloy. At the 60% purity level, it was not flammable at pressures up to 0.27 MPa. Reducing the oxygen purity down to 50% increased the non-flammable zone to 0.79 MPa. At 30 and 40% oxygen purity, the Nb-45Ti was non-flammable up to the maximum test pressure of 1.48 MPa.

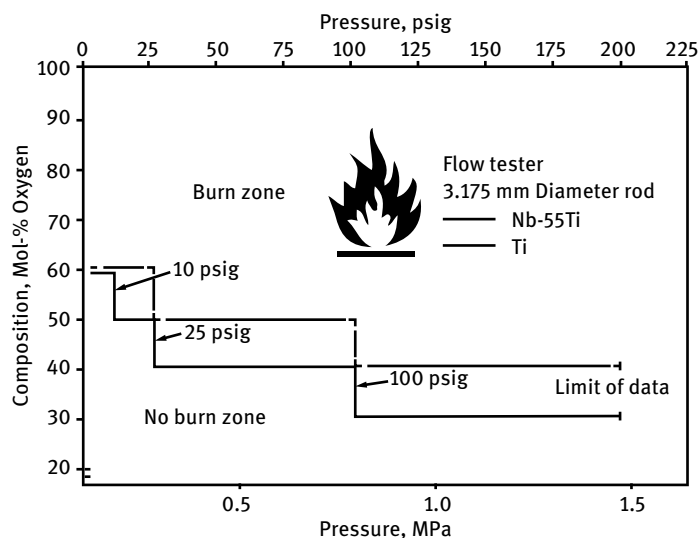


Figure 45: Flammability boundaries between burn and no burn zones for titanium and niobium/55 titanium alloy (reprinted, with permission from *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Seventh Volume*, © 1995 ASTM International)

The ignition propensity of titanium was determined by frictional ignition testing and the combustibility determined by promoted combustion testing [521]. Results indicated that the pressure $\times$ volume (PV) energy per unit surface area product required for ignition by friction was $0.0035 \times 10^3 \text{ W/m}^2$ ($0.01 \times 10^6 \text{ psi ft/min}$) and in 100% oxygen titanium is combustible at pressures as low as 13.8 kPa (2 psia).

The *Frictional Heating Test* apparatus consisted of a high-pressure test chamber, an electrical motor and transmission assembly, and a pneumatic actuation cylinder [522, 523]. The high-pressure test chamber, fabricated from Monel 400, consisted of a cylindrical chamber with a replaceable nickel sleeve. The chamber contained a rotating shaft that extended through the chamber by a series of bearings and seals. The shaft was connected at one end to a drive motor and transmission assembly that could rotate the shaft up to 30000 rpm. The other end of the shaft was connected to a pneumatically actuated cylinder capable of applying up to 4450 N (1000 lbf) normal load on the test specimens. The rotating test specimen was mounted on the shaft, and the stationary test specimen was affixed to the test chamber. Tests were conducted in GOX at 6.9 MPa (1000 psia) and 17000 rpm while increasing the load at a rate of 35 N/s (7.8 lb ft/s) until ignition occurred.

In addition to the frictional ignition test, the metals were also tested in a *Promoted Combustion Test*. The promoted combustion test system consisted of a cylindrical stainless steel chamber with an internal volume of approximately 740 cm^3 (45 cu. in.). The chamber could be pressurized to 68.9 MPa (10000 psia) and had a copper

liner and a copper base plate to protect it from the burning metal. The test specimen was ignited with an aluminum or magnesium wire wad. Titanium alloy Ti-6Al-4V, was easily ignited by friction. Ti-6Al-4V was tested at 2250, 4500, and 6750 rpm, while Al-6061 and Inconel MA 754 were tested at 17000 rpm. Ti-6Al-4V samples tested in GOX tended to friction weld at 2250 rpm.

Diaphragms of thin titanium and aluminum alloy stainless steel sheet have been pressurized with liquid or gaseous oxygen and gaseous nitrogen, and subjected to impact from a high velocity, small steel projectile [524]. Titanium alloys burned in the oxygen environment but did not burn in either the sea level air environment or pure nitrogen at pressures up to 414 kPa (60 psi). Although stainless steel and aluminum are relatively unreactive in the oxygen environment, these metals will burn sympathetically when placed in contact with burning titanium.

Once ignited, the combustion of solid titanium metal in oxygen may extinguish under a crust of titanium oxide. The combustion of bulk titanium in oxygen at sea level atmospheric pressure was studied using laser ignition, high-speed color cinematography, time and space resolved spectra in the visible region, metallography of specimens quenched in argon gas, XRD, and chemical product analyses [525]. The results indicated that an initial vapor phase reaction immediately adjacent to the molten surface starts rapidly, but as the oxygen uptake progressed, the evaporation rate slowed down. The accumulation of the various soluble oxides soon drove the reaction zone below the surface where gas formation caused boiling and ejection of particles. The build-up of a titanium oxide coating may cut off the oxygen supply and cause the reaction to cease.

The flammability of commercially pure (CP) titanium rods in oxygen-enriched atmospheres as a function of diameter and test gas pressure was determined [526]. Test samples of varying diameters were ignited at the bottom and burned upward in gaseous 70% O₂/balance N₂ and in 99.5+% O₂ atmospheres at various pressures. Test samples were 15.2-cm (6.0-in.) long rods having diameters of 0.8 mm (1/32 in.), 1.6 mm (1/16 in.), 3.2 mm (1/8 in.), 4.8 mm (3/16 in.), and 6.4 mm (1/4 in.). The burning rate of each ignited sample was determined by observing the apparent regression rate of the melting interface of the burning samples. The burning rate increased with decreasing test sample diameter and with increasing test gas pressure and oxygen concentration. The regression rate of the melting interface (burning rate, RRMI) was plotted as a function of test gas pressure and a least squares curve fit through the burning rate data yielded a logarithmic curve which describes the burning rate as follows:

$$\text{RRMI} = 1.1135 \ln(A)^{-2.8163}$$

where RRMI is the regression rate of the melting interface (burning rate) in in./s and A is the test sample cross-sectional area in in.².

11.6.1.4 Nickel Alloy Combustion in Oxygen

It was found that compact samples of nickel and its alloys heated in “cold” (323 K) and “hot” (≤ 1573 K) oxygen ignited only at temperatures exceeding the melting point of the materials [527]. The ignition temperature was independent of the oxygen pressure up to 70 MPa. It was suggested that the drop in the ignition temperature of alloys with rising oxygen pressure reported in other papers is related to systematic errors in measuring the surface temperature of the samples.

11.6.2 Refractory Alloys in Oxidizing Environments

Turbine blades driven by lean-operating gas generators and pump impellers are exposed to extreme conditions that may lead to ignition of the metals. Turbine blades and pump impellers are typically made from oxidation-resistant superalloys. Nevertheless, several of these metals were tested [528]. In the particle impact tests, nickel 200, Monel 400, and silicon carbide were the most resistant to ignition; Monel K-500 and zirconium copper were slightly less resistant to ignition; and Hastelloy X, Invar 36, and stainless steel 316 were the least resistant to ignition. In frictional heating tests of pairs of like materials, the ranking was generally upheld, with the materials ranked in order of decreasing resistance to ignition as follows: nickel 200, Inconel 600, Monel 400, Monel K-500, Hastelloy X, Invar 36, and stainless steel 316.

11.7 Drop Weight Impact and Shock Sensitivity of Liquid Oxygen/Contaminant Mixtures

In accordance with ASTM test procedure D2512-95 [529], a sample of the test material is placed in a specimen cup, precooled and covered with liquid oxygen and placed in the cup holder located in the anvil region assembly of the impact tester. A precooled striker pin is then centered in the cup. The plummet is dropped from selected heights onto the pin, which transmits the energy to the test specimen. Observation for any reaction is made and the liquid oxygen impact sensitivity of the test material is noted. Drop tests are continued using a fresh specimen cup and striker pin for each drop, until the threshold value is achieved. A series of drop tests are conducted at an energy level of 98 J (72 ft-lb_f) or as specified for the pass-fail tests and a 50% point calculated by the Bruceton up-and-down method. This test apparatus is similar to the BAM apparatus illustrated in Figure 35.

Mixtures of LOX and organic compounds can have friction and impact sensitivity properties similar to those of the much-feared nitroglycerin [253].

The impact sensitivity of organic compounds in LOX was tested with a modified ABMA drop-weight tester [530]. For 18 of the 24 compounds tested, there was a correlation between the flash point in air and the impact sensitivity in mixtures with LOX. See also reference [531].

A study was conducted to evaluate the repeatability of the LOX mechanical impact test used by NASA to screen materials for oxygen service (NHB 8060.1B Test 12 Part 1, which is based on the ASTM method) [276, 532]. Four materials were tested: Teflon, Vespel SP-21, Viton A, and Nylon 6/6. Each test material was subjected to several series of tests that were conducted at different impact energy levels. The results showed that the variability from series to series in the reaction threshold energy level was within the precision statement of the ASTM method; however, this precision was considerably broader than the reaction threshold implied by the NHB 8060.1B test criteria.

The impact ignition mechanism in LOX is a real combustion ignition mechanism that needs to be understood in the design of oxygen systems. The use of test data from this test method has been questioned due to the lack of a clear method of application of the data and variability found between tests, material batches, and facilities [533]. A large database has accumulated over several years, but data are not always consistent. Testing was performed to determine the statistical nature of the test procedure to help establish sample size guidelines for material characterization. The common method of determining a pass/fail criterion based on either light emission or sound report or material charring was questioned.

In addition to impact testing of mixtures with LOX [534], similar test methods have been applied to impact or adiabatic compression testing of materials in gaseous oxygen. NASA JSC and Southwest Research Institute have developed a GOX drop weight impact sensitivity test method [535–538].

Adiabatic compression testing of components in GOX is a test method that is utilized worldwide and is commonly required to qualify a component for ignition tolerance under its intended service [539]. This testing is required by many industrial standards organizations and government agencies. Ignition may occur during rapid pressure surges.

There may be a correlation between dynamic pneumatic adiabatic compression ignition pressure ratios per ASTM G 74 and the autoignition temperature of polymeric materials in a static test [540]. The data obtained on five polymers resulted in a strong correlation between the 50% reactivity level and the AIT of polymers, indicating similar ignition mechanisms.

11.8 Bullet Impact Sensitivity of Liquid Oxygen

A .50 caliber incendiary bullet was fired into a titanium LOX tank [289, 541]. A huge flash was observed, and a violent reaction occurred, resulting in fragmentation of the vessel. Fusion and burning were noted on the fracture surfaces of some of the pieces. Similar tanks of type 304L stainless steel apparently failed to react and did not shatter unless they were faulty or had defects at the grain boundaries.

The nature of the problem incurred by meteoroid impacts in space flight is ill-defined. Although much work has been reported in this field, there still exists a very high degree of uncertainty of predictions of meteoroid impacts and their effects on space vehicles. The results of the previous puncture tests strongly indicated that penetration of titanium tanks containing LOX by a single meteoroid encountered in space flight could result in a catastrophe. Consequently, it was decided to investigate the behavior of titanium diaphragms, pressurized with LOX, upon simulated meteoroid punctures. In one test series, 0.1–0.2-g steel projectiles were fired through air at velocities from 2.77 to 4.85 km/s (9100–15900 ft/s) into titanium, aluminum, and stainless-steel diaphragms, internally pressurized with LOX. Diaphragms of thin titanium and aluminum alloy stainless steel sheet have been pressurized with LOX or GOX and gaseous nitrogen, and subjected to impact from a high velocity small steel projectile [287, 542]. Titanium alloys burned in the oxygen environment but did not burn in either the sea level air environment or pure nitrogen at pressures up to 414 kPa (60 psi). Although stainless steel and aluminum are relatively unreactive in the oxygen environment, these metals will burn sympathetically when placed in contact with burning titanium. In this study, two diaphragms were tested simultaneously by use as front and back closures for a cylinder aligned with the path of the projectile. Using titanium discs, the back diaphragm ignited and burnt violently 15 times in 16 tests. Test conditions included both the Ti-5Al-2.5Sn alloy and the Ti-6Al-4V alloy, in thicknesses of 0.63, 0.4, and 0.35 mm (0.025, 0.016, and 0.014 in.), GOX at room temperature or LOX, and pressures of 138 and 414 kPa (gauge) (20 and 60 psig). The front diaphragm reacted less often, but still reacted in over one half of the tests. Control tests using 414 kPa (gauge = 60 psig) GN_2 or zero psig air with titanium diaphragms produced no reactions. Eight trials with 0.4-mm (0.016-in.) thick 2024-T3 aluminum discs and seven trials with 0.25-mm (0.010-in.) thick 301-XFH stainless steel also failed to react; however, slight oxidation was noted around some of the penetrations in aluminum. It was also investigated whether sandwiching of the titanium between aluminum or stainless steel plates would diminish the reactivity, but the titanium reaction ignited the aluminum or stainless steel, which also burnt violently. Results from these sandwich tests show that cladding titanium with aluminum or stainless steel will not prevent Ti/LOX reactions.

11.8.1 Cap Sensitivity of Liquid Oxygen/Contaminant Mixtures

In one test, 37 L ethanol and 37 L LOX were mixed and initiated by a detonator. The resulting explosion was equivalent to that of 25–50 kg TNT [543].

The explosive limits and energy output of LOX/liquid methane system were determined at 90 K for mixtures containing 6–80 mol-% or 3–67 mass-% liquid methane [143]. The methane used for these experiments had a composition of 96.77% methane and 3.37% ethane. The charge was confined in an iron can (5 cm = 2 in. in outside diameter, 5.7–9.5 cm high, 0.25 mm = 0.01-in. wall thickness) filled with 100 g of the mixture

and initiated by means of Primacord and a No. 6 electric blasting cap. When the charge was detonated on the 4.8 mm (3/16 in.) thick steel plate, a hole may be punctured into the steel plate, or the steel plate may be ruptured, bent downward, or only dented, depending on the brisance of the explosive. The lower limit of the LOX/liquid methane mixtures was between 3 and 6 mass-% (6 and 11 mol-%) methane while the upper limit was between 30 and 67 mass-% (67 and 80 mol-%) methane. These explosive limits differ from the flammability limits of the gaseous mixtures. The measured and theoretically calculated detonation velocity of LOX/LCH₄ and GOX/GCH₄ mixtures is illustrated in Figure 46. The maximum detonation velocity occurs with stoichiometric mixtures.

Liquid oxygen/liquid methane mixtures have been proposed as cryogenic mono-propellants, but their handling safety remains in doubt [544].

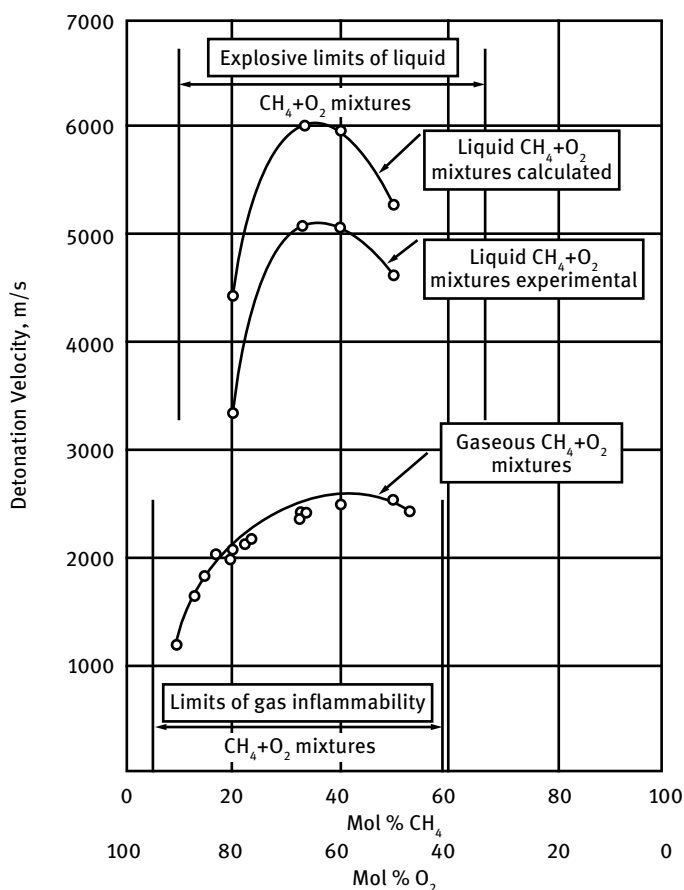


Figure 46: Experimental and theoretical detonation velocities of LOX/LCH₄ and GOX/GCH₄ mixtures (reprinted and modified from [143], with permission from © 1959 American Chemical Society; permission conveyed through RightsLink)

11.8.2 Bullet Impact Sensitivity of Liquid Oxygen/Contaminant Mixtures

The sensitivity of a LOX/liquid methane mixture which had the fastest rate of detonation (33 mol-% methane and 67 mol-% oxygen) to bullet impact was tested by firing a 22-caliber, short copper bullet through a can (2 in. diameter and 4 in. high) containing the explosive liquid mixture, the nozzle of the gun being 40 feet from the mixtures [143]. In testing the sensitivity to sparks, a 1500V discharge from a 0.1 μ Farad condenser was passed through the liquid mixture, using 1–3 mm gaps. The energy discharged was 113 millijoules. Explosions were initiated in all these tests.

The sensitivity of solid oxygen + liquid hydrogen + diluent and liquid oxygen + solid hydrocarbon + diluent mixtures was investigated employing a projectile impact to determine the shock required to detonate these mixtures [545]. With no diluent, each explosive system could be initiated by a shock stimulus of 1.0–2.5 kbar. The explosive yields were such that a mass unit of cryogenic mixture was equivalent to 0.6–2.0 mass units of TNT. Large volumes of detonable, gaseous hydrogen-oxygen mixtures would result from a massive spill of LH₂-LOX. Inhibition of detonation initiation by dry powder particle additives was investigated. The powder additives produced insignificant inhibition in comparison to that produced by gaseous diluents.

11.9 Explosive Yield of Liquid Oxygen/Fuel Mixture Explosions

In case of launch pad accidents, LOX and fuels may have an opportunity to pre-mix before they are ignited by an external source of ignition. The worst-case explosive yield of such explosions has been predicted by model experiments and by calculations [546–552].

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Oxygen Fluorides

Oxygen fluorides are very useful rocket propellant ingredients, both as the main oxidizer and also in small quantities to add hypergolicity to otherwise non-reactive or insufficiently reactive oxidizers. The advantage of oxygen fluorides over nitrogen fluorides is that both the fluorine and the central atom contribute to the oxidation reaction in the combustion chamber of a rocket. There are at least four known oxygen fluorides with varying fluorine contents (Table 1).

Table 1: Fluorine content of oxygen fluorides.

Compound Name	Formula	Fluorine content, mass-% F	CAS RN
Oxygen difluoride (oxygen fluoride)	F—O—F	70.36	7783-41-7
Dioxygen difluoride	F—O—O—F	54.29	7783-44-0
Trioxygen difluoride (ozone fluoride)	F—O—O—O—F	44.19	16829-28-0
Tetraoxygen difluoride	O ₄ F ₂	37.26	

The oxygen fluorides containing more than one oxygen are less stable than the lowest member of the group, oxygen difluoride. They are hypergolic with most fuels, but oxygen difluoride is hypergolic only with a few fuels. Oxygen fluorides have found the attention of rocketeers for quite some time, but no real applications have materialized in all those years [1]. At the moment, the reason for summarizing the physical and chemical properties of oxygen fluorides in this book is mostly for historical interest [2]. No stone shall be left unturned when looking for better and more energetic rocket propellants. Before starting new efforts for the development of new rocket propellants, the information gathered during past decades needs to be summarized in a systematic manner and made available to future researchers. This is the reason why fluorine and non-metallic fluorides are discussed in some detail in this book, in spite of continuing environmental and safety concerns about their use. Some of the fluorine compounds find applications in chemical lasers. Oxygen as the central atom in non-metallic fluorides has the advantage over nitrogen that it is an oxidizer in its own right and it contributes to the combustion energy released in the rocket chamber, whereas nitrogen would only be carried along as ballast. Compared to halogens, such as chlorine or bromine, oxygen as the central atom in non-metallic fluorides for rocket propellants has the advantage of a lower atomic mass, resulting in a higher exhaust velocity. Compared to elemental fluorine, oxygen difluoride, nitrogen trifluoride and tetrafluorohydrazine are relatively easy to handle because they have higher boiling points. Oxygen difluoride (OF₂) has been categorized as a “space storable” propellant.

It was discovered that hydrocarbons as fuels in rocket engines will give higher specific impulse with physical mixtures of oxygen and fluorine (FLOX) than with either oxidizer by itself. The mixture ratio of fluorine and oxygen in such physical mixtures can change with age and progressive evaporation. It would be desirable to synthesize chemical compounds in which the fluorine: oxygen atomic ratio is fixed. One such compound is oxygen difluoride (OF_2), a chemical compound that is thermally stable and maintains its fluorine: oxygen ratio indefinitely. Of all the known oxygen fluorides (OF_2 , O_2F_2 , O_3F_2 , and O_4F_2), oxygen difluoride is so far the only one that has actually been test-fired as the main oxidizer in a rocket engine. As a sideline, it should be mentioned that there is an interest in trioxygen difluoride in admixture with liquid oxygen which renders liquid oxygen (LOX) hypergolic with many common rocket fuels. This potential application will be described in a forthcoming section in this chapter.

There are several publications which deal with oxygen fluorides as a group and discuss the similarities and difference in their molecular structures and physical and chemical properties. Some of these publications are summarized in the next section.

1 Literature on Oxygen Fluorides

Soon after the discovery of the first (and most stable) oxygen fluoride, OF_2 , there was speculation that other fluorides of oxygen might form under different conditions (i.e., in absence of water) [3]. Two very good summaries of the literature on oxygen fluorides were compiled in 1963, reference [4] with 109 literature citations, and reference [5]. These two publications were good references for the first edition of a book on rocket propellants in 1968, but of course 10 times more publications have appeared in the interim that all would need to be included here if we had the space. An excellent review of oxygen fluorides and dioxygenyl salts contains 124 references [6]. Another summary on the fluorides of oxygen was published in France [7] but has not yet been translated.

Much of the original research work on oxygen fluorides other than OF_2 was done at Temple University [8].

The effort at Jet Propulsion Laboratory (JPL) in Pasadena, CA, in the 1960s to develop high-energy space-storable bipropellant combinations for challenging deep space missions with high total impulse requirements, such as those to outer planets or comets, has resulted in a series of summary publications in support of the simultaneously on-going experimental effort to bring this oxidizer closer to full-scale use [9, 10], but this oxidizer never reached flight status and only limited ground testing in rocket engines was done.

A good summary on oxygen fluorides is the “Fluorine and Oxygen” chapter in *Gmelin Handbook of Inorganic Chemistry* [11]. This chapter focuses on oxygen fluorides O_nF_2 , $n = 1-6$, oxygen fluoride radicals O_xF , $x = 1-4$, and hypofluorous acid, HOF .

It is known that all halogens, mostly chlorine and bromine, contribute to the seasonal demise of the ozone layer in the upper atmosphere of Earth. The main man-made vehicles bringing halogens to the upper atmosphere were the fluorocarbons used as

refrigerants and aerosol propellants. To a limited extent, fluorine and oxygen fluorides are also involved in ozone reactions and the formation and destruction of O—F bonds is a key step in those reactions. This is why there are many publications on the formation of $\cdot\text{OF}$ free radicals which support atmospheric chemistry but have very little to do with rocket propellants. The thermochemical properties of all oxygen fluorides and their associated free radicals that were listed in the Joint Army Navy Air Force (JANAF) thermochemical tables going all the way up to O_8F_2 have been updated by the National Institute of Standards and Technology (NIST) [12]. That publication contains an annotated bibliography (over 600 references) for all neutral oxygen fluorides which have been reported in the literature. There is a need for additional experimental and theoretical data. See also reference [13].

2 Oxygen Difluoride

At room temperature, oxygen difluoride, also known as oxygen bifluoride, OF_2 , oxygen fluoride, monooxygen difluoride, difluorine monoxide, CAS RN [7783-41-7] is a colorless gas, that condenses at $127\text{ K} = -145.3^\circ\text{C}$ forming a yellow liquid. It is very toxic and has a pungent, unpleasant odor. The name “fluorine monoxide” has occasionally been used to describe this compound as F_2O but is chemically incorrect. That name was patterned after the name for “chlorine monoxide” for Cl_2O which is more often used in this form.

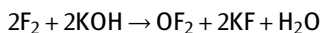
As an oxidizer for rocket propellants, OF_2 has the advantage (compared to NF_3) that both the fluorine and the central atom, oxygen, act as oxidizers, as opposed to NF_3 where the central atom nitrogen is carried along as useless ballast.

2.1 Literature Summaries on Oxygen Difluoride

The most complete accumulation of OF_2 data is in the *OF₂ Handbook* released (with only limited distribution) in 1970 [14]. See also [15, 16].

2.2 Preparation of Oxygen Difluoride

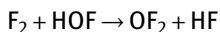
Oxygen difluoride forms when fluorine gas is passed through a dilute caustic solution containing 2% KOH



The concentration of the caustic solution must be maintained constant because if the concentration is too low, the reaction proceeds too slowly. If the caustic concentration is too high, the reaction product oxygen difluoride will hydrolyze [17]. The process can be carried out as a process with continuous replacement of the caustic solution through which the F_2 is bubbled [18–20]. Adding an excess of alkali metal fluorides

to just a little water can improve the OF_2 yield from 50 to 80% [21]. In particular, CsF addition allowed optimized OF_2 production with 86% yield. NaF was less effective.

In the course of studies of the preparation of hypofluorous acid, HOF , it was observed that substantial amounts of OF_2 were always formed as a byproduct of the synthesis of HOF . It was theorized that HOF was probably involved as an intermediate in the production of OF_2 involving the reaction [22]:



Besides by reaction of fluorine with water in alkaline solutions, OF_2 can also be obtained by electrolysis of wet hydrofluoric acid. It was known for a long time that oxygen difluoride was formed as an unwanted byproduct during the fluorine production by electrolysis of KHF_2 melts when the electrolyte was not painstakingly dry. It took a while before this method was improved in a way that OF_2 became the main product and not just a byproduct. In an effort to optimize water content and current density, initial experiments were carried out in H_2F_2 that contained 1% KF as the conductivity enhancer [23–25]. Electrolysis was carried out with nickel anodes at 7.0–7.6 V in a static cell at 0–3 °C. A method was developed to monitor the water concentration in the electrolyte on-line. OF_2 , F_2 , O_2 , and O_3 were formed at the anode and were analyzed by gas chromatography (GC). The gases were passed through a cold trap at dry ice temperature and an absorption tower with dry NaF to absorb the HF vapors. When plotting the product yield and product distribution as a function of water content, it could be seen that the OF_2 yield dropped very rapidly once the water content exceeded 0.5 mol % and leveled off at a current yield of 10% for water concentrations of 5–35 mol %. The coulombic yield of OF_2 can reach 45% and is at an optimum in H_2F_2 electrolytes containing 0.5–5 mol % H_2O . The maximum current densities could be maintained at 0.5–1 mol % H_2O . Removal of ozone by adsorption on silica gel is dangerous because OF_2 and SiO_2 can react explosively.

For electrolytic generation of OF_2 from wet HF , the ohmic overvoltage at the nickel anode was determined by both potential decay and superimposed square waves [26].

Ozone is an undesirable contaminant in the production of OF_2 . The ozone content in the electrolysis products of wet HF can be determined by GC [27]. The gases are separated on a silica gel column that is temperature-programmed from 198 to 263 K (–75 to –10 °C) to minimize decomposition.

Other investigators used 10 mass-% NaF as auxiliary electrolyte and examined water contents from 1–25 mass-% and reported yields of up to 60% [28]. Electrical conductivity in the $\text{H}_2\text{F}_2/\text{H}_2\text{O}$ system goes through a maximum at 74% H_2F_2 .

Oxygen difluoride can be produced electrochemically by introducing an oxygen-containing gas into the pores of a porous anode in an electrolysis cell containing anhydrous liquid hydrogen fluoride as the electrolyte [29].

Oxygen difluoride (OF_2) in addition to O_2 and O_3 was formed by electrolysis of H_2F_2 in the range of 0.5% < H_2O < 20% beginning at a voltage of 4 V [30]. The OF_2 yield decreased with increasing water concentration and voltage. The maximum of the OF_2

formation appeared at 2% H_2O in the range between 5 and 9 V with a concentration of ~45% by volume of OF_2 in the anodic gas. Below 2% water the formation of elementary fluorine as byproduct can be observed. The formation of OF_2 depended on the formation of a black layer on the surface of the nickel anode, which was formed during an induction period. K_2NiF_6 was shown to be one constituent of this black layer.

Oxygen difluoride has been observed as a byproduct in the production of perchloryl fluoride ClO_4F by reaction of elemental fluorine with 60% perchloric acid in a trickle column packed with glass chips [31]. It appears that the fluorine reacted with H_2O before it began to react with HClO_4 , concentrating the HClO_4 in the process.

Oxygen difluoride may be an unwanted byproduct of the fluorine production if the $\text{KF} \cdot 2\text{HF}$ electrolyte is not carefully dried to start with. The fluorine thus produced contains oxygen difluoride as a contaminant which needs to be separated to prevent clogging of liquid fluorine feed systems in rocket engines.

The economics of OF_2 production based on four processes described in the literature were reinvestigated [32]. These four processes were: **(1)** fluorine-caustic **(2)** fluorine-water catalyzed by alkali fluorides, **(3)** electrolysis of water in hydrogen fluoride, and **(4)** electrolysis of oxygen in hydrogen fluoride using a porous anode. Oxygen difluoride was produced at Air Products & Chemicals Inc. Allentown, PA, USA, without purification in 65–70% yield by the caustic-fluorine process at fluorine feed rates of 0.1 and 0.2 lb/h over a wide range of operating variables. Oxygen difluoride selling prices calculated for the caustic-fluorine method, the fluorine-water method, and the direct electrolytic method were estimated from \$55/lb at 4000 lb/year down to \$8/lb at approximately 60000 lb/year (as of 1970). From previous work it appeared that the fluorine-caustic process was the easiest to develop. Unless the process can operate continuously, the on-stream efficiency may be low because of operating problems in the fluorine section of the plant. Further scale-up was planned to gain more information on corrosion and heat effects on yield and on-stream efficiency with a 2 lb/h fluorine reactor. The economic comparison of the fluorine-caustic, fluorine-water, and direct electrolysis methods showed that the processes were rate and investment rather than process-dependent, and that the final price hinged on how the equipment was depreciated. It was concluded that at that time (1970) the fluorine-caustic offered the least expensive method for making OF_2 at rates at or below 10000 lb/year.

After OF_2 was no longer commercially available, for a short time NASA/JPL operated a pilot plant for production of OF_2 by reaction of fluorine with potassium hydroxide in water at 283 K (10 °C) [33]. Excess OF_2 and F_2 was dissipated by combustion of charcoal in a burn barrel. Byproduct potassium fluoride was reacted with calcium hydroxide to form insoluble, non-toxic calcium fluoride and to regenerate potassium hydroxide. The pilot plant was located at the JPL Edwards Air Force Base facility [34]. They achieved a yield of 78% of a high purity OF_2 product.

As of 2014, research quantities of OF_2 were available from at least one supplier, BOC Sciences, but it is no longer listed as of 2021 [35].

2.3 Physical Properties of Oxygen Difluoride

A good starting point for a summary of physical properties of oxygen difluoride was the product information bulletin once provided by Allied Chemical to its customers and prospective customers, but it is no longer available [36]. For additional information see also [4, 9, 10].

2.3.1 Boiling and Freezing Point of Oxygen Difluoride

Physical properties of oxygen difluoride are summarized in Table 2.

Table 2: Physical properties of oxygen difluoride.

Property	SI units	MKS units	Source	Year	References
Molecular mass	53.9962 g/mol	18.5198 mol/kg	NIST	1959	[37]
Freezing/melting point	49.35 K	−223.8 °C	Chemistry		
Freezing/melting point	49.4 K	−223.7 °C	WebBook		
Boiling point	127.85 K	−145.3 °C	Schnizlein et al.	1952	[38]
Boiling point	127.9 K	−145.2 °C	NIST Chem WebBook	1959	[37]

2.3.2 Density of Oxygen Difluoride

Data for the density of liquid oxygen difluoride are listed in Table 3. The density of liquid oxygen difluoride at 83 K = −190 °C is 1.65 g/cm³.

2.3.3 Vapor Pressure of Oxygen Difluoride

Vapor pressure data from two different sources are compared in Figure 1. The vapor pressure data in Table 4 have been curve-fitted and can be expressed by the equation:

$$\log p_v = 7.2242 - 555.42/T$$

where p_v is the vapor pressure in mmHg and T in the temperature in kelvin. A different Antoine equation applicable for the temperature range 77.0–128.5 K can be downloaded from the NIST Chem WebBook:

$$\log (P)_{10} = 5.26568 - (758.401/(T + 15.742))$$

where P is the vapor pressure in bar and T is the temperature in kelvin. The vapor pressure equation from NIST Chem WebBook (solid black line in Figure 1) gives notably lower vapor pressures than the equation from Schnizlein et al. (dashed line). Vapor pressure data for oxygen difluoride are summarized in Table 4.

Table 3: Density of liquid oxygen difluoride.

Temperature		Density
K	°C	g/cm ³
127.9	−145.3	(1.521 extrapolated)
127.4	−145.8	1.523
126.0	−147.2	1.529
125.8	−147.4	1.530
125.7	−147.5	1.531
125.3	−147.9	1.533
124.5	−148.7	1.537
124.4	−148.8	1.537
122.6	−150.6	1.546
122.4	−150.8	1.547
122.2	−151.0	1.548
122.1	−151.1	1.549
121.9	−151.3	1.550
121.7	−151.5	1.551
121.2	−152	1.533
120.4	−152.8	1.557

Data source: [39]

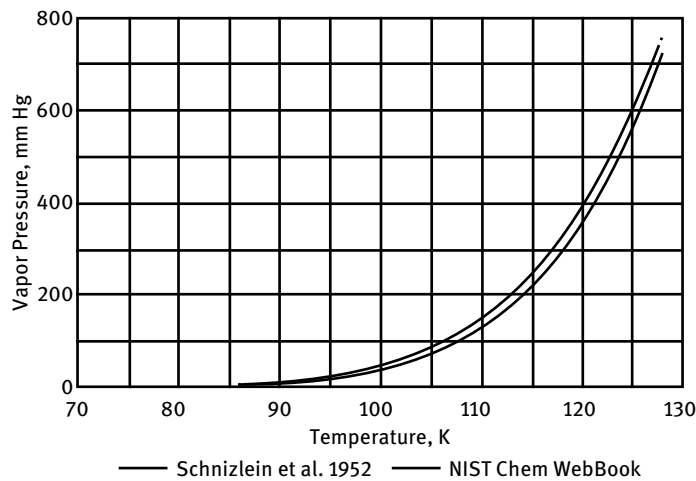


Figure 1: Vapor pressure of oxygen difluoride. Comparison of data from two sources.

Table 4: Vapor pressure of oxygen difluoride.

Temperature		Vapor pressure, mm Hg		kPa
K	°C	Measured	Calculated from curve-fitted data ^a	Measured
77.8	−195.4	1.4	1.2	0.19
81.1	−192.1	2.9	2.4	0.39
83.1	−190.1	4.7	3.5	0.63
87.5	−185.7	7.6	7.5	1.01
89.2	−184	11.6	9.9	1.55
91.5	−181.7	14.3	14.3	1.9
91.9	−181.3	15.4	15.2	2.1
92.3	−180.9	16.3	16.1	2.2
93.3	−179.9	18.3	18.7	2.4
94.1	−179.1	20.6	21.0	2.7
95.1	−178.1	24.1	24.2	3.2
100.5	−172.7	47.3	49.8	6.3
103.6	−169.6	72.6	72.9	9.7
103.7	−169.5	73.9	73.8	9.9
110	−163.2	141	149.6	18.8
115.9	−157.3	273	270.4	36.4
116.2	−157	279.1	278.2	37.2
121.2	−152	423.6	438.1	56.5
121.8	−151.4	471.9	461.4	62.9
122	−151.2	471.3	469.4	62.8
124.8	−148.4	577	593.9	76.9
125.3	−147.9	618.8	618.7	82.5
127.2	−146	735	720.6	98
127.9	−145.3	740	761.4	98.7

Data source: [38]

^a Calculated from the curve-fitted equation $\log p_v = 7.2242 - 555.42/T$; p in mmHg; T in K

Vapor pressure data from a Thiokol RMD report [40] illustrated in Figure 2 cover a wider range than the Schnizlein data.

2.3.4 Viscosity of Liquid Oxygen Difluoride

Viscosity data for saturated liquid OF₂ are available only over a narrow temperature range from 120 to 127 K, just below the normal boiling point. The dynamic (=absolute) viscosity in this range can be expressed by the equation

$$\log \eta = 131.5/T - 1.5768$$

where η is the viscosity in cPs and T is the temperature in kelvin. The viscosity derived from this equation is listed in the last column of Table 5.

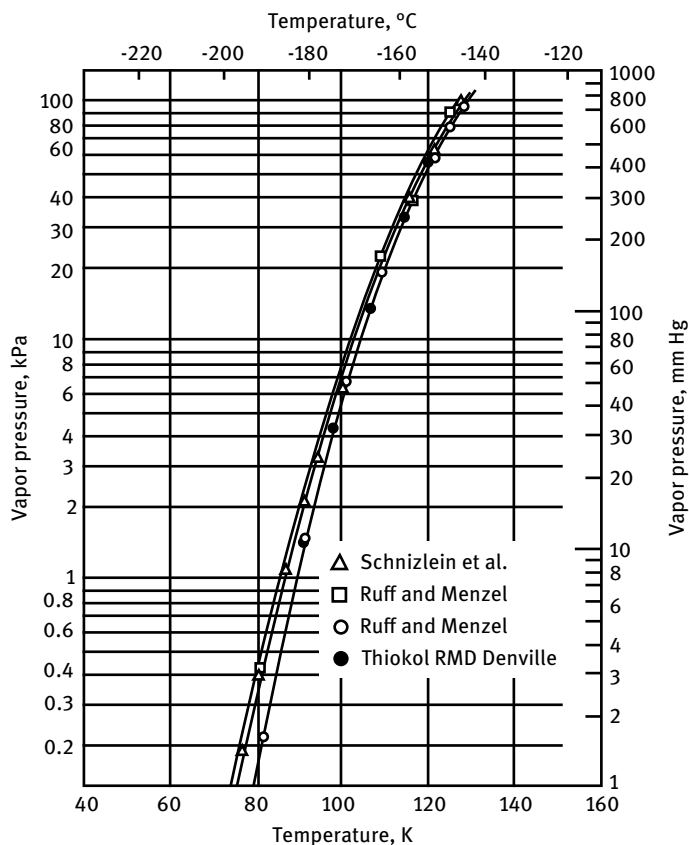


Figure 2: Vapor pressure of liquid OF_2 as a function of temperature (reproduced and modified from [9])

A different equation for the viscosity of liquid OF_2 was extrapolated over a wider temperature range:

$$\log \eta = 112.4/T - 1.4508$$

where η is the viscosity in cPs and T is the temperature in kelvin. Viscosity data are graphed in Figure 3 and listed in Table 6.

The critical point property data of oxygen difluoride are listed in Table 7.

2.3.5 Miscibility of Liquid Oxygen Difluoride with Other Oxidizers

Because liquid oxygen difluoride is not hypergolic with most fuels at the temperature of its normal boiling point, more energetic fluorine oxidizers have been sought to make it hypergolic.

Table 5: Dynamic viscosity of liquid oxygen difluoride.

Temperature		Density	Viscosity, measured	Viscosity, calculated ^a
°C	K	g/cm ³	cPs	cPs
-145.8	127.3	1.523	0.2852	0.2859
-147.2	125.9	1.529	0.2937	0.2935
-147.4	125.7	1.53	0.2933	0.2947
-147.5	125.6	1.531	0.2962	0.2952
-147.9	125.2	1.533	0.2998	0.2975
-148.7	124.4	1.537	0.3014	0.3022
-148.8	124.3	1.537	0.3024	0.3028
-150.6	122.5	1.546	0.314	0.3138
-150.8	122.3	1.547	0.3129	0.3151
-151	122.1	1.548	0.3134	0.3164
-151.1	122	1.549	0.3176	0.3170
-151.3	121.8	1.55	0.3171	0.3183
-151.5	121.6	1.551	0.3188	0.3196
-152	121.1	1.553	0.3227	0.3229
-152.8	120.3	1.557	0.3259	0.3283

Data source: [39]

^a Calculated from $\log \eta = 131.5/T - 1.5768$; η in cPs; T in K

For its potential use as an oxidizer in rocket propellants, it is important to know if and to what extent OF₂ is miscible with other liquid oxidizers, in particular those containing oxygen. A wide range of oxidizers (NOF, NO₂F, NF₃, N₂F₄, ClO₃F, ClF₃) were tested for miscibility and potential inadvertent interactions with OF₂ [41, 42]. The binary systems NF₃/OF₂, ClO₃F/OF₂, and N₂F₄/OF₂ exhibited complete miscibility over the entire range of mixture ratios, as did a ternary mixture of ClF₃/ClO₃F/OF₂ (under pressure at 195 K = -78 °C).

Liquid OF₂ was miscible in a molar ratio of 1:1 with liquid CF₄ at 90 K, CClF₃ at 90 K, CH₄ at 90 K, N₂F₄ at 110 K, and Kr at 120 K [43]. Liquid oxygen difluoride mixes homogeneously in all proportions with liquid F₂ at 77 K, with LOX and liquid ozone (LOZ) at 90 K, with liquid O₃F₂ at 116 K, and with liquid ClF at 125 K. It also mixes homogeneously with liquid CH₄ at 90 K, but this mixture is very **dangerous**. It may detonate upon the slightest stimulus or temperature rise.

Chlorine monofluoride theoretically would be expected to be miscible with OF₂ because of the similarities in molecular weight, boiling points and the lack of intermolecular forces between the similar molecules. This has, in fact, been experimentally verified; however, when attempts were made to increase the fluorine content of the additive, for example, with ClF₃ instead of ClF, theoretical analysis of the system indicated that ClF₃ and OF₂ would not be expected to exhibit much solubility or miscibility because of the dissimilarity in their molecular weights and their boiling points (boiling point of OF₂ is 128 K = -145 °C and the boiling point of ClF₃ is 284 K = +11 °C). Experi-

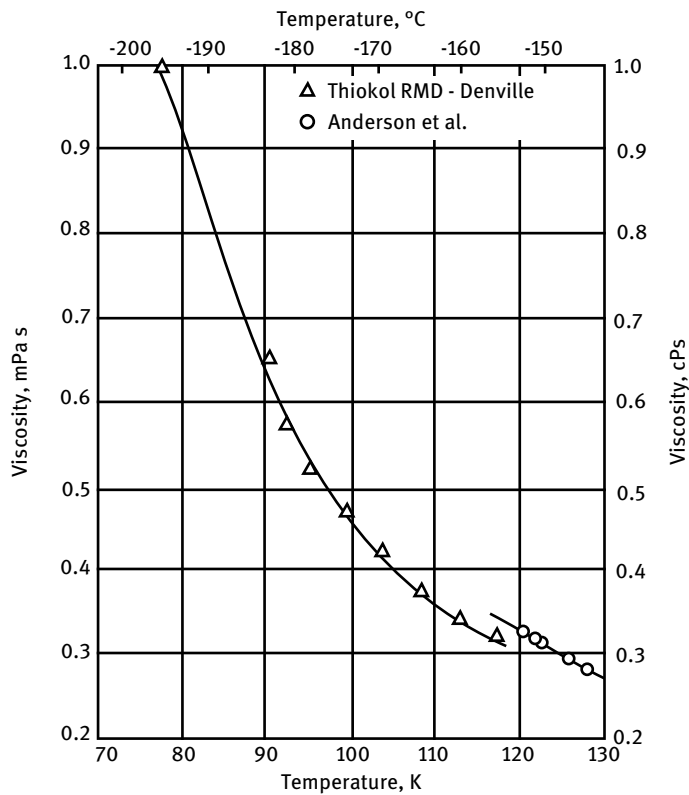


Figure 3: Viscosity of liquid OF₂ as a function of temperature (reproduced and modified from [9])

Table 6: Viscosity of liquid oxygen difluoride as a function of temperature.

Temperature		Density	Kinematic viscosity	Absolute viscosity	Calculated viscosity	Deviation
°C	K	g/cm ³	cSt	cPs	cPs	%
-195.7	77.4	1.776	0.566	1.004	1.000	0.004
-183.0	90.1	1.711	0.382	0.654	0.628	0.026
-180.2	92.9	1.700	0.336	0.572	0.572	0.000
-177.8	95.3	1.688	0.309	0.522	0.534	-0.012
-174.1	99.0	1.669	0.282	0.470	0.482	-0.012
-169.6	103.5	1.647	0.256	0.422	0.431	-0.009
-165.0	108.1	1.625	0.238	0.376	0.387	-0.001
-160.5	112.6	1.604	0.215	0.344	0.352	-0.008
-155.8	117.3	1.581	0.205	0.323	0.321	0.001

Data source: [9]

Table 7: Critical point properties of oxygen difluoride.

Critical data	SI units	MKS units
$t_{\text{crit.}}$	$215 \pm 1 \text{ K}$	$-58.0 \pm 1 \text{ }^\circ\text{C}$
$P_{\text{crit.}}$	4.954 MPa	$48.9 \text{ atm} = 719 \text{ psia}$
$V_{\text{crit.}}$	$9.76 \times 10^{-5} \text{ m}^3/\text{mol}$	$97.6 \text{ cm}^3/\text{mol}$
$\rho_{\text{crit.}}$	0.553 kg/m^3	0.553 g/cm^3

Data source: [39]

mentally, there was no apparent solubility of ClF_3 in liquid OF_2 . Because of the even greater differences in molecular weight between ClF_5 and OF_2 , it was at first expected that OF_2 and ClF_5 would be miscible; however, contrary to the theoretical prediction, it was discovered that ClF_5 has some solubility in OF_2 even at liquid OF_2 temperatures and furthermore that it is possible to form completely miscible systems of OF_2 and ClF_5 at intermediate temperatures [44]. To investigate solubility of ClF_5 in OF_2 at liquid OF_2 temperatures, ClF_5 was condensed in a glass tube and then frozen therein. OF_2 was then condensed onto the solid ClF_5 in amounts of approximately 84% by volume OF_2 , 16% ClF_5 . The mixture was agitated and gradually warmed. The interface between the ClF_5 and OF_2 was observed to recede, indicating that there was some solubility of ClF_5 in OF_2 even at temperatures of about 128 K (-145°C). Although ClF_5 is slightly soluble in OF_2 at liquid OF_2 temperatures of approximately 128 K (-145°C), the system at that temperature does not appear to be completely miscible. It was found that at temperatures above 194.6 K (-78.5°C), the systems will be completely miscible up to the critical temperature of the system. The vapor pressure of OF_2/ClF_5 mixtures at 194.6 K (-78.5°C) was measured as a function of mixture ratio and showed a slight positive deviation from ideal behavior. A vapor pressure chart was included in the patent specification.

Oxygen difluoride is a good solvent for liquid ozone. Ozone solvents have been sought that would attenuate the detonability of pure liquid ozone without detracting too much from its performance as a rocket oxidizer. These solvents should not have a solubility gap such as the one found with LOX. Fluorocarbons were tried first, but they are inert diluents which detract from performance. Oxygen difluoride has the advantage that it is not only a good solvent for liquid ozone, but also a powerful oxidizer in its own right. Oxygen difluoride/ozone systems have been investigated and it appeared that ozone and oxygen difluoride are completely miscible over the entire range of mixture ratios and temperatures.

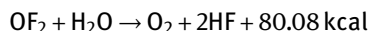
The ozone-oxygen difluoride system has shown promise as a rocket oxidizer [45]. The viscosities, densities, and surface tensions of binary mixtures showed no deviations from expected linear interpolation values. The vapor pressure indicated, as was the case with fluorine, that the ozone-oxygen difluoride system is completely homogeneous. No sensitivity measurements have been made, but no unusual hazards were

noted. Therefore, it appeared, at the very least, that ozone could be used to upgrade the performance of either fluorine or oxygen difluoride.

Stabilized liquid ozone was burned with gaseous hydrogen in a rocket engine [46]. Stabilization was accomplished by dissolving liquid ozone in liquid OF_2 . In two experiments, the O_3 concentration was 40 mass-% and when burned with GH_2 , resulted in an explosion in one case and calm burning in another; however, an explosion also occurred in one experiment with 10% O_3 and 90% OF_2 and very irregular combustion chamber pressures were encountered in several other experiments.

2.3.6 Solubility of Liquid Oxygen Difluoride in Inert Solvents

Solubility of OF_2 in water at $273\text{ K} = 0^\circ\text{C}$ and 11 atm is $6.8\text{ cm}^3\text{ OF}_2/100\text{ cm}^3\text{ H}_2\text{O}$. At atmospheric pressure it is $4.3\text{ cm}^3\text{ OF}_2/100\text{ cm}^3\text{ H}_2\text{O}$. Gaseous OF_2 is slightly soluble in water, and the solution obeys Henry's law with an absorption coefficient (liters of gas in 1 L of water) of 0.04297 at $293\text{ K} = 20^\circ\text{C}$ and 0.068 at $273 = 0^\circ\text{C}$. The solutions are not stable because a slow hydrolysis reaction takes place at room temperature:



Solutions of oxygen difluoride in partially or perfluorinated organic solvents, such as 1-fluoropropane or monofluoromethane have been patented as monopropellants [47].

2.3.7 Thermal Conductivity of Oxygen Difluoride

The thermal conductivity of liquid OF_2 is $0.26\text{ W m}^{-1}\text{ K}^{-1}$ at 90 K ($0.00061\text{ cal cm}^{-1}\text{ s}^{-1}\text{ K}^{-1}$ at -183°C , from reference [48]).

2.3.8 Thermodynamic Properties of Liquid and Gaseous Oxygen Difluoride

There is a wide scatter in the enthalpy of formation data reported for oxygen difluoride, in particular the liquid (Table 8). It seems that the experts cannot even agree on if the enthalpy of formation is positive or negative. Numbers range all over the ballpark. The best summary of thermodynamic data for gaseous OF_2 compiled by NIST contains a table listing 28 different numbers for the enthalpy of formation, ranging all the way from $+10.6$ to $+76\text{ kJ/mol}$, collected over a time span from 1930 to 1990 and originating from both experimental measurements and quantum mechanical computational chemistry predictions.

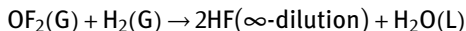
Based on the three fundamentals of $\gamma_1 = 833\text{ cm}^{-1}$, $\gamma_2 = 492\text{ cm}^{-1}$, and $\gamma_3 = 1110\text{ cm}^{-1}$, the thermodynamic functions of OF_2 gas between 298 and 1500 K were calculated [53]. The numbers for 298 K were $-(F_0 - H_0)/T = 210.6\text{ J mol}^{-1}\text{ K}^{-1} = 50.31\text{ cal mol}^{-1}\text{ }^\circ\text{C}^{-1}$, $S_0 = 246.7\text{ J mol}^{-1}\text{ K}^{-1} = 58.93\text{ cal mol}^{-1}\text{ }^\circ\text{C}^{-1}$, and $C_p = 42.2\text{ J mol}^{-1}\text{ K}^{-1} = 10.08\text{ cal mol}^{-1}\text{ }^\circ\text{C}^{-1}$. Their tentative proposed enthalpy of formation $(\Delta H_f)_{298}$ was $+23.0\text{ kJ/mol} = +5.5\text{ kcal/mol}$.

Table 8: Thermodynamic properties of liquid and gaseous oxygen difluoride.

	SI units	MKS units	Source	Year	References
Molar heat capacity, C_p , gaseous at 298 K	43.32 J mol ⁻¹ K ⁻¹	10.349 cal mol ⁻¹ °C ⁻¹	JANAF	1969	[49]
Enthalpy of formation (ΔH) ₂₉₈ gaseous	+24.52 ± 1.59 kJ/mol -18.4 ± 3.4 kJ/mol +31.7 kJ/mol	+5.86 ± 0.38 kcal/mol -4.40 ± 0.82 kcal/mol +7.6 kcal/mol	JANAF and NIST Chem WebBook Bisbee et al. Evans, Munson, and Wagman	1969 1965 1955	[37] [50] [51]
	+24.52 ± 1.59 kJ/mol	+5.86 ± 0.38 kcal/mol	King and Armstrong	1968	[52]
Enthalpy of formation (ΔH) ₂₉₈ liquid	-35.6 kJ/mol	-8.5 kcal/mol			
Entropy S°_{gas} , 1 bar	247.46 J mol ⁻¹ K ⁻¹	59.14 cal mol ⁻¹ °C ⁻¹	NIST Chem Web-Book, Chase	1998	[37]
Heat of evaporation (ΔH) _{evap.}	11.2 kJ/mol at 123.8 K 11.08 kJ/mol at 127.8 K	2.680 kcal/mol at -144.8 °C 2.650 kcal/mol at -145.3 °C	Allied Chemical Streng	1959 1963	[36] [4]
Entropy of evaporation (ΔS) _{evap.}	86.4 J mol ⁻¹ K ⁻¹	20.65 cal mol ⁻¹ °C ⁻¹	Allied Chemical	1959	[36]

The widely cited number (+7.6 ± 2 kcal/mol) listed in Evans, Munson, and Wagman [51], which was an average of three numbers reported by earlier investigators, is generally considered unreliable and should be ignored.

The most accurate enthalpy of formation of OF₂ was obtained from constant pressure flame calorimetry measurements at NIST (former NBS) by burning OF₂ with H₂ and absorbing the formed HF and H₂O [52]. The enthalpy of formation of OF₂ was measured in a calorimeter by allowing OF₂ to react with H₂ in a closed bomb with a bottom layer of water to absorb the HF formed in the reaction:



The standard enthalpy of formation of gaseous OF₂ calculated from the known heats of formation of the products was -18.4 ± 3.4 kJ/mol (-4.40 ± 0.82 kcal/mol) [50, 54], but this number is totally out of line with all the other measurements and there must have been an instrumental or computational error leading to the negative number.

The gas phase heat capacity of OF_2 can be calculated by a Shomate equation

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + \frac{E}{\tau^2}$$

where C_p is the heat capacity in $\text{J mol}^{-1} \text{K}^{-1}$, τ is the temperature in kelvin divided by 1000: $\tau = \text{K}/1000$, and A, B, C, D, and E are constants listed in Table 9 for two temperature ranges.

Table 9: Coefficients for thermodynamic property Shomate equations for oxygen difluoride.

Temperature range, K	298–600	600–6000
A	15.06976	57.26808
B	136.2612	0.640466
C	–172.8088	–0.150702
D	81.40767	0.011677
E	0.071893	–1.898625
F	15.57553	1.585041
G	232.4333	307.3976
H	24.51803	24.51803

Data source: [37, 49]; data last reviewed in September 1995

According to the *NIST Chemistry WebBook* web site, the standard enthalpy of formation of the OF_2 gas is $\Delta H_f^{298} \text{ gas} = +24.52 \pm 1.59 \text{ kJ/mol}$. The differential enthalpy of formation of gaseous oxygen difluoride as a function of temperature can be expressed by the equation

$$H^\circ - H_{298.15}^\circ = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{\tau} + F - H$$

where H° is the standard enthalpy in J mol^{-1} , τ is the temperature in kelvin divided by 1000: $\tau = \text{K}/1000$, and A, B, C, D, E, F, and H are constants listed in Table 9 for two temperature ranges. The standard entropy of gaseous oxygen difluoride as a function of temperature can be expressed by the equation

$$S^\circ = A \times \ln(\tau) + B\tau + \frac{C\tau^2}{2} + \frac{D\tau^3}{3} - \frac{E}{2\tau^2} + G$$

where S° is the standard entropy in $\text{J mol}^{-1} \text{K}^{-1}$, τ is the temperature in kelvin divided by 1000: $\tau = \text{K}/1000$, and A, B, C, D, E, and G are constants listed in Table 9 for two temperature ranges.

The thermochemical properties of all oxygen fluorides and their associated free radicals have been summarized and the JANAF thermochemical tables for oxygen fluorides going all the way up to O_8F_2 have been updated by NIST, but sufficient infor-

mation was not available to generate thermochemical tables for any condensed phase species [12]. Table 10 gives a summary of recommended thermochemical data for gas phase oxygen fluorides including some free radicals. The [] brackets indicate estimated values.

Table 10: Thermodynamic properties of the gaseous oxygen fluorides.

Temperature, K	0	298.15	298.15	298.15	298.15
Compound	ΔH_0 kJ/mol	ΔH_f kJ/mol	ΔG_f° kJ/mol	C_p° J mol ⁻¹ K ⁻¹	S_0 J mol ⁻¹ K ⁻¹
OF(G)	+108 ± 10	+109 ± 10	105	32.0	216.40 ± 0.3
FOO(G)	+27.2 ± 2	+25.4 ± 2	39.4	44.5	259.5 ± 0.2
OF0(G)	[+381.2 ± 20]	[+378.6 ± 20]	[395]	[41.1]	[251 ± 1]
FOF(G)	+26.8 ± 2	+24.5 ± 2	41.8	43.3	247.5 ± 0.4
FOOF(G)	+22.9 ± 0.8	+19.2 ± 0.8	58.2	62.1	277.2 ± 0.2

Data source: [12]

The NIST-JANAF thermochemical table values for the thermochemical properties of oxygen fluorides issued in 1996 were critically examined on the basis of high-level density functional and *ab initio* G2 calculations [55]. Special attention was given to the enthalpies of formation and it was concluded that, although the proposed values for OF(G), FOO(G) and FOF(G) were reasonable and in agreement with previously recommended values, the enthalpy of formation recommended for FOOF was too low. Instead, a value about 50% larger was proposed and it was recommended that the original 1959 experimental determination of this enthalpy of formation should be repeated.

The theoretical enthalpy of formation ΔH_f (298 K) value obtained for gaseous FOF (¹A₁) was +24.68 ± 1.25 kJ/mol (+5.9 ± 0.3 kcal/mol), and for FOOF (¹A) it was +26.78 ± 2.93 kJ/mol = +6.4 ± 0.7 kcal/mol [56]. The value for FOF is different from experimental results which gave +19.20 ± 2.09 kJ/mol = +4.59 ± 0.5 kcal/mol. See also reference [57].

A narrow range of values (155–197 kJ/mol = 37–47 kcal/mol) for the O–F bond energy was obtained from the heat of formation and normal assumptions for the other bonds present in molecules with O–F bonds for the species for which data were available [58]. The average value for the energy of the O–F bond for all O–F bonded species was found to be 180 kJ/mol (43 kcal/mol), which corresponds very closely to the value of 188 kJ/mol (45 kcal/mol) derived from the heat of formation of oxygen difluoride. The variation found in the O–F bond energies for the species is less than that observed for other bonds, depending on the nature of the compound they are attached to.

2.3.9 Molecular Structure of Oxygen Difluoride

The energy release that drives a rocket is founded in the energy of chemical bonds being broken and made. In order to select the best rocket propellant from the group of oxygen fluorides, the energy of the O—F bond must be known. An excellent summary of bond lengths, bond angles and force constants in several of the O—F molecules was provided in [12].

The predicted heats of formation at 298.15 K and structures of 5 small oxygen fluoride molecules have been calculated by computational chemistry [56]. Good agreement with experiment was found for several structures.

In studying the molecular structure of OF₂ (is it similar to that of OH₂?), it was useful to have microwave spectra [59]. The values for the rotational constants together with the effective moments of inertia calculated from them were derived from 13 rotational absorption lines of which 9 of the lines could be assigned to rotational transitions of OF₂. It is highly unlikely that OF₂ would have the structure of a fluorosyl fluoride F—F=O but CAS has assigned this structure a CAS Registry number [86825-57-2], nevertheless.

The interatomic distance between the central oxygen atom and the two equivalent fluorine atoms and the angle formed between them were measured by several investigators, but the results vary, as summarized in Table 11.

Table 11: Molecular constants of the oxygen difluoride molecule.

Property	Result	Author	Year	References
O—F distance	1.3896 Å	Hilton et al.	1961	[59]
O—F distance	1.409 Å	Pierce, Jackson, and di Cianni	1961	[60, 61]
O—F distance	1.412 Å	JANAF	1969	
F—O—F bond angle	$2\theta = 104.163^\circ$	Hilton et al.	1961	[59]
F—O—F bond angle	$103^\circ 18'$	Pierce, Jackson, and di Cianni	1961a, 1961b	[60, 61]
Dipole moment	0.297 ± 0.005 D	Pierce, Jackson, and di Cianni	1961a, 1961b	[60, 61]

The publication by Chase [12] contains an excellent summary of bond lengths, bond angles, and force constants in the OF₂ molecule covering the time period from 1935 to 1994 with about 30 different sources of experimental measurements or theoretical calculations for the O—F bond length, many more than shown in above table [12].

A total of 17 rotational transitions of F₂O were measured in the region 13–60 GHz with Stark module spectrometers [60, 61]. Rotational constants, moments of inertia, the inertial defect and structural parameters of F₂O were derived from these measurements. A dipole moment of 0.297 ± 0.005 D was obtained.

Four valence force constants have been evaluated on the basis of Wilson's group theoretical method for OF₂ [62]. The observed fundamental frequencies were then utilized for the calculation of molar thermodynamic functions assuming a rigid rotator,

harmonic oscillator approximation for the temperature range from 100 to 1700 K. The O—F bond energy is 58 kcal/bond = 2.52 eV.

Self-consistent field and large-scale configuration interaction studies with double zeta and extended basis sets were performed on F₂O for its geometry, vertical electronic excitation energies, and vertical ionization potentials [63]. Large-scale configuration interaction methods gave the best agreement with the experimentally measured distance (1.41 Å).

Ab initio predictions at the self-consistent field (SCF), double excitation configuration interaction (CISD) and double excitation coupled cluster (CCSD) levels were reported for OF₂ using the double zeta plus polarization (DZP) and triple-zeta plus polarization (TZP) basis sets [64]. The calculated geometries, rotational constants, dipole moments, fundamental frequencies, isotopic frequency shifts, vibration-rotation interaction constants, centrifugal distortion constants, Coriolis coupling constants and IR band intensities were compared with experimental data. The best agreement was usually found for the CCSD results. The experimentally derived cubic force field of OF₂ was reproduced well so that the predicted quartic force field of OF₂ was also expected to be realistic.

2.3.10 Dipole Moment of Oxygen Difluoride

The dipole moment of OF₂ has been determined from the Stark effect on two rotational frequencies [65]. The dipole moment of 0.1759 ± 0.0010 debye was about 2.1% of that calculated for a simple ionic model. The dielectric constant, polarization and dipole moment of OF₂ were compared to those of SF₄ [66]. A condenser was mounted in a cylindrical glass vessel which was immersed in the thermostat bath. Capacities were measured with the OF₂ gas at atmospheric pressure over the temperature ranges 195–353 K (–78° to +80 °C). The dipole moment of OF₂ gas was 0.4 ± 0.1 D for a polarization of 5 cm³/mol. The value for OF₂ is much smaller than that for OH₂. The dipole moment of OF₂ was reported as 0.297 ± 0.005 D [60, 61].

2.3.11 Optical Properties of Oxygen Difluoride

2.3.11.1 UV/Visible Spectra of Oxygen Difluoride

In the visible/UV spectrum between 8000 and 2100 Å, absorption of light starts at about 5400 cm^{–1}, is purely continuous and shows maxima at 4210 Å = 23800 cm^{–1}, 3580 Å = 28000 cm^{–1}, and 2940 Å = 34000 cm^{–1}. A very abrupt ascent of absorption is observed at about 2640 Å = 38000 cm^{–1}, but the maximum of absorption is not yet reached at 2130 Å = 47000 cm^{–1}.

The photoabsorption and dissociation processes of Cl₂O₂ and Cl₂O have attracted considerable attention since these processes are involved in the ozone depletion in the Antarctic stratosphere. By analogy, the photoabsorption and dissociation processes of O₂F₂ and OF₂ are of interest. The excitation spectrum of OF₂ up to about 13.0 eV was calculated and compared to theoretical results. The shape and main features of

the calculated OF_2 spectrum was found to be very similar to that of Cl_2O , each state being blue-shifted by 2–3 eV, and the valence and Rydberg excited states were clearly discriminated [67].

2.3.11.2 Infrared Spectra of Oxygen Difluoride

The infrared spectrum of OF_2 has been re-examined from 2–25 μm with a prism spectrometer and selected regions further examined with a grating spectrometer [68]. Several bands observed by previous investigators were shown to be caused by impurities. An assignment of fundamental modes could be made which was consistent with dimensions of the molecule obtained from electron diffraction data. Two new bands were observed and assigned to combinations of the fundamentals. The observed frequencies and their assignments were: $\nu_1 = 928 \text{ cm}^{-1}$, $\nu_2 = 461 \text{ cm}^{-1}$, $\nu_3 = 831 \text{ cm}^{-1}$, $\nu_1 + \nu_3$, and $2\nu_2 + \nu_3$ at 1731 cm^{-1} , $3\nu_3 = 2460 \text{ cm}^{-1}$, $2\nu_1 + \nu_3 = 2643 \text{ cm}^{-1}$.

The absorption spectrum of OF_2 dissolved in liquid N_2 at 80 K was obtained and the frequency and intensity of the absorption bands were determined [69].

The IR spectra of highly purified OF_2 were measured in standard 10-cm gas cells equipped with silver chloride windows at pressures up to one atmosphere in the region from 350 to 4000 cm^{-1} [70]. Figure 4 is a composite of three IR spectra of gaseous OF_2 taken at different partial pressures and path lengths. The sharp drop-off at the low frequency side is due to absorption by the AgCl windows on the cell. Note that the wavenumber scale is not continuous but composed of four sections showing different parts of the spectrum.

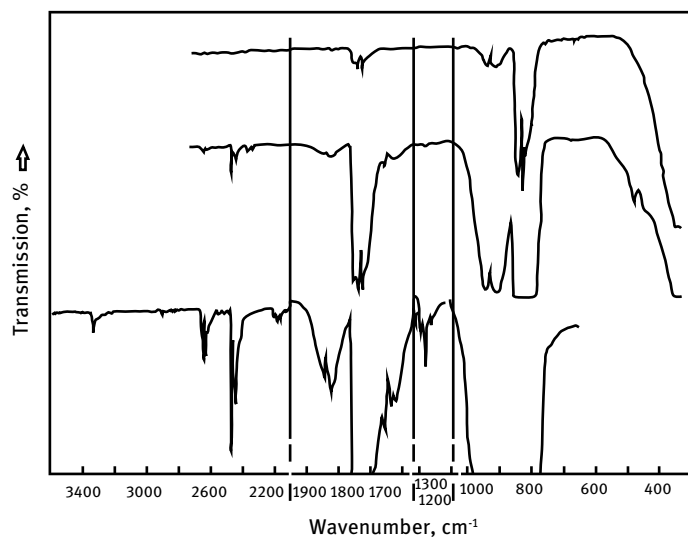


Figure 4: Composite of three IR spectra of OF_2 taken at different partial pressures and path lengths (reprinted and modified from [70], with permission from © 1966 Elsevier; permission conveyed through RightsLink.)

The study of gaseous OF_2 IR spectra indicated that a simple harmonic oscillator model is inadequate to describe the vibrational spectrum and that Fermi resonances must be taken into consideration. Several transitions fall within a 100-cm^{-1} range of each other introducing the possibility of widespread resonance effects in the molecule. These effects are evident in the complicated spectra patterns exhibited in the overtones and combinations observed.

Portions of the ν_3 asymmetrical stretch band of OF_2 were measured under conditions of Doppler-limited resolution and the frequencies of 176 transitions were measured with a nominal accuracy of 0.001 cm^{-1} , see reference [71]. The remaining band constants were determined by constraining the ground state parameters to the values determined earlier and carrying out a simultaneous fit of the existing IR and $\nu_3 = 1$ microwave data. No evidence for the anticipated effects of weak Coriolis coupling for levels with $K - 1 = 16$ and $J = 30$ was observed although such effects may be present in levels with much higher quantum numbers.

2.3.11.3 Raman Spectra of Oxygen Difluoride

The Raman spectra of liquid OF_2 were obtained and compared to IR spectra [72]. Polarization studies confirmed earlier infrared band assignments and supported the existence of Fermi resonance between ν_1 and $2\nu_2$.

The Raman spectra of solid OF_2 proved to be difficult to obtain because of the colored nature of this compound. The liquid is yellowish brown whereas the solid still retains a light brown coloration. A comparison of Raman and IR of crystalline OF_2 indicated that this solid is not centro-symmetric and contains at least two molecules per primitive cell, on sites of symmetry C_s or C_1 [73]. Absorption bands at 461, 821, and 925 cm^{-1} were found in gas IR, liquid Raman, and solid Raman and solid IR spectra. The most striking feature in the IR spectrum of crystalline OF_2 was the broad band on the high-frequency side of the 812 cm^{-1} peak. In the Raman spectrum, a sharp peak was observed at 845 cm^{-1} , its frequency being approximately coincident with the limit of the IR reflection band. The far-IR spectrum of crystalline OF_2 showed seven bands in the $40\text{--}90\text{ cm}^{-1}$ region, all of these having Raman-active counterparts with almost identical frequencies.

The argon matrix Raman spectra of $^{16}\text{OF}_2$ and $^{18}\text{OF}_2$ at 16 K had frequencies within one wave number of analogous IR spectra [74]. In addition, laser photo-detachment of fluorine atoms has provided significant yields of the $\bullet\text{OF}$ and $\bullet^{18}\text{OF}$ free radicals. Temperature cycling and depolarization ratio measurements aided in identifying new chemical species and making vibrational assignments.

2.3.12 Microwave Spectra of Oxygen Difluoride

The molecular structure of OF_2 has been studied by microwave spectroscopy based on 13 rotational absorption lines [75]. The frequencies of the lines were measured with a precise frequency standard. Nine of the lines were assigned to rotational transitions

of OF_2 using a graphical method. The values for the rotational constants together with the effective moments of inertia calculated from them were $A = 61567.71 \text{ MHz}$, $I_A = 8.21096 \text{ amu, \AA}^2$; $B = 11066.54 \text{ MHz}$, $I_B = 45.6809$; $C = 9343.85 \text{ MHz}$; $I_C = 54.1088 \text{ amu, \AA}^2$. The effective values for the O—F interatomic distance and the apex angle 2θ calculated from I_A and I_B were $r = 1.3896 \text{ \AA}$, $2\theta = 104.163^\circ$.

Microwave absorption spectra of the OF_2 molecule in the vibrationally excited states with $\nu_1 = 1$, $\nu_2 = 1$ and 2, and $\nu_3 = 1$ were measured and analyzed with consideration for the Fermi resonance between ν_1 and $2\nu_2$ vibrational levels [76]. The degree of mixing between the two states and quadratic force field were determined from the inertia defects. Cubic potential constants and equilibrium structures were obtained from the vibration-rotation interaction constants.

Radio frequency transitions within six different rotational levels of oxygen difluoride have been observed in the presence of external electric fields [77]. These data were analyzed in terms of the dipole moment, polarizability anisotropies, spin rotation and spin-spin interactions: $\mu = 0.30818(3) \text{ D}$, $aaa-abb = 1.389(8) \text{ \AA}^3$, $aaa-acc = 1.883(10) \text{ \AA}^3$, $Maa = 59.60(7) \text{ kHz}$, $Mbb = 25.05(11) \text{ kHz}$, $Mcc = 51.39(8) \text{ kHz}$, and $1/R^3 = 0.0941(5) \text{ \AA}^{-3}$.

A very detailed analysis of the rotational and centrifugal distortion constants of OF_2 has been posted on a NIST web site as part of their triatomic species spectral data file [78]. Historically, the analysis of the rotational and centrifugal distortion constants for OF_2 had caused considerable difficulty. The first spectra on OF_2 had been incorrectly interpreted and later Pierce, di Cianni, and Jackson [79] provided the correct assignments from a detailed centrifugal distortion analysis of new spectral measurements.

2.3.13 Photoelectron Spectra of Oxygen Difluoride

Additional information on bonding states and ionization energies in OF_2 can be obtained from photoelectron spectra. The photoelectron spectrum of OF_2 pertaining to ionizations to the ground and low-lying excited electronic states of F_2O^+ was investigated theoretically [80]. The near equilibrium potential energy surfaces of the ground electronic state of OF_2 and the mentioned ground and excited electronic states of F_2O^+ reported by others for the C_{2v} configuration are extended for the C_s geometry assuming a harmonic vibration along the asymmetric stretching mode [81].

2.3.14 Electrical Properties of Oxygen Difluoride

Liquid oxygen difluoride does not autodissociate like BrF_3 and the electrical conductivity is not measurable. Oxygen difluoride in the dark does not have an electronic spin resonance (ESR) signal and is not paramagnetic [82, 83]. When illuminated with UV at $3660 \text{ \AA}$, an ESR signal (a strong doublet with a hyperfine splitting of 13.5 Gauss) of a free radical was observed, but it was not positively identified. Most likely it was $\cdot\text{OF}$ free radical and not a multi-oxygen fluoride. The intensity of the ESR signal increased

with continued illumination, reached a maximum and then decayed. The rate of photolysis was temperature dependent.

The electrical conductivity of liquid OF_2 is $\leq 1.4 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$ and $\leq 5.16 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$ at 77 and 113 K (−196 and −160 °C), respectively [84]. Only few chemicals that dissolve in OF_2 will cause an increase in conductivity.

2.3.15 Magnetic Properties of Oxygen Difluoride

2.3.15.1 Nuclear Magnetic Resonance Spectra of Oxygen Difluoride

Direct comparisons between ^{19}F nuclear magnetic resonance (NMR) spectra of liquid and gaseous F_2 , OF_2 , and NF_3 had not been reported prior to 1966 [85]. The chemical shifts of liquid and gaseous F_2 , OF_2 , and NF_3 are listed in Table 12.

Table 12: ^{19}F NMR shifts in liquid and gaseous F_2 , OF_2 , and NF_3 .

	^{19}F NMR shifts ^a		
	F_2 (ppm)	OF_2 (ppm)	NF_3 (ppm)
Liquid at 77 K	-422 ± 1	-249 ± 1	-142 ± 1
Gas	-419 ± 1	-248 ± 1	-138 ± 1
Difference gas–liquid	3	1	4

^a In relation to CFCl_3 reference.

Data source: [85]

As can be seen in Table 12, the chemical shifts for liquid F_2 , OF_2 , and NF_3 were all lower than the corresponding shifts in the gas. This downfield shift due to liquefaction is similar to that observed in the proton magnetic resonance studies of the first row hydrides.

The ^{19}F NMR spectra of liquid F_2 , OF_2 , O_2F_2 , and O_3F_2 were measured and compared [86]. The shifts of O_2F_2 and O_3F_2 were the furthest downfield of any simple fluorine compound yet reported. In order to completely understand the NMR shifts, they have to be measured at several temperatures. The vast difference in chemical shift of O_2F_2 and O_3F_2 indicated that the fluorine nuclei (hence fluorine-oxygen bonding) are considerably different in O_2F_2 and O_3F_2 as compared to OF_2 . The structures of F_2 , OF_2 , and O_2F_2 can be well characterized, and hence their ^{19}F NMR signals can be interpreted in accordance with their structures. The “one-electron” bond model in O_2F_2 would result in a ^{19}F nucleus, which has a very low shielding constant and is thus consistent with the ^{19}F NMR spectrum. A summary of chemical shifts is presented in Table 13. The O_3F_2 is given in quotation marks, since there is some uncertainty about the reality of the compound. A model for O_3F_2 is postulated in which this species is made up of O_2F_2 and “interstitial” O_2 .

Table 13: ^{19}F NMR shifts for liquid F_2 , OF_2 , O_2F_2 , and O_3F_2 .

Compound	Temperature, K	Shift, ppm ^a
F_2	77	-422 ± 1
OF_2	77	-249 ± 1
O_2F_2	145	-865 ± 1
" O_3F_2 "	<145	-877 ± 5

^a In relation to CFCl_3 reference.

Data source: [86]

Indirect spin-spin coupling tensors, $\mathbf{J}$, are of importance in interpreting NMR spectra. For example, a great deal of experimental and theoretical work has focused on the characterization of $\mathbf{J}$ couplings observed across hydrogen bonds. Similar couplings may occur between fluorine bonds and contribute to the association of molecules. Symmetry properties of indirect nuclear spin-spin coupling tensors can be calculated by a first principles method and results for OF_2 were shown [87]. Measured $\mathbf{J}_{\text{iso}}(^{19}\text{F}, ^{17}\text{O})$ in OF_2 is $\pm 300 \pm 30$ Hz and the predicted number was very close. See also reference [88].

2.4 Chemical Properties of Oxygen Difluoride

Oxygen difluoride is a weaker oxidizer than elemental fluorine or halogen fluorides. It will eventually react with most organic substances, but only at higher temperatures than fluorine or halogen fluorides. In contradistinction to fluorine it does not autoignite with methane, kerosene, charcoal or ammonia at room temperature. Once ignited, the combustion reaction is just as energetic as those supported by fluorine as an oxidizer. The reaction with diborane is hypergolic at room temperature and this makes a good rocket propellant combination [89].

2.4.1 Decomposition of Oxygen Difluoride

2.4.1.1 Thermal Decomposition of Oxygen Difluoride

Oxygen difluoride is thermally stable under normal storage conditions. Above 523 K (250 °C) it begins to decompose into its constituents. The activation energy of the homogeneous gas phase reaction is 172 kJ/mol (41 kcal/mol). Other sources reported the activation energy of thermal decomposition as 169.8 ± 12.5 kJ/mol (40.6 ± 3 kcal/mol). The reaction has been found to be about first-order with respect to OF_2 when a large excess of inert diluent gas is present, with the pseudo first-order constant proportional to total pressure and found to be approximately second-order when only pure OF_2 is used. The reported activation energies were in the range of 130–176 kJ/mol (31–42 kcal/mol).

Although the kinetics of the thermal decomposition of OF_2 have been studied extensively, there remained considerable doubt as to the exact mechanism of pyrolysis. This reaction has been investigated with static reactors, flow reactors, and shock tubes. This reaction would often precede the ignition of OF_2 with fuels at elevated temperature and therefore must be understood in developing OF_2 as a rocket propellant.

The thermal decomposition of oxygen difluoride has been investigated in aluminum static reactors at 563–634 K [90]. The reaction had an induction period followed by an apparent first-order decay in the pressure region of 10–5500 mm Hg. The decomposition of OF_2 is a complex process, possibly proceeding via a chain reaction. The observed first-order constant was

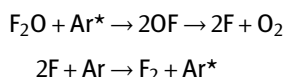
$$k_1 = 10^{9.0} \exp(-31000/RT) \text{ s}^{-1}$$

The thermal dissociation of Ar-diluted OF_2 behind incident shock waves was investigated in the temperature range 860–1300 K [91]. The course of the dissociation was followed by means of UV absorption spectroscopy utilizing a light beam centered at 220 nm. The dissociation exhibited two phases: a slow initiation phase followed by an accelerating rate. Initial slope measurements gave a second-order rate constant of

$$k = 10^{14.2} \exp(31500/RT) \text{ mL mol}^{-1} \text{ s}^{-1}$$

The results were interpreted as being indicative of a chain mechanism.

The thermal decomposition of OF_2 was studied in a single-pulse shock tube over the temperature range 770–1390 K [92]. For temperatures below 1000 K these results were in excellent agreement with the previous shock tube data; however, all rates obtained by conventional techniques, either in static or in flow systems, proved to be higher than those derived from the shock tube techniques. This was attributed to surface effects which cannot be avoided in conventional systems. The following scheme was proposed:



with

$$k_1 = 10^{17.3 \pm 1.4} \exp(-42.5 \pm 4.1) \text{ mL mol}^{-1} \text{ s}^{-1}$$

and

$$k_2 = 10^{12.10 \pm 0.12} \text{ mL mol}^{-1} \text{ s}^{-1}$$

The reverse reactions cannot be neglected even in the early stages of reaction. The bond dissociation energy $D(\text{FO}-\text{F})$, was found to be $178.6 \pm 17.1 \text{ kJ/mol}$ ($42.7 \pm 4.1 \text{ kcal/mol}$). The mechanism of the OF_2 decomposition was also discussed.

It was already shown that oxygen inhibits OF_2 decomposition. Another free radical scavenger, CO was therefore also tested for its effect on OF_2 decomposition [93]. The

kinetics of the reaction between oxygen difluoride with carbon monoxide were studied in shock tubes between 800 and 1400 K. Some of the experiments were done with a single pulse tube. These provided data on the production of CO_2 , O_2 , and F_2CO . In addition, time-resolved optical measurements were made behind incident shock waves. The reaction between OF_2 and CO leads to the production of significant amounts of F_2CO , which results in a temperature increase that becomes more important at the lower temperatures. For shock tube OF_2 kinetic studies, see also reference [94].

Oxygen difluoride in helium gas carrier has been decomposed at temperatures from 773 to 973 K and at residence times from 1 to 10 ms using a tubular flow reactor coupled to a mass spectrometer [95]. The reactor was made from nickel and was 7.5 cm (3 in.) long and had a diameter of 6.1 mm (0.25 in.). The rate expression found for the bimolecular rate coefficient over the temperature range from 723 to 923 K was

$$\log k = 9.78 - \frac{7065}{T} \text{ L mol}^{-1} \text{ s}^{-1}$$

No evidence for the oxy fluoride ($\cdot\text{OF}$) radical was found. This thermal decomposition does not appear to be a simple unimolecular decomposition. Additional tests were planned to be done in a shock tube [96]. The activation energy of OF_2 decomposition in a flow reactor was 142 kJ/mol (34 kcal/mol) [237].

The rate and mechanism of pyrolysis of OF_2 has been studied over the temperature range of 603–704 K (330–431 °C) in a stirred-flow Monel reactor, and a concentration range of 1–10 mol % OF_2 in helium at a total pressure of 1 atmosphere [97]. The only observed products were oxygen and fluorine. The reaction was somewhat less than first order with respect to reactant concentration. The initial rate data could be represented by the following equation:

$$-[\text{d}(\text{OF}_2)/\text{d}t]_0 = k_2(M)(\text{OF}_2)_0 + k_{3/2}(M)(\text{OF}_2)^{1/2}$$

where k_2 and $k_{3/2}$ are the second-order and 3/2-order rate constants and M is the total concentration of species in the reactor. The Arrhenius plot of the k_2 values gave the following equation:

$$k_2 = 10^{16.9 \pm 0.6} \exp(39200 \pm 1700/RT)$$

where k_2 is the second-order rate constant in $\text{mL mol}^{-1} \text{ s}^{-1}$ and T is the temperature in kelvin.

The thermal decomposition of OF_2 has been investigated in reactors made of Mg, Al or quartz using a static method [98]. The temperature was varied between 501 and 583 K and the total pressure between 1.3 and 100 kPa (10 and 750 mm Hg). The reaction was homogeneous and at moderate and high pressures essentially of second order. In the absence of foreign gases the second-order constant increased slowly with decreasing pressure. All added gases increased the reaction rate.

2.4.2 Photolysis of Oxygen Difluoride

Because the decomposition of OF_2 can also be initiated by intense light, it should be stored only in the dark [99].

Oxygen difluoride is an effective fluorinating agent, but for many fluorinating reactions the reacting mixture has to be illuminated with UV to achieve the desired products at a reasonable rate of formation.

The photoionization efficiencies of the ions F_2O^+ and OF^+ have been measured in a photoionization mass spectrometric study of gaseous OF_2 [100]. The adiabatic first ionization potential of OF_2 was 13.11 ± 0.01 eV. The region near threshold (13.11 – 13.6 eV) had a structure that was interpreted as vibrational autoionization. Additional peaks at 13.81 , ~ 15 , and ~ 15.5 eV were interpreted as Rydberg levels that decay by an electronic autoionization mechanism and which converge to the second ionization potential at 16.17 eV. An upper limit for the appearance potential of OF^+ (0 K) was 14.438 eV, quite different from the electron impact value of 15.8 ± 0.2 eV. That implies $\Delta H^\circ_f(\text{OF}) = +109.2 \pm 9.6$ kJ/mol ($+26.1 \pm 2.3$ kcal/mol) and an ionization potential of $(\text{OF}) = 12.79 \pm 0.10$ eV.

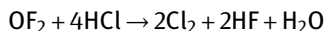
2.4.3 Radiolysis of Oxygen Difluoride

A study of the radiolysis of liquid oxygen difluoride with γ -radiation from a ^{60}Co source was performed at a dose rate of 6.00×10^5 rad/h in stainless steel vessels and at a temperature of 77 K (-196°C) [101]. Samples were loaded into the vessels and pressure over the liquid was determined. Each vessel contained 5.0 g of OF_2 liquid, which filled about 20% of the available volume. When plotting the mols of gaseous decomposition products, O_2 and F_2 , as a function of radiation dose, it was noted that in this case the yield of decomposition products was not linear with dose as were other chemicals subjected to radiolysis. The fact that the yield was not constant but decreasing probably indicated a secondary reaction which was removing the gaseous products at a slow but definite rate. One such reaction which immediately suggests itself is the reverse reaction of O_2 and F_2 gas to reform OF_2 liquid. It is also possible that some O_2F_2 could be formed which would also condense at the temperature of these experiments and lead to an apparent decrease in the rate of decomposition of OF_2 . Since the rate of formation of decomposition products, and hence the G -value, decreased with increasing dose, the value at low doses is most important since that gives the maximum value and indicates the maximum rate of radiation-induced decomposition. The initial value was $G(\text{gas}) = 0.30$ molecules/100 eV. A G -value this low indicates liquid OF_2 is rather radiation resistant. The data further indicated a maximum gas build-up rate of about 6.9×10^3 mL/megarad. Assuming one and a half molecules of gaseous products for each molecule of liquid OF_2 decomposed, the G -value is $G(\text{OF}_2) = 0.20$ molecules/100 eV. This is equivalent to about $1 \times 10^{-3}\%$ decomposition per megarad.

2.4.4 Reactions of Oxygen Difluoride

Oxygen difluoride does not react with F_2 either in gaseous phase at temperatures up to 573 K (300 °C) or in liquid phase at cryogenic temperatures. No OF_3 or OF_4 was formed under these conditions. The O^{+2} just seems to be the highest state of oxidation we can oxidize oxygen to (for now). The mixtures of OF_2 with the other halogens, Cl_2 , Br_2 or I_2 , explode upon warming.

At elevated temperatures OF_2 reacts with glass forming SiF_4 and oxygen. With aqueous solutions of HCl, HBr, or HI oxygen difluoride reacts quantitatively, liberating free halogens:



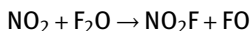
The other three halogens are displaced also from their halide salts. Gaseous OF_2 does not ignite hypergolically when mixed with H_2 , CH_4 or CO , but the mixtures will explode when sparked. Oxygen difluoride reacts slowly with anhydrous NH_3 yielding NH_4F . A mixture of OF_2 with NO is slowly colored brown; NOF and NOF_2 are formed. A gaseous NO - OF_2 mixture may explode from a spark.

Pure NOF should not react with OF_2 . An explosion that was reported in the literature has later been blamed on NO contamination in the NOF that was used for the experiment.

Oxygen difluoride can be made to react with hot mercury to form mercury(II) fluoride and with platinum powder it will react at 473 K (200 °C) to form PtF_4 and O_2 .

The reaction of OF_2 with NO_2 leads to a mixture of NO_2F , NO_3F , and O_2 , and the proportions of products depend on the operating pressure. At low pressure, this is a useful method for preparation of NO_2F .

The thermal reaction between OF_2 and NO_2 was studied at 333–353 K (60–80 °C) [102]. The reaction took place with a pressure decrease, one mol of OF_2 being used up for each two mols of NO_2 . The reaction products varied with the total operating pressure and consisted of NO_2F , NO_3F , and O_2 . In the case of extremely high pressure, only the two fluorides and no O_2 are formed, the pressure change being 50% of the initial NO_2 content when using an excess of OF_2 . At very low pressure, only NO_2F and O_2 are formed in the mol ratio 4 : 1. The rate-determining step of the overall reaction is a bimolecular reaction:



with

$$k = 1.28 \times 10^8 e^{(-14475/RT)} \text{ L mol}^{-1} \text{ s}^{-1}$$

Liquid OF_2 does not react with liquid ozone. Liquid OF_2 has been tested as a non-reactive solvent for ozone.

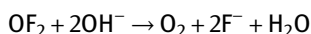
The reaction of OF_2 with nitrosyl fluoride, FNO , resulted in a mixture containing FNO_2 , F_2 , NF_3 , and O_2 [103]. No ONF_3 was detected as a major product. Likely mechanisms to account for the formation of the observed products have been proposed on

the basis of high-level *ab initio* computations. According to those *ab initio* calculations, OF₂ should react in a bimolecular reaction with FNO forming either **(1)** FNO₂ and F₂ directly or **(2)** forming the peroxide species F₂N—O—O—F as an unstable intermediate, which then decomposes in a unimolecular reaction to yield NF₃ and O₂. Using quantum chemical calculations, the likely intermediate compound F₂N—O—O—F was shown to possess a true minimum on its potential energy surface and the structure and vibrational data of F₂N—O—O—F were calculated.

2.4.4.1 Hydrolysis of Oxygen Difluoride

The freshly synthesized OF₂ gas must be carefully dried prior to storage because it may slowly hydrolyze (corrosion by HF) or water (ice) crystals may cause clogging of orifices if liquid OF₂ is pumped into a rocket engine.

The basic hydrolysis of oxygen difluoride has previously been studied [104], but under such conditions that the rate-controlling step was the rate of dissolving of the gas in the water rather than the rate of hydrolysis when in solution. The hydrolysis of OF₂ follows the reaction

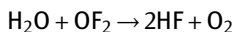


Oxygen difluoride does not behave as the anhydride of an acid. It has only a low solubility in water or even in cold 40% KOH. The progress of the hydrolysis of dissolved OF₂ in water was monitored with an ion-selective fluoride electrode and a pH electrode (which being a glass electrode, could only be used for pH up to 11) [105]. Runs were made with buffered solutions at preselected pH or with NaOH solutions. The presence of ions other than OH[−] in the buffered solutions had little or no influence upon the rate of hydrolysis of OF₂. At constant pH and temperature the rate was directly proportional to the concentration of OF₂. The rate equation may be written as

$$d[\text{OF}_2]/dt = -k[\text{OF}_2][\text{OH}^-]^{1/3} - 0.0105$$

where *k* is time was measured in seconds. The straight line in a graph (not shown) corresponded to *k* having a numerical value at 293 K (20 °C) of 4.1×10^{-3} where time is in seconds and concentrations are in mol/L.

Water steam reacts with oxygen difluoride producing mainly hydrogen fluoride and oxygen



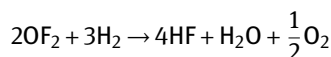
The reaction is exothermic. At the conditions of a premixed burner similar to the one used for fluorine/steam flames, the components did not ignite spontaneously, but when properly initiated the reaction proceeded with a flame [106]. The burner used consisted of two concentric tubes. The inner tube was copper or stainless steel with an i.d. = 0.40 or 0.50 cm and a wall thickness of about 0.2 mm. The outer tube had an i.d. of 1.90 cm and was made of brass or Pyrex glass. Both steam and oxygen difluoride

were preheated to about 373 K (100 °C). The oxygen difluoride-steam diffusion flame was stable and weakly luminous.

2.4.4.2 Oxygen Difluoride/Hydrogen Reactions

The oxygen difluoride/hydrogen reaction is potentially useful in chemical lasers. The kinetics of the $\text{OF}_2 + \text{H}_2$ reaction was studied at 383–463 K (110–190 °C) in a flow reactor with helium dilution [107]. Oxygen at or in excess of 5 mol-% inhibited the reaction. This reaction had a significant heterogeneous component and is dependent on the reactor material.

The kinetics of the $\text{OF}_2 + \text{H}_2$ reaction in the temperature range of 383–493 K (110–220 °C) at 1 atm total pressure was studied in a Monel stirred-flow reactor with helium as the carrier gas [108]. The products approximate stoichiometry was represented the equation



The rate was strongly inhibited by oxygen and was unaffected by the other products. The reaction was first order with respect to oxygen difluoride.

The kinetics of the $\text{OF}_2 + \text{H}_2$ reaction was further studied in the temperature range of 433–583 K (160–310 °C) at 1 atm total pressure in a magnesium stirred-flow reactor with helium as the diluent [109].

2.4.4.3 Oxygenyl Fluoronium Salts

Oxygen difluoride may be used as the starting product for formation of oxygenyl fluoronium salts. These are potential rocket propellant or gas generant oxidizers. Dioxygenyl fluoronium salts are described in the section “Dioxygenyl(II) Complex Fluoride Salts”.

2.4.5 Analysis of Oxygen Difluoride

The reaction of OF_2 with mercury or potassium iodide can be used to analyze the assay of OF_2 samples [110, 111]; however, both reagents will also respond to free fluorine that may be contained in the OF_2 sample as a contaminant. For the quick and less sophisticated detection of OF_2 in the air in rocket test sites a gas detection tube has been developed that contains potassium bromide and fluorescein on a silica gel carrier. The reaction with OF_2 (or many other oxidizers) liberates bromine that converts fluorescein to eosin and produces a distinct color change [112]. The length of the colored zone is proportional to the quantity of oxygen fluoride. Optimum conditions for the determination were established.

Mixtures of OF_2 with NF_3 , CF_4 , SiF_4 , N_2 or O_2 can be analyzed by GC on a silica gel column which was dried and desorbed by first heating to 1173 K (900 °C) and then coated with 30% halocarbon oil and proved to be sufficiently resistant to the mostly

very aggressive gases, while still giving good separations. The retention volumes of a series of inorganic gases on this column were measured and the height equivalent to a theoretical plate (HETP) calculated [113].

Oxygen difluoride and other even more corrosive oxidizers can be analyzed by mass spectrometry in a mass spectrometer that was modified by removing all glass parts and replacing them with Monel and Teflon [114]. Oxygen difluoride mass spectra displayed rhenium oxyfluorides as the result of sample corrosive interaction with a rhenium filament in the source.

A GC method was used for purification of commercial OF_2 containing O_2 and CF_4 [115]. Components in GC effluent gases were determined and identified. Pure OF_2 was collected in a cold trap and subsequently used for calibration of mass and IR spectrometers and physical measurements.

Quantitative and qualitative analysis of OF_2 was possible by GC through a $1\text{ m} \times 0.25\text{-in.}$ copper column filled with 40–60 mesh silica gel, helium as carrier gas and a thermal conductivity detector, except that OF_2 and CF_4 were not separated [116]. The possible CF_4 content would have to be determined by IR in a separate analysis.

The adsorption of OF_2 on SH-functionalized $\text{B}_{24}\text{N}_{24}$ or $\text{B}_{24}\text{P}_{24}$ nanocages has been evaluated theoretically as a potential sensor for OF_2 detection in the gas phase, but this work lacks experimental verification [117].

2.5 Handling of Oxygen Difluoride

2.5.1 Materials of Construction for Oxygen Difluoride

The selection of materials of construction for OF_2 systems is relatively easy. At room temperature, the dry gas does not attack glass, quartz, or metals. It can be stored in glass vessels in the gaseous or liquid state. Vessels containing liquid OF_2 should be hermetically sealed from the atmosphere to prevent escape of OF_2 vapors and to prevent intrusion of atmospheric moisture.

All components for OF_2 use must be thoroughly cleaned and degreased before they come into contact with OF_2 . Once the system is assembled and leak-checked, it can be gradually passivated with either diluted elemental fluorine or OF_2 .

There are several good design manuals for OF_2 systems which contain detailed information on material compatibility and system design and operating instructions, such as cleaning and passivation [19, 20, 48].

2.5.1.1 Compatibility of Metallic Materials of Construction with Oxygen Difluoride

Most metals react with OF_2 only after they are heated to several hundred degrees C. Polished, shiny copper will tarnish when heated in OF_2 . Most metals such as stainless steel, copper, aluminum, Monel or nickel can be used for OF_2 service up to a temperature of 473 K (200 °C). Above this temperature the suitability of a metal has to be tested from case to case. Anodized aluminum has been used for parts that come

in contact only with gaseous OF_2 such as in pressurant lines or vent lines. Venturi orifices for OF_2 were made from CRES-303. Nickel or copper were used for injector heads in rocket engines operating on OF_2 oxidizer.

The corrosive attack is accelerated when materials are immersed in a rapidly flowing liquid at high pressure, or when bubbles in the flowing liquid impinge on the surface, thus preventing the maintenance of a passivating layer. A simple rotation of the specimen is not satisfactory for investigating corrosive attack at such high velocities because the liquid tends to move with the specimen, and the actual rate of liquid movement with respect to the metal surface is not definitely known. An apparatus was developed to conduct accelerated corrosion tests of materials with fluorine oxidizers at cryogenic temperatures. It consisted of a closed loop with a diaphragm pump inserted in a cryostat. Rapidly flowing OF_2 flowed through an orifice made of the test material and impinged on a coupon of the same material to see if immediate reaction or slow corrosion would take place. A number of structural alloys were selected from materials that had shown good corrosion resistance in long-term immersion corrosion tests. Test times ranged from 8 to 30 min. Tests with O_3F_2 in LOX were run in the same apparatus. A wide range of metals was tested for compatibility with flowing OF_2 in the gaseous or liquid state, including Al-1100-0, Al-2014-T6, Al-6061-T6, CRES-316, CRES-347, Ni-200, Monel-400, columbium, and Cufenloy 40A [118]. The effect of flow velocity on corrosion rate was most pronounced with Al-1100-0 and barely noticeable with Monel. Orifice diameters eroded and increased with the less compatible materials and erosion damage in the impingement area was obvious, but no immediate ignition took place.

The static corrosion rates of metals and alloys in fluorine-containing oxidizers at cryogenic temperatures are small due to the formation of passivation fluoride films. Low corrosion rates are difficult to measure with conventional methods since the total mass change is very small. The corrosion resistance of platinum, copper, nickel, and tantalum in liquid OF_2 was estimated from changes in solution capacitance and conductance between two plates of these materials [119]. Capacitance and electrical conductivity increased as the result of film formation and dissolution of metal ions. Both comparisons indicated that Ta was more susceptible to corrosion than Ni. A marked increase in capacitance and a decrease in solution resistance between Ta electrodes occurred when the temperature of OF_2 was increased from 117 to 181 K (-156 to -92°C). Therefore, an appreciable increase in corrosion attack of tantalum by OF_2 was to be expected at the higher temperatures. For comparison, the corrosion rates of metals in OF_2 determined by mass change measurements were given, as shown in Table 14.

Impact sensitivity, static immersion corrosion rates, susceptibility to stress corrosion, corrosion in flowing liquids and effects of weldments and impurities on corrosion of OF_2 in contact with various materials of construction were tested and the results of tests were presented in a form that should be useful to rocket designers [120, 121]. Three stainless steels, 301 (full hardened), 316 (annealed), and 347 (annealed) were stressed and exposed to OF_2 for 21 days at 194 K (-110°F). No stress corrosion

Table 14: Corrosion rate of metals in liquid oxygen difluoride at 194 K (−110 °F).

Material	Test duration				Test duration			
	1 Day	21 Days	4 Months	1 Year	1 Day	21 Days	4 Months	1 Year
	mil per year ^a				μm/year			
Copper	0	0.01	0.005	0.0007	0.000	0.254	0.127	0.018
Nickel	0.9	0.02	0.002	0.0007	22.86	0.508	0.051	0.018
Tantalum	—	0.02	—	—	—	0.508	—	—

^a 1 mil = 1/1000 of an inch

Data source: [119; 120]

failure occurred. Three welded aluminum alloys were stressed to or beyond their yield strength (0.2% offset) and exposed to OF₂ for 21 days at 194 K (−110 °F) under a pressure varying from 342 to 580 psig. The test coupons were double tensile test specimens in geometry, with one end exposed to the gas and the other to the liquid phase. All specimens were observed to have a narrow band of corrosion attack next to the weld zone. The stressed 2219-T6 welded aluminum alloy failed in the section exposed to the gas phase. None of the other plastically deformed test coupons broke. Studies with impure oxidizer (OF₂ with 1% water addition) were conducted on aluminum alloys, magnesium alloy, columbium, tantalum, stainless alloys, copper, brass, nickel alloys, and titanium alloys. In general, corrosion was considerably accelerated, though not to the extent seen in earlier tests with moist N₂F₄—ClO₃F.

A survey of pretreatment methods for metal surfaces that are to come into contact with OF₂ and other storable propellants suggested that for most other oxidizers special pretreatment is not necessary as long as the surfaces are free of contaminants, but in the case of OF₂ and FLOX it may be advantageous to practice gradual exposure of metal surfaces to the fluorine compound to ensure deactivation of contaminants which may have resisted the cleaning process [122]. Details of a general procedure were given for pretreatment of metal systems to be used with OF₂, ClF₃, or FLOX: **(1)** descale, degrease, dry, and **(2)** deactivate residual contaminants with a controlled fluorination treatment. The recommended fluorination treatment is merely a step in the cleaning procedure and not a deliberate attempt to provide “passivation”. Passivation leads to the formation of protective fluoride films. The thickness and adherence of passivating fluoride films determines corrosion rates during long-term storage. Reports on the compatibilities and corrosion rates of metals and fluorine oxidizers were reviewed.

Crush gaskets can be made from soft copper. Pliable gaskets and O-rings can be made from Teflon. Perfluorinated oils can be used as lubricants. If one wants to measure low pressures with a U-gauge, mercury cannot be used as the manometer fluid because it reacts with OF₂. A layer of a perfluorinated oil may protect the mercury for short-term service.

Flow decay studies examined clogging materials not only in oxygen difluoride, but also in dinitrogen tetroxide (NTO), hydrazine, and diborane, all in the category of space-storable propellants [123, 124]. Liquid oxygen difluoride was flowed through a 0.25-mm (0.010-in.) diameter orifice, a 2–10 μm filter and a 10- μm surface tension acquisition screen, but showed no evidence of flow clogging or flow decay [125]. The propellant was run both neat and doped with contaminants in a controlled way for the orifice and filter test runs. Temperature conditioned runs ranged from 155 to 122 K (–180 to –240 °F). Approximately a 10% variation in flow was noted during a single run for several runs. Some difficulty was experienced in controlling flow. In several runs flow rate increased and then decreased and increased again indicating erratic flow control. The flow control may be inherent in the flow bench or instrumentation. Temperature variations may have been responsible causing changes in density and viscosity; however, in all cases, no trends were apparent which indicated flow clogging or flow decay behavior of oxygen difluoride.

Radioactive tracer test methods that were successfully used to study metals corrosion in N_2O_4 can possibly also be used for OF_2 [126–128]. See also [129, 130].

2.5.1.2 Compatibility of Non-metallic Materials of Construction with Oxygen Difluoride

Fluorocarbon plastics and silicone rubber are suitable for use with OF_2 , and Teflon, polyethylene, and ethylene propylene rubber can withstand a perchloryl fluoride-tetrafluorohydrazine mixture for a short time [131].

Shock sensitivity tests showed that both Teflon and graphite in OF_2 at 194 K (–110 °F) could be exploded with a planar shock wave of 827 MPa (120000 psi), but no reaction took place at 620 MPa (90000 psi) or at 77 K (–320 °F) [120, 132].

Preliminary compatibility experiments have shown that silica filler in conventional elastomer compositions provided a site for progressive attack by OF_2 . To improve the resistance of *cis*-1,4-poly(butadiene) elastomers to attack by OF_2 at low temperatures, it was therefore attempted to replace the silica filler with less reactive substances, for example, alumina [133]. An elastomer was compounded with “fumed” alumina, i.e., submicron alumina produced by condensation of alumina formed in a vapor phase hydrolysis reaction. Dynamic tests (tensile strength and elongation at break in propellant) showed the new elastomer compound to be especially rugged, even at 194.6 K (–78.5 °C). Long-term compatibility tests showed that both relaxed and stressed elastomer compounds did not undergo significant degradation in OF_2 and, moreover, the compound had a very low permeability coefficient at 194.6 K (–78.5 °C).

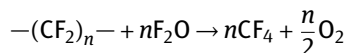
2.6 Disposal of Surplus Oxygen Difluoride

The disposal of surplus OF_2 uses methods similar to those recommended for elemental fluorine. The gas can be diluted with air or nitrogen and then fed into a fuel-rich

methane or propane flame. If the activated charcoal disposal method is used, the charcoal canister has to be preheated externally because the reaction with OF_2 does not start by itself at room temperature. The stack gases of either disposal reactor must be tested periodically with potassium iodide-starch paper for the presence of unreacted OF_2 or F_2 . The USAF has tested OF_2 propellants at Arnold AFB in Tennessee and reported on experience in handling and disposal of OF_2 at rocket test sites [134].

2.7 History of Accidents with Oxygen Difluoride

One phase of a materials compatibility test program consisted of immersion of structural materials in gaseous and liquid OF_2 for short periods of 1 and 21 days, and for longer periods of 4 and 12 months in a dry ice bath at 195 K (-109°F) at a saturation pressure of 3.44 MPa (500 psi). On 15 October 1963, during maintenance of the immersion baths of the long-term test containers, an explosive reaction or deflagration occurred [135]. It was confined to one test bay but resulted in the destruction of the long-term immersion test set-up and caused severe physical injury to the research technician attending to the immersion bath in the test bay. The accidental explosion which resulted in the destruction of the immersion test set-up and severe personal injury occurred while the research technician was replenishing the cold bath with crushed dry ice. Four long-term exposure tests were in progress in the test bay on the day of the accident. Two of them (both exploded) were tests involving OF_2 , and two involved a mixture of 50% perchloryl fluoride–50% tetrafluorohydrazine. The latter ones did not explode. The technician later reported that he felt a tremendous blow and a sensation like a strong electric shock. The ladder was blown from under him, and he was knocked down to the floor of the bay. His boots, shirts, and part of his trousers pants were blown off, and both legs and one arm received severe injuries. He was taken to hospital in a critical condition. There were two distinct explosions approximately 1/10 s apart. This was heard by persons away from the test facility; the technician and the project scientist did not perceive two separate blasts. A violent physical jolt and a flash of light accompanied the detonations. Both OF_2 exposure tests had been destroyed, and fragments of the test bombs and test coupons were strewn over a wide area. From the condition of the Teflon pieces used as a rack to hold the immersed metal samples, it appears that this material was involved in a reaction with oxygen difluoride



This reaction is highly exothermic and gives 4.6 kcal/formula weight. See also reference [136].

2.8 Gelled Oxygen Difluoride

In an effort to reduce the leakage hazard of liquid oxygen difluoride and at the same time improve its ignition characteristics and rocket engine performance, a variety of gelling agents have been tested with OF_2 , including frozen ClF_3 . Chlorine trifluoride is not soluble in liquid OF_2 and microcrystalline, finely dispersed solid ClF_3 suspended in liquid OF_2 can create a gelled propellant with high viscosity [137–140]. During the development, ClF_3 -gelled liquid nitrogen was used as a more inert simulant for the ClF_3/OF_2 gel. It was found that liquid nitrogen gelled with solid chlorine trifluoride possesses static and dynamic flow properties which closely approximate those of the OF_2/ClF_3 gels. Thus, LN_2/ClF_3 gels may be used as suitable simulants for OF_2/ClF_3 gels. The ClF_3/OF_2 gel was found to be chemically and mechanically stable in static tests. Samples of the gel were stored for 30 days. ClF_3 as a volatile gellant has the advantage over fumed silica that it will not leave residues which might clog the injector orifices. Other gelling agents (not using ClF_3) were developed for gelling of B_2H_6 [141].

Inorganic fluorides and oxides were screened as potential gelling agents for OF_2 . Liquid OF_2 was gelled with Alon C, fumed TiO_2 , and Cab-O-Sil fumed silica [142]. The best gel properties were obtained with Cab-O-Sil. Gel samples were evaluated for thermal stability, mechanical stability, evaporation rate relative to ungelled OF_2 , and shock sensitivity. It was later found that OF_2/SiO_2 gels are potentially explosive [143].

Another gelling agent tested was finely divided lithium fluoride with particle lengths of $0.4\text{ }\mu\text{m}$ [144]. The liquid OF_2/LiF gel was thermally stable and shock insensitive but was not stable under flow conditions in a rheometer.

Other gelling agents proposed for non-metallic fluoride liquid oxidizers were barium hexafluoroantimonate and barium hexafluorobismuthate [145].

2.9 Toxic Properties of Oxygen Difluoride

Oxygen difluoride is assumed to pass intact into the pulmonary cells where it reacts with biochemical reducing systems to ultimately cause cell death and structural failure. OF_2 is fairly stable in aqueous systems and would be expected to survive chemically in the atmosphere of the lungs and in the gas transport processes without immediate reaction on pulmonary surfaces. It is soluble enough ($608\text{ mL OF}_2/\text{L}$ of water at $273\text{ K} = 0^\circ\text{C}$) to permit transport into cells in the low amounts evidently necessary for lethal effects. OF_2 degasses quickly from saturated aqueous solutions when its partial pressure in the atmosphere falls. In the course of an exposure, the gas should therefore be present in the lungs only during the period of exposure, leaving a minor amount of HF resulting from the limited reaction of OF_2 with the aqueous phase of the pulmonary membrane complex.

Oxygen difluoride is very toxic and must be handled with the same precautions as elemental fluorine. In some instances, it has been observed that OF_2 is actually more

toxic than F_2 . Ruff and Menzel [17] attributed this to the fact that OF_2 initially dissolves in the tissue and diffuses to the lower layers before it hydrolyzes and unfolds its toxic action, whereas with elemental fluorine the action is limited to the surface and the tissue forms a scar layer. Inhalation of an aerosol of calcium chloride or magnesium acetate solution has been recommended as a first aid measure in the treatment of OF_2 victims. The olfactory threshold of OF_2 in air is 0.1 ppm and it can be recognized by its odor at 0.5 ppm. Based on animal tests with rats, the LC50 after a 5-min inhalation was 20 ppm, and after a 20-min inhalation it was 5 ppm [146, 147]. Chronic inhalation of 0.5 ppm OF_2 in rats caused some casualties. Chronic long-term inhalation tests with rats (6 h/day, 5 days/week, cumulative exposure of 165 h) at 0.1 ppm OF_2 did not cause any adverse effects. In order to maintain sufficient margin of safety, it is recommended to keep the working place concentration below 0.005 ppm [148]. There are analytical instruments available that can detect fluorine and OF_2 at very low levels.

The acute inhalation toxicity of oxygen difluoride in the albino rat has been determined at concentrations of 5–40 ppm for 5–15 min [149]. A concentration $\times$ time (CT) product (ppm-min) of about 100 results in 50% mortality. At the levels studied, gross and microscopic pulmonary damage developed 7 h after termination of the exposure, and, if death did not intervene, repair began after the third day. The extreme toxicity of oxygen difluoride and its insidious character make it imperative to exclude any potential for inhalation by personnel in the laboratory.

Oxygen difluoride exposures of groups of rats were made in an $18 \times 18 \times 27$ in. aluminum chamber fitted with transparent Kel-F view ports and lined with Teflon-surfaced glass cloth [150, 151]. Groups of 10 rats were exposed to 15 ppm (by volume) OF_2 for 10, 15, 22.5 or 34 min and observed for up to 5 days afterwards. The survival time was measured and ranged from 2 to 37 h (and a few survivors at 5 days) in the 10-min group and from 0.2 to 5.7 h in the 34-min group. Groups of 4 rats were exposed to 30 ppm OF_2 for 10, 15 or 22.5 min and survival times ranged from 3 to 4 h in the 10-min group (no survivors) and 0.3–3.6 h in the 22.5 min group (no survivors). Tissue and blood samples were taken from deceased and surviving animals and analyzed for fluoride content. Clinical chemistry observations showed little change over a 20-h period following OF_2 exposure for 10 min at 15 ppm. This dose was high enough that a few animals of the series observed died before they could be sampled. Blood glucose rose moderately and remained somewhat higher than normal for the entire period of observation. The limited damage found in organs and tissues other than the lungs indicated that OF_2 had not achieved more than limited distribution, but reacted primarily in the pulmonary cells.

Four species of animals (monkeys, dogs, rats, and mice) were exposed to various concentrations of 8, 16, 21, and 32 ppm OF_2 in air for 15 or 60 min [152]. The acute effects of OF_2 inhalation were shown mainly to be respiratory in nature. Tachypnea was the most prominent toxic sign observed in rodents. Upper respiratory and gastrointestinal tract irritations were observed in dogs and monkeys. The mortality response demonstrated a significant difference in the susceptibility of the various species to

Table 15: Mortality LC50 for oxygen difluoride inhalation in four animal species.

Animal species	LC50, ppm by volume		CT dose, ppm × min	
	60 Min	15 Min	60 Min	15 Min
Mouse	1.5	7.5	90	113
Rat	2.6	12.7	156	191
Dog	26	90	1560	1350
Monkey	26	108	1560	1620

Data source: [152]

the toxic effects of the gas. Rats and mice were found to be much more susceptible than monkeys or dogs (Table 15). In mice a certain amount of tolerance developed if the animals were conditioned in 1 ppm OF₂ for 1–7 days prior to a 1–8 day exposure to 3.5–4.25 ppm which produced some mortality. There was no tolerance developed in animals preconditioned at 0.25 or 0.5 ppm prior to the more severe exposure.

The lungs of rats exposed to OF₂ were examined by light and electron microscopy [153]. The exposures were for 30–60 min to an average of 4.5 ppm OF₂, the minimal lethal dose. Animals were sacrificed after 30 (group 1) and 60 min (group 2) exposure and 1 (group 3) and 2h (group 4) following 60 min exposure. Mild gross changes were observed in groups 3 and 4, but no light microscopic visible lesions were found. Alterations were noted in all four groups using electron microscopy. These were mostly indicative of fluid change and consisted of blebbing of the endothelial and epithelial layers of the alveolocapillary wall and rarefication of the cytoplasm of these cells. The lamellar bodies of the type II cells showed an increasing and consistent loss of matrix structure and density. These fine structural changes increased in quantity and severity as time of exposure or post-exposure period increased.

In about 1968, a student was transferring OF₂ vapor from a 1-lb tank to his apparatus through Tygon tubing that had been cleaned with benzene, but the tubing ignited and the tank fell on the floor, bending the shut-off valve while gas was still leaking. The student went to a workbench to grab a wrench and shut the valve, but by then most of the gas had leaked out. The student was sent to a hospital and developed severe lung edema and was put on oxygen when he had trouble breathing. The lung edema resolved after 3 days and the patient was released from the hospital after 10 days. It was estimated that he had breathed 1000 ppm for 2–3 min which by all estimates should have been fatal. Other people in the building were exposed to smaller concentrations as the gas diffused through the building but they did not need hospitalization [154].

Raw toxicity data of inhalation toxicity tests with mice, rats, guinea pigs, and rabbits are summarized in Table 16.

The acute toxicity data for oxygen difluoride are summarized again in Table 17, including some of the data already referenced individually above.

Table 16: Inhalation toxicity of oxygen difluoride.

Concentration ppm	Duration h	Mortality, %			
		Mice	Rats	Guinea pigs	Rabbits
10	1.0	7	8	15	0
10	1.5	20	100	50	0
10	2.0	74	100	90	0
10	2.5	100	100	100	0
10	3.0	100	100	100	25
10	4.0	100	100	100	88
10	4.5	100	100	100	100
5	1.0	0	4	0	0
5	2.5	0	28	0	0
5	3.0	0	28	20	0
5	3.3	10	88	67	0
5	4.0	50	96	87	0
5	4.5	50	100	100	0
5	5.0	80	100	100	13
5	5.5	90	100	100	43
5	7.0	100	100	100	100
1 (26 h elapsed)	7	100	100	100	100
1	9	75	40	—	—
0.5	15.25	5	—	—	—
0.5	28.75	—	10	—	—

Data source: [155]

Table 17: Acute toxicity data and lethal concentration data of oxygen difluoride.

Species	LC50 (ppm)	Duration	Adjusted 0.5–h LC (CF)	Derived value
Rat	2.6	1 h	3.3 ppm (1.25)	0.3 ppm
Mouse	1.5	1 h	1.9 ppm (1.25)	0.2 ppm
Dog	26	1 h	33 ppm (1.25)	3.3 ppm
Monkey	16	1 h	20 ppm (1.25)	2.0 ppm

Data source: [156, 157]

The recommended maximum tolerable concentrations of OF₂ in workroom air are: NIOSH REL: 0.05 ppm (0.1 mg/m³) ceiling; OSHA PEL: 0.05 ppm (0.1 mg/m³) TWA; 1989 OSHA PEL: 0.05 ppm (0.1 mg/m³) ceiling; 1993–1994 ACGIH TLV: 0.05 ppm (0.11 mg/m³) ceiling [158]. At one time the National Research Council (NRC) Emergency Exposure Limits (EELs) recommended to military and space agencies were: 10-min EEL: 0.5 ppm; 30-min EEL: 0.2 ppm; 60-min EEL: 0.1 ppm. The NIOSH revised IDLH was 0.5 ppm.

2.10 Detonability Properties of Oxygen Difluoride

Oxygen difluoride is not shock sensitive. Tests using Trauzl block techniques indicated that OF_2 is insensitive to shock at 77 K (-196°C). The cavity volume of the lead block increased 40%, which is more than with a blank test with water (17%), most likely due to a chemical reaction between the OF_2 and the lead. For comparison, the cavity volume increase with RDX was 130%. A cylinder of liquid OF_2 was subjected to a bullet impact test which ruptured the cylinder but failed to detonate the OF_2 [159].

3 Dioxygen Difluoride

Dioxygen difluoride, O_2F_2 , $\text{F}-\text{O}-\text{O}-\text{F}$, oxygen subfluoride, perfluoroperoxide, dihydroxydifluoride, dioxydifluoride, CAS RN [7783-44-0] is not very stable and cannot be used as a rocket propellant. It is included in this book only as an intermediate in the synthesis of other fluorine oxidizers or as a decomposition product of higher multi-oxygen fluorides. There is a lot of interest in trioxygen difluoride (“ozone fluoride”) as a means to hypergolize LOX, and O_2F_2 is either a byproduct of O_3F_2 preparation or the end product of O_3F_2 or O_4F_2 decomposition. This is why this chapter on O_2F_2 was added to this book at this point. Dioxygen difluoride has received a lot of attention from atmospheric chemists because a free radical derived from O_2F_2 , the free radical $\cdot\text{OOF}$ is suspected of playing a role in the ozone layer destruction in the upper atmosphere of Earth where it forms in the photolysis of man-made fluorocarbons that leaked from refrigeration units and cosmetic aerosol sprays. $\cdot\text{OOF}$ is relatively stable and there are more publications on $\cdot\text{OOF}$ than on O_2F_2 itself.

3.1 Preparation of Dioxygen Difluoride

Dioxygen difluoride, O_2F_2 forms as an orange liquid if one passes a equimolar mixture of oxygen and fluorine at 2000–2660 Pa (15–20 mm Hg) and 83 K (-190°C) through a glow discharge [160, 161]. The formation of dioxygen difluoride from the elements in a glow discharge was investigated at a pressure of ~ 1 mm Hg, current strengths 10, 20, and 40 mA, and gas velocities from 0.4 to 11 L/h [162–164]. The amount of O_2F_2 obtained was proportional to the volume velocity of the gases. The dependence of the degree of conversion on the fluorine-oxygen mixture ratio and specific energy was established. A stationary value of the degree of conversion for these experiments is reached at a specific energy of ~ 30 Wh/L. A scheme of formation of dioxygen difluoride in a discharge was proposed.

The destruction of the ozone layer in Earth’s stratosphere as the result of halocarbon atmospheric pollution involves reactions of $\text{FO}\cdot$ and $\text{FOO}\cdot$ radicals. The photochemical reaction of F_2 and O_3 was studied at 195 and 120 K in order to test for the

presence of the $\text{FO}^\bullet$ radical [165]. The product composition was dependent on operating temperature. In experiments at 120 K, a gaseous mixture of F_2 and O_3 was UV-irradiated at 3660 Å for 4 h. After irradiation, the reaction vessel contained a colorless gas and a yellow deposit on its walls, and the gas consisted of OF_2 , O_2 , and F_2 . O_3 was no longer detected. The yellow deposit was soluble in CClF_3 . An electron paramagnetic resonance (EPR) spectrum of the solution was identical with a solution of O_2F_2 , namely that of the $\text{FOO}^\bullet$ radical. The yields of O_2F_2 and OF_2 were 36 and 20%, respectively. In additional experiments at 195 K, irradiated mixtures of F_2 and O_3 yielded only OF_2 , and O_2F_2 was not detected.

Dioxygen difluoride can be prepared by photosynthesis directly from the elements by illuminating a liquid mixture of oxygen and fluorine with UV light at 77 K (−196 °C) [166].

Low-energy pathways of the reaction $\text{F}_2 + \text{O}_2 \rightarrow \text{O}_2\text{F} + \text{F}$ or O_2F_2 through excitation of F_2 or O_2 in a frozen oxygen matrix were measured as a function of laser irradiation frequency [167]. The F_2 absorption detected in this experiment extended more than 200 nm to longer wavelengths than any electronic absorption of molecular difluorine reported so far.

When $\text{F}^\bullet$ atoms produced by a microwave discharge through NF_3 in argon carrier gas were codeposited with O_2 in an argon matrix at 14 K, prominent IR absorptions, including several overtone and combination bands of $\text{FO}_2^\bullet$ and of O_2F_2 were found [168].

Dioxygen difluoride is not alone with its X_2O_2 structure in the family of halogen oxides. The other halogen oxides and their ions and radicals are also known and their structures have been compared to that of O_2F_2 [169].

The plasma chemistry in an O_2/F_2 low-pressure high-density discharge and the plasma parameters, electron temperature T_e , DC plasma potential V_{pl} , electronegativity as well as the densities of the reacting species were calculated as a function of F_2 content and discharge pressure in the pressure range 0.13–13 Pa (1–100 μm Hg) [170]. The difluorine is highly dissociated. The prevalence of fluorine atoms increased as F_2 was added to the discharge and for mixtures with ~35% F_2 atomic fluorine $\bullet\text{F}$ was the dominating species in the discharge. The dominant positive ions changed from O^+ and F^+ at low pressure (<0.67 Pa = <5 μm Hg) to O^{2+} and F^{2+} at high pressure (>6.7 Pa = >50 μm Hg).

Dioxygen difluoride (O_2F_2) can be produced directly in the liquid phase at temperatures above 119 K (−154 °C) [171]. An O_2/F_2 gas mixture was heated to 973 K (700 °C) and was then rapidly cooled on the outer surface of stainless steel cold fingers refrigerated by a liquid oxygen bath pressurized to >1 MPa with helium. This produced 6 g of O_2F_2 in less than 1 h. Color of the viscous liquid in the O_2F_2 generator ranged from copper red to straw yellow. Different O_xF_y compounds existed simultaneously on the tubes. Audible “pings” and pressure excursions occurred when liquid O_2F_2 was dripped onto uncooled portions of the apparatus and decomposed spontaneously.

Several low-temperature oxygen fluorides that are stable only at cryogenic temperatures were synthesized and their mass spectra were studied between 77 and 260 K, but neither the parent ion of O_2F_2 , O_3F_2 or O_4F_2 nor the unambiguously assignable fragment ions of O_3F_2 or O_4F_2 were observed [172]; however, the appearance potentials of O_2F^+ and OF^+ were measured to be 14.0 eV and 17.6 ± 0.2 eV, respectively, at 130 K. These values were consistent with other related data and indicated that these ions were produced by electron impact fragmentation of O_2F_2 .

3.2 Physical Properties of Dioxygen Difluoride

Dioxygen difluoride is not very stable and decomposes even at 223 K (-50°C) in reversal of its formation. Because it decomposes so rapidly, the boiling point of this compound could not be determined by direct measurement, but it had to be extrapolated from vapor pressure curve measurements up to 216 K (-57°C). The orange color of the condensate can give rise to confusion with other O_xF_y compounds, such as trioxygen difluoride O_3F_2 that forms under the same conditions but is obtained by starting with a different $\text{F}_2:\text{O}_2$ ratio. Other differences between the two compounds are the melting points (O_2F_2 m.p. 109.6 K = -163.5°C ; O_3F_2 m.p. 82.2 K = -190.9°C) and the densities (O_2F_2 ρ_{liq} at 216 K = -57°C : 1.45 g/cm³; ρ_{solid} at 108 K = -165°C : 1.912 g/cm³, O_3F_2 ρ_{liq} at 90 K = -183°C : 1.756 g/cm³). Because of its lack of thermal stability, O_2F_2 is not useful as a rocket propellant. Nevertheless, we are summarizing here some of its properties because O_2F_2 may serve as an intermediate in the synthesis of other oxygen fluorides or it is encountered as a decomposition product of some of the other polyoxygen fluorides.

Pure O_2F_2 is an orange solid melting at 109.7 K. It is thermally unstable and decomposes to oxygen and fluorine in the neighborhood of its boiling point at 216 K.

3.2.1 Optical Properties of Dioxygen Difluoride

In the visible/UV spectrum, the maximum absorption of O_2F_2 at 140 K is at 360 μm . It changes color with temperature.

The infrared spectrum of solid O_2F_2 , produced by radiolysis of a mixture of liquid O_2 and F_2 , has been obtained at 77 K [173]. With the help of isotopic labeling, all fundamental vibrations could be located and assigned. The results showed that the O—O bond in O_2F_2 has considerable double bond character, resembling O_2 more than it does H_2O_2 , and having a significant barrier to internal rotation. There is considerable participation of the fluorine p electrons in the bonding orbitals.

A complete absorption spectrum of gaseous dioxygen difluoride was obtained using a very long path length, temperature-programmable cell and an FT-IR spectrometer [174]. All six fundamental vibrational frequencies were deduced from three fundamental bands and four binary combination bands. A significant deviation of the ν

frequency was observed from the matrix studies of solid FOOF. All data indicated that O_2F_2 is a linear molecule and does not exist in the branched $\text{O}=\text{OF}_2$ form.

The unusual bond lengths in FOOF were compared to the structure of FNNF in an effort to explain the electronic structure of σ -bonds and π -bonds in these molecules [175]. If a double-quartet modification of the octet rule is used, ten structures, including semipolar bonds, would be possible for this molecule, assuming that around every atom, the four electrons of a given spin have a tetrahedral arrangement. Structures are favored that (a) have small formal charges on the atom, and (b) reduce interelectron repulsion. Formal charges of $+1/2$ and $-1/2$ on oxygen and fluorine would seem to be allowable energetically.

Photolysis of F_2 and O_2 suspended in solid N_2 , Ar or O_2 produced IR absorptions of an oxyfluoride other than OF_2 and O_2F_2 [176]. Isotopic labeling, concentration dependence, diffusion behavior, and normal coordinate analysis permitted assignment of these bands, at 1499.7, 586.4, and 376 cm^{-1} , to the free radical or cation O_2F . On diffusion at low temperatures, this molecule formed only loosely bound aggregates, $(\text{O}_2\text{F})_n$, though it is a free radical. Normal coordinate analysis showed that the O—O bond of O_2F is a double bond, like those in O_2 and in O_2F_2 and that the O—F bond is much weaker than those in OF_2 . Thus, O_2F resembles O_2F_2 in its bonding.

3.2.2 Magnetic Properties of Dioxygen Difluoride

The chemical shift of ^{19}F in O_2F_2 is unusually low. A dilute solution of O_2F_2 in CF_3Cl showed a single peak at 865 ± 10 ppm. The peak position relative to that of CF_3Cl did not change much with temperature in the range 193–143 K (-80 to -130°C). Dioxygen difluoride contains a paramagnetic species ($\bullet\text{OOF}??$). Exchange between $\bullet\text{OOF}$ and FOOF could explain the line shift and also the line width of the NMR signal. It was concluded that either no exchange is taking place, or that the concentration of free radicals is much too low to greatly affect the NMR spectrum [177].

The ^{19}F NMR spectra of liquid O_2F_2 were already discussed in the OF_2 section [86]. The shifts of O_2F_2 and O_3F_2 were the furthest downfield of any simple fluorine compound yet reported.

3.2.3 Thermodynamic Properties of Dioxygen Difluoride

Thermodynamic properties of O_2F_2 were included in earlier tables where it was listed along with the other oxygen fluorides. A very detailed summary of thermophysical properties of O_2F_2 is available in [12] and [178]. The most recent recommended value for the standard enthalpy of formation of O_2F_2 gas was $-19.163\text{ kJ/mol} = -4.58 \pm 0.2\text{ kcal/mol}$. The data for ΔH_f and ΔG_f in the Lyman paper may be too low by 5.65 kJ/mol . Other sources [4] give the heat of formation as $+4.73 \pm 0.30\text{ kcal/mol}$.

The NIST-JANAF thermochemical table values for the thermochemical properties of oxygen fluorides issued in 1996 were critically examined on the basis of high-level density functional and *ab initio* G2 calculations [55]. Special attention was given to the

enthalpies of formation and it was concluded that although the proposed values for $\text{OF}(\text{G})$, $\text{FOO}(\text{G})$, and $\text{FOF}(\text{G})$ are reasonable and in agreement with previously recommended values, the enthalpy of formation recommended for FOOF is too low. Instead, a value about 50% larger was proposed and it was recommended that the original 1959 experimental determination of this enthalpy of formation should be repeated.

3.2.4 Molecular Structure of Dioxygen Difluoride

The vibrations and microwave absorption spectra lines of O_2F_2 were assigned by isotope labeling and demonstrated that the structure is a chain, $\text{F}-\text{O}-\text{O}-\text{F}$, with the structural parameters: $r(\text{O}-\text{O}) = 1.217 \pm 0.003 \text{ \AA}$, $r(\text{F}-\text{O}) = 1.575 \pm 0.003 \text{ \AA}$, $\angle\text{OOF} = 109^\circ 30'$, and dihedral angle $= 87^\circ 30'$ [179]. The $\text{O}-\text{O}$ distance is particularly short and the $\text{O}-\text{F}$ distance is particularly long. The oxygen-oxygen distance $r(\text{O}-\text{O})$ in OF_2 is much shorter than in H_2O_2 and $r(\text{O}-\text{F})$ is much longer than in OF_2 . The fact that $r(\text{O}-\text{O})$ in OF_2 is very similar to that found for the dioxygen molecule indicated that there must be some multiple bonding between the two atoms. The barrier to internal rotation must be fairly high. The dipole moment of the molecule as derived from measurements of the Stark effect was $1.44 \pm 0.04 \text{ D}$.

The structure of O_2F_2 is a non-linear $\text{F}-\text{O}-\text{O}-\text{F}$ chain with an $\angle\text{OOF}$ angle of $109^\circ 30'$, a dihedral angle of $87^\circ 30'$, an $\text{O}-\text{O}$ bond length of $1.217 \text{ \AA}$, and an $\text{F}-\text{O}$ bond length of $1.575 \text{ \AA}$. Infrared spectra help to determine the molecular structure and the bond energies in the gaseous O_2F_2 molecule [174]. All data indicated that O_2F_2 is a linear molecule and does not exist in the branched $\text{O}=\text{OF}_2$ form.

Equilibrium structures of $\bullet\text{OOF}$, FOOF , OOF_2 , and FOOOF calculated using the density functional theory (DFT) methods were compared with those generated using the *ab initio* calculations and when possible the experimental data [180].

According to some other DFT calculations, the affiliation of lone pair electrons toward the fluorine atom decreased from OF_2 to O_3F_2 as the number of oxygen molecules increased [181]. The strength of $\text{O}-\text{O}$ bond decreased from O_2F_2 to O_3F_2 . The shorter $\text{O}-\text{F}$ bond of O_3F_2 could readily change to longer one and *vice versa* through a transition state with energy barrier of 11.06 kJ/mol . The $\text{O}-\text{F}$ bond is much stronger than the $\text{O}-\text{O}$ bond in O_3F_2 . On the contrary, the $\text{O}-\text{F}$ bond is much weaker than the $\text{O}-\text{O}$ bond in O_2F_2 . O_2F and O_3F can be regarded as weakly bound $\text{OO}-\text{F}$ and $\text{OO}-\text{OF}$ adducts, respectively. O_3F_2 could be regarded as a weakly bound $\text{FO}\cdots\text{OOF}$ adduct. The standard enthalpies and free energies of formation for the binary compounds can be predicted, but experimental verification is lacking in most cases.

3.3 Chemical Properties of Dioxygen Difluoride

3.3.1 Decomposition of Dioxygen Difluoride

Dioxygen difluoride is said to decompose into fluorine and oxygen with a half-life time at 223 K (−50 °C) of 3 h for the homogeneous unimolecular decomposition. The decomposition and many reactions of O_2F_2 and the higher multi-oxygen fluorides O_nF_2 , $n > 2$ involve the dioxygen fluoride $\bullet O_2F$ free radical as an intermediate. The free radical has been characterized by ESR. It may also play a role in the reaction of fluorine with ozone in the upper atmosphere. The ESR spectrum of $\bullet O_2F$ was found to contain normally “forbidden” lines in which the electron spin transition is accompanied by a nuclear spin flip [182].

Electron paramagnetic resonance spectra of O_2F_2 and O_3F_2 both showed identical EPR spectra which could be attributed to the free radical $\bullet OOF$, the concentration being 0.1 and 5 mol %, respectively [183]. In either system the radical is formed as the result of the ongoing decomposition process.

The reactions of fluorine atoms with dioxygen produce (and consume) the species $\bullet OOF$ and O_2F_2 [184]. The fluorine atoms can be produced by photolysis of molecular fluorine with an excimer laser (KrF, 248 nm).

The decomposition of gaseous dioxygen difluoride (FOOF) and dioxygen fluoride $\bullet OOF$ to F_2 and O_2 at ambient temperature has been studied by EPR spectroscopy, Fourier transform infrared (FTIR) spectroscopy and transient gas pressure measurements [185]. EPR spectroscopy detected neither F atoms nor $\bullet OOF$ radicals as intermediates despite the presence of $\bullet OOF$ radicals shown by complementary FTIR experiments. The FTIR spectra of gaseous FOOF undergoing decomposition at ambient temperature showed prominent, isolated bands near 1210 cm^{-1} (FOOF) and near 1490 cm^{-1} ($\bullet OOF$). Oxygen-carrier FTIR experiments strongly suggested that a reversible reaction between FOOF and O_2 forms $\bullet OOF$, and that this reaction was rapid relative to FOOF/ $\bullet OOF$ decomposition.

The equilibrium between dioxygen monofluoride $\bullet OOF$, dioxygen difluoride FOOF, and dioxygen O_2 has been studied in the temperature range 286–195 K and forward and reverse reaction rate constants were determined [186]. An activation energy of 54.4 kJ/mol (13 kcal/mol) was found for both reactions. The equilibrium constant in the middle of the temperature range was 21.5. The estimated heats of formation of gaseous $\bullet OOF$ and FOOF were +10.9 and 18.8 kJ/mol (+2.6 and +4.5 kcal/mol), respectively.

3.3.2 Reactions of Dioxygen Difluoride

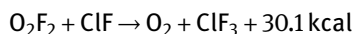
Dioxygen difluoride can undergo a wide range of reactions with inorganic and organic reactants [187–189]. Liquid O_2F_2 reacted vigorously when added to solid anhydrous ammonia at temperatures close to 110 K. It caused explosions when added to water ice

at 130–140 K and reacted also with traces of water if dissolved in HF containing H₂O at 195 K, the brown color of the solution disappearing and O₂ gas escaping.

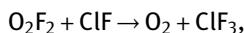
Investigations of the chemical reactions of O₂F₂ and other oxygen subfluorides were made in an effort to discover new reactions leading to solid oxidizers containing oxygen and fluorine [190].

Two new oxygen fluorides, O₅F₂ and O₆F₂, were discovered and methods of preparation and some of the properties of these new oxygen fluorides were described [191, 192]. Synthesis of polyoxygen difluorides by electrical discharge in the liquid phase or ultraviolet irradiation was accomplished. Thermal stability, sensitivity, solubility, and the EPR spectrum for O₅F₂ were determined. Free radicals play an important role in synthesis and decomposition of oxygen fluorides. Chemical reactions of O₄F₂ and N₂F₄ with O₃ were studied and additional data on solubility of O₄F₂ in LOX of liquid OF₂ were obtained. Diffusion flames of OF₂ with various fuels were obtained and characterized. Attempts were made to synthesize OF₄, which were so far unsuccessful.

Chlorine monofluoride ClF abstracts the fluorine from O₂F₂, forming ClF₃ and liberating O₂. The reaction of O₂F₂ with ClF showed that if the reaction is carried out without special precautions at temperatures above 140 K, the two substances react violently with heat evolution following the stoichiometric equation:



A deep violet compound was obtained by the reaction of O₂F₂ with ClF at 240–119 K (–33 to –154 °C). This compound was a strong oxidizer and was stable at 195 K (–78 °C). It was soluble in anhydrous HF at 195 K (–78 °C) and was not an electrolyte. Its thermal decomposition was suppressed by oxygen. Based on the observed stoichiometry of the overall reaction



the violet compound was postulated to have the composition (ClF₃O₂)_n. The same material was also obtained by the interaction of O₂F₂ with Cl₂ or HCl or by UV photolysis of mixtures of ClF₃ and O₂ at –78 °C [193].

Being a high energy oxidizer, dioxygen difluoride reacted vigorously with organic compounds, even at temperatures close to its melting point. It reacted instantaneously with solid ethyl alcohol, producing a blue flame and an explosion. When a drop of liquid O₂F₂ was added to liquid methane cooled at 90 K, a white flame was produced instantaneously, which turned green upon further burning. When 0.2 mL of liquid O₂F₂ was added to 0.5 mL of liquid CH₄ at 90 K, a violent explosion occurred.

In trying to identify differences in the reactive behavior of O₂F₂ and O₃F₂, each of these compounds was reacted with sulfur dioxide or nitrogen dioxide. This does not make a good rocket propellant, but it helped to understand the differences in reactivity of these two compounds [194, 195]. The reaction of SO₂ with O₂F₂ produced SO₂F₂ and byproducts FSO₂OF and FSO₂OOF. The products of the reaction of O₃F₂ with SO₂ were essentially the same as those obtained with O₂F₂, except that the relative quantities

were different. The mechanism of the formation of these products was studied by the use of NMR analysis of the compounds. The reaction of NO_2 with O_2F_2 did not produce FNO_3 , but only simple fluorination occurred, resulting in FNO_2 .

When running similar experiments with O_4F_2 in comparison to O_2F_2 , a comparison of the products formed in the reaction of SO_2 with O_2F_2 and O_4F_2 showed that the major product in both cases was F_2SO_2 , but the yield was lower in the O_4F_2 reaction [196, 197]. The yield of $\text{F}_2\text{S}_2\text{O}_5$ in the O_4F_2 reaction was also considerably lower than in the O_2F_2 reaction. Perhaps the most interesting observation was the comparison of the yields of FSO_2OOF (5% from O_2F_2 and 32% from O_4F_2). It was concluded that the primary reactions of both O_2F_2 and O_4F_2 are similar, i.e., simple fluorination predominates; however, O_4F_2 appears to be a better source of $\cdot\text{OOF}$ than O_2F_2 .

3.3.3 Dioxygenyl(II) Complex Fluoride Salts

The synthesis of $\text{O}_2^+ \text{PtF}_6^-$, the first known example of a dioxygenyl salt, was reported in 1962 by Bartlett and Lohmann. Since then numerous other O_2^+ salts have been synthesized and studied. These salts are potential oxidizers for high energy solid propellants.

Dioxygen fluoronium and dioxygenyl saline compounds, such as $[\text{O}_2][\text{BF}_4]$ or $[\text{O}_2][\text{PF}_6]$ were obtained from O_2F_2 with Lewis acids [198, 199] and from O_2F_2 with BF_3 or PF_5 [200]. O_2PF_6 is unstable at room temperature, but O_2AsF_6 and O_2SbF_6 are stable under inert gas up to 373 K (100 °C).

Irradiation of mixtures of liquid oxygen and fluorine at 77 K appeared to result in the formation of appreciable yields of ozone difluoride and oxygen difluoride via a short chain reaction [201]. Treatment of the irradiated mixtures with boron trifluoride at 77 K led to the recovery of a white powder, reasonably stable at room temperature in dry air, in amounts from 20 to 250 mg. The powder was identified as $[\text{O}_2^+][\text{BF}_4^-]$ from elemental analysis, paramagnetic resonance and XRD.

The structure of solid $[\text{O}_2][\text{BF}_4]$ and the kinetics of decomposition of this salts were examined using ^{18}F tracer methods and the presence of OOF free radicals during $[\text{O}_2][\text{BF}_4]$ decomposition was theorized [202].

The reactivity of O_2F_2 with other fluorides such as ClF_3 , SbF_5 , BF_3 , MoF_6 , WF_6 , and SiF_4 has been studied in the search for Lewis adducts or ionic salt formation [203].

Both oxygen difluoride and a mixture of oxygen and fluorine react with AsF_5 or SbF_5 to give dioxygenyl salts under moderate pressures and elevated temperatures [204]. Initial attempts to prepare dioxygenyl salts from BF_3 , PF_5 , SiF_4 , BrF_3 , BrF_5 , or IF_5 with OF_2 were unsuccessful. Instead, dioxygenyl tetrafluoroborate was prepared by reaction of O_2F_2 or O_4F_2 with BF_3 at low temperatures [205]. Isotopic tracer studies of the reaction indicated that the compound is dioxygenyl tetrafluoroborate, $[\text{O}_2^+][\text{BF}_4^-]$ rather than a coordination compound, $\text{FO}_2 \rightarrow \text{BF}_3$. It was suggested that O_2F is the intermediate in both the preparation and decomposition of $[\text{O}_2^+][\text{BF}_4^-]$.

Electron spin resonance spectra of polycrystalline O_2BF_4 , O_2AsF_6 , O_2SbF_6 , and $\text{O}_2\text{Sb}_2\text{F}_{11}$ were recorded over the temperature range from 83 to 293 K (–190 to +20 °C) at 9.35 GHz and indicated that the ions are in sites of orthorhombic or lower symmetry [206].

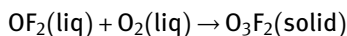
A deep violet compound was obtained by the reaction of O_2F_2 with ClF at 140–119 K (–133 to –154 °C) [207]. This compound was a strong oxidizer and was stable at 195 K (–78 °C). It was soluble in anhydrous HF at 195 K (–78 °C) and was not an electrolyte. The violet and the blue compound exhibited an infrared absorption at 1535 and 1527 cm^{-1} , respectively, and were interpreted in terms of the peroxides F_2ClOOF and $\text{F}_2\text{ClOOCIF}_2$, respectively.

Dioxygenyl salts containing doubly charged mononuclear counterions such as $(\text{O}_2^+)_2[\text{MF}_6]^{2-}$ ($\text{M} = \text{Ni}, \text{Mn}$) are marginally stable up to about 263 K (10 °C) and are characterized by an O–O stretching frequency of about 1805 cm^{-1} [208].

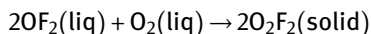
It was attempted to react sodium azide or hydrazinium azide with various dioxygenyl salts to make a new oxidizer, but under no circumstances could the formation of dioxygenyl azide, O_2N_3 , be observed [209, 210]. Another oxygen-fluorine cation that forms stable salts is the trifluorooxonium cation OF_3^+ [211].

4 Trioxygen Difluoride and Tetraoxygen Difluoride

The synthesis of trioxygen difluoride, O_3F_2 , “ozone fluoride”, CAS RN [16829-28-0] from the elements was first reported by Japanese scientists in 1938 [212, 213] but the news was received with skepticism by others. They had reported that under illumination with ultraviolet light the reactions



and



take place to some extent. Two compounds, $\text{O}_2\text{F}_2(\text{solid})$ and $\text{O}_3\text{F}_2(\text{solid})$, were also formed by silent discharges in the mixture of $\text{O}_2(\text{liq}) + \text{F}_2(\text{gas})$. It was not until 20 years later that the reaction was reproduced and the existence of O_3F_2 confirmed by work at the Research Institute of Temple University in Philadelphia, PA. Since then this compound has received attention as a potential hypergolic ignition aid in rocket propellants [214]. A trace (0.05 mass-%) of ozone fluoride in LOX makes the oxidizer hypergolic with many fuels (hydrocarbons, amines, gaseous hydrogen) and results in more stable combustion in a rocket engine.

Trioxygen difluoride is thermally unstable and even less stable than dioxygen difluoride, but under the anticipated conditions of usage it would always be dissolved in liquid oxygen and kept at cryogenic temperatures all the time.

The conditions under which dioxygen difluoride, trioxxygen difluoride, and tetraoxygen difluoride form from fluorine and oxygen are all very similar and the only difference in the operating conditions is the different molar ratio of the reactants [215]. The discussion of the preparation, physical and chemical properties of tetraoxygen difluoride has been combined in this chapter with those for trioxxygen difluoride.

4.1 Preparation of Trioxxygen Difluoride and Tetraoxygen Difluoride

Trioxxygen difluoride is formed if one passes a mixture of gaseous oxygen and fluorine (molar ratio 3 : 2) at low pressure (1.6 kPa = 12 mm Hg) and low temperatures (83–90 K = –190 to –183 °C) through a glow discharge [214, 216, 217]. The apparatus used by the early investigators is illustrated in Figure 5.

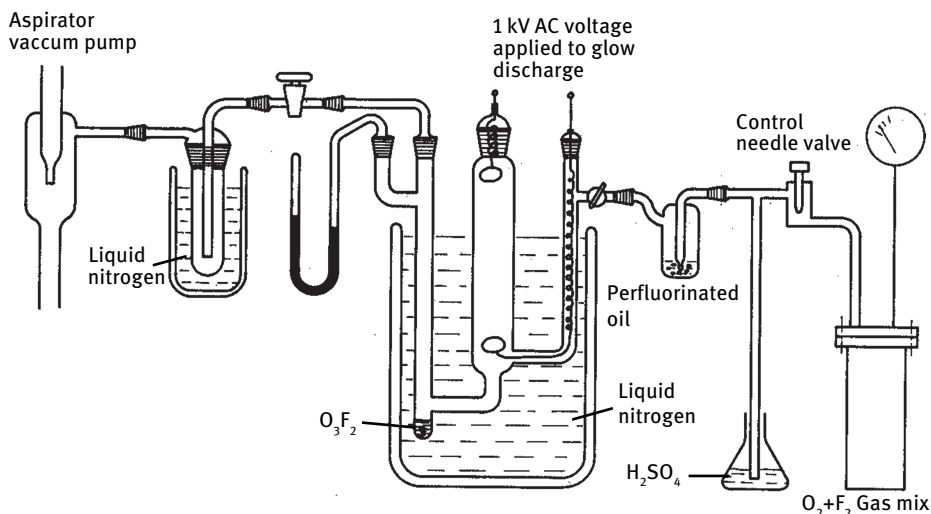


Figure 5: Apparatus for synthesis of trioxxygen difluoride (reproduced and modified after [216])

The compound condenses on the walls of the discharge vessel as a red, viscous liquid that can be freed from contaminating dissolved oxygen, fluorine or oxygen difluoride by evacuation. In contradistinction to O_2F_2 , the O_3F_2 is still a liquid at the temperature of liquid oxygen (90 K = –183 °C) and one can tell the difference by observing the condensate at this temperature. As long as all necessary precautions are observed, O_3F_2 can even be distilled (sublimed) in a high vacuum at 96–114 K and 0.1–1.5 mm Hg. One must be careful not to allow the temperature to rise above 115 K as O_3F_2 decomposes in an exothermic reaction, first to O_2F_2 and oxygen, and then to the elements.

If the temperature increases beyond 200 K, then O_2F_2 decomposes into its elements. The decomposition reaction is not explosive between 90 and 115 K. Liquid O_3F_2 cannot be made to detonate by an electric spark or a detonator [218]. In this respect it is less dangerous than liquid ozone.

By making slight changes in the operating conditions of the glow discharge synthesis of O_3F_2 (lower temperature 60–77 K instead of 90 K, and lower current and voltage i.e. 4.5–4.8 mA at 840–1280 V instead of 20–30 mA at 2000–3000 V), Grosse and co-workers succeeded in synthesizing another polyoxygen-fluorine compound, tetraoxygen difluoride O_4F_2 , which they called “oxozone fluoride”. O_4F_2 can be produced by an electrical discharge at low temperatures and pressures by using a mixture of 2 mols O_2 to 1 mol F_2 by cooling more effectively and to lower temperatures, i.e., 60–77 K (instead of 90 K) [215]. Improved O_4F_2 yields were obtained when the apparatus was made of copper instead of Pyrex because the unstable product could be quenched faster [219]. Tetraoxygen difluoride is a solid at 77 K and sometime condenses on the cold wall between the electrodes in the form of red-brown crystal bundles. At 90 K its vapor pressure is much less than 1 mm Hg. At 90 K it can be stored for several hours and no decomposition takes place (based on pressure rise measurements). At 77 K O_4F_2 is a reddish brown solid, depositing on the glass walls of the discharge vessel between the electrodes. O_4F_2 differs in color from O_3F_2 , and sometimes forms clusters of long needle-like brown crystals. It is a liquid and stable at least for a couple of hours at 90 K, since no noticeable rise in pressure occurs. Between 90 and 110 K, O_4F_2 decomposes slowly into O_2 and O_3F_2 and the latter at 110 K to O_2 and O_2F_2 . Since O_2F_2 , in turn forms $O_2 + F_2$ at about 200 K, the whole O_4F_2 is decomposed entirely into O_2 and F_2 gas. The chemical composition of O_4F_2 was established both by synthesis and analysis. One had to make sure that the condensate did not contain O_3 . The condensate was extracted with LOX in which ozone is quite soluble and the LOX was analyzed for O_3 , but none was found. It has been proven that O_4F_2 is not an adduct of O_3F_2 with oxygen or ozone, but it is a chemical compound in its own right. Careful analysis showed the F:O ratio to be $1.98 \pm 0.005:1$ (theoretical 2:1). Tetraoxygen difluoride is somewhat soluble in liquid oxygen at 77 K and forms a faintly brown solution. No additional properties could be obtained so far. Other work indicated that there may be even higher oxygen-fluorine compounds such as O_5F_2 and O_6F_2 (see Section 5).

Instead of starting with a mixture of elemental oxygen and fluorine, the polyoxygen difluorides can also be made starting with mixtures of oxygen difluoride and fluorine [220].

A continuous process of preparing solutions of O_3F_2 in LOX by bubbling gaseous fluorine through LOX in a quartz Dewar while illuminating it with UV light is described in a patent [221].

The effects of electrode geometry and operating conditions on the O_3F_2 yield were studied [222].

4.2 Physical Properties of Trioxygen Difluoride

Trioxygen difluoride is a solid at the temperature of liquid nitrogen (77 K), a liquid at the temperature of liquid oxygen (90 K) and decomposes at 120 K. Because the compound is difficult to obtain in the pure state and thermally unstable, only very little work has been done in characterizing its physical and thermodynamic properties. The melting point of O_4F_2 was found to be 82 ± 2 K. The extrapolated normal boiling point of O_4F_2 is 194 K. The compound decomposes completely below this temperature. The density of liquid O_3F_2 can be calculated from the following linear equation which is a curve fit of the data shown in Figure 6.

$$\rho = 2.357 - 0.00676T$$

where ρ is the density in g/cm^3 and T is the temperature in kelvin.

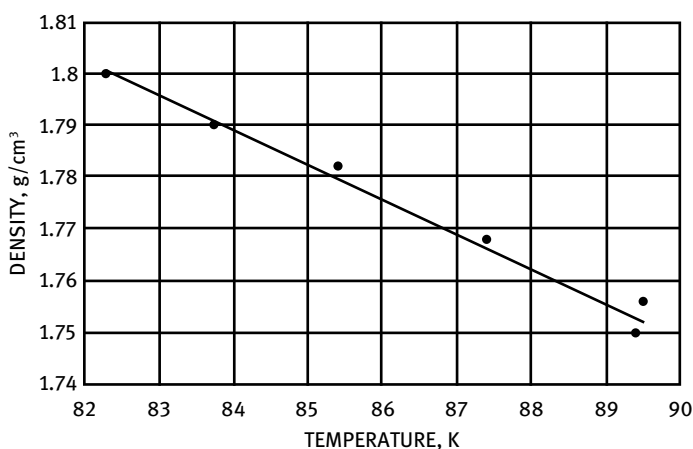


Figure 6: Density of trioxygen difluoride (chart created by Schmidt 2016, based on data from [216]). Solid circles: data points, solid line: curve-fit linear equation

The vapor pressure of O_3F_2 can be calculated from the following logarithmic equation, which is a curve fit of the data shown in Figure 7.

$$\log p_v = 4.7277 - 520.7/T$$

where p_v is the vapor pressure in mm Hg and T is the temperature in kelvin.

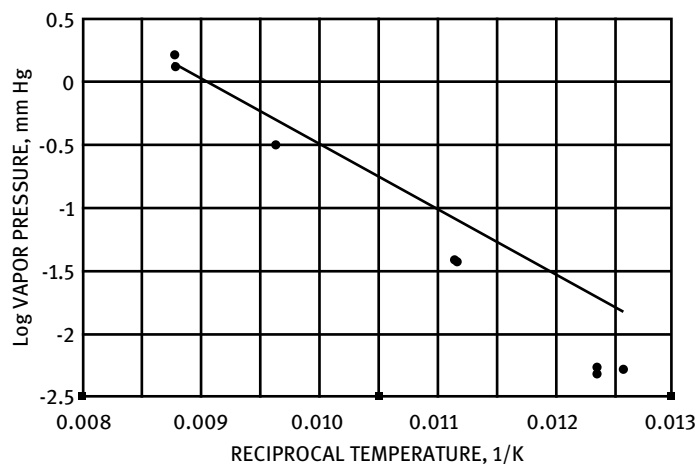
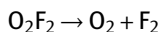
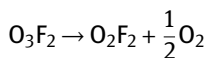


Figure 7: Vapor pressure of trioxxygen difluoride (chart created by Schmidt 2016, based on data from [216]). Solid circles: data points, solid line: curve-fit equation

4.2.1 Thermodynamic Properties of Trioxxygen Difluoride

The enthalpy of formation of O_3F_2 was calculated from the heat of reaction of the following two decomposition reactions:



The standard enthalpy of formation ΔH_f^{298} of $\text{O}_3\text{F}_2(\text{g})$ is $+26.1 \pm 3.1 \text{ kJ/mol} = +6.24 \pm 0.75 \text{ kcal/mol}$ [223]. Trioxxygen difluoride is an endothermic compound and its autodecomposition is an exothermic reaction and measured in a calorimeter to determine its heat of formation. In the same apparatus the standard enthalpy of formation ΔH_f^{298} of gaseous dioxygen difluoride was measured and it was found to be $+19.8 \pm 1.2 \text{ kJ/mol}$ ($+4.73 \pm 0.3 \text{ kcal/mol}$).

4.2.2 Optical Properties of Trioxxygen Difluoride

Trioxxygen difluoride is soluble in perhalogenated solvents. A mixture of trifluorochloromethane and difluorodichloromethane was used as a solvent to measure the absorption spectrum of O_3F_2 in the visible range at 77 K [224]. Trioxxygen difluoride absorbs at 380–430 nm (molar coefficient of extinction = $\epsilon = 17.0 \pm 0.5 \text{ cm}^{-1} \text{ mol}^{-1}$) (Figure 8). This maximum absorption is somewhat shifted toward the long wavelength end of the spectrum compared to that of dioxygen difluoride O_2F_2 ($\epsilon = 14.0 \text{ cm}^{-1} \text{ mol}^{-1}$ at 360 nm).

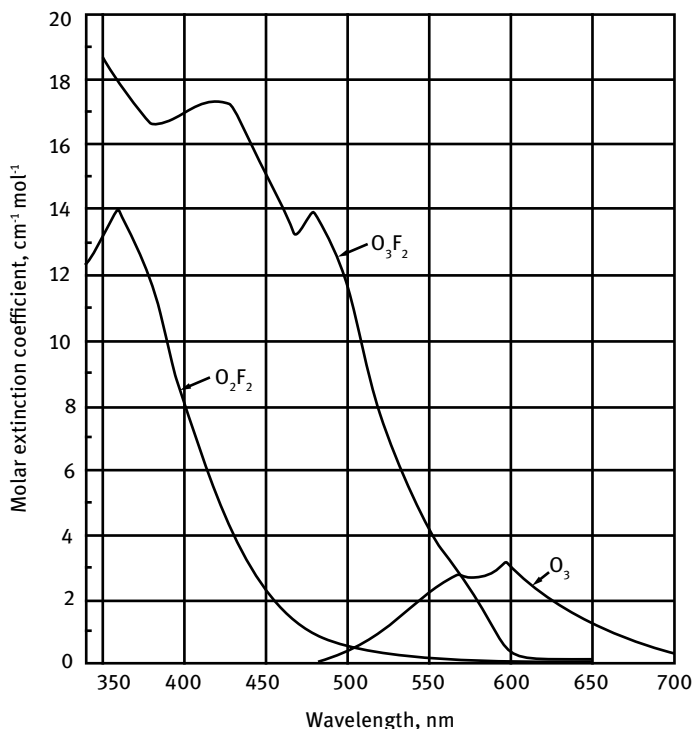


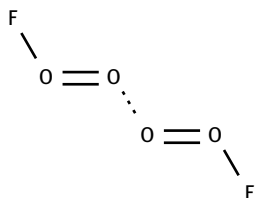
Figure 8: Absorption spectra of trioxygen difluoride, dioxygen difluoride and ozone solutions in Freon 12/13 mixture at 77 K (republished and modified from [224], with permission granted by © 1961 American Institute of Physics; permission conveyed through Copyright Clearance Center, Inc.)

The maximum absorption for liquid O_3F_2 occurred in the region of 380–430 nm, the molar extinction coefficient being $17.0 \pm 0.5 L cm^{-1} mol^{-1}$. Liquid O_2F_2 has its maximum at 360 nm ($14.0 L cm^{-1} mol^{-1}$). Neither liquid O_3F_2 nor liquid O_2F_2 has any absorption at the wavelength that ozone has at its maximum ($3.1 L cm^{-1} mol^{-1}$ at 600 nm). The effect of temperature on the absorption of liquid O_2F_2 in the Freon mixture was studied. It was observed that the higher the temperature, the greater the absorption. Its molar extinction coefficient at 360 nm was 14.10 at 77 K, 15.27 at 140 K, and $15.65 L cm^{-1} mol^{-1}$ at 175 K. This agreed nicely with the color change of O_2F_2 with temperature (cherry-red liquid at 175 K and yellow-orange solid at 77 K).

During the study of EPR spectra of O_2F_2 and O_3F_2 , a free radical giving an asymmetric spectrum was discovered [183]. In continuation of these studies, when the EPR spectrum of undiluted solid O_4F_2 was studied at 77 K, a single broad band signal was obtained having a peak-to-peak line width value of 52 ± 1 gauss and a g value of 2.003 [225]; however, a different EPR spectrum was obtained for dilute samples (~ 0.2 mol %) in CF_4 prepared at 90 K and studied at 77 K. That spectrum consisted of a strong,

sharp doublet and not completely resolved shoulders on either side of the doublet. The hyperfine splitting of the doublet was 14 ± 1 gauss and the g value was 2.005. These observations indicated that there were two different species in the sample, most likely $\bullet\text{OOF}$ and its dimer O_4F_2 .

Tetraoxxygen difluoride (O_4F_2), a red unstable solid with a melting point of 82 K, can be prepared by electrical discharge in an oxygen/fluorine gas mixture ($\text{O}_2:\text{F}_2 = 2:1$) in a Pyrex vessel cooled to 77 K. Because of its instability, information about its structure is limited. ESR and NMR data in solution showed that O_4F_2 is in equilibrium with the radical $\bullet\text{OOF}$. Infrared spectra were consistent with $2\text{O}_2\text{F} = \text{O}_4\text{F}_2$, the spectrum of O_4F_2 being very little different from $\bullet\text{OOF}$. Raman spectra for O_4F_2 were obtained by photolyzing a low-temperature solution of oxygen difluoride (OF_2) in liquid oxygen at about 90 K [226]. The solution of OF_2 in O_2 (approx. 3:1 by volume) was prepared in a simple quartz still. After photolysis with a Pyrex-filtered mercury arc ($\lambda > 320 \text{ nm}$) for some 15 min the solution was deep orange in color and the Raman spectrum was obtained. The closeness of the frequencies for $\nu(\text{O}-\text{O}-\text{F})$ and $\nu(\text{O}-\text{F})$ in matrix and solution suggested that the perturbing influence of the matrix or solution on the vibrational potential function was very small. The position of the $\text{O}-\text{O}$ stretching frequencies suggested that the species produced in solution was O_4F_2 and not $\bullet\text{O}_2\text{F}$. It was noted that the degree of interaction between two $\bullet\text{O}_2\text{F}$ radicals shifted the $\text{O}-\text{O}$ stretch only by 2.5 cm^{-1} and the other vibrations not at all. There is strong evidence that the O_4F_2 molecule is bonded through the oxygens in some manner:



The ESR spectra of oxygen fluoride radicals have been studied extensively, and spectra with varied structures have been assigned to these radicals, with the exception of the well-characterized doublet spectrum for $\bullet\text{O}_2\text{F}$ radicals (splitting 13–16 oersted, g 2.0046–2.0033), and also the anisotropic spectrum, which has been analyzed in detail [227]. The assignment of the other types of ESR spectra to $\bullet\text{O}_2\text{F}$ radicals was extremely arbitrary. At the same time, certain specific features of $\bullet\text{O}_2\text{F}$ radicals required sufficiently reliable identification, since ESR data have been used to reach important conclusions regarding the nature of a number of fluorine-oxygen compounds like O_3F_2 or O_4F_2 . Unlike familiar unstable free radicals, the stabilization of which is achieved by isolating them from each other in a rigid matrix, $\bullet\text{O}_2\text{F}$ radicals are stable both in the form of the individual substance, solid at 77 K, and in solvents that are inert with

respect to $\cdot\text{O}_2\text{F}$ (O_2F_2 , OF_2 , O_2 , CF_4 , etc.). $\cdot\text{O}_2\text{F}$ radicals are sensitive to light in the visible and ultraviolet ranges, and disappear at an appreciable rate at temperatures above 90 K. Since $\cdot\text{O}_2\text{F}$ radicals are sensitive to light with <600 nm, which brings about their transformation, all the operations involving them must be carried out under dark conditions.

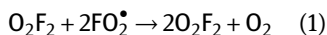
4.2.3 Molecular Structure of Trioxygen Difluoride

Because all the oxygen fluorides with more than one oxygen atom at the center are very unstable, it is difficult to determine physical properties (spectra) that would help to determine the structure of these molecules. In many cases, computational chemistry with *ab initio* or DFT methods comes to the aid with predictions on how the electron clouds will hold the atoms together in a labile fashion.

Surface tension, viscosity, dielectric constant, paramagnetic susceptibility, specific susceptibility, molar magnetic moment, electron paramagnetic resonance, nuclear magnetic resonance and infrared spectra of O_3F_2 were measured to determine the molecular structure of trioxygen difluoride [228]. The structure of O_3F_2 could not be clearly defined. There was evidence to support the presence of $\cdot\text{O}_2\text{F}$ and $\cdot\text{OF}$ radicals. The possibility that O_3F_2 is a trimer, at least in the liquid state, could not be ruled out. O_3F_2 is not a compound of ozone. A linear molecular configuration is not possible.

The molecular structure of O_3F_2 has been the subject of heated discussion. It is difficult to analyze the material because it often starts to decompose before a decent spectrum can be obtained.

Cryogenic mass spectrometry led some to conclude that “ O_3F_2 ” consists of loosely bonded $\cdot\text{O}_2\text{F}$ and $\cdot\text{OF}$ radicals [229]. There were no m/e signals attributable to O_2F_2 , O_3F_2 or O_4F_2 , but peaks attributable to OF^+ , F_2O^+ , O_2^+ , O_2F^+ , and F_2^+ . It was concluded that “ O_3F_2 ” is basically an $\cdot\text{O}_2\text{F}$ and an $\cdot\text{OF}$ radical loosely bonded together and that it undergoes thermal decomposition to $\cdot\text{O}_2\text{F}$ and $\cdot\text{OF}$ via the reversible reaction shown in Eq. 2. These conclusions were based mainly on the fact that OF^+ and F_2O^+ were observed in the mass spectrometry studies.



↗ fast

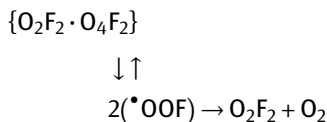


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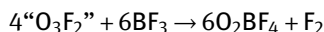


Another far-fetched theory, based on the ^{19}F NMR spectrum of “ O_3F_2 ” postulated that “ O_3F_2 ” consists of O_2F_2 and interstitial oxygen [85, 86].

Finally, work on both ^{19}F and ^{17}O NMR spectroscopy of “ O_3F_2 ” [88, 230–232] led investigators to conclude that the system is best explained as



It was also determined that under ordinary conditions the oxygen atom of OF_2 does not exchange with those of either O_2F_2 or so-called O_3F_2 . The reaction of “ O_3F_2 ” with BF_3



without the release of oxygen also seemed to support a “ O_3F_2 ” consisting of a mixture of O_2F_2 and $(\text{OOF})_2$. All of the evidence obtained supports the conclusion that “ O_3F_2 ” is actually a mixture of O_2F_2 and $(\text{OOF})_2$.

Equilibrium structures of FOOOF in comparison to $\cdot\text{OOF}$, FOOF, and OOF_2 were calculated using a density functional theory (DFT) method and compared with those generated using the *ab initio* calculations and experimental data [180]. The structures of oxygen-fluoride molecules that are known to be problematic for computation were studied using DFT methods. The structures were compared with those generated using the *ab initio* calculations and, when possible, some experimental data. The suitability of the DFT methods for the theoretical study of these molecules is still under discussion.

Coupled-cluster calculations to study the FOOOF isomer of O_3F_2 showed two local minima of similar energy, conformers of C_2 and C_s symmetry [233]. Structures, harmonic vibrational frequencies and standard enthalpies and free energies of formation were calculated. The calculated bond lengths of O_3F_2 were more characteristic of those in OF_2 and a normal peroxide than the unusual bond lengths in O_2F_2 . Both conformers had equal F—O and O—O bond lengths, contrary to suggestions by others of an unsymmetrical structure. The calculated ΔH_f° and ΔG_f° were +110 and +173 kJ/mol, respectively. O_3F_2 was calculated to be stable to decomposition to either $\text{FO} + \text{FOO}$ or $\text{F}_2 + \text{O}_3$, but unstable to decomposition to its elements, to $\text{O}_2\text{F}_2 + \frac{1}{2}\text{O}_2$, and to $\text{OF}_2 + \text{O}_2$.

4.2.4 Magnetic Properties of Trioxygen Difluoride

The ^{19}F NMR spectra of liquid F_2 , OF_2 , O_2F_2 , and O_3F_2 were measured and compared [86]. The results were already discussed in the OF_2 NMR chapter and the O_3F_2 molecular structure chapter. In discussing the molecular structure of O_3F_2 , it was suggested that O_3F_2 is a 1:1 adduct of O_2F_2 and O_4F_2 or an adduct of $2\text{O}_2\text{F}_2$ and O_2 . See also reference [88].

4.2.5 Solubility of Trioxygen Difluoride and Tetraoxygen Difluoride

Trioxygen difluoride is nearly insoluble in liquid fluorine, liquid nitrogen or liquid oxygen at 77 K. At 90 K its solubility in liquid oxygen is very small (0.1 mass-%) and it forms a pale yellow liquid. The solubility of O_3F_2 in LOX is illustrated in Figure 9.

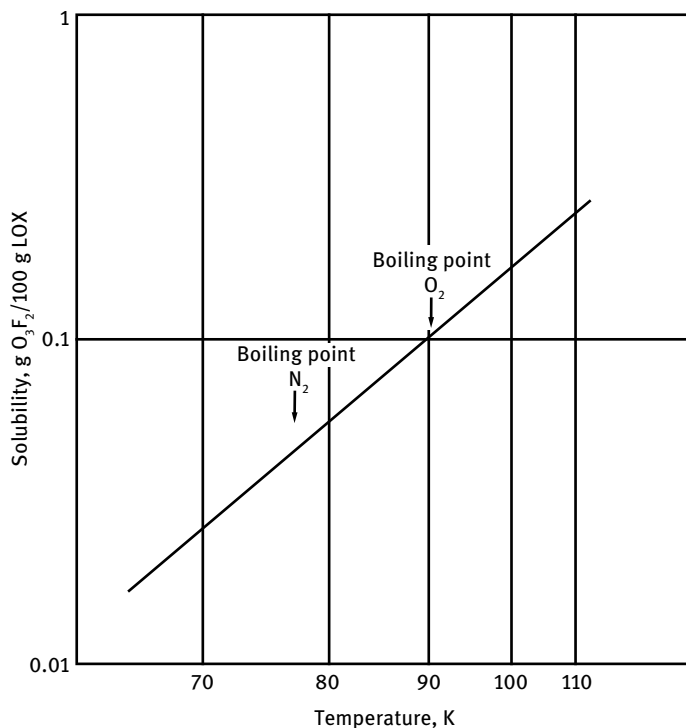


Figure 9: Solubility of trioxygen difluoride in liquid oxygen (based on data from [216])

Trioxygen difluoride is miscible with dioxygen difluoride in all proportions. Perfluorinated or perhalogenated organic solvents (e.g., Cl_2CF_2 or ClCF_3 = halocarbon 12 or 13) can be used to study properties of O_3F_2 in solutions.

Solid O_4F_2 is practically insoluble (less than 0.01 mol %) in liquid nitrogen at 77 K, and in liquid argon at 85 K. In liquid oxygen at 77 K the solubility of O_4F_2 is about 0.05 mol %. Carbon tetrafluoride (Freon-14) dissolves appreciable amounts of O_4F_2 at 90 K (melting point of CF_4 = 89.2 K). The solution containing 1 mol % of O_4F_2 is reddish brown [219].

4.3 Chemical Properties of Trioxygen Difluoride

4.3.1 Decomposition of Trioxygen Difluoride and Tetraoxygen Difluoride

Trioxygen difluoride is thermally unstable. Even at the temperature of liquid oxygen, at 90 K, the rate of decomposition is measurable and amounts to 4%/day. The half-life time at the temperature of liquid nitrogen, at 77 K, is estimated to be 2 years. If one plots the logarithm of the rate of decomposition versus the reciprocal absolute temperature, one obtains a straight line indicating that this is a first-order reaction. From the slope of the line one can calculate the energy of activation of the decomposition reaction ($15.5 \text{ kJ/mol} = 3.7 \text{ kcal/mol}$).

Tetraoxygen difluoride decomposes at 90 K with about a 16-day half-life time to trioxygen difluoride and oxygen. Trioxygen difluoride decomposes in turn, at 90–115 K to O_2F_2 and finally to O_2 and F_2 . Pure O_4F_2 , or its solidified solutions containing about 1 mol % of O_4F_2 in CF_4 has been kept at liquid nitrogen temperature for weeks without noticeable decomposition. O_4F_2 explodes on fast warming.

4.3.2 Storability of Trioxygen Difluoride and Trioxygen Difluoride/ Liquid Oxygen Solutions

The storage life of O_3F_2 solutions in LOX at 90 K was not expected to exceed 1 month. In the 1960s, Air Reduction Co. installed a 25-gallon pilot plant for production of LOX/ O_3F_2 (TOFLOX) with 0.05–0.10% O_3F_2 in LOX in Huntsville, AL, but it is not known if it actually has produced sizable amounts of TOFLOX [234].

4.3.3 Reactions of Trioxygen Difluoride and Tetraoxygen Difluoride

Trioxygen difluoride is a very strong oxidizer and it reacts with all hydrogen-containing substances vigorously with ignition. The reaction with liquid methane, solid hydrazine or solid ammonia at 90 K is so energetic that the glass test tubes used for the reaction are fragmented to small pieces.

Trioxygen difluoride reacts with elemental sulfur, bromine, iodine, red phosphorus, and charcoal in flame reactions, sometimes explosively. A mixture of trioxygen difluoride and ethanol did not react at 90 K but exploded when thawed. The enormous reactivity of trioxygen difluoride is maintained after the compound is dissolved in liquid oxygen. This mixture reacts hypergolically with most rocket fuels [194].

Reactions of O_2F_2 and O_4F_2 with nitrogen oxides produced inconclusive results. Some evidence for NO_2OOF was obtained, but it could not be identified before it decomposed to O_2 and NO_2F [202].

4.3.3.1 Hypergolic Ignition Tests with Trioxygen Difluoride

This chapter actually belongs in a future volume on hypergolic bipropellant combinations, but we summarize the ignition characteristics of O_3F_2 and $\text{O}_3\text{F}_2/\text{LOX}$ solutions

here to better characterize this chemical and to explain why we devoted that much space to it in this chapter.

The first tests of the hypergolization of LOX by addition of O_3F_2 were conducted at Temple University [235, 236]. A dilute solution (0.05%) of O_3F_2 in LOX was used as an oxidizer in an ignition test apparatus and proved to be hypergolic with gaseous H_2 , unsymmetrical dimethylhydrazine (UDMH), UDMH-diethylenetriamine (UDMH-DETA), EtOH, C_3H_8 , *n*-hexane, jet propellant 4 (JP-4) and mixtures of JP-4 and UDMH. Compatibility tests (by simple contact) showed that dilute O_3F_2 /LOX solutions do not react hypergolically with most materials of construction commonly used in LOX systems. Similar tests with emphasis on ignition of hydrogen were conducted at Stanford Research Institute, Menlo Park, CA [237, 238].

4.4 Handling and Safety Properties of Trioxxygen Difluoride

Because pure trioxxygen difluoride cannot be used as a rocket propellant, the concern about safe handling of this energetic material deals mostly with the handling during its manufacture in the pure state and later, in the form of solutions in other oxidizers, predominantly LOX. The lack of thermal stability of trioxxygen difluoride makes it necessary to store it at very low temperatures, typically at the temperature of liquid nitrogen. One will want to make sure that there is always sufficient cryogenic coolant on hand and that contact of the product with organic, combustible substances is avoided. Toxicity concerns are the same as those when dealing with fluorine (liquid or gas) since fluorine is one of the decomposition products once the trioxxygen difluoride starts decomposing. Adding trioxxygen difluoride to liquid oxygen results in stricter safety precautions required for the solution than one is used to for LOX. The LOX/ O_3F_2 tank will be designed with a cooling jacket that holds a supply of liquid nitrogen. If one stores pure LOX, it does not matter how much of the cryogenic oxidizer evaporates, the remaining oxygen will still be pure enough for the intended use. Not so with LOX/ O_3F_2 solutions: if more than 50% of the oxygen is allowed to evaporate, the solubility limit of O_3F_2 in LOX will be exceeded and pure O_3F_2 segregates on the bottom of the tank. Transferring LOX/ O_3F_2 from one tank to another requires additional safety precautions. Unlike LOX transfer where the lines can be allowed to cool by evaporating some LOX and tolerating evaporation losses, for the transfer of LOX/ O_3F_2 the lines must be precooled with LOX from a separate supply or must be externally cooled.

If LOX/ O_3F_2 solutions are stored for a long time, the O_3F_2 content must be examined from time to time and, if necessary, fresh O_3F_2 must be added to maintain the desired O_3F_2 level and its hypergolic ignition capability. Accidental spills of LOX/ O_3F_2 solutions constitute a more significant hazard than LOX spills because the probability of accidental ignition of structural materials in the vicinity of the spill is so much higher. Rocket propellant test personnel are used to prevent air intrusion into LOX to prevent ice formation and clogging of filters and orifices, but for LOX/ O_3F_2 solutions

moisture must be excluded very carefully for an additional reason: O_3F_2 will hydrolyze and lose its hypergolic ignition capability and hydrogen fluoride, one of the hydrolysis products, will cause nasty corrosion problems.

4.5 Materials Compatibility with Trioxxygen Difluoride

The dry, water-free, cryogenic LOX/ O_3F_2 solution (typically containing 0.05% O_3F_2) can be stored in CRES-303, CRES-316, CRES-321, CRES-347, aluminum, copper, brass, or titanium alloy 120-VCA.

Allpax-500, Teflon, and Duroid-3400 have been used as gasket materials and Molycote-Z and Oxylube-702 have been used as lubricants. For higher concentrations (0.11% O_3F_2 in LOX) the following materials of construction are no longer resistant: Kel-F, polyethylene, Kel-F Oil 464, Halocarbon 11,14 Oil or AR-1 F-LOX-lube, but CRES-303 is acceptable even for the higher concentrations [214].

The compatibility of metallic and organic structural materials with 0.05% solution of O_3F_2 in LOX was investigated under static and flow conditions [118, 120].

4.6 Detonability of Trioxxygen Difluoride

In a 1-in. diameter $\times$ 8 in. length steel pipe initiated with two 1 in. $\times$ 1 5/8 in. diameter tetryl pellets as the booster charges, a charge of liquid trioxxygen difluoride was not detonable [239, 240].

5 Other Oxygen Fluorides

Speculation had it that oxygen as the central atom might be pushed to higher, hypervalent states of oxidation and that higher oxygen fluorides like OF_5 or OF_6 might be possible. Two new oxygen fluorides, O_5F_2 and O_6F_2 , were discovered and methods of preparation and some of the properties of these new oxygen fluorides were described [191, 192]. Synthesis of polyoxxygen difluorides by electrical discharge in the liquid phase or ultraviolet irradiation was accomplished. Thermal stability, sensitivity, solubility, and the EPR spectrum for O_5F_2 were determined.

An *ab initio* study of the electronic structure of OF_6 has been undertaken [241]. Optimized geometries were calculated at the self-consistent field (SCF) and Moeller-Plesset (MP2) levels of theory using several basis sets. Vibrational analyses indicated that OF_6 has stability in $[O_h]$ symmetry at both the SCF and MP2 level. The calculations suggested a stability competition between the covalent $[O_h]$ structure and the $[\text{C}_{4v}]$ OF_5^+F^- ion-pair structure.

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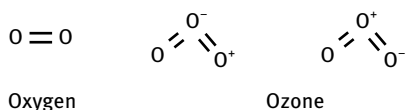
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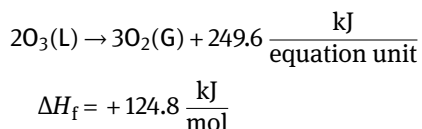
Ozone and Ozone/Oxygen Mixtures

1 Introduction

Ozone, O₃, also known as 1λ,1,3λ,1-trioxidane, μ-oxidodioxygen, trioxygen, triatomic oxygen, CAS RN [10028-15-6], is an allotrope of dioxygen consisting of three instead of only two oxygen atoms. Ozone, O₃ (in the liquid form frequently abbreviated as LOZ = **L**iquid **O**Zone), is a more energetic form of oxygen, and its safe use as a rocket propellant would give a higher specific impulse than liquid oxygen with all fuels. The various reactions that will be discussed in this chapter convert one form of oxygen into an other:



Ozone is an even more powerful oxidizing agent than dioxygen and has been experimentally tested as a rocket propellant, but it has never been demonstrated to be safe or practical to use. To our knowledge, it has never actually flown in a rocket. Compared to another high-energy oxidizer, fluorine, ozone has the advantage that exhaust products from a bipropellant rocket engine running on ozone are non-toxic. Another advantage is that the starting raw material, dioxygen, is in abundant supply. A significant disadvantage is that liquid ozone is very shock sensitive and unstable, decaying to dioxygen through the exothermic reaction



This reaction proceeds more rapidly with increasing temperature and decreasing pressure but is very slow at cryogenic storage temperatures.

In addition to very active research into ozone as an energetic chemical and potential rocket propellant, much effort has been devoted to looking for polyoxygens with four or more oxygen atoms joined in one molecule. If such compounds could be made and stabilized, they would make powerful rocket propellants. Thus, we present a detailed account of ozone chemistry here because it would be the jumping board from which to start in the search for even more energetic all-oxygen oxidizers.

1.1 Ozone History and Literature Summaries

An excellent summary of the history of the discovery and characterization of ozone is given in [1]. Ozone has been known for a long time, and many published books and monographs have dealt with the chemistry and general aspects of this chemical. Some of these titles are now only of historical interest. Judging by the number of books published, it seems that the interest in ozone as a chemical culminated in the year 1916: [2–4]. Then, following a quiet period of four decades, ozone chemistry experienced a resurgence when NACA and other rocket propulsion organizations began to look at ozone as a rocket propellant and a series of good summaries became available [5–10]. Among those, the two-volume bibliography by Thorp is a valuable source of information.

When the concern about the toxicity of chloroform and other halogenated organics in drinking water caused water treatment facility operators to look at other means of disinfecting drinking water, ozone stepped up as a clean, residue-free disinfectant to replace chlorine. It is quite possible that today's widespread use of ozone as a water treatment chemical has benefited from the extensive research done in the 1950s with government funding when ozone was slated for use as a rocket propellant.

Then, after interest in ozone as a rocket propellant waned, it was the atmospheric research enabled by high-altitude sounding rockets and satellites in the 1960s and 1970s that identified the deleterious effect of halocarbons on the protective ozone layer on Earth and on the formation of an so-called ozone hole over the poles that spurred an increase, by several orders of magnitude, in the annual number of publications on the ozone, mostly on atmospheric chemistry. There exists a dual concern about ozone: the unwanted abundance of ozone in smog at the bottom of the polluted atmosphere where we live and breathe and a shortage of ozone at the top of the atmosphere, where it is supposed to absorb skin- and vegetation-damaging UV rays from the Sun and protect us from sunburns. There is even a scientific society dedicated exclusively to the study of ozone for industrial uses in water treatment and its significance for life on Earth. Since 1979, the society has even been publishing a bimonthly journal: *Ozone: The Journal of the International Ozone Association* [11].

The first preparation of pure ozone and determination of several of its physical properties was done by E. H. Riesenfeld at the University of Berlin during the period 1922–1926 [12, 13]. Ever since the pioneering work of Riesenfeld there has been no lack of attempts to liquefy ozone and use it as a rocket propellant. These efforts were frustrated by the explosive sensitivity and explosive power of liquid ozone, which has been the cause of frequent accidents, which led other investigators to the conclusion that the utilization of pure ozone as a rocket propellant would be impossible.

Karrer and Wulf also reported the preparation of pure liquid ozone and determination of its molecular mass in 1922 but were frustrated by frequent explosions at various stages of their experiments [14].

Some of the early work on ozone with the intent of using it as a rocket propellant was conducted by Schumacher in cooperation with rocket pioneer Eugen Sänger [15–17].

Following the end of World War II, efforts aimed at the production of ozone as a rocket propellant continued undiminished in the USA and in what was then the USSR. In the United States, Armour Research Foundation, in conjunction with Linde Air Products and Air Reduction Co. (Murray Hills, NJ), was one of the leading ozone research organizations at that time [18]. This group succeeded in 1955 in preparing extremely pure ozone and identifying some of the causes of explosive sensitivity of samples prepared by earlier investigators [19].

If not for its hazardous properties (explosivity and toxicity), liquid ozone would make a good oxidizer in combination with fuels such as liquid hydrogen or hydrocarbons. The advantage over liquid fluorine would be not only that some ozone combinations give higher specific impulse, but also that the exhaust gases are non-toxic. It was expected that the production of liquid ozone would be less expensive than that of liquid fluorine. Despite this, liquid fluorine appeared to be the leading oxidizer candidate in the 1960s when high-energy propellants were the name of the game, regardless of their toxicity. It was argued that the hazards of liquid fluorine are somewhat more predictable, whereas the handling of liquid ozone sometimes resulted in unexpected, unpredictable, and hard-to-explain explosions.

1.2 Advantages and Disadvantages of Ozone as a Rocket Propellant

In a comparison of the advantages and disadvantages of fluorine versus ozone conducted in 1959, it was argued (but without substantiation of claims by hard numbers) that neither of the two oxidizers justifies the high expense of research and development, because non-chemical propulsion systems would soon replace all high-energy chemical rocket propellants in satellites and space probes [20]. This pessimistic view was not immediately confirmed, at least not for the next 10 years while the development of the NOMAD upper stage using liquid fluorine as the oxidizer continued until it also was abandoned as impractical.

With regard to future applications of ozone as a rocket propellant, initial developments will, in all likelihood, use not pure ozone but mixtures of liquid ozone with liquid oxygen or liquid fluorine. For this reason, this chapter combines a discussion of the physical and chemical properties of pure ozone by itself with those of its mixtures.

The following historical literature summaries (only second-hand sources of information) may be useful as an introduction to the use of ozone as a rocket propellant and its hazards: [21–23].

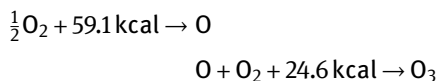
Today the main applications of ozone are in drinking water purification and sterilization and the treatment of industrial waste waters. It has the advantage that it can destroy infection-bearing bacteria and organic contaminants without forming danger-

ous halocarbons (in particular, chloroform) as happens with treatment using elemental chlorine or hypochlorite.

2 Preparation, Production, and Availability of Ozone

Ozone is produced by a silent discharge (“corona discharge”) in oxygen or air at sea level pressure by an endothermic reaction. The resulting ozone has a positive enthalpy of formation. Good yields are achieved with oxygen flowing past large surface area electrodes connected to alternating-current voltages of 5 to 10 kV.

Dissociation of molecular oxygen:



Depending on the operating conditions, the product gas can contain 3 to 15% ozone. The reaction product can be condensed into a cold trap in liquid nitrogen, and the residual gas can be recycled into the closed-loop apparatus. If one connects several ozonizers in series, the maximum concentration of ozone in the product is limited to a stationary concentration of about 20% because some ozone decomposes back to oxygen under the conditions of its formation in the silent discharge.

Ozone can also be formed by UV illumination of oxygen in analogy to processes in the upper atmosphere of Earth leading to the formation of a protective ozone layer. Regardless of the method of stimulation, electric discharge or UV light, the maximum concentration of ozone in the products of a single-pass ozonizer is limited. There is a dynamic equilibrium that can be shifted only by condensing ozone and removing it from the reaction zone.

If the ozonizer is operated on dry air instead of pure oxygen, the resulting ozone is contaminated by nitrogen oxides, mostly dinitrogen pentoxide, which can also be obtained in separate reactions of nitrogen dioxide with ozone. The percentage conversion of oxygen to ozone in dry air can be higher than in pure oxygen [24, 25]. Traces of moisture, however, reduce the ozone yield substantially. Commercial ozonizers are available in a wide range of models [26].

For all these devices, the ozone yield as a function of electric power consumption is an important evaluation criterion [27]. A group of Russian scientists conducted a systematic evaluation of the fundamental operating parameters of ozonizers to optimize the yield of ozone and published two long series of publications with 12 sequels. The variables studied included the electrode geometry, the space velocity of oxygen feed gas, the admixture of inert diluent gases, the discharge voltage, the discharge current, and the frequency of the alternating current. The results obtained with different reactor designs were normalized by the power : volume ratio of the reactors. The pressure and temperature of the feed gas also have an influence on the ozone yield. These

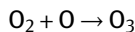
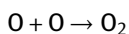
publications deal with the kinetics of the synthesis of ozone under flow conditions [28], the synthesis of ozone from oxygen-argon mixtures [29], the effect of electrode temperature [30], operation under reduced pressure [31], steady-state conditions [32], ozone formation in oxygen-nitrogen mixtures [33], the power effect of discharge [34], kinetics in a closed-loop ozonizer [35], and combining several ozonizers [36]. Another series of publications dealt with the electrical theory of ozonizers [37–46]. The best ozone yields are achieved if the pressure and flow rate in the ozonizer are carefully controlled [47]. See also [48].

The design criteria for laboratory-scale ozonizers were described in [49] and [50]. Ozonizers can also be operated at high pressures [51]. One must avoid electrode materials that might catalyze the decomposition of ozone [52]. Sometimes it is best to encase electrodes in glass.

The explosive sensitivity of liquid ozone has been blamed on the presence of organic contaminants [19]. The most likely source of contaminants is the oxygen derived from air liquefaction by compression and adiabatic expansion. The compressors used for compressing air must be lubricated, and some parts run very hot. At that temperature, some of the oil is thermally cracked to form lower, more volatile hydrocarbons, including acetylene, which is difficult to separate from liquid oxygen by distillation or freezing and filtering. Liquid oxygen may typically contain up to 3 ppm acetylene at 90 K (–183 °C). Lowering the acetylene concentration to 0.003 ppm did not totally alleviate the explosive problem because sporadic explosions still rendered the ozone product unsafe.

Extremely pure oxygen suitable for ozone production can be obtained by passing the gas over hot copper(II) oxide, which destroys all organic contaminants [53]. Ozone that was prepared from oxygen purified in this manner could be liquefied without problem and was much less sensitive to shock and vibration than previously prepared samples.

To study ozone formation in the solid state, gaseous oxygen was passed through an electrodeless discharge and condensed, either alone or in a matrix of inert gases, at liquid helium temperature [54]. On warming through a temperature range of 13–30 K, the blue solid deposits became more deeply colored. The amount of ozone formed as a function of time was determined. It was concluded that ozone was formed upon condensation by the predominant reactions from atomic oxygen



The experimentally observed conversion to ozone of 58% agreed well with that calculated from a rate law with $k_1/k_2 = 1.3$. The activation energy of these reactions was estimated to be less than 6.3 kJ/mol (1.5 kcal/mol). At one point, atomic oxygen was considered for use as a cryogenic solid rocket propellant. This reaction would essentially limit the useful life of atomic oxygen before it recombines.

Ozone can form by the reaction of fluorine gas with water or during the decomposition of peroxides. Ozone is formed in good yield by reacting O^{2+} salts with water in HF at 195 K ($-78^{\circ}C$). Using isotopically labeled water, ^{17}O - ^{16}O - ^{16}O and ^{18}O - ^{16}O - ^{16}O can be prepared, and other isotopomers could be made starting with $^{17}O^{2+}$ and $^{18}O^{2+}$ precursors [55]. ^{17}O nuclear magnetic resonance (NMR) spectroscopy and IR matrix spectroscopy were used for the detection and a study of the decay of the isotopomers. The ^{17}O or ^{18}O label remained at the terminal position as long as the sample was kept at or below 195 K ($-78^{\circ}C$), but at higher temperatures scrambling of the atoms was observed.

In most cases of rocket applications, one will not want to use pure ozone, but ozone solutions in liquid oxygen. Such solutions can be prepared by bubbling ozonized oxygen through a sample of liquid oxygen that is externally cooled by a bath of liquid air or liquid nitrogen. Liquid oxygen and liquid ozone are not miscible over the entire range of compositions at the temperature of liquid oxygen. Instead, at the temperature of liquid oxygen, there are two phases, a lower one containing 30 mass-% oxygen dissolved in ozone and the upper layer of 30 mass-% ozone dissolved in oxygen. In the hope that all explosive hazards of ozone/oxygen solutions can be brought under control, some companies started with the design of plants for the production of liquid ozone/liquid oxygen (LOZ/LOX) in 1952 [56]. However, none of these projects was brought to fruition.

Some organizations were overly optimistic in believing it would be possible to use liquid ozone as a rocket propellant on a large scale and in making preparations to produce tonnage quantities of the chemical [57]. However, they advised against the preparation and storage of solid ozone.

A simple method for producing (100%) pure ozone in the laboratory is the silent electric discharge technique [58]. The specific production costs of ozone were estimated for a capacity range of 1 to 1000 kg/h ozone for various plant configurations and air or oxygen as feed gas and for air preparation, onsite liquid oxygen delivery, onsite oxygen production, and/or oxygen recycling systems [59].

The γ -irradiation of liquid or solid oxygen is one method for producing ozone [60, 61]. In undiluted oxygen at 77 or 90 K, the G-value was 6 molecule/100 eV absorbed. The presence of nitrogen will cause the formation of unwanted NO_2 .

2.1 Natural Occurrence of Ozone

2.1.1 Natural Occurrence of Ozone on Earth

Ozone in small quantities is formed by several physical and chemical processes. Lightning strikes leave behind the telltale odor of ozone. Ionizing radiation from radioactive isotopes will ozonize the surrounding air. The cabin air of airplanes flying at high altitudes and using ambient air may contain irritating amounts of ozone. Ozone can often be smelled in the vicinity of laser printers or copy machines. Federal and state

regulations limit the allowable concentration of ozone in the air in places of employment (Section 6.1). Ozone is indisputably a minor atmospheric constituent, but it plays a major role in the physico-chemistry of the atmosphere. At the height of the sometimes hyped public concern about the ozone hole and before the legally enforced reduction in halocarbon emissions began to take effect, one of the most absurd proposals to patch the ozone hole was to load several rockets with a payload consisting of tons of liquid ozone (if not as the oxidizer that propelled the rocket) and disperse it in the ozonosphere.

2.1.2 Natural Occurrence of Ozone on Extraterrestrial Planetary Bodies

There has been speculation that some ozone might have formed under the influence of energetic radiation on dioxygen and condensed in a matrix of ice or solid oxygen in cold parts of the Universe, where it might be preserved for a long time.

The detection of ozone on Europa and Callisto was surprising, since the vapor pressure of solid oxygen exceeds the atmospheric pressures of these satellites. Condensed O_2 and O_3 on the surfaces of some icy satellites are thought to originate from the radiolytic decomposition of surface water ice by the impact of energetic magnetospheric ions, but decades of laboratory studies have produced no evidence for ozone from the radiolysis of pure water ice. In trying to reproduce those conditions in a laboratory on Earth, it was found that codeposition during radiation caused the burial of a high concentration of radiolytic O_2 from which ozone was formed [62, 63]. Irradiation was done at 130 K with 100 keV Ar^+ ions. The UV reflectance spectra of the irradiated ice matched those observed on the icy satellites Ganymede and Rhea.

The mass uptake of ambient oxygen in nanoporous ice could be enhanced by irradiation with 193-nm photons, due to conversion of O_2 into H_2O_2 and O_3 , with an efficiency that increased with decreasing temperature [64]. These findings showed a new way to form H_2O_2 and O_3 on icy surfaces in the outer solar system at depths much larger than are accessible by typical ionizing radiation, which has possible astrobiological implications. In the search for *in situ* resource utilization (ISRU) resources, one must be prepared to encounter ozone in addition to the more desirable hoped for discovery of water and oxygen. The question is whether this discovery of ozone should be considered a detriment, making the oxygen unfit for breathing, or a benefit, allowing one to scoop up a more energetic oxidizer propellant for the trip home. The discovery of ozone and/or hydrogen peroxide on the surface of Mars and its icy satellites would make the extraterrestrial existence of life forms as we know them highly unlikely because both are very effective disinfectants.

3 Physical Properties of Ozone

The molecular mass of ozone is 47.9982 g/mol. In the liquid phase, ozone has an indigo-blue color. At temperatures around 90 K (–183 °C), liquid ozone may be kept without noticeable decomposition for long periods. Fast warming to the boiling point or rapid cooling may cause explosions. The liquid ozone must be evaporated or frozen very slowly with appropriate precautions. Liquid ozone has a tendency to supercool instead of crystallizing. Solid ozone has a deep blue-violet color. A layer 0.2 to 0.5 mm is transparent, but solid ozone in a layer 1 mm thick is almost opaque. Solid ozone (at 77.35 K) was compressed to 22.5 atm without any difficulty. Slight impact and slight friction at that temperature did not cause an explosion. Gaseous, liquid, or solid ozone explodes easily if it is exposed to heat, sparks, flames, or shocks. The presence of contaminants enhances its sensitivity.

Quite often physical properties of pure ozone are listed in the same publications that also deal with its mixtures with oxygen. We had to decide whether properties of ozone/oxygen mixtures should be listed immediately following the property of pure ozone or if mixtures should be moved to a separate subsection at the end of the ozone chapter. The decision was made to list the properties of mixtures of ozone and oxygen at the end of each property chapter. A discussion of mixtures of ozone with other oxidizers (fluorine, nitric acid) appears at the end of this chapter.

The density, melting points, and boiling points of ozone are higher than those of oxygen.

Because it is difficult to work with pure ozone, the physical properties of this compound have not yet been determined with the same accuracy as those of oxygen. In particular, physical properties reported in older publications must be treated with a good amount of distrust. Discrepancies were caused by impurities in the ozone and shortcomings inherent in the experimental methods used. In cases of discrepancies, it is difficult to decide which values are correct without repeating the experiments with modern methods.

Good summaries of physical properties of ozone were published at a time when hopes for the future use of ozone as a rocket propellant were still running high [6, 7, 18, 65, 66].

3.1 Freezing Point and Phase Diagrams of Ozone

It is difficult to measure the freezing point of LOZ and LOX/LOZ mixtures because it has a tendency to supercool. Warming frozen ozone to determine the melting point is a hazardous operation. Melting point data for ozone are summarized in Table 1.

In one experiment, ozone was frozen in a bath of liquid/solid nitrogen slush at the triple point of nitrogen, then the liquid nitrogen bath was warmed by slow addition of oxygen at a rate of 0.06°/min ([67]). Melting of solidified ozone was observed to begin

Table 1: Melting point of ozone.

Melting point		Authors	Year	References
K	°C			
80 ± 0.5	-193 ± 0.5	Brown, Berger, and Hersh	1954	[67]
80.7 ± 0.4	-192.5 ± 0.4	Jenkins	1956	[68]

at 79.7 K (-193.4°C), and melting was complete at 80.6 K (-192.5°C). The true melting point of solid ozone is $80 \pm 0.5\text{ K} = -193 \pm 0.5^\circ\text{C}$.

3.1.1 Phase Diagram of Ozone/Oxygen System

Ozone and oxygen are miscible over the entire range of compositions only above a critical mixing temperature, for which various sources give 93.2 K (-179.9°C) or 92.6 K (-180.5°C). Below this temperature the mixtures separate into two phases. The lower phase is an ozone-rich phase. The lower phase, containing 44–65 mol-% ozone, is much more sensitive than the homogeneous solution. Phase separation must be avoided if one wants to use LOX/LOZ mixtures as rocket propellants. Several investigators have been looking for an additive that will prevent phase separation.

The phase diagrams of the binary system liquid and solid ozone and oxygen have been studied extensively [69–71].

Table 2–4, and Figure 1 and 2 give the composition of the ozone-rich phase and the oxygen-rich phase in the two-phase region of ozone/oxygen mixtures.

Table 2: Composition of immiscible O_3/O_2 phases in two-phase region.

Temperature		Composition, mol-% O_3	
K	°C	Oxygen-rich phase	Ozone-rich phase
78	–195	5.3	65
85	–188	10.0	58
88	–185	18.0	48
91	–182	—	44.5
92	–181	24.5	—

Data source: [69]

Curve I in Figure 2 gives the experimental results. Curve II is the “theoretical” curve, assuming Raoult’s law will hold. Curves I and II are quite different. The “experimental” curve I shows a small but distinct maximum at $167.8 \pm 1\text{ K}$ ($-105.3 \pm 1^\circ\text{C}$). At this temperature and a pressure of 760 mm Hg the gas and liquid phases have the same composition. The large difference between the shapes of curves I and II should not

Table 3: Phase boundaries of ozone/oxygen mixtures.

Temperature		Mol-% ozone	
K	°C	in upper phase	in lower phase
90	−183.2	17.6	67.2
77.5	−195.7	6.9	84.3

Data source: [71, 72]

Table 4: Physical properties of ozone/oxygen mixtures.

Temperature, K	Mass-% ozone in starting mixture	Mass-% ozone in upper phase	Mass-% ozone in lower phase
90.2	24.27	24.27	Only one phase, homogeneous
90.2	25.0	23.92	1.80
90.2	40.0	16.–80	23.20
90.2	50.0	12.04	37.96
90.2	60.0	7.32	52.68
90.2	75.0	0.21	74.79
90.2	75.45	Only one phase, homogeneous	75.45
77.5	10.0	10.0	Only one phase, homogeneous
77.5	25.0	8.10	16.90
77.5	40.0	6.20	33.80
77.5	50.0	4.93	45.07
77.5	60.0	3.67	56.33
77.5	75.0	1.77	73.23
77.5	89.0	Only one phase, homogeneous	89.00

Data source: [73]

come as a surprise because the van der Waals forces between the different types of molecules in the liquid phase (O_2 , O_3) will be quite different (see also Figure 7).

3.1.2 Phase Distribution

The significant structure theory of liquids was applied to the partially miscible system of the O_3/O_2 mixture, which exhibits partial miscibility in a temperature range of 77.6 to 93.2 K (−195.5 to −179.9 °C) [74]. A partition function for the binary liquid mixture was developed using the significant liquid structure theory. A coexistence curve of the O_3/O_2 system was obtained by varying the mol fractions of the components to find the temperature at which the two liquids separate. The agreement between theory and experiment was satisfactory.

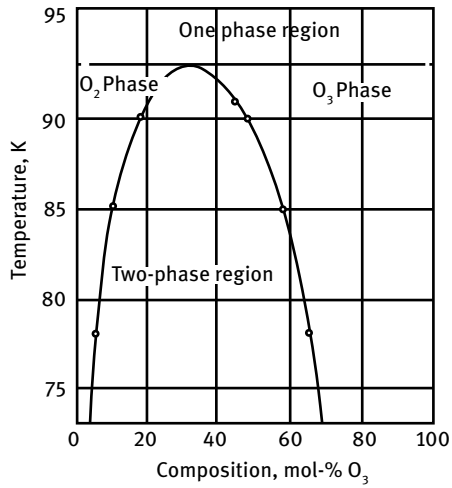


Figure 1: Solubility phase diagram of LOX/LOZ system. (Republished and modified from [69], with permission of © 1953 American Institute of Physics; permission conveyed through Copyright Clearance Center Inc.)

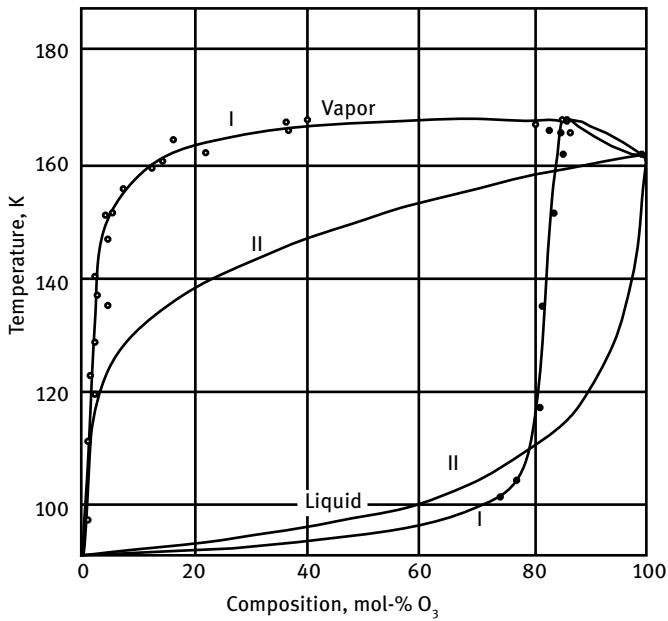


Figure 2: Phase diagram of LOX/LOZ system. (Republished and modified from [69], with permission of © 1953 American Institute of Physics; permission conveyed through Copyright Clearance Center Inc.)

3.2 Boiling Point of Ozone

Literature data for the boiling point of ozone are summarized in Table 5, and those for ozone/oxygen mixtures are summarized in Table 6.

Table 5: Boiling point of ozone.

Boiling point		Authors	Year	References
K	°C			
161.3 ± 0.3	-111.9 ± 0.3	Jenkins and Birdsall	1952	[70]
161.3	-111.9	Streng	1971	[75]
161.6	-111.5 ± 0.5	Riesenfeld and Beja	1924	[13]

Table 6: Boiling point of liquid ozone/liquid oxygen mixtures.

Mol-% ozone	Boiling point ^a	
	K	°C
85.0	94.1	-179.1
90.0	97.2	-176.0
95.0	106.1	-167.1
98.0	122.3	-150.9

^a At 101 kPa, extrapolated from vapor pressure data
Data source: [71]

3.3 Density and Partial Molar Volumina of Ozone

The density of gaseous ozone at 101 kPa and 273 K is 2.1415 g/L [65]. The density of liquid ozone was measured over a range of 77.4 to 174.2 K using ozone thermometers, and the data are shown in Figure 3. The density of liquid ozone is an almost linear function of temperature [76].

The classical method of calculating coefficients of thermal expansion is by a polynomial equation of the form

$$V = \alpha + \beta T + \gamma T^2 + \delta T^3 + \dots$$

where α , β , γ , and δ are the coefficients, V is the specific volume, and T is the temperature in kelvin. An equation relating the specific volume of liquid ozone to the absolute temperature was determined by the method of least squares. This equation,

$$V = 0.551 + (6.25 \times 10^{-4})T + (3.35 \times 10^{-6})T^2$$

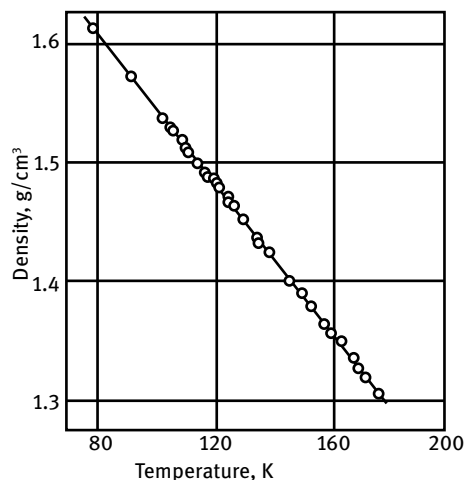


Figure 3: Density of liquid ozone as a function of temperature. (Republished and modified from [76], with permission from © 1957 American Institute of Physics, permission conveyed through Copyright Clearance Center, Inc.)

where V is the specific volume in cm^3/g and T is the temperature in kelvin, is accurate to within 0.2% of the experimental data. From the equation and the table, three coefficients of thermal expansion over the range of 77 to 175 K were derived:

$$\alpha = 0.551, \quad \beta = 6.25 \times 10^{-4}, \quad \text{and} \quad \gamma = 3.35 \times 10^{-6}$$

Table 7: Density of liquid and solid ozone.

Physical state	Temperature		Density
	°C	K	g/cm^3
Liquid	−195.8	77.3	1.6137 ± 0.0004
Liquid	−195.8	77.3	1.613 (supercooled)
Liquid	−195.6	77.5	1.619 ± 0.0004
Liquid	−195.6	77.5	1.613 ± 0.0004
Liquid	−195.4	77.7	1.614 ± 0.004
Liquid	−188.0	85.1	1.595 ± 0.003
Liquid	−185.6	87.5	1.5839 ± 0.0011
Liquid	−183.0	90.1	1.571 ± 0.003
Liquid	−183.0	90.1	1.574
Liquid	−182.9	90.2	1.5727
Liquid	−170.0	103.1	1.536
Liquid	−150.0	123.1	1.473
Liquid	−120.0	153.1	1.376
Liquid	−112.0	161.1	1.354 ± 0.001
Solid	−195.8	77.5	1.728 ± 0.002

Data source: [68, 78]

Table 8: Density of liquid ozone and liquid ozone/liquid oxygen mixtures (at 101 kPa).

Temperature		Composition		Density	Authors	Year	References
K	°C	Mol-% ozone	Mass-% ozone	g/cm ³			
90	−183.2	72.2	79.4	1.4596	Jenkins and Dipaolo	1956	[68]
90	−183.2	81.1	86.6	1.5050			
90	−183.1	83.8	88.6	1.5086			
77.3	−195.8	88.0	91.7	1.5678 ± 0.07			
77.4	−195.7	89.0	92.4	1.5738 ± 0.09			
90	−183.2	95.2	96.8	1.5489			
90	−183.2	100.0	100.0	1.574			
90.2	−182.9	100.0	100.0	1.5727 ± 0.0004			
87.5	−185.6	100.0	100.0	1.5839 ± 0.0011			
77.5	−195.6	100.0	100.0	1.6130 ± 0.0004			
77	−195.5	6.2	9.0	1.230 ± 0.004	Hersh, Berger, and Brown	1959	[66]
77	−195.5	86.8	90.8	1.563 ± 0.005			
90	−183	22.1	29.8	1.245 ± 0.003			
90	−183	63.6	72.4	1.426 ± 0.004			
90	−183	100.0	100.0	1.571 ± 0.003			
85	−188	100.0	100.0	1.595 ± 0.003			
77	−195	100.0	100.0	1.614 ± 0.003			

See also Figure 4

The density of ozone at its boiling point, 161 K, was determined to be $1.354 \pm 0.001 \text{ g/cm}^3$. The volume increase on melting is +7.1% [77]. Additional density data for liquid and solid ozone are listed in Table 7. The densities of ozone/oxygen mixtures are listed in Table 8.

For the conversion of mol-% ozone to mass-% ozone and vice versa in ozone/oxygen mixtures, one can use the following formulas:

$$\text{Mass-\% O}_3 = 100 - \frac{100}{1 + \left(\frac{\text{Mol-\% O}_3}{100 - \text{Mol-\% O}_3} \right) \left(\frac{47.9982}{31.9988} \right)}$$

$$\text{Mol-\% O}_3 = 100 - \frac{100}{1 + \left(\frac{\text{Mass-\% O}_3}{100 - \text{Mass-\% O}_3} \right) \left(\frac{31.9988}{47.9982} \right)}$$

For the interpolation of density as a function of composition relationships, the following equations derived from the foregoing table come in handy:

$$\begin{aligned} \text{at } 77.7 \text{ K} = -195.5^\circ\text{C}: \quad \rho &= 0.833 - 0.213\chi_{\text{O}_3} \\ \text{at } 90.2 \text{ K} = -183.0^\circ\text{C}: \quad \rho &= 0.877 - 0.240\chi_{\text{O}_3} \end{aligned}$$

where ρ is the density in g/cm^3 , and χ_{O_3} is the mass fraction ozone.

It was found that the densities of liquid ozone-liquid oxygen mixtures could be calculated accurately from the additive behavior of densities of pure liquid ozone and liquid oxygen at the same temperature by means of the relation

$$1\bar{d} = \frac{X_1}{d_1} + \frac{X_2}{d_2}$$

where $\bar{d}$ is the density of the mixture, d_1 and d_2 are the densities, and X_1 and X_2 are the weight fractions of pure oxygen and pure ozone, respectively. This linear relationship is also evident from the data illustrated in Figure 4. See also [79].

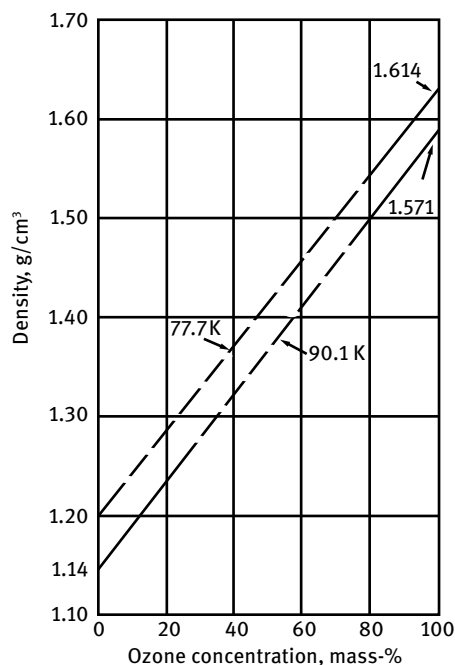


Figure 4: Density of liquid ozone/oxygen mixtures. (Reproduced and modified from [80].)

3.4 Compressibility of Ozone

Experimental determination of the compressibilities of ozone and ozone/oxygen mixtures would be difficult because of the unstable nature of ozone, so they were calculated from critical constants for pure ozone and from well-established data for oxygen [81]. Equation of state virial parameters of ozone/oxygen mixtures data for pure ozone, pure oxygen, and mixtures containing 20, 40, 60, and 80 mol-% ozone were presented in table format. The calculated compressibilities of pure ozone were used to correct thermodynamic quantities for the ideal gas, computed from spectroscopic data, to real gas conditions.

3.5 Vapor Pressure and Vapor Phase Composition of Ozone

3.5.1 Vapor Pressure of Solid and Liquid Ozone

The vapor pressure between 90.2 and 243.2 K (−183 and −30 °C) can be calculated from the equation [82]

$$\log P = 8.25313 - 814.941587/T - 0.001966943T$$

where P is the vapor pressure in mm Hg and T is the temperature in kelvin. The normal boiling point is 161.2 ± 0.3 K (−111.9 ± 0.3 °C). The critical temperature was determined experimentally and found to be 261 ± 0.1 K (−12.1 ± 0.1 °C). The critical pressure derived from this critical temperature and the vapor pressure equation is 5.51 MPa (54.6 atm absolute). Results were in good agreement with the data in the literature. The precision of the vapor pressure data measurement is limited by the unstable nature of ozone and the necessarily small samples that must be used for measurements in the interests in the interests of safety. See also [83].

Vapor pressure data for solid and liquid ozone are listed in Table 9. Figure 5 shows vapor pressure data to higher temperatures, significantly above the normal boiling point.

Table 9: Vapor pressure of ozone.

Physical state	Temperature			Vapor pressure	Authors	Year	References
	K	°C		mm Hg			
Solid at melting point	80.1	−193.0	Triple point	0.00859	Jenkins and Birdsall	1952	[70]
Liquid	90	−183	Boiling point of liquid oxygen	0.10	Jenkins and Birdsall	1952	[70]
Liquid	194.9	−78.2	Dry ice	6.18 atm	Jenkins and Birdsall	1952	[70]
Liquid	87.2	−185.9	Boiling point of liquid argon	4.03×10^{-2}	Hanson and Mauersberger	1985	[84]
Liquid	87.2	−185.9	Boiling point of liquid argon	4.05×10^{-2}	Mauersberger, Hanson, and Morton	1985	[85]
Solid	68	−205		1×10^{-5}	Hanson and Mauersberger	1986	[86]

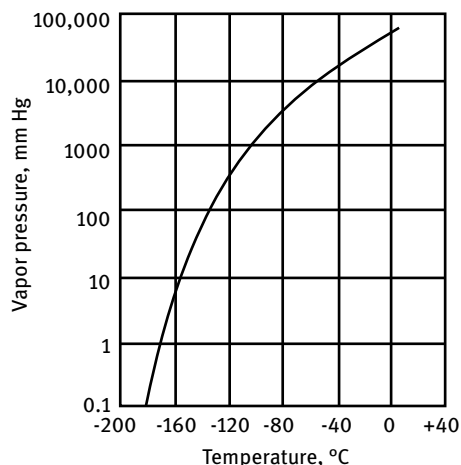


Figure 5: Vapor pressure of ozone. (Based on data from [82].)

The vapor pressure above liquid ozone was measured with high accuracy in a temperature range of 85 to 95 K. High-precision vapor pressure data will aid research in atmospheric ozone measurements, and ozone/diluent gas streams with known ozone partial pressures will help in calibrating instruments in many laboratory ozone studies such as measurements of cross sections and reaction rates [84, 85]. At the boiling point of liquid argon (87.3 K = -185.9°C), an ozone vapor pressure of 4.03×10^{-2} to 4.05×10^{-2} mm Hg was obtained with an accuracy of $\pm 0.7\%$. Increases and decreases in liquid argon temperatures raised and lowered the ozone vapor pressure, respectively. A least-squares fit of the data provided the Clausius-Clapeyron equation for liquid ozone, and a latent heat of vaporization of 82.7 cal/g was calculated.

Vapor pressures of liquid and solid ozone were measured over a temperature range of 87 to below 66 K. The experiment was performed under flow conditions, and the gas was analyzed by a precision mass spectrometer system to make sure that no premature decomposition had occurred [86]. In the range of solid ozone, two forms, supercooled and crystalline ozone, were found. A least-squares fit of the data for crystalline ozone resulted in the following linear relationship between pressure and the reciprocal of temperature for the crystalline form of ozone:

$$P = 10.460 - 1021.6/T$$

where P is the vapor pressure in mm Hg and T is the temperature in kelvin. The estimated uncertainty of the data is $\pm 1.0\%$. A triple point temperature of 79.6 ± 0.3 K was found where supercooled and crystalline ozone data intersect. For example, the vapor pressure of ozone at 68 K (-205°C) is 1×10^{-5} mm Hg, from which the latent heat of sublimation was calculated to be 407 J/g (97.4 cal/g).

The vapor pressure of ozone in a temperature range of 92.8 to 162.0 K can be calculated by the Antoine equation

$$\log_{10}(P) = 4.23637 - [712.487/(T + 6.982)]$$

where P is the vapor pressure in bar and T is the temperature in kelvin (from [87]).

3.5.2 Vapor Pressure and Vapor Phase Composition of Ozone/Oxygen Mixtures

Phase diagrams and vapor pressure composition data for liquid ozone/oxygen mixtures were obtained at 77.6 to 93 K (−195.5 to −180 °C) [88]. The vapor pressure isotherms (Figure 6) were used to construct the boiling point-composition line at atmospheric pressure (Figure 7). The vapor pressure of pure liquid ozone defines an upper limit for the partial pressure of ozone in the vapor in equilibrium with boiling liquid. The vapor pressure of ozone/oxygen solutions deviated markedly from Raoult's law in a positive direction. Liquid-liquid equilibrium indicated that 93 K (−180 °C) was an upper bound for the consolute temperature. The region of two liquid phases extended from 9 to 91 mass-% ozone at 77.6 K (−195.5 °C) and 29.8 to 72.4 mass-% ozone at 90 K (−183 °C).

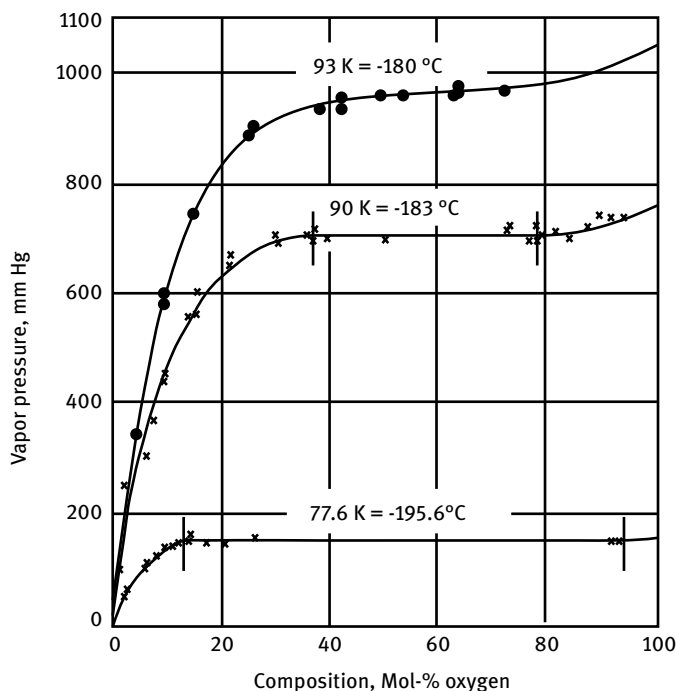


Figure 6: Vapor pressure isotherms for ozone/oxygen system at three temperatures. (Republished and modified from [88], with permission from © 1955 American Institute of Physics, permission conveyed through Copyright Clearance Center, Inc.)

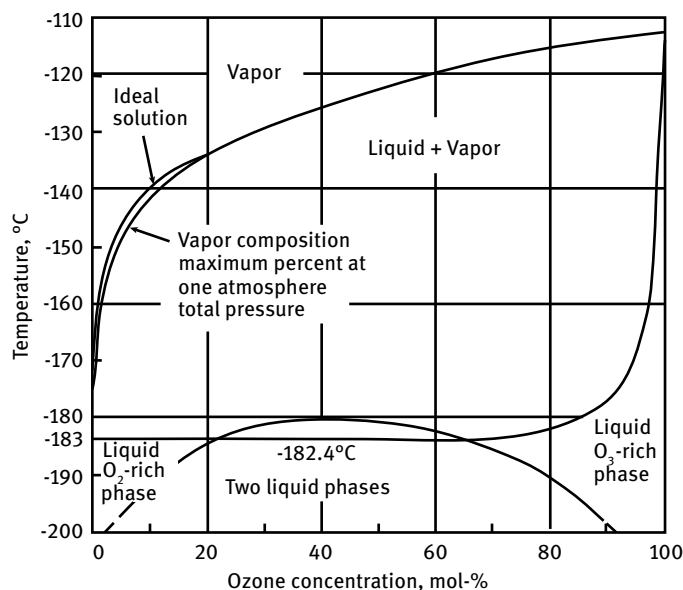


Figure 7: Phase diagram for ozone/oxygen system at 1 atm total pressure. (Republished and modified from [88], with permission from © 1955 American Institute of Physics, permission conveyed through Copyright Clearance Center, Inc.)

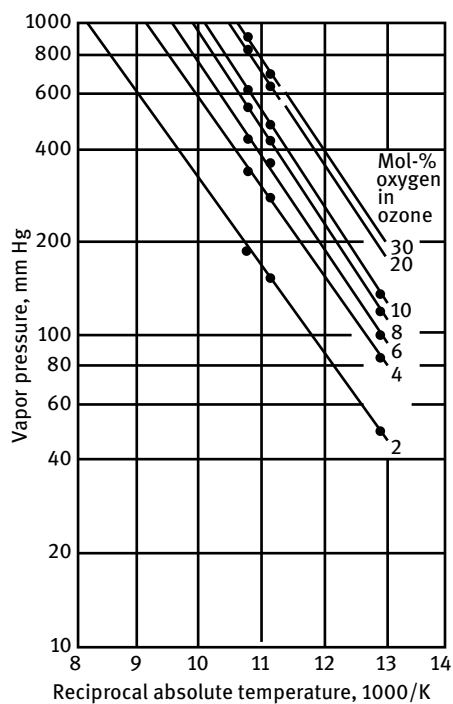


Figure 8: Vapor pressure of ozone/oxygen mixtures at below atmospheric pressure. (Republished and modified from [88], with permission from © 1955 American Institute of Physics, permission conveyed through Copyright Clearance Center, Inc.)

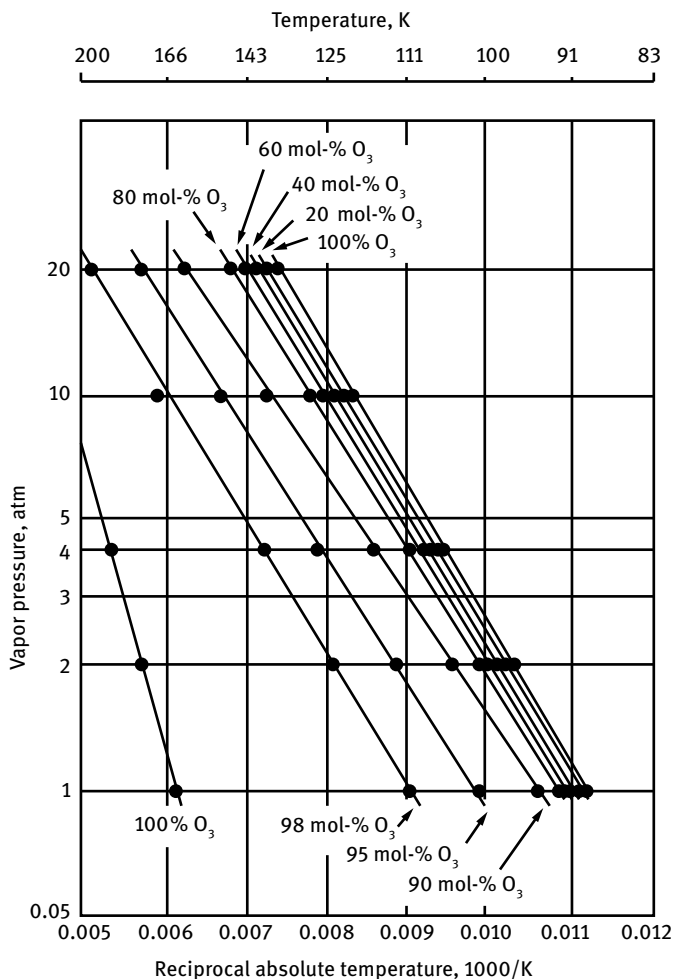


Figure 9: Vapor pressure of liquid ozone/oxygen mixtures at above atmospheric pressure. (Republished and modified from [83], with permission of © 1960 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

Plotting the data from Figure 6 in an Arrhenius-type graph gives straight lines for the logarithm of the vapor pressure when plotted versus reciprocal absolute temperature (Figure 8). This figure is for below atmospheric pressures. A later illustration (Figure 9) shows similar data for above atmospheric pressure.

Figure 10 combines vapor pressure and vapor phase composition data with the phase boundaries in the liquid ozone-liquid oxygen system.

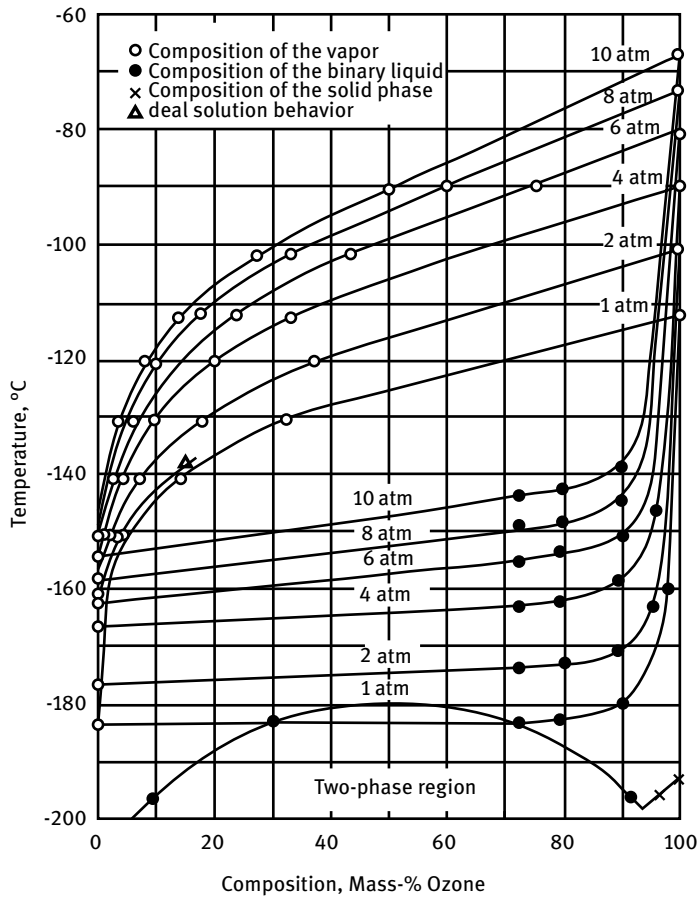


Figure 10: Vapor pressure phase diagram of ozone/oxygen mixtures. (Reproduced and modified from [7].)

3.6 Viscosity of Ozone

The viscosity data for gaseous and liquid ozone are summarized in Table 10. The viscosity of liquid ozone/oxygen mixtures is illustrated in Figure 11. The viscosity of liquid ozone/oxygen mixtures can be interpolated to an accuracy of less than $\pm 5\%$ from the following equations [68]:

$$\log \eta = (\chi_1 \log \eta_{O_2} + \chi_2 \log \eta_{O_3})$$

where χ_1 = mol fraction oxygen, η_{O_2} = viscosity of liquid oxygen = 0.190 cPs at -183°C , χ_2 = mol fraction ozone, and η_{O_3} = viscosity of liquid ozone = 1.56 cPs at -183°C . Similar viscosity data are compiled in Table 11.

Table 10: Viscosity of gaseous and liquid ozone.

Physical state	Temperature		Viscosity		Source	Year	References
	K	°C	Pa s	Ps			
Gaseous	298	25	133×10^{-7}	133×10^{-6}	Streng	1961	[65]
Gaseous	273	0	127×10^{-7}	127×10^{-6}	Streng	1961	[65]
Gaseous	195	-78	107×10^{-7}	107×10^{-6}	Streng	1961	[65]
Liquid (supercooled)	77.6	-195.6	0.00414 ± 0.00005	0.0414 ± 0.0005	Jenkins and Dipaolo	1956	[68]
Liquid	90.2	-183.0	0.00156 ± 0.00002	0.0156 ± 0.0002	Jenkins and Dipaolo	1956	[68]
Liquid	161.3	-111.9	0.000272	0.00272	Streng	1961	[65]

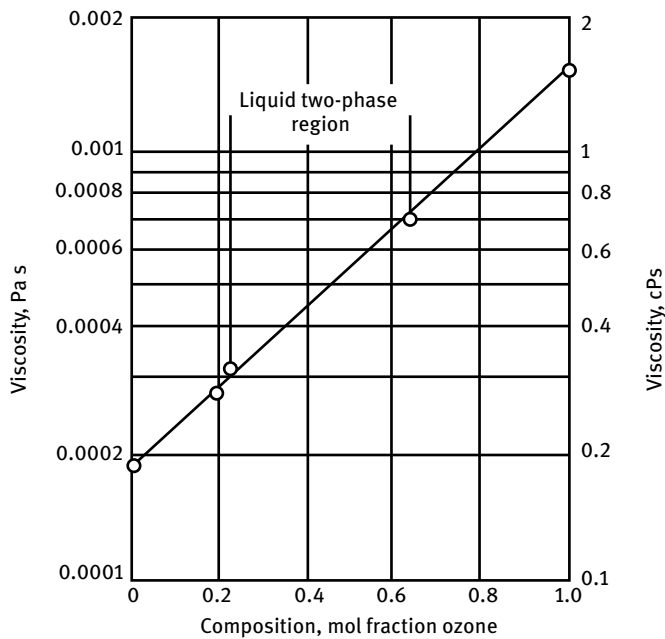


Figure 11: Viscosity of liquid ozone/oxygen mixtures at 90 K. (Republished and modified from [68], with permission of © 1956 American Institute of Physics; permission conveyed through Copyright Clearance Center Inc.)

Table 11: Viscosity of liquid ozone/oxygen mixtures.

Mass-% ozone	Viscosity, Pa s		Viscosity, cPs	
	at 78 K	at 90 K	at -195 °C	at -183 °C
100.0	0.0042 ± 0.00001	0.00157 ± 0.00002	4.20 ± 0.01	1.57 ± 0.02
72.4		0.00079 ± 0.00001		0.79 ± 0.01
29.8		0.00031 ± 0.00001		0.31 ± 0.01
26.0		0.00027 ± 0.00001		0.27 ± 0.01
9.0	0.00034 ± 0.00001		0.34 ± 0.01	
0.0		0.000189		0.189

Data source: [66]

3.7 Surface Tension of Ozone

Surface tension data of liquid ozone are listed in Table 12.

Table 12: Surface tension of liquid ozone.

Temperature		Surface tension		Authors	Year	References
K	°C	dyn/cm	N/m			
77.2	-196.0	43.8 ± 0.1	0.0438 ± 0.0001	Hersh, Berger, and Brown	1959	[66]
90.2	-183.0	38.4 ± 0.7	0.0384 ± 0.0007	Hersh, Berger, and Brown	1959	[66]
90.5	-182.7	38.1 ± 0.2	0.0381 ± 0.0002	Jenkins and Dipaolo	1956	[68]

As referenced in [65]

1 dyn = 10⁻⁵ N; 1 dyn/cm = 10⁻³ N/m

3.8 Thermal Conductivity of Ozone

The thermal conductivity of liquid ozone is very similar to that of liquid oxygen (Table 13).

Table 13: Thermal conductivity of liquid ozone.

Temperature		Thermal conductivity	
K	°C	cal s ⁻¹ cm ⁻¹ °C ⁻¹	W cm ⁻¹ K ⁻¹
145.2	-128.0	5.52 × 10 ⁻⁴ ± 5%	0.00231
108.2	-165.0	5.42 × 10 ⁻⁴ ± 5%	0.00227
90.2	-183.0	5.31 × 10 ⁻⁴ ± 5%	0.00222
77.4	-195.8	5.21 × 10 ⁻⁴ ± 5%	0.00218
For comparison: Liquid oxygen			
91.1	-182.0	5.36 × 10 ⁻⁴	0.00224

Data source: [89–91].

3.9 Critical Constants of Ozone

The critical constants of ozone are listed in Table 14. Chances are that ozone would explode before it reached its critical point when warmed up.

Table 14: Critical point properties of ozone.

Property	SI unit	Other unit
$T_{\text{crit.}}$	261.15 K	-12.1 °C
$P_{\text{crit.}}$	5.514 MPa	54.6 atm
$V_{\text{crit.}}$	147.1 cm ³ /mol	

Data source: [65]

3.10 Solubility, Miscibility, Mixtures, Solutions of Ozone

3.10.1 Mixtures of Inorganic Substances with Ozone

At the temperature of liquid oxygen or liquid nitrogen, liquid ozone and liquid oxygen form two immiscible layers with the lower layer consisting of 30% oxygen dissolved in ozone and the upper layer of 30% ozone dissolved in oxygen. The composition of the two layers varied with temperature. Above a critical temperature for this two-phase phenomenon homogeneous mixtures could be obtained.

3.10.1.1 Solubility of Ozone in Solvents

The solubility of ozone in water is 0.688 g/L at 293 K and 101 kPa and the Bunsen coefficient is 0.321 L gas/L water. This solubility is important for wastewater and drinking water treatment using ozone as the disinfectant. To store dissolved gaseous ozone for later use, perfluorinated organic solvents exhibit high solubility for both oxygen and ozone. The solubility in other solvents has been measured and reported [92]. At one time, dissolved ozone in compressed gas cylinders has been offered for sale for laboratory use where the operation of an ozonizer was not practical.

Ozone forms homogeneous mixtures when mixed with the following chemicals (not all of them oxidizers) in a 1:1 molar ratio at the temperatures (in K) indicated in parentheses following the chemical's formula: CO (77), NF₃ (90), NF₃ (90), CH₄ (90), CClF₃ (90), ClO₃F (116), O₂F₂ (120), CCl₂F₂ (130), ClF₃ (195) [75].

Solutions of ozone in inert halocarbons, such as CF₄, ClCF₃, and CHClF₂, are suitable to measure its spectroscopic properties [93] or as a convenient and safe method to store ozone. Many different inert solvents have been proposed for extraction and storage of ozone. Proposed solvents for the extraction and storage of ozone include CClF₃ or CHClF₂ at <178 K (<-95 °C) [94], mixtures of oxygen and argon [95], mixtures of CCl₂F₂ and CClF₃ [96], and a wide range of 20 different fluorochlorocarbons [97], e.g., CF₄ [98] and CCl₂F₂ [99].

Table 15: Thermodynamic properties of gaseous ozone at pressure of 1 bar.

Tempera- ture K	Molar heat capacity, C_p $J \cdot K^{-1} \text{ mol}^{-1}$	Entropy S $J \cdot K^{-1} \text{ mol}^{-1}$	$-[G - H(T_r)]/T$ kJ/mol	$H - H(T_r)$ kJ/mol	ΔH_f kJ/mol	ΔG_f kJ/mol	Equilibrium constant, $\log K_f$
0	0.000	0.000	Infinite	-10.351	145.348	145.348	Infinite
100	33.292	200.791	271.040	-7.025	144.318	150.235	-78.474
200	35.058	224.221	242.401	-3.636	143.340	156.541	-40.884
298.15	39.238	238.932	238.932	0.000	142.674	163.184	-28.589
300	39.330	239.175	238.933	0.073	142.665	163.311	-28.435
400	43.744	251.116	240.531	4.234	142.370	170.247	-22.232
500	47.262	261.272	243.688	8.792	142.340	177.224	-18.514
600	49.857	270.129	247.373	13.654	142.462	184.191	-16.035
700	51.752	277.963	251.194	18.738	142.665	191.130	-14.262
800	53.154	284.969	254.986	23.986	142.907	198.037	-12.931
900	54.208	291.292	258.674	29.356	143.169	204.913	-11.893
1000	55.024	297.048	262.228	34.819	143.439	211.759	-11.061

Data source: [87]

The French company Air Liquide France was one of the first chemical companies to offer ozone solutions commercially for sale. Ozone can be stored in solution under high pressure [100]. It is recommended to store these compressed gas cylinders below 250 K = -23°C to extend the shelf life of this chemical. As an alternate solvent, anhydrous white fuming nitric acid has been patented as a solvent for gaseous ozone [101]. This would make a good rocket propellant oxidizer.

It was discovered that a low concentration of CF_3Cl (Freon-13) on the order of 3 to 5 mass-% added to ozone/oxygen solutions completely eliminated the two-phase regions [17]. Thus, it became possible to handle these solutions without the dangers that would attend the separation of an ozone-rich phase.

3.11 Thermodynamic Properties and Thermal Properties of Ozone

The thermodynamic properties of gaseous ozone are listed in Table 15. The data in the NIST online table [87] go all the way to 6000 K, but ozone would not be stable at those temperatures. Only the data below 1000 K are shown.

3.11.1 Heat Capacity of Ozone

The specific heat of liquid ozone has been measured over a temperature range of 97 to 121 K. The heat capacity was found to be a linear function of temperature and could be represented by the equation

$$c_p = 0.425 + 0.0014(T - 90)$$

where c_p is the heat capacity in $\text{cal g}^{-1}^{\circ}\text{C}^{-1}$ and T is the temperature in K [102]. This equation was considered sufficiently accurate for engineering purposes over the temperature range of 90 to 150 K. Thus, the values reported for the specific heat of liquid ozone at 90 and 150 K in the following table (Table 16) are compatible with the preceding equation.

Table 16: Heat capacity of liquid ozone.

Temperature		Heat capacity			
K	$^{\circ}\text{C}$	$\text{J mol}^{-1} \text{K}^{-1}$	$\text{J g}^{-1} \text{K}^{-1}$	$\text{cal mol}^{-1}^{\circ}\text{C}^{-1}$	$\text{cal g}^{-1}^{\circ}\text{C}^{-1}$
90	-183	85.35	1.7782	20.39	0.425
150	-123	102.2	2.1297	24.43	0.509

Data source: [102]

Molecular mass: 47.9982 g/mol

3.11.2 Enthalpy of Formation of Ozone

Enthalpy of formation data for solid, liquid, and gaseous ozone are listed in Table 17.

Table 17: Enthalpy of formation of ozone.

Physical state	Temperature		Enthalpy of formation	
	K	°C	kJ/mol	kcal/mol
$(\Delta E)_f$ Gaseous	291 K under constant volume	18	$+143.2 \pm 0.7$	$+34.220 \pm 0.180$
$(\Delta H)_f$ Gaseous	291 K under constant pressure	18	$+141.9 \pm 0.7$	$+33.923 \pm 0.180$
Liquid	90.19	-183	$+124.8 \pm 0.8$	$+29.83 \pm 0.20$
Solid	80.7	-192.5	+122.6	+29.3
Gaseous as ideal gas	298.15	+25	$+142.7 \pm 1.7$	$+34.1 \pm 0.4$

Data source: [65, 87]

3.11.3 Heat of Fusion and Solid-State Phase Transitions of Ozone

The heat of fusion $(\Delta H)_{\text{melt}}$ of solid ozone was estimated at about 2.09 kJ/mol = 0.5 kcal/mol [65].

3.11.4 Heat of Vaporization of Ozone

Heat of vaporization data for liquid ozone are listed in Table 18.

Table 18: Heat of vaporization of liquid ozone.

Heat of vaporization ^a $(\Delta H)_{\text{vap}}$				Source	Year	References
kJ/mol	kcal/mol	J/g	cal/g			
15.19	3.63	316.4	75.63	Hersh	1959	[103]
14.35	3.43	299.0	71.46	Jenkins and Birdsall	1952	[70]
16.61	3.97	346.0	82.7	Hanson and Mauersberger	1985	[84]

^a At normal boiling point

Molecular mass: 47.9982 g/mol

A latent heat of vaporization of liquid ozone of 82.7 cal/g was calculated from vapor pressure data [84]. The latent heat of sublimation of solid ozone was calculated to be 407 J/g (97.4 cal/g) [86]. See also [83].

3.11.5 Heat of Dissociation of Ozone

The activation energy of thermal decomposition of gaseous ozone at low pressure is 100.4 kJ/mol = 24.0 kcal/mol [65]. The bond dissociation energy of 105 kJ/mol (25 kcal/mol), defined as the energy necessary to break the first bond, is far less than

the mean thermochemical value of 299 kJ/mol (71.5 kcal/mol). The bond dissociation energy and the activation energy are essentially identical.

3.11.6 Entropy of Ozone

Thermodynamic functions of ozone are listed in Table 19.

Table 19: Thermodynamic functions of gaseous ozone.

Temperature	Enthalpy function ($H_0 - H_{00}$)/ T		Entropy S		Free energy function ($F_0 - H_{00}$)/ T		Molar heat capacity C_p	
	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ °C ⁻¹
As ideal gas at 1 atm								
150	33.31	7.961	214.10	51.171	180.78	43.208	33.72	8.059
200	33.56	8.022	223.92	53.519	190.39	45.505	35.04	8.374
250	34.05	8.138	231.98	55.444	197.94	47.308	37.02	8.847
298.15	34.71	8.297	238.68	57.046	203.97	48.749	39.19	9.367
300	34.73	8.301	238.93	57.105	204.17	48.798	39.28	9.387
350	35.55	8.497	245.14	58.59	209.60	50.095	41.54	9.929
400	36.43	8.708	250.83	59.949	214.41	51.245	43.65	10.432
450	37.35	8.926	256.14	61.219	218.75	52.282	45.49	10.873
500	38.24	9.139	260.98	62.375	222.72	53.231	47.10	11.258
550	39.11	9.347	265.52	63.46	226.40	54.111	48.47	11.584
As real gas at 1 atm								
200	33.27	7.951	223.74	53.474	190.50	45.531	35.55	8.497
298.15	34.61	8.272	238.61	57.03	204.00	48.757	39.35	9.406
350	35.48	8.481	245.09	58.579	209.62	50.1	41.65	9.955
As real gas at 5 atm								
200	32.07	7.665	209.59	50.094	177.55	42.436	37.60	8.987
298.15	34.20	8.173	224.95	53.765	190.76	45.593	40.02	9.564
350	35.21	8.415	231.52	55.335	196.32	46.922	42.09	10.059
As real gas at 10 atm								
298.15	33.67	8.048	218.84	52.305	185.17	44.257	40.84	9.761
350	34.86	8.332	225.52	53.901	190.66	45.57	42.63	10.19

Data source: [81, 65]

3.12 Molecular Properties, Structure, Dipole Moment, Molecular Orbital Calculations of Ozone

3.12.1 Molecular Properties of Ozone

The molecular structure of ozone is an open V, as shown in Figure 12. The V-shape structure of ozone (116.8° bend angle and 1.27 Å bond distance) is well established. The

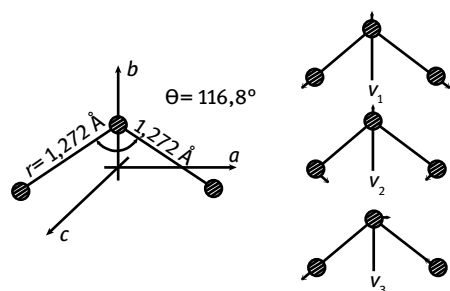


Figure 12: Open-form and fundamental vibrations of ozone molecule. (Reproduced from [105] with permission © Uspekhi Fizicheskikh Nauk 1994.)

microwave spectrum gives structural information that can be interpreted unambiguously and that is more accurate than that obtained by other methods. The rotational spectra have been obtained for six different isotope-labeled ozone molecules between 9 and 45 GHz [104]. Although the resultant bond length of $1.278 \pm 0.002 \text{ \AA}$ was consistent with the electron diffraction value of $1.26 \pm 0.02 \text{ \AA}$, the apex angle value of $116^\circ 45' \pm 30'$ was inconsistent with the diffraction value of $127 \pm 3^\circ$. The dipole moment of ozone was determined to be 0.58 ± 0.05 Debye unit from the Stark effects of two low J-transitions.

However, there is some evidence of an alternate form of the ozone molecule in the shape of a closed equilateral triangle (Figure 13), which may be an intermediate in the decomposition or formation of bent (V-shaped) ozone. This isomer is referred to as the metastable cyclic isomer of ozone, or cyclic ozone. Theoretical evidence for the stability of cyclic ozone has been conflicting [106–108]. The cyclic ozone should decompose more easily than the bent ozone because it contains three single bonds. The $\angle \text{O—O—O}$ bond angle in the triangular form should be close to 60° . This molecule is isoelectronic with cyclopropane.

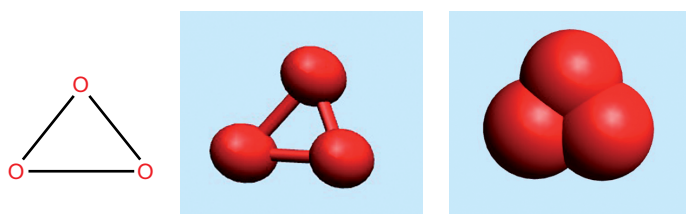
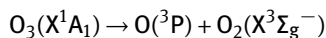


Figure 13: Molecular structure of cyclic ozone.

Because oxygen as a starting material is in abundant supply, oxygen-derived high-energy rocket propellants have received significant attention in recent decades. Theoretically, the cyclic form of ozone is an even more powerful oxidizer than conventional ozone. The predicted enthalpy of formation of cyclic ozone vapor is above that

of V-shaped ozone with an angle of $116^{\circ}48'$, which is $+142.7\text{ kJ/mol}$. Theoretically, the cyclic structure is energetically more favorable by 200 kJ/mol (48 kcal/mol), contrary to the value obtained in experiments [109]. The theoretical enthalpy of reaction of metastable cyclic solid ozone with liquid hydrogen is 17.15 MJ/kg (going to water vapor), compared to 14.65 MJ/kg for frozen normal ozone/LH2 compared to only 12.56 MJ/kg for LOX/LH2, which is what is currently flying in many rockets. Other *ab initio* calculations predicted that the energy level of the cyclic conformer of ozone should be 67 kJ/mol (16 kcal/mol) above the preferred (open-chain) form of this substance. The theoretical rocket performance of cyclic ozone is about 35% higher than that of LOX/LH2 [110]. That should be enough motivation to continue to search for more energetic forms of oxygen and/or ozone [111]. The cyclic ozone should decompose more easily than the V-shaped bent ozone because it contains three single bonds.

Several *ab initio* quantum mechanical investigations have predicted that the stability of the cyclic ozone molecule may be sufficient for future use as a rocket propellant, indicating that a significant energy barrier prevents its spontaneous conversion to the open form, and an even bigger barrier prevents its decomposition to dioxygen and atomic oxygen [112, 113]. *Ab initio* calculations of the equilibrium structure of the D_{3h} form of ozone and the energy difference (ΔE) between the open and cyclic forms of ozone indicated that ΔE is 121.7 kJ/mol (29.1 kcal/mol), of which triple excitations contributed 24.3 kJ/mol (5.8 kcal/mol) [114]. Zero-point vibrational energies decreased ΔE by 1.67 kJ/mol (0.4 kcal/mol), yielding a final estimate of 120 kJ/mol (28.7 kcal/mol). These results demonstrated that cyclic ozone is above the



dissociation limit ($109.2\text{ kJ/mol} = 26.1\text{ kcal/mol}$). The existence of a cyclic ozone seems proven because cyclic ozone rings were found adsorbed to a magnesium oxide surface using transmission electron diffraction [115]. The first experimental evidence of the cyclic form of ozone was found in three air-stable surface reconstructions of MgO (111) surfaces on single crystals annealed above 1450°C . The oxygen trimers appeared to be centered over underlying Mg atoms. Charge transfer may explain the cyclic O_3 stabilization of the polar MgO (111) surface, and it may not be possible to remove cyclic O_3 from the surface and into a rocket without it suffering premature decomposition. But most investigations into the short-lived existence of cyclic O_3 and ways to stabilize it were initiated by studies of the formation and decomposition in Earth's atmosphere, and only few had the use of ozone as a rocket propellant in mind.

If ring-shaped polyoxygen molecules contain more than three oxygens, the strain energy would decrease, and the stability should increase [116]. In analogy of dioxygen forming a dimer $(\text{O}_2)_2$, ozone may also exist in the form of a dimer $(\text{O}_3)_2$ [117].

The half-life of cyclic ozone was estimated to be only 10 s at 200 K and 70 s below 100 K, which might partly explain the unsuccessful attempts for its experimental identification [118]. The kinetic isotope effects (KIEs) for various ^{18}O substitution reactions were calculated as a function of temperature and were predicted to be as high as

10 at very low temperature. Because of the large KIEs, the experimental identification of cyclic $^{18}\text{O}_3$ seems more promising than cyclic $^{16}\text{O}_3$.

From a propulsion standpoint, the biggest question with cyclic ozone is how to make it. Some researchers are pursuing cyclic ozone production via organometallic chemistry using a transition metal ligand to bind and stabilize the cyclic ozone molecule. Cyclic ozone has not been isolated so far, despite its computed kinetic persistence. Possibilities of “trapping” this molecule (or the valence-isoelectronic cyclic thiozone, S_3) in transition metal complexes were investigated.

In 2005, Temple University’s Center for Advanced Photonics Research was awarded a Defense Advanced Research Projects Agency (DARPA) grant to develop cyclic ozone using laser-based chemistry methods [119]. They calculated the lifetime of cyclic ozone to be essentially infinity at liquid nitrogen temperatures. Whether this molecule is stable or sensitive to spontaneous explosion remains unknown. Coherent anti-Stokes Raman spectroscopy (CARS) schemes for detecting the synthesis of cyclic ozone were suggested.

A fourth allotropic form of oxygen is called tetraoxygen (O_4 , oxozone), most likely a dimer of dioxygen (O_2)₂, with potentially even higher rocket performance than the ozones. Very little is known about tetraoxygen. The exact shape of this molecule is still uncertain, but *ab initio* calculations indicate that some forms of the O_4 molecule should be stable. Best estimates based on *ab initio* calculations estimated an enthalpy of formation in a range of 93–95 kcal/mol [120]. The existence of tetraoxygen was predicted theoretically in the 1920s, and recent experiments have demonstrated its existence. The various aspects of tetraoxygen relate closely to ozone chemistry. A metastable energized state of tetraoxygen at low pressure was detected experimentally in 1997 [121].

A metastable state of tetraoxygen was produced and directly detected in a molecular beam, both by means of a direct-current discharge and by photodissociation of ozone in the collision region [121]. The O_4^* produced a complex spectrum from which general conclusions were drawn about its energetics and structure. The energy for this species is about 4 eV above that of two isolated O_2 molecules. A predominance of peak frequency differences in the range 411–419 cm^{-1} supports a cyclic D_{2d} geometry as predicted by *ab initio* calculations. Evidence of solid tetraoxygen was found at extremely high pressures (about 20 GPa) [122]. Intact O_4 as a gas-phase species had a lifetime in excess of 1 μs , and its dissociation requires overcoming a barrier on the order of 42 kJ/mol (10 kcal/mol) [123].

Condensation of gaseous ozone at 10–20 K gave solid ozone, which was used for X-ray diffraction (XRD) and neutron powder diffraction analysis. The solid had a bent structure with an O—O—O angle of 117.9°, in good agreement with the gas-phase structure. Measurement of the unit cell dimensions over the range 5–54 K provided no evidence for a phase transition. The crystal structure of ozone was determined from conventional XRD and high-resolution neutron powder diffraction data [124]. Ozone crystallizes in the orthorhombic space group P_{bca} with eight formula units per unit

cell. The lattice parameters at 5 K are as follows: $a = 778.88(2)$ pm, $b = 669.73(2)$ pm, $c = 684.13(2)$ pm. The geometry determined for an ozone molecule in the solid was found to be in good agreement with the well-known gas phase structure. There was no significant deviation from ideal C_{2v} symmetry. An ozone dimer with C_i point symmetry is feasible.

The $(O_3)_2$ dimer potential energy surface was explored by *ab initio* calculations, identifying five minima with binding energies between 1.46 and 9.37 kJ/mol (0.35 and 2.24 kcal/mol) [125]. The most stable may be characterized as slipped parallel, with the two O_3 monomers situated in parallel planes.

3.12.1.1 Search for Other Polyoxygens in Frozen Ozone

The search for higher polyoxygens and the triangular form of ozone has concentrated on frozen ozone, prepared in various ways and kept at very low temperatures, often in a matrix of frozen oxygen or frozen argon. One had to rely on spectroscopic methods to determine if the frozen mass contained anything other than frozen ozone.

Solid oxygen can serve as a matrix and stabilizer for solid ozone and other polyoxygens (if they exist) [126]. Experiments of this type were part of the development of rocket propellants that significantly improve the performance of the conventional liquid oxygen rocket propellant. One of the species believed to exist in frozen ozone was a weakly bound $O \cdots O_3$ complex isolated in solid oxygen, but later experiments suggested the Fourier transform infrared (FTIR) absorption spectra to be due to an ozone dimer formed by nanosecond tunable UV laser light irradiation between 210 and 240 nm to generate specifically oriented ozone dimers in solid oxygen. Other absorptions are due to defect sites, and they disappear during annealing [127]. Ozone was either generated *in situ* by irradiation of frozen oxygen or deposited onto a cold finger from a stream of oxygen seeded with low concentration of ozone [128, 129].

Cyclic O_4 is of interest both as a potential high-energy-density material (HEDM) species and because of its possible role in the ozone deficit problem in atmospheric chemistry. The pathway for decomposition from the D_{2d} minimum through a saddle point of C_2 symmetry and the approximate location of the singlet triplet crossing were calculated by computing the triplet energies at the geometries along the pathway for the singlet state [130]. The barrier to decomposition was found to be about 9 kcal/mol.

In preparation for inverse hybrid engine tests with frozen ozone/frozen oxygen in the chamber and gaseous hydrogen injected as a fuel, rocket engine tests with frozen oxygen (no ozone yet) were conducted at US Air Force Research Laboratory (AFRL), Phillips Laboratory at Edwards Air Force Base. An inverse hybrid rocket engine developed at Orbitec using a grain of solid oxygen burning in an atmosphere of gaseous hydrogen was tested at AFRL. In an effort to achieve higher I_{sp} , it was planned to replace the solid oxygen grain with a grain composed of solid oxygen enriched with solid ozone. Before this test could be done, the safety properties of solid oxygen-solid ozone mixtures had to be characterized [131, 132].

3.12.2 Dipole Moment of Ozone

Two properties, the dipole moment and the magnetic susceptibility of ozone, were of special interest for the characterization of the ozone molecule. A fully symmetrical (triangular) molecule should not have a dipole moment. The dipole moment, which was very important in the long debate about the structure of the ozone molecule, was first reported in 1939 using conventional methods on the liquid ozone/oxygen mixture obtained from condensation of the product of silent discharge with liquid oxygen [133]. The value of 0.49 D ruled out linear and symmetrical triangular structures for ozone.

From the Stark splitting of a microwave spectrum, the dipole moment was derived to be 0.53 ± 0.02 debye. Zeeman splittings of this transition showed that ozone is not significantly paramagnetic [134].

The dipole moment of ozone was determined to be 0.58 ± 0.05 debye from the Stark effects of two low J transitions in the microwave spectrum [104].

3.12.3 Molecular Orbital Calculations of Ozone

Because ozone is often too unstable to allow detailed experimental determination of many of its molecular properties, computational chemistry has stepped in to fill the gap. Predicted absorption spectra of open-form V-shaped O_3 and its excited states and predissociation states and those of postulated cyclic ozone can then be compared to measured spectra. The vibrational energies of ozone up to the dissociation threshold were calculated and compared to measured spectra [135]. The three lowest transition energies predicted for $^{16}O_3$ are 1101.9 cm^{-1} (1103.14 cm^{-1}), 698.5 cm^{-1} (700.93 cm^{-1}), and 1043.9 cm^{-1} (1042.14 cm^{-1}) for the symmetric stretch, the bending, and the antisymmetric stretch modes, respectively. The numbers in parentheses are the experimental values.

The effective ground state potential energy function of the ozone molecule near the C_{2v} equilibrium configuration was obtained in a least-squares fit to the largest sample of experimental, high-resolution vibration-rotation data used for this purpose so far [136]. The long-range behavior of the fitted potential at the dissociation limit $O_3 \rightarrow O_2 + O$ showed very good agreement with experimental data. The new potential energy surface was used to predict the band centers of the isotopomers $^{17}O_3$ and $^{18}O_3$.

3.13 Absorption, Emission, and Fluorescence Spectra of Ozone

The spectra of ozone are extremely important in determining its prevalence in the atmosphere, either as an air pollutant near the surface or as the key ingredient of the ozone layer in the upper atmosphere that protects us from the damaging UV radiation of the Sun. Spectroscopy would also be the method of choice to identify contaminants in liquid ozone, some of which are responsible for its hazardous explosion sensitivity. Spectroscopy is used to identify kinetic mechanisms that lead to the formation

of ozone or its decomposition and to identify intermediates in those reactions. Isotopic labeling and comparison of spectra of labeled compounds with natural ozone is a frequently used method to assign frequencies in the spectra to specific vibrations in the molecule and clarify its structure and energy levels. If we are looking for superoxidizers like O_4 , O_6 , or O_8 as future rocket propellants, the best way to find them is to predict from quantum mechanical calculations what their spectra might look like and then start looking at the predicted frequencies of molecular vibrations, rotations, or electronic levels. If ozone is in use at the workplace (any workplace, not just rocket test sites), the ozone concentration in the air needs to be monitored to protect the workers and spectroscopic methods are the fastest and most accurate methods to do that, even by remote sensing without direct contact with the sample.

3.13.1 Visible-Range Absorption Spectra of Ozone

The extinction coefficients of ozone dissolved in liquid oxygen or a Freon 12/13 mix at 77 K in the visible range were compared to the extinction coefficient of gaseous ozone in air (Table 20).

Table 20: Molar extinction coefficients of dissolved ozone.

Solvent	Temperature, K	Molar extinction coefficient, $L\ cm^{-1}\ mol^{-1}$	
Freon mixture	77	2.81 at 570 μm	3.10 at 600 μm
Liquid O_2	77	1.44 at 560 μm	2.00 at 600 μm
Gaseous	295	1.23 at 575 μm	1.32 at 605 μm

Data source: [93]

As shown in Table 20 and Figure 14, the molar extinction coefficient of ozone was greatest when dissolved in the Freon mix. The molar extinction coefficient of liquid ozone at 77 K was greater than that of gaseous ozone at 295 K.

3.13.2 Infrared Absorption Spectra of Ozone

In view of the great significance of ozone in atmospheric chemistry, and the use of IR spectroscopy for remote sensing, IR spectra of ozone have been thoroughly investigated. A low-resolution IR spectrum of gaseous ozone is shown in Figure 15. See also [137, 138].

Fourteen IR absorption bands of ozone between 500 and $3300\ cm^{-1}$ were measured and identified and values of the vibrational anharmonic constants determined [140]. The integrated band absorbances of many of these bands were measured from spectra taken on a spectrometer with a 32-m optical path length sample cell near 298 K

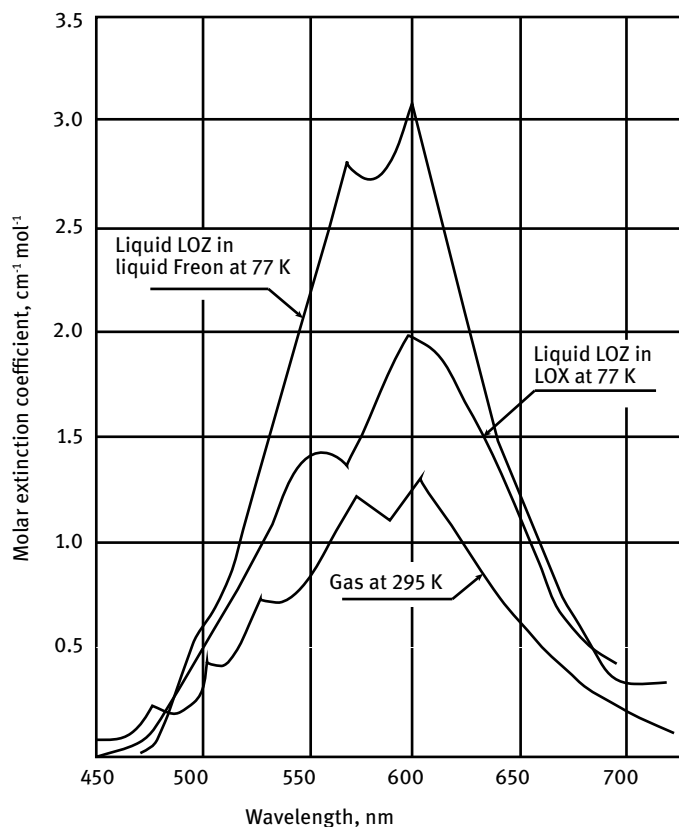


Figure 14: Ozone light absorption spectra in visible range. (Republished and modified from [93], with permission granted by © 1961 American Institute of Physics; permission conveyed through Copyright Clearance Center, Inc.)

(25°C). It was shown that the statistical band model described the behavior of the bands reasonably well for the ranges of experimental variables used.

A very complete history of the development of IR and microwave (vibrational-rotational) spectroscopy of ozone from the mid-19th century to 1994, including a bibliography of 254 references, was offered in [105]. It covered the development of both linear and non-linear spectroscopy and applications in fields of physics and chemistry of ozone, monitoring in the atmosphere, laser stimulation of chemical reactions, and study of relaxation processes.

IR spectra have helped to identify cyclic ozone, an unstable isomer of the open-chain normal ozone [141, 142]. The extinction coefficient of gaseous ozone in the IR range at 9.49μ is $80\text{ cm}^{-1}\text{ mol}^{-1}\text{ L}$.

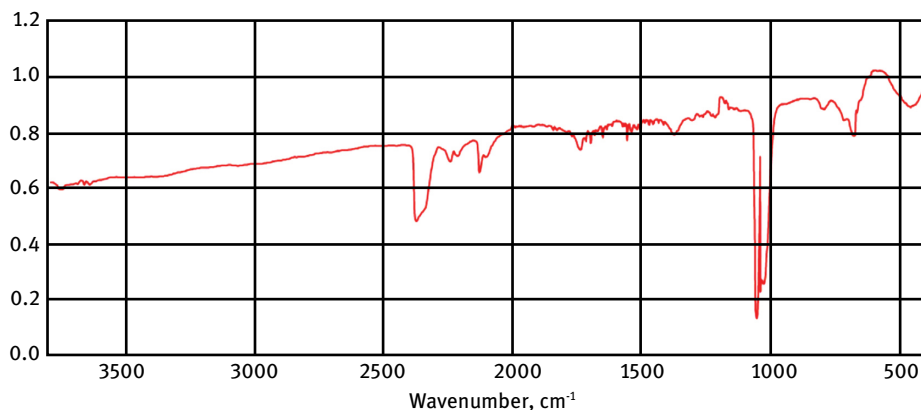


Figure 15: Low-resolution IR spectrum of gaseous ozone. (Reproduced and modified with permission from [139].)

A review of efforts to experimentally determine absolute line intensities for ozone transitions in the 9- to 11- μm spectral region over the last several decades explained that much of this effort has been driven by the requirements for remote sensing of terrestrial atmospheric ozone [143]. While significant progress has been achieved, discrepancies continue to persist among various IR measurements, and the relation between IR and UV standards is vague.

The IR spectra of liquid ozone films were measured at 78–85 K and ozone dissolved in liquid argon at 91–95 K [144]. Maxima of ozone bands in Ar solution were shifted toward lower frequencies compared to those in the gas phase by 1–30 cm^{-1} .

3.13.2.1 Infrared Absorption Band Assignments to Fundamental Vibrations in Ozone
Calculations of vibrations leading to the decomposition of ozone using valence-force potential functions tried to explain how molecules become energized in events leading to monomolecular decomposition reactions [145].

Some of the isotopic ozone molecules of different combinations of oxygen-16 and oxygen-18 have been synthesized and isolated in rare-gas matrices at 20 K and their IR absorption bands identified [146]. The isotope effects were calculated for symmetrical as well as unsymmetrical isotopic ozone molecules.

The vibrational frequencies of the six antisymmetric stretching modes of the ozone isotopomers $^{16}\text{O}_3$, $^{16}\text{O}_2^{18}\text{O}$, and $^{18}\text{O}_3$, in both Ar and Kr matrices, have been measured [147]. The ozone molecule has very anharmonic antisymmetric vibrations compared to other known molecules. Upper and lower limits to the valence bond angle were calculated and compared to each other and to the gas-phase bond angle. The bond angles of O_3 in both Ar and Kr, which were derived from measured

frequencies agreed with one another within the experimental uncertainty ($\pm 0.4^\circ$), and these angles were also in agreement with the gas-phase angle, $116.8 \pm 0.5^\circ$.

FTIR spectra of six ozone isotopomers of ^{18}O -enriched ozones were studied in LOX solution at 77 K in the spectral range $650\text{--}3200\text{ cm}^{-1}$ [148]. Full vibrational assignments could be made, and relative transition strengths were measured for many previously unobserved absorption bands of ^{18}O -enriched species.

3.13.3 Raman Fluorescence Spectra of Ozone

The problem with Raman spectroscopy of ozone is that ozone photolyzes under the influence of exciting illumination before fluorescence spectra can be recorded. It is therefore best to keep the ozone cool in a matrix of a frozen inert gas while the Raman spectra are recorded.

The Raman spectra of argon matrix-isolated ozone and oxygen-18-enriched ozone were obtained using reduced-power argon ion laser excitation [149]. Photodecomposition of ozone was sufficiently moderated to obtain excellent Raman spectra, with the following $^{18}\text{O}_3$ assignments: ν_1 1104 cm^{-1} , very strong; ν_2 701 cm^{-1} , strong; ν_3 1038 cm^{-1} , weak. IR spectra provided complementary data. An ozone valence angle of $116.3 \pm 4^\circ$ was calculated, in excellent agreement with microwave results. See also [150].

3.13.4 Ultraviolet/Visible Range Absorption Spectra of Ozone

The problem with measuring the UV spectra of ozone is that ozone photolyzes under the influence of a light beam before absorption spectra can be recorded. Strangely enough, not even the NIST Chemistry WebBook web site has UV spectra of O_3 . It is therefore best to keep the ozone cool in a matrix of a frozen inert gas while the spectra are recorded. For the visible region, some references about experimental absorption measurements are very old since the first absorption spectrum (between 520 and 650 nm) was observed by Chappuis in the year 1880, and this absorption range was named after him. Only with improved instrumentation was it possible to obtain accurate measurements of the absorption coefficient of ozone in the visible and UV ranges [151].

The absorption coefficient of gaseous ozone was measured for mercury lines at 2537, 2894, 2967, 3021, 3342, and $5770\text{ \AA}$ by measuring both the optical absorption and the pressure rise as the ozone decayed in a sealed quartz absorption tube [152]. This avoided a chemical determination of the ozone. The absorption cross-section σ is related to the absorption coefficient α by the equation $\sigma = \alpha/N$, where N is the atomic number density.

The absorption coefficients of ozone have been measured in the UV and visible regions using essentially 100% pure ozone [153]. The technique was based on a pure preparation of O_3 . Owing to the low variation of pressure in the cell, the ozone decom-

position was assumed to be negligible. Measurement of ozone concentration would then be a simple measurement of the total pressure.

The ozone absorption cross section at the 253.7 nm mercury line was measured very accurately and can be used as a reference line for other measurements. The partial pressure of ozone in the absorption cell was measured by simultaneously measuring the composition of the mixture (O_2/O_3) with a mass spectrometer and the total pressure of the gaseous system with a calibrated pressure sensor [154]. The method was precise but involved lots of instrumentation and is limited to measurements at some specified wavelengths.

Absorption cross sections of ozone at ambient temperature for the whole spectral region within the 195- to 345-nm range were measured and compared with all of the previous data [155]. The agreement among more recent works was relatively good. The absorption spectrum of ozone in the UV region (Figure 16) shows a large continuum from 200 to 350 nm with a maximum near 250 nm (Hartley band) on which some small diffuse undulations spaced by approximately 200 cm^{-1} can be seen. At the higher wavelengths (310–350 nm), the spectrum is dominated by more intense but also diffuse vibrational bands corresponding to the Huggins bands. At the mercury resonance line wavelength ($\lambda = 254\text{ nm}$), the value $\sigma(O_3)$ was found to be $1.130 \pm 0.011 \times 10^{-17}\text{ cm}^2$.

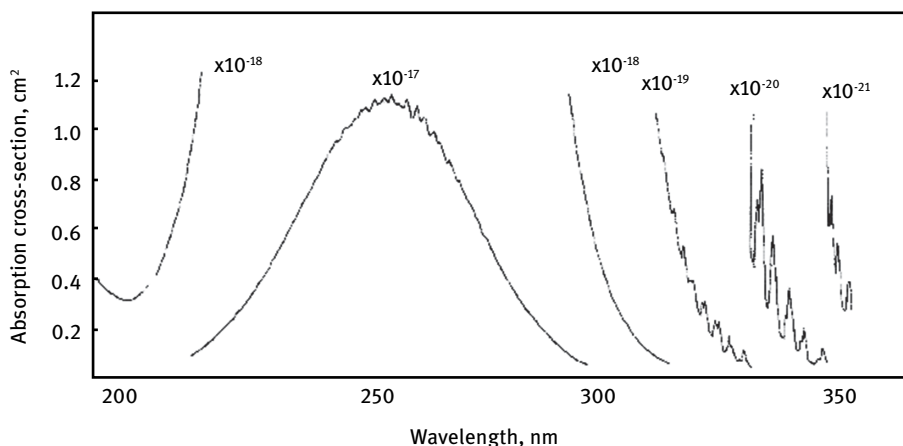


Figure 16: Absorption cross sections of ozone in UV. (Republished and modified from [155], with permission of © 1991 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

Absolute absorption cross sections of ozone have been measured at ambient (295 K) and low temperature (218 K) in the visible region. The temperature effect was very small. Ozone has an absorption band between 420 and 830 nm, with a large continuum with two maximum absorptions, $\sigma = 4.83 \times 10^{-21}\text{ cm}^2$ at 575 nm and $\sigma =$

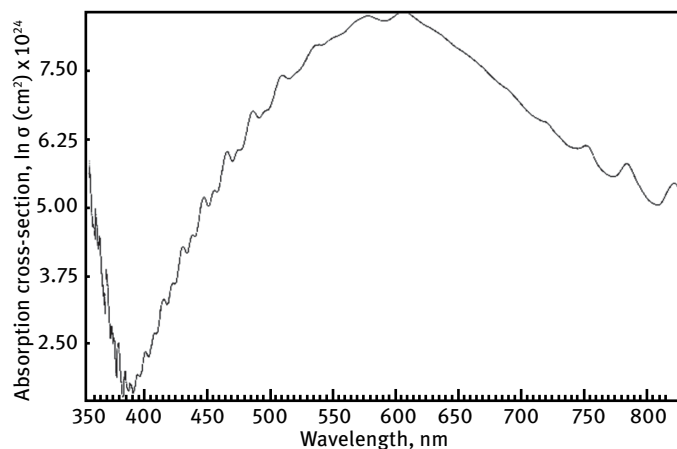


Figure 17: Absorption cross sections of ozone in the visible range at ambient temperature. (Republished and modified from [156], with permission of © 1998 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

$5.23 \times 10^{-21} \text{ cm}^2$ at 603 nm, overlapped by diffuse vibrational structure (Figure 17) [156]. The minimum of the absorption between the Hartley and the Chappuis bands was observed for the first time at 377.5 nm.

The extinction coefficient of gaseous ozone in the UV range at 252 nm, where the absorption is very strong, is $3360 \text{ cm}^{-1} \text{ mol}^{-1} \text{ L}$. This is what protects us from even worse sunburns, but enough UV is coming through to pose a skin hazard.

3.13.5 Microwave Absorption Spectra of Ozone

The microwave spectra give structural information that can be interpreted unambiguously and that is more accurate than that obtained by other methods. Microwave spectra in the region of four low- J rotational transitions of $^{16}\text{O}_3$ were measured in the region from 42 to 118 GHz, and the rotational spectroscopic constants found were $A = 106530.0 \pm 1.1 \text{ MHz}$, $B = 13349.06 \pm 0.06 \text{ MHz}$, $C = 11834.3 \pm 1.1 \text{ MHz}$. The oxygen nuclei form an isosceles triangle (which is a triangle that has two sides of equal length) with an apex angle of $116^\circ 49' \pm 30'$, and the two equal internuclear distances are $1.278 \pm 0.003 \text{ Å}$ [134]. The dipole moment was derived from the Stark splitting to be 0.53 ± 0.02 debye. Zeeman splittings of this transition showed that ozone is not significantly paramagnetic.

The rotational spectra of six isotope-labeled ozone molecules were measured between 9 and 45 GHz [104]. The spectra of four of the molecules have been identified to the extent necessary to determine the spectral constants, from which moments of inertia have been calculated. The structural parameters of the molecules were calculated by taking the moments of inertia for a molecule two at a time (Section 3.12).

The microwave spectrum of O_3 was reanalyzed to include the effect of centrifugal distortion [157]. The rotational constants determined in this manner were $A = 106534.74$ MHz, $B = 13348.95$ MHz, $C = 11834.30$ MHz. The force constants were then used to calculate distortion constants for $^{16}O^{18}O^{16}O$, and these in turn were used to analyze its rotational spectrum. See also [158–162].

3.14 Dielectric Constant of Ozone

Numerical data for the dielectric constant of liquid ozone are listed in Table 21, and the dielectric constants of liquid ozone/oxygen mixtures are listed in Table 22.

Table 21: Dielectric constant of liquid ozone (at 1 kHz).

Temperature		ϵ	Temperature		ϵ
K	°C		K	°C	
77	–195	5.45	147	–126	3.33
90	–183	4.75 ± 0.02	162	–111	3.01
103	–170	4.33	175	–98	2.91
118	–155	3.85	185	–88	2.78

Data source: [103], as referenced in [65]

Table 22: Dielectric constant of liquid ozone/oxygen mixtures (at 90 K = –183 °C).

Ozone in oxygen		Dielectric constant ϵ (dimensionless)	Molar polarization, cm^3
Mass-% O_3	Mol-% O_3		
0	0	1.46 ± 0.01	—
14.9	10.5	1.82	26.352
17.6	12.5	1.90	26.296
19.2	13.7	1.93	25.642
29.8	22.1	2.20	23.774
100.0	100.0	4.75 ± 0.02	—

Data source: [103, 133]

3.15 Magnetic Properties of Ozone

It is interesting to note that in contradistinction to oxygen, ozone is not paramagnetic. The paramagnetic properties of ozone/oxygen mixtures can be used to analyze the composition (as long as no other diluents are in the mixture) (Section 4.1.2.6).

The data needed for the analysis of liquid ozone/oxygen mixtures by measurement of magnetic susceptibility were determined by the Quincke (U-tube) method for

magnetic susceptibility with a permanent magnet [163]. Results at 78 K (−195 °C) and 90 K (−183 °C) showed a linear relation between the magnetic susceptibility of the solutions and mass percentage oxygen at low oxygen content. Above about 10% oxygen the specific susceptibility of oxygen in solution decreased significantly. At 90 K (−183 °C), the ratio of specific susceptibility of oxygen in solution to that of pure liquid oxygen decreased from 1.30 at low concentrations to 1.13 at 27.6% oxygen, the two-liquid phase boundary. The limiting ratio at 78 K (−195 °C) was 1.42. The discontinuity in magnetic susceptibility was used to establish the compositions at the phase boundaries, 9.2 and 91 mass-% oxygen at 78 K (−195 °C), 27.6 and 70.2% at 90 K (−183 °C).

The magnetic susceptibility of gaseous ozone was reported as 0.002×10^{-6} centimeter gram system (CGS) units and that of liquid ozone was 0.150×10^{-6} CGS units (from [7] as referenced in [65]). For comparison, the magnetic susceptibility of liquid oxygen is 260×10^{-6} CGS units.

4 Chemical Properties of Ozone

4.1 Chemical Reactivity of Ozone

At ordinary temperatures, ozone is a gas, light blue in color. When inhaled, the gas has a characteristic pungent odor from which its name was derived from the Greek word *ozein*, to smell. The odor permits recognition of ozone in concentrations down to about 0.1 ppm. Gaseous ozone is a highly active, irritating, oxidizing substance. Ozone is a strong oxidizer. Its oxidizing power liberates elemental iodine from an acidified aqueous potassium iodide solution. The addition of a trace amount of starch makes this popular test even more sensitive when the iodine-starch adduct turns dark blue. Often potassium iodide/starch paper is available from chemical supply houses and can be used to detect ozone leaks. An excellent summary of the chemical and catalytic properties of ozone and its participation in many different types of reactions was published with many literature references [164].

Gaseous ozone does not react with hydrogen gas at 195 to 294 K (−78 to +21 °C) and 67 to 141 kPa (504 to 1061 mm Hg). In a range of 195 to 273 K (−78 to 0 °C) ozone will initially not visibly react with cyanogen or nitrous oxide. At 296 K (23 °C) and 74 kPa (557 mm Hg), ozone will react slowly with cyanogen over the course of 18 h. Ozone will explode when mixed with carbon monoxide, nitric oxide or phosphine at 195 K (−78 °C). Ozone will immediately explode if mixed with ammonia at 273 K (0 °C). On the other hand, at lower temperatures, it has been postulated that *ammonium ozonide* is formed by the slow oxidation of solid NH_3 by gaseous O_3 at low temperatures [165]. It proceeds through an unstable intermediate:



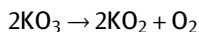
A red solid appears on warming around 143 K (-130°C), reaches a maximum concentration at $\sim 158\text{ K}$ ($\sim -115^{\circ}\text{C}$), and is entirely decomposed as soon as the mixture warms to 183 K (-90°C). The IR spectra show two strong bands at 800 and 1140 cm^{-1} and two faint ones at 1260 and 2053 cm^{-1} , besides the characteristic bands of the NH_4^+ and NO_3^- ions. The explosion properties of the frozen mixture have not been established.

Liquid ozone is stable toward and miscible with liquid methane (at 90 K = -183°C), liquid fluorine (at 77 K = -196°C), liquid oxygen difluoride (at 77 K = -196°C), and liquid nitrogen trifluoride (at 90 K = -183°). With perchloryl fluoride it is miscible at 116 K = -157°C but no longer miscible at lower temperatures at 90 K = -183°C . Ozone dissolves in halocarbon-12 (Cl_2CF_2) or halocarbon-13 (ClCF_3) at 116 K = -157°C without reactions [99]. The saturation concentration of ozone in tetrafluoromethane at 90 K = -183°C is 12 mass-% O_3 [98]. The saturation concentration of ozone in liquid argon at 90 K = -188°C is only 10 mass-% O_3 . Mixtures of liquid nitrogen and liquid ozone separate at 77 K = -196°C into two phases. The upper phase contains 5.1 mol-% O_3 , and the lower contains 8.8 ± 0.9 mol-% nitrogen. Ozone is completely homogeneously miscible with ozone fluoride O_3F_2 at 90 K = -183°C , and ozone fluoride decomposes only slowly at these temperatures in ozone solutions. However, if the mixture is warmed to 116 K = -157°C , it will explode.

Whereas ozone is miscible with oxygen difluoride OF_2 , its miscibility with dioxygen difluoride O_2F_2 is only limited. A homogeneous mixture can be obtained at 116 K = -157°C , but when this mixture is cooled to 90 K = -183°C , the O_2F_2 precipitates as a solid, and if one attempts to warm the mixture to 195 K (-78°C), it will explode. Ozone does not mix with chlorine trifluoride at 133 K = -140°C .

4.1.1.1 Alkali Metal Ozonides

It would be nice if the alkali metal or tetraalkylammonium ozonides could be stabilized and used as a storable stable solid form of ozone. Alkali metal ozonides form as deep orange compounds by the reaction of ozone with alkali metal (Na, K, Rb, Cs) hydroxides or the metals themselves. It would be possible to obtain 93% pure KO_3 by exposing dry powdered KOH to oxygen containing 6–8% ozone at 263 to 258 K (-10 to -15°C) [166]. The product was extracted with liquid ammonia to yield red-brown needles of KO_3 . KO_3 decomposed completely in 11 d in the following manner:



The enthalpy of formation of KO_3 was estimated as $+260 \pm 4\text{ kJ/mol}$ ($+62.1 \pm 0.9\text{ kcal/mol}$). The molecular structure of alkali metal ozonides contains an O—O—O linkage. Ammonium ozonide, formed as an orange solution from bubbling ozone in oxygen into liquid ammonia, is thermally unstable and decomposed to ammonium nitrate, oxygen, and water. Ozonides have been treated as solid propellant oxidizers, but experiments failed to produce enough stable materials to actually fire it in a rocket engine.

KO_3 dissolved in liquid NH_3 absorbs strongly in the UV from 300 nm, in addition to the strong band in the visible violet-blue range [167]. Other species, such as O_3 , O_2^- , and HO_2 , also absorb in that region.

4.1.1.2 Reactions of Ozone with Inorganic Compounds

Ozone will burn with hydrogen gas if the mixture is ignited, but at low temperatures with liquid ozone, a new type of chemistry of peroxides and superoxides begins to unfold. The composition of low-temperature condensates obtained by the reaction of hydrogen atoms with liquid ozone has been determined from the Raman spectra and data of the molar ratio of O_2 to H_2O_2 in the decomposition products [168]. The main constituents are hydrogen tetroxide, H_2O_4 , hydrogen trioxide, H_2O_3 , and hydrogen peroxide, H_2O_2 , in comparable amounts, and some water, H_2O . H_2O_4 , H_2O_3 , and H_2O_2 are formed in diffusion-controlled reactions between OH and HO_2 in the liquid ozone layer and stabilized by transfer to the solid phase. $\cdot\text{OH}$ and $\cdot\text{O}_2\text{H}$ radicals are generated via a sequence of the reactions initiated by the interaction $\text{H} + \text{O}_3(\text{L})$.

4.1.1.3 Reactions of Ozone with Organic Compounds

Ozone will react with many organic compounds under the destruction of the carbon skeleton. The destruction of organic matter is the key mechanism for the bactericidal and disinfecting properties of ozone. Such reactions can take place in aqueous solutions as well in the dry state. If the concentration of ozone is high enough and the organic compound (e.g., an olefin) is reactive enough, the reacting mixture may ignite and burst in flames [169].

In industrial areas with high levels of air pollutants, ozone destroys and embrittles rubber in automobile tires and brake, fuel, and coolant hoses. Rubber formulators have tried to delay this reaction by adding antioxidants (antiozonants) to the rubber compositions. Antiozonants leach from tires and tire dust and contribute to water pollution and fish poisoning. Sometimes antioxidants are added to solid propellant binders for rockets that need to be stored in air for a long time.

In organic chemistry, ozone is used in ozonolysis (ozonation, ozonization) reactions to convert olefins to oxygenated products and to determine the number of double bonds in polymers. Ozonolysis is the cleavage of alkenes or alkynes by reaction with ozone to form organic compounds in which the multiple carbon-carbon bond has been converted to a carbonyl group. The outcome of the reaction depends on the type of multiple bond being oxidized and the workup conditions. Intermediates of such reactions with alkenes are cyclic ozonides formed in a 1,3-dipolar cycloaddition. Alkenes can be oxidized with ozone to form alcohols, aldehydes, ketones, or carboxylic acids. Ozone will bleach many dyes and stains, but without the formation of unwanted chlorinated byproducts like polychlorinated biphenyls (PCBs) or chloroform.

4.1.2 Analysis of Ozone

Analytical tasks in the preparation and handling of ozone include the analysis of liquid and solid ozone mixtures and the detection of gaseous ozone in the air. The analysis of mixtures of liquid and solid ozone with other chemicals must be conducted with physical methods of measurement because the mixtures can often not be vaporized without premature decomposition or even explosions.

4.1.2.1 Analysis of Gaseous Ozone in Air

Because ozone plays an important role in atmospheric chemistry and pollution control, there are many analytical methods for analysis of ozone in air.

For occasional spot checks of ozone concentration in air at the workplace, the easiest method involves using gas detection tubes made from glass tubes that contain an indicator supported on a granular material, which changes color when exposed to ozone. Such tubes are available from Draeger, MSA, Kitagawa, and others. Gas detection tubes are sensitive to as little as 0.05 ppm O₃ and can measure up to 300 ppm O₃ with 10 strokes. Draeger ozone gas detection tubes are available for two ranges of concentration (Table 23).

Table 23: Draeger ozone gas detection tubes.

Tube designation	Concentration range	Draeger part number
Ozone 0.05/b	0.05–1.4 ppm	67 33 181
Ozone 10/a	10–300 ppm	CH 21 001

Data source: [170]

4.1.2.2 Analysis of Gaseous Ozone Grab Samples

The detection and quantification of ozone in air can be done with wet chemical and common gas absorption methods. The bibliography by Thorp [6] contains detailed chapters on the analysis of gaseous ozone.

4.1.2.3 Instrumental Analysis of In-Situ Real-Time Concentration of Gaseous Ozone in Air

Ozonizers are widely used for sterilization of drinking water and for wastewater treatment. To avoid the formation of NO_x, the ozonizers are fed with pure oxygen instead of air. The ozone concentration in the effluent oxygen needs to be monitored to make sure that the ozonizer works properly and to adjust the dilution with air before the gas stream is bubbled through the water that needs to be treated.

Four continuous automatic analyzers for measuring atmospheric levels of ozone were used in a calibration and field study [171]. These were (1) a colorimetric instrument based on the detection of iodine released from neutral potassium iodide reagent,

(2) a coulometric instrument utilizing the polarization current as a measurement of iodine released by ozone in a cell contacted by potassium iodide reagent, (3) a galvanic cell measuring bromine release by ozone, and (4) a UV photometer.

Continuous ozone analyzers are based on chemiluminescent reactions of ozone with dyes (eosin) or electrochemical methods or semiconducting gas sensors based on metal oxides (In_2O_3 , SnO_2). In an evaluation of different sensing techniques, sensors based on indium oxides performed best in detecting ozone [172]. They had the best sensor sensitivity as well as the smallest cross-sensitivities.

Ozone in air will liberate bromine from a bromide solution which is then measured potentiometrically [173]. At an air flow rate of 0.2 L/min the measurable range is 0–1 ppm O_3 for a 1-mV full span recorder.

Ozone concentrations in the atmosphere can be sensed remotely by their IR absorption [174]. The absorptivity at $9.48\text{ }\mu\text{m}$ at 101 kPa is 3.74×10^{-4} ppm m^{-1} .

4.1.2.4 Analysis of Liquid Ozone Mixtures

The analysis of mixtures of liquid or solid ozone with other chemicals must be conducted with physical methods of measurement because the mixtures can often not be vaporized without premature decomposition or even explosions of the ozone contained in the mixture. Because the physical properties of binary ozone mixtures are well known, also at low temperatures where the ozone content remains stable, one can interpolate from measurements of physical properties back to the chemical composition of the mixture. Physical methods are of interest mostly for the analysis of LOZ/LOX mixtures. The physical properties that are easily measured and vary almost linearly with the composition of the mixture are light absorption in the visible range, magnetic susceptibility, and the dielectric constant.

As we review past efforts to dope LOX with ozone to increase its specific impulse and endorse continued efforts with this non-polluting (non-polluting once it is all burned) oxidizer, we wonder how much ozone we have already unwittingly been flying as a contaminant in the millions of tons of LOX that has powered most of our space launches to date. If LOX is produced in a polluted industrial area with a high O_3 content in the atmosphere, where is it going to end up in the air liquefaction plant? In LOX that is intended to be vaporized as breathing oxygen, what is the maximum ozone content allowed?

A crude method of estimating the ozone concentration in LOZ/LOX mixtures is possible based on the knowledge of the phase diagram (the miscibility gap) and by visual observation of the phase separation at $90\text{ K} = -183^\circ\text{C}$. If no darker, heavier phase is formed on cooling, the overall ozone concentration in the mixture is below 24 mass-% O_3 . On the other hand, if there is no lighter, less intensely colored phase floating on the dark liquid ozone, the overall ozone concentration is above 75 mass-% O_3 . Magnetic susceptibility (see below) was a very sensitive criterion of purity of ozone after most of the oxygen had been pumped off.

4.1.2.5 Photometric Methods for Analysis of Liquid Ozone Mixtures

Owing to the intensely blue color of liquid ozone, it can be determined photometrically in mixtures with liquid oxygen by its absorption in the visible range near 600 nm as well as in the UV range at 260 nm. This method is typically used for determining LOZ in LOX in the range 0 to 28 mass-% O_3 . Ozone in solvents (such as CCl_4 , $ClCF_3$, or H_2O) other than LOX can be determined by the same method, but that is less relevant for a rocket propellant application.

As a side note, it is the UV absorption at 260 nm by ozone in the high atmosphere that protects all living beings on Earth from the intense UV radiation of the Sun.

In carrying out photometric measurements at cryogenic temperatures, one must make sure that the cells are constantly cooled to temperatures below 90 K = -183°C and that the cell windows are not covered by frost. One may use double-walled cells like a transparent Dewar flask, or one has to purge the apparatus with cold, dry gas to prevent ambient moisture from entering.

4.1.2.6 Magnetic Susceptibility Methods for Analysis of Liquid Ozone Mixtures

Because LOX is paramagnetic, but LOZ is not, this difference in physical properties can be used for analysis of LOZ/LOX mixtures. The modest diamagnetism of LOZ does not interfere with these measurements. This rapid and easy-to-perform method is best used for the analysis of mixtures containing 72 to 100 mass-% LOZ [163]. The sample to be analyzed is contained in a U-shaped capillary tube and cooled to 78 to 90 K (-195 to -183°C). Initially the tube is carefully leveled and the liquid level recorded. One of the legs of the U tube is surrounded by a powerful permanent magnet. If the magnet is raised, the liquid in one leg of the U tube rises and the amount of rise is proportional to the amount of oxygen in the sample. If the magnet has a flux density of 8000 Gauss, pure oxygen would rise 100 mm. It was claimed that the method is accurate to within $\pm 0.01\%$ absolute.

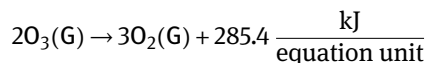
4.1.2.7 Dielectric Constant Measurements for Analysis of Liquid Ozone Mixtures

The dielectric constant of pure ozone at 77 K = -196°C is 5.45 ± 0.1 . For LOZ/LOX mixtures at 90 K = -183°C the dielectric constant was measured over a wide range of compositions [175]. For instance, at 6 mass-% O_3 , the constant was $\epsilon = 1.595$. This agreed well with measurements by other authors [133].

4.2 Thermal Stability, Decomposition, Radiation Stability of Ozone

Ozone will decompose, sometimes catastrophically, in all physical states, depending on the energy of the stimulus. We are discussing here slow homogeneous decomposition in the gas phase, stationary decomposition flames in the gas phase, explosive

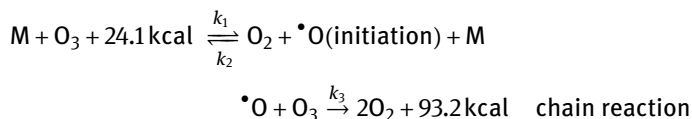
decomposition in the gas phase, and explosions or even detonations in the liquid and solid state. The decomposition reaction



is strongly exothermic and explains the high energy release during ozone explosions (in reversal of its enthalpy of formation, which is positive).

4.2.1 Kinetics of Ozone Decomposition

The ozone decomposition reaction is thought to proceed as a chain reaction as follows:



where M may be a third body that could be another ozone molecule, an inert diluent gas molecule, or the hot wall of the container. There is no evidence for a direct bimolecular reaction of ozone to produce O_2 , nor is there any evidence for important surface effects or energy chains [176]. On the other hand, the results at very fast rates of decomposition indicated an acceleration that can be accounted for in terms of temperature gradients in the system. This region is usually very close to the thermal explosion limit. The values found for the rate constants are (for M equal to O_3) as follows [177]:

$$\begin{aligned} k_1 &= 4.61 \pm 0.25 \times 10^{12} \exp(-24000/RT) \text{ L mol}^{-1} \text{ s}^{-1} \\ k_2 &= 6.00 \pm 0.33 \times 10^7 \exp(+600/RT) \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1} \\ k_3 &= 2.96 \pm 0.21 \times 10^{10} \exp(-6000/RT) \text{ L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

As with many energy transfer processes, k_1 has an abnormally high preexponential factor, and k_2 has a correspondingly negative energy of activation. It was further inferred that the reaction that produces two O_2 molecules with 99 kcal of excess energy between them does not produce more than one excited electronic state of O_2 and that these hot O_2 molecules are not very efficient in exciting O_3 to decomposition. Reevaluating the constants based on a different enthalpy of formation of atomic oxygen, the numbers (evaluated at 363 K) are as follows [178]:

$$\begin{aligned} k_1 &= 6.8 \times 10^4 \exp(-24890/RT) \text{ mol/L} \\ k_2 &= 2.96 \times 10^7 \exp(+890/RT) \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1} \\ k_3 &= 3.37 \times 10^{10} \exp(-5700/RT) \text{ L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

Other investigators found similar numbers for the rate constant k_1 , such as [179]

$$k_1 = 4.31 \times 10^{14} \exp(-22.2/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \quad 300 \leq T \leq 3000 \text{ K}$$

or [180]

$$k_1 = 1.6 \times 10^{12} \exp(-24300/RT) \text{ L mol}^{-1} \text{ s}^{-1}$$

(at 11–52 mmHg and 388 to 403 K (115–130 °C))

The photolysis of ozone may follow a different pathway than the thermal decomposition.

The slow decomposition of ozone in the gas phase has been studied extensively by kineticists because it is a relatively simple reaction, with no or only a few byproducts, and well suited to demonstrate gas-phase kinetics and fundamental reaction orders. This reaction is merely a limitation in our ability to store and pump ozone as a rocket propellant. A summary of all the kinetic studies on the decomposition of ozone would fill an entire book. In a book on rocket propellants, the only justification for dealing with the kinetics of ozone decomposition would be the promise that it could help us find an inhibitor that would stabilize ozone sufficiently so it could be safely used as a rocket propellant. Such an inhibitor has not been found, and the success of inhibiting the premature decomposition of ozone is as unlikely as trying to stop or slow down the radioactive decay of a radioactive isotope.

4.2.1.1 Thermal Decomposition of Gaseous Ozone

There are hundreds of publications on the slow thermal homogeneous gas-phase decomposition (pyrolysis) of ozone in the dark. Those studies were done mostly in support of atmospheric chemistry and to derive kinetic equations. The storage stability of gaseous ozone in the laboratory closely relates to those studies and will be discussed in Section 4.2.8. Many of those studies were done in the search for additives that might slow down the rate of ozone decomposition. It is impossible to include a complete summary of all publications on the thermal decomposition of ozone in this book. References to a few typical publications may suffice. The slow thermal decomposition of ozone is the slowest of the three basic modes of ozone decomposition: **(1)** slow decomposition in the dark, **(2)** stationary flames, and **(3)** detonation.

The bond dissociation energy of ozone, defined as the energy necessary to break the first bond, is 104.6 kJ/mol (25 kcal/mol), far less than the mean thermochemical value of 299 kJ/mol (71.5 kcal/mol) per bond. See also [181–183].

4.2.1.2 Catalytic Decomposition of Gaseous Ozone

The ozone molecule is very labile, and it does not take much energy stimulation or lowering of the activation energy to decompose it. On the surface of catalysts, the rate of decomposition of ozone is accelerated. Unreacted ozone gas that has passed through drinking water in order to disinfect and sterilize it must be destroyed by catalytic converters before it may be vented above the roof.

Thirty-five materials, including charcoal, metals, and metal oxides, were tested for their catalytic efficiency in decomposing ozone at room temperature [184]. Charcoal and nickel(II) oxide were found to be the best catalysts. A 0.5-in.-thick filter bed of these active materials initially removed 95 and 80%, respectively, of the ozone from a 1 ft³/min air stream containing 250 ppb of ozone. The catalytic efficiency of all the materials tested was found to degrade with time. Operating parameter tests with the charcoal and nickel(II) oxide showed that their efficiencies at a constant flow rate were nearly invariant over input ozone concentrations ranging from 45 ppb to 1.0 ppm and that at a constant input ozone concentration, their efficiencies decreased with an increase in flow rate over the range 0.14–1.17 ft³/min. Palladium-impregnated manganese(IV) oxide is an active ozone decomposition catalyst [185].

Aerosol particulates suspended in the atmosphere may cause ozone decomposition and catalyze interaction of ozone with other atmospheric pollutants. Many of the ozone reactions with organic compounds that are used on a large scale every day in the chemical process industry may be enabled or accelerated by catalysts. The primary method of destroying unwanted ozone (e.g., ozone that has completed drinking water sterilization) before releasing it into the atmosphere is by catalytic decomposition by passing it over a heated catalyst bed. Catalysts might destroy toxic ozone from the ambient air pumped into pressurized cabin passenger aircraft cruising at high altitudes. If ozone were more stable, one might envision monopropellant rocket thrusters with packed catalyst beds operating on gaseous ozone like hydrazine or hydrogen peroxide monopropellant thrusters.

4.2.2 Storage Stability of Ozone

Ozone will decompose slowly if stored as a gas at room temperature. Examples of ozone losses in gas are summarized in Table 24. The source of these data unfortunately does not state the container materials (presumed to be glass) and whether the samples were kept in the dark. The rate of decomposition probably depends on the absence of any catalytic contaminants in the container material. Gaseous ozone would preferably be stored in glass or quartz vessels [186].

The rate of decomposition of gaseous ozone can be slowed down by adsorbing the gas on large-surface-area materials, such as silica gel or glass wool. Aqueous solutions of ozone decompose more slowly in alkaline than in acidic solutions. It has been suggested that even the decomposition of gaseous ozone can be delayed if the walls of the storage containers are coated with strongly alkaline chemicals [188]. The yields and lifetimes of ozone and ozonide produced by the photochemical decomposition of hydrogen peroxide and sodium persulfate in water made alkaline with sodium hydroxide were improved by an increase in sodium hydroxide and oxygen concentration.

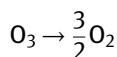
Table 24: Decomposition of gaseous ozone during storage.

O ₃ Mol-%	T, K	P, mm Hg	Amount of O ₃ decomposed	Rate of decomposition, %/d
40	296–299	740	4.2% in 7 d	0.6
50	273	766	2.9% in 3 d	0.9
50	296–297	600	4.5% in 5 d	0.9
100	195	754	No noticeable decomposition in 8 d	0.0
100	296	757	0.9% in 1 d	~0.9

Data source: [187]

4.2.3 Stationary Ozone Decomposition Flames

The decomposition reaction of gaseous ozone proceeds via



and is strongly exothermic ($143.17 \pm 0.753 \text{ kJ/mol} = 34.220 \pm 0.180 \text{ kcal/mol}$) at constant pressure $p = \text{const} = 1 \text{ atm}$ and $T_a = 291 \text{ K}$. The flame can be stabilized on a burner if the burner has a properly designed flame holder and if the entrance velocity is sufficiently high to prevent flashback of the flame into the feed system [73, 77, 187, 189]. The flame temperature of pure ozone is appreciably hotter than the temperature of methane-air (2148 K) or carbon monoxide-air (2370 K) flames.

Because only very few species are involved in ozone decomposition flames, this simple reaction constitutes a suitable model reaction to validate flame combustion models. The stability of a steady-state solution of a model for ozone decomposition flames has been investigated for five different cases of ozone flame propagation [190]. The cases chosen were all for $T_0 = 573 \text{ K}$ (300 °C) and at 83 kPa (0.821 atm), so that the experimental data of Hirschfelder, Curtiss, and Campbell could be used to verify the model. The predicted flame speed for an adiabatic flame temperature of 3153 K was 986 cm/s with diffusion and 1560 cm/s without back diffusion.

4.2.3.1 Flammable Range of Ozone Decomposition Flames

Ozone will sustain a decomposition flame over a wide range of pressures and compositions in dilution with inert gases. The range of conditions where ozone decomposition flames propagate and can be stabilized on a burner depends on the ozone content of the gas, operating pressure, preheat temperature of the gas, mode of ignition, and burner diameter. If the flow rate of the gas is too slow, the combustion zone will flash back into the supply lines. If the ozone concentration is at the upper end of the safe range, the combustion could at any time transition into a detonation and destroy the apparatus.

Most ozone generators do not produce ozone concentrations higher than 10 vol-%. In many industrial applications where ozone is used as a reactant and disinfectant, it

would be desirable to use higher concentrations, but they are limited by the explosion potential of gaseous ozone once the concentration exceeds 10 vol-%. Using ozone to sterilize medical equipment at concentrations higher than 10% would entail the same explosion hazard as the medical equipment industry experienced with ethylene oxide, which has caused severe explosions in medical equipment factories.

At atmospheric pressure (298 K at 101 kPa), ozone will sustain a decomposition if initiated by a shock wave as long as the ozone concentration in a mixture with oxygen is above 9.2 mol-% [191]. Thermal ignition with a hot wire or a spark will ignite only above 10 mol-%.

4.2.3.2 Flame Burning Velocity of Ozone Decomposition Flames

Flame Burning Velocity of Decomposition Flames in Pure (Undiluted) Gaseous Ozone

The thermodynamic data for ozone and oxygen are very accurate and formed the basis for calculations of the theoretical flame temperatures and flame speeds of the gaseous ozone flame summarized in Table 25 and 26 from several literature sources [187, 189, 192].

Spectrometric investigations indicate that some of the energy transport in gaseous ozone decomposition flames and detonations occurs through radiative transport. If the radiative energy loss can be quantified, one can use it to correct the measured flame temperature and calculate the adiabatic flame temperature [193, 194]. A kinetic scheme capable of representing both the observed UV quantum yields in pure ozone and the thermal decomposition rates in O_3/O_2 mixtures was designed for the calcu-

Table 25: Theoretical flame speeds of decomposition flames with gaseous ozone.

Initial conditions			Calculated flame speed
Temperature		Pressure	
K	°C	atm	cm/s
298	25	1	472 ± 12^a
298	25	5	488
298	25	10	504
298	25	100	529
273	0	1	420
233	-40	1	325
161	-112	1	205
195	-78	1	270 ± 7^a
195	-78	2	282
195	-78	5	295
195	-78	10	304
195	-78	100	317

^a Experimental values for comparison

Data source: [65]

Table 26: Theoretical flame temperature of ozone decomposition flame.

Initial conditions		Flame temperature
Pressure	Temperature	
Atm	K	K
1	298	2677
2	298	2716
5	298	2761
10	298	2789
1	195	2648
2	195	2683
5	195	2723
10	195	2748

Data source: [65]

lation of temperature-composition histories during photo-initiated ozone explosions [195].

The theoretical equations developed for the prediction of ozone flames at atmospheric pressure [196] were then extended to predict the flame velocities for gaseous ozone flames burning at higher pressures [197] (Table 27).

Table 27: Theoretical decomposition flame velocities in pure (undiluted) ozone.

Initial temperature $T_0 = 195$ K					
p , atm	1	2	5	10	100
T , K	2648	2683	2723	2748	2784
V_0 , cm/s	270	282	295	301	317
Initial temperature $T_0 = 300$ K					
p , atm	1	2	5	10	100
T , K	2678	2716	2761	2789	2834
V_0 , cm/s	444	464	488	504	529

Data source: [197]

Because the kinetics of decomposing ozone are relatively simple (compared to the combustion of other monopropellants like nitromethane or hydrazine), the ozone decomposition reaction was selected to test the validity of several models for the prediction of laminar flame speeds [198]. Model predictions were compared with available experimental data for ozone decomposition flames, and the agreement was satisfactory.

Species and temperature profiles and the burning velocities were predicted over a range of initial ozone mol fractions of 0.25 to 1.00 [199]. The computed burning ve-

locities were no more than 30% greater than the measurements of Streng and Grosse. Comparison with the computed results of Warnatz showed agreement within $\pm 12\%$, even though they used quite different expressions for some of the kinetic coefficients. Differences are most likely due to different methods to account for atomic oxygen. See also [183].

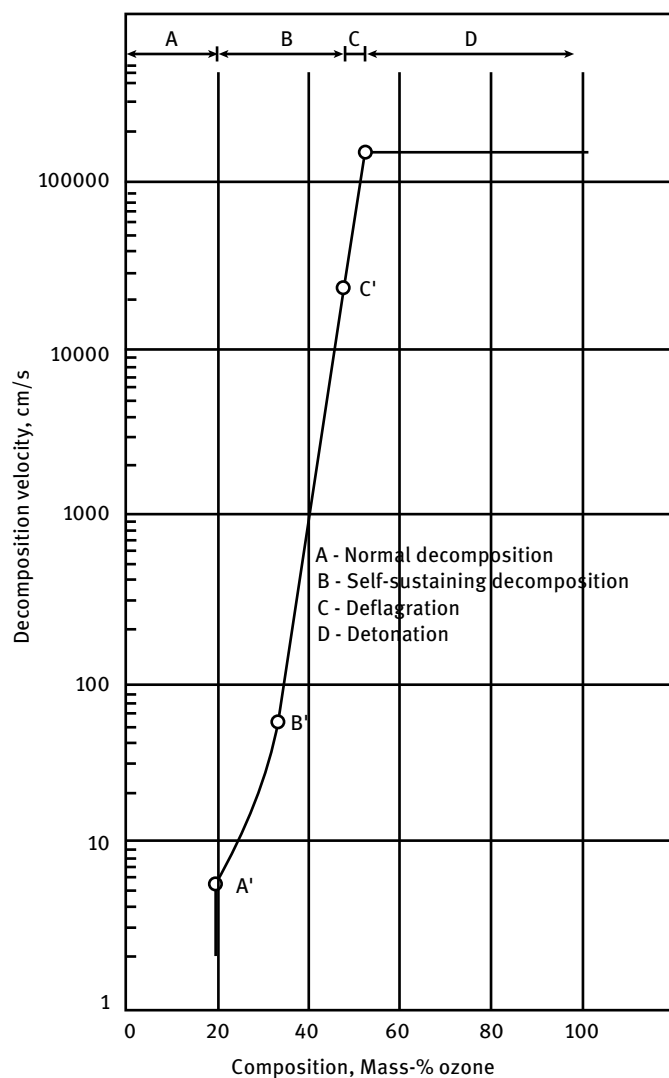


Figure 18: Decomposition velocities of gaseous ozone/oxygen mixtures. (Reprinted and modified from [187], with permission from Elsevier © 1957, permission conveyed through RightsLink.)

Flame Burning Velocity of Decomposition Flames of Gaseous Ozone/Oxygen

The speed of flame propagation in ozone/oxygen gas decomposition flames in the absence of any fuels increased steeply with increasing ozone concentration, starting at 20 mass-% ozone where a flame can be maintained, progressing through combustion, deflagration, and all the way to detonation. The ranges of reactivity are illustrated in Figure 18.

The theoretical flame speeds of gaseous oxygen/ozone mixtures were calculated using a method similar to that described earlier for pure ozone. The results are summarized in Table 28, and a comparison with experimental values shows moderate agreement between the two sets of data. Table 29 gives the theoretical flame temperatures of ozone/oxygen decomposition flames.

Table 28: Flame speeds of gaseous ozone/oxygen mixtures.

Ozone concentration Mol-%	Calculated		Measured
	298 K, 1 atm cm/s	195 K, 1 atm cm/s	298 K, 1 atm cm/s
17	9.2		
20	18.2		
24	18.0		
25			41
28	52.2		
36		44.0	
40	128.4		139
46	165.9		
50			214
53	210.1		
58		132.0	
60			290
70			349
75	331		
80			386
82		209.0	
90			411

Data source: [189, 187]

Table 29: Theoretical flame temperatures of ozone/oxygen decomposition flames.

Ozone concentration, mol-% O ₃	Flame temperature, K
18.18	1027
40.00	1687
66.7	2277
100	2677

Data source: [187]

It has been shown that that no steady flame can be produced in concentrated ozone and that detonation would invariably result with ozone/oxygen mixtures above 54 mass-% ozone.

The theory of flame propagation in gaseous ozone/oxygen mixtures was applied to mixtures containing 50–100 mol-% ozone [196, 200]. The formulas were modified to allow for comparatively high concentration of atomic oxygen. The results for $T_0 = 298\text{ K}$ shown in Table 30 were found to be in good agreement with three experimental values. Additional data were calculated for $T_0 = 195\text{ K}$ (dry-ice temperature).

Table 30: Calculated flame velocities and flame temperatures in gaseous ozone/oxygen mixture decomposition flames.

Initial temperature $T_0 = 298\text{ K}$								
Mol fraction ozone	0.25	0.40	0.50	0.60	0.70	0.80	0.90	1.00
T , K	1250	1687	1934	2155	2333	2475	2587	2677
V_0^a , cm/s	41	139	214	290	349	386	411	430
V_0^b , cm/s	50	130	190	249	307	362	418	474
V_0^c , cm/s	55	141	160					
Initial temperature $T_0 = 195\text{ K}$								
Mol fraction ozone	0.25	0.40	0.50	0.60	0.70	0.80	0.90	1.00
T , K	1172	1610	1867	2090	2279	2430	2552	2650
V_0^a , cm/s	17.1	70	119	164	204	232	250	260

^a Calculated by [200] for diffusion coefficient $\delta = 0.94$

^b Calculated from empirical equation found by Streng and Grosse $V_0 = 563 \times \text{mol fraction } \text{O}_3 - 88.8\text{ cm/s}$

^c Measured by Lewis and von Elbe

Data source: [200] and [197]

A calculation method for predicting flame velocities of ozone and ozone/oxygen decomposition flames was developed that included complete multi-component diffusion and heat conduction solving the time-dependent mass and energy conservation equations of a laminar flame [201]. Calculations with simplified transport models were made for comparison. The flame speed could be predicted as a function of the initial $\text{O}_3 : \text{O}_2$ ratio, and it agreed reasonably well with experimental data. See also [202–205].

4.2.3.3 Quenching Diameter of Gaseous Ozone Decomposition Flames

The quenching diameter (“critical diameter”) of flames in a cylinder as a function of pressure (at 298 K) can be expressed by the equation

$$\log d_c = 1.953 - 1.111 \log P$$

where d_c is the quenching diameter in micrometer (μm) and P is the pressure in atm [206]. For example, in a cylinder at 1 atm and 298 K, the quenching diameter is 90 μm ,

the smallest of any gaseous reactant known. The quenching diameter of flames in a cylinder as a function of temperature (at 101 kPa) can be expressed by the equation

$$d_c = 347.5 - 0.864 T$$

where d_c is the quenching diameter in micrometer (μm) and T is the temperature in kelvin.

Table 31 gives an overview of some quenching diameter measurements obtained under different conditions.

Table 31: Quenching diameter of ozone and ozone/oxygen flames.

Ozone concentration Mol-%	Temperature K	Pressure atm	Quenching diameter mm
15	298	1	5.000
25	298	1	1.650
50	298	1	0.390
75	298	1	0.165
100	298	1	0.090

Data source: [206]

For information on the critical diameter of capillary passages through which ozone decomposition may propagate, see also [207].

The minimum gas flow to prevent flashback of an ozone flame is a function of the burner diameter (Table 32).

Table 32: Minimum gas flow or flashback flow at 1 atm and 298 K = 25 °C.

Burner tube internal diameter, cm	Minimum flow, flow rate, cm^3/s
0.065	7
0.1	29
0.2	232
0.3	725
0.6	6090
0.8	14500
1.0	29000
2.0	232000

Data source: [77]

4.2.4 Detonation of Gaseous Ozone

A flame front propagating unimpeded into gaseous ozone or ozone/oxygen mixtures may undergo a deflagration-to-detonation transition (DDT), and the remaining un-

reacted gas detonates. Numerous investigators have measured the critical diameter above which explosions become possible, and the critical quenching diameter in capillary tubes below which an established detonation becomes extinguished and fails to propagate. The critical quenching diameter of pure ozone is the smallest of all known detonable gases and gas mixtures.

When curve fitting the data and expressing the quenching diameter d_c of gaseous ozone/oxygen mixtures as a function of chemical composition, the quenching diameter could be expressed by the following equations:

$$\log d_c = 6.189 - 2.118 \log x \quad \text{at 1 atm and 298 K}$$

$$\log d_c = 6.403 - 2.113 \log x \quad \text{at 1 atm and 195 K}$$

where d_c is the quenching diameter in micrometers (10^{-6} m), and x is the ozone concentration in vol-% O_3 .

Determination of the critical quenching diameter has practical significance insofar in terms of preventing the detonation of gaseous ozone by filling the storage volume with inert, porous particles. The pore size and interstitial spaces of these particles should be on the same order of magnitude as or smaller than the quenching diameter ($\sim 200 \mu\text{m}$). Ozone did not decompose when stored in containers of various materials under test (glass, aluminum, stainless steel) at dry-ice temperature [208].

The detonation velocity of gaseous ozone and ozone/oxygen mixtures are presented in Table 33, where we can compare experimental and theoretical results which agree quite well.

Table 33: Theoretical and experimental detonation velocities of gaseous ozone and gaseous ozone/oxygen mixtures.

Ozone concentration Mol-%	Detonation temperature K	Detonation pressure atm	Detonation velocity ^a m/s	
			Calculated	Measured
100	3340	30.78	1878	1863 $\pm$ 20
75	3110	25.50	1795	1782 $\pm$ 40
50	2645	19.15	1637	1633 $\pm$ 20
25	1705	10.89	1290	—

^a at 298 K = 25 °C and 101 kPa = 1 at, based on data from [209] and [192]

Similar results were reported by others and are summarized in Table 34 and 35.

The effect of diluents and critical ignition energy on the ignition of gaseous ozone in a range of 153 to 326 K (-120 to $+53$ °C) was examined with either spark ignition or thermal ignition on hot surfaces [212]. O_2 , CO_2 , H_2O , and SiF_4 were tested as diluents. The nature of the diluent gas had only a slight effect on the location of the lower limit

Table 34: Calculated and measured detonation velocities of gaseous ozone/oxygen mixtures.

Ozone concentration Mol-%	Initial pressure mm Hg	Detonation velocity m/s		Deviation of measured vs. calculated % relative
		Measured	Calculated theoretical Chapman-Jouguet (C-J) detonation velocity	
77	110	1733	1765	-1.8
77	112	1727	1765	-2.2
73	99	1720	1747	-1.6
64	133	1691	1710	-1.2
64	109	1691	1708	-1.0
45.5	130	1498	1577	-5.0
36.8	105	1406	1481	-5.1
25.0	275	1273	1302	-2.2
17.3	399	1140	1144	-0.4
10.5	486	932	964	-3.3
9.2	497	879	921	-4.6

Data source: [210]

Table 35: Comparison of detonation velocities of gaseous and liquid ozone/oxygen mixtures.

Gaseous		Liquid	
Mol-% O ₃	m/s	Mol-% O ₃	m/s
25.0	1290	58.0	4160 ± 140
50.0	1633 ± 20	65.1	4500 ± 80
75.0	1782 ± 40	77.6	5100 ± 180
100.0	1863 ± 20	89.5	5600 ± 60

Data sources: Gaseous, 1 atm, 298 K = 25 °C [209]; Liquid [211]

of detonability. The autoignition temperatures could be calculated based on the Semenov theory and agreed well with the data measured by Kamenetskaya. Thermal ignition experiments were conducted with gaseous ozone [213].

To test ignition limits, the calculated amount of 100% pure gaseous ozone was introduced into an evacuated cylindrical phosphor bronze vessel, 90 mm in diameter and 180 mm high. The ozone was then diluted with oxygen to the required concentration, and the mixture ignited by a spark from a 4-μF capacitor [214]. Test with sparks from a Tesla coil of considerable higher energy produced practically identical results. When it was found that the explosive limits of gaseous ozone/oxygen mixtures depended on the container material (glass or metal), the investigators assumed that

a chain reaction is sustained and that the wall material might be a chain terminator. However, this interpretation was challenged by others.

Attempts were made to predict the detonability of gases from theoretical considerations, and the reliability of those predictions was tested against experimental data for nitric oxide or ozone. It was predicted that ozone would detonate but nitric oxide would not [215]. Additional information on ozone detonations can be found in the following references: [191, 216–218].

The velocities of steady detonation waves in gaseous ozone were measured over a wide range of conditions in tubes with diameters between 1 and 25.4 mm, at initial pressures between 10.66 and 29.3 kPa (80 and 220 mm Hg), and in mixtures containing from 72.5 to 96.6 vol-% O_3 in oxygen or argon. The experimental velocities, extrapolated to infinite tube diameter, agreed within experimental error with those calculated by the classical theory of Chapman and Jouguet [219, 220].

Experimental and theoretical studies have been conducted on the nature of concentrated ozone decomposition [221]. Ozone with concentrations above 50 vol-% can produce a passivated layer on the surface of stainless steel, which is considerably less active to ozone decomposition. The ozone decomposition rate was strongly dependent on temperature, concentration, and pressure. The activation energy and order of reaction for the decomposition was reaffirmed. N_2 , Ar, and He dilution had no effects on ozone decomposition, while CH_4 and H_2 acted as catalysts, and CO reacted with ozone under room temperature and pressure conditions.

A series of ignition experiments using electric spark ignition was conducted to investigate the explosion hazards of gaseous ozone with concentrations of up to 60 vol-% [222]. The results showed that the lower explosion limit of ozone in oxygen at room temperature and atmospheric pressure was about 10 vol-%. Partial decomposition of ozone in the ignition vessel was observed in a range of 10 to 12 vol-%, and only ozone with a concentration exceeding 12 vol-% could cause an explosive chain decomposition and convert to oxygen completely. The lower explosion limit shifted to higher concentrations with decreasing initial pressures. For instance, at 100 mm Hg the lower limit was 25 vol-% O_3 . The explosion limit sharply increased at a pressure of 100 mm Hg or less. For example, the lower explosion limits at 600, 200, 80, and 20 mm Hg were estimated to be 12, 12.5, 15, and 30 vol-% O_3 , respectively. It seems that carbon dioxide has a weak inhibiting effect on ozone explosions. Adding 70 vol-% carbon dioxide to an ozone/oxygen mixture raised the lower explosion limit from 10 to 12 vol-% O_3 .

The explosion trigger energy (minimum ignition energy) is strongly dependent on ozone concentration and pressure. For example, the minimum trigger energy for 15 vol-% ozone at a pressure of 76 mm Hg (about 220 mJ) was more than 20-fold that at atmospheric pressure (about 10 mJ), and that for 13 vol-% ozone (about 580 mJ) was approximately 30 times higher than that for 20 vol-% (about 20 mJ) at the same pressure of 76 mm Hg [223]. A slight change in ozone concentration resulted in a large

difference in the minimum trigger energy. There was a 16-fold difference in ignition energy between 12.4 and 14.3 vol-% O_3 at a pressure of 200 mm Hg.

The detonation and deflagration properties of ozone/oxygen mixtures of up to 20 vol-% O_3 in oxygen under high pressures of up to 1.0 MPa in a closed cylindrical tube were experimentally investigated [224]. The mixtures were ignited by an electric spark at one end of the tube. Flame propagation properties such as flame velocity and pressure were measured with thermocouples and piezoelectric transducers mounted along the tube. Slow and constant flame propagation profiles were obtained. Figure 19 shows the steady flame velocity as a function of ozone concentration between 14 and 20% O_3 at an initial pressure of 0.1 MPa.

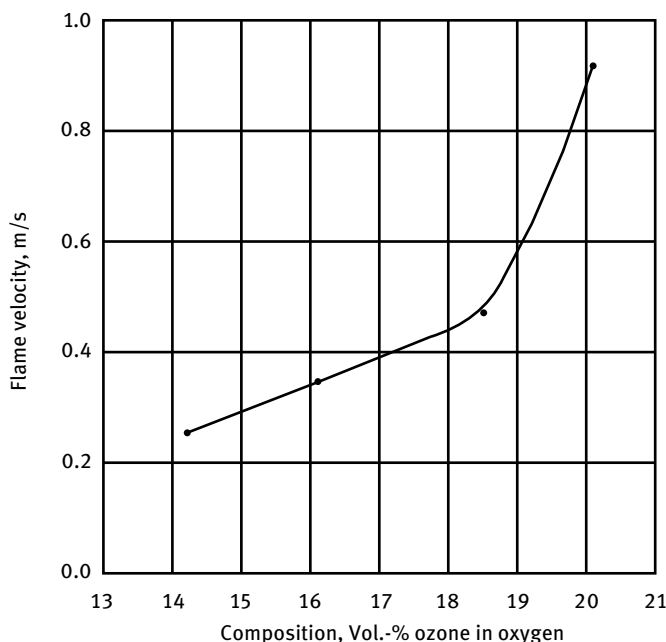


Figure 19: Steady flame velocity of ozone decomposition flames at 0.1 MPa. (Republished and modified from [224], with permission of © 2001 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center, Inc.)

Figure 20 shows the flame speed as a function of pressure for a constant ozone composition. The flame speed increased only moderately when the pressure of a mixture containing 13.4 to 14.3 vol-% ozone was increased from 0.1 to 1 MPa.

The quenching ability of a wire gauze was tested as a flame arrestor. A 20-mesh stainless-steel wire gauze was inserted in the middle of the test section. A 15 vol-% O_3 flame was quenched at atmospheric pressure. However, when the mixture was flowing, the flame was trapped by the gauze and kept burning on the surface of the gauze.

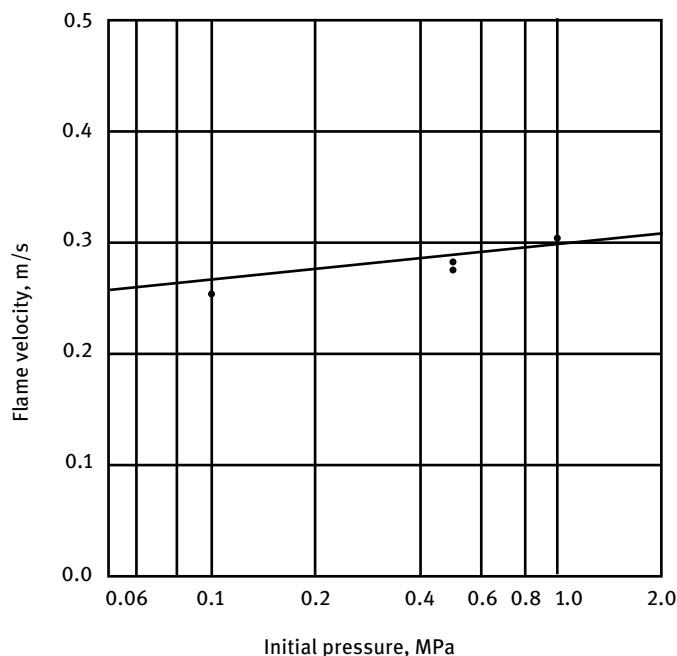


Figure 20: Steady flame velocity of ozone decomposition flames as a function of initial pressure. (Republished and modified from [224], with permission of © 2001 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center, Inc.)

The wire gauze acted as a flame holder. The lower concentration limit for flame propagation was measured under different conditions. Deflagration-to-detonation transition by an electric spark ignition was not achieved under these experimental conditions. In near-limit mixtures, despite slow flame propagation velocity and easy flame quenching properties, direct initiation of detonation by a driver (donor section) detonation of a stoichiometric oxygen-hydrogen mixture was easily achieved at much lower O_3 concentrations than the limit of deflagration. The observed detonation properties, such as wave velocity and pressure, agreed well with Chapman-Jouguet (C-J) calculated values. The detonation velocity (900–1200 m/s) and the pressure ratio of final to initial pressures (5–9.5) were not affected by the initial pressure of the mixtures. Near the detonation limit, typical spinning detonations with oscillatory pressure waves were observed. Figure 21 shows the detonation velocity of an oxygen-hydrogen donor-driven ozone detonation as a function of O_3 concentration. The solid line denotes the theoretical detonation velocity from a C-J calculation. Little change in the detonation velocity with tests at different initial pressures in the target section of the shock tube.

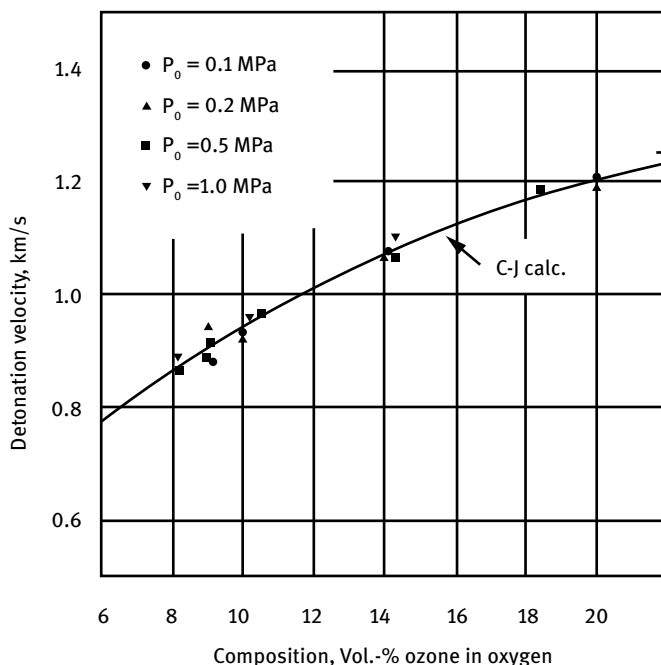


Figure 21: Detonation velocity of ozone/oxygen mixtures at various initial pressures. (Republished and modified from [224], with permission of © 2001 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center, Inc.)

4.2.5 Strand Burning of Liquid or Solid Ozone and Their Mixtures with Oxygen

When taking certain safety precautions, it is possible to burn solid or liquid ozone in thin strands unconfined or confined in capillary tubes. The ignition energy must be kept at a minimum so that it just ignites combustion but does not initiate a detonation. A condensed-phase ozone strand burns like many monopropellants, even in the absence of other fuels. However, if hot spots develop unintentionally, the apparatus may explode.

Calculated theoretical strand burn rates and flame temperatures of ozone combustion are summarized in Table 36.

The burn rate and flame temperature of solid ozone and ozone/oxygen mixtures (with 50 and 75% O_3) are lower than corresponding data in the liquid state. The difference between liquid and solid samples is least with pure ozone. The burn rate is dependent on the sample starting temperature, which is most pronounced with the mixtures and least noticeable with pure ozone.

The strand burning of solid ozone, with or without intermediate formation of a liquid melt layer, has been used as a simple example to test computational models for homogeneous solid propellant (monophasic energetic materials like RDX)

Table 36: Calculated theoretical strand burn rates and flame temperatures of combustion of ozone and ozone/oxygen mixtures.

Physical state	Starting conditions		Ozone concentration mol-%	Burn rate cm/s	Flame temperature K
	Pressure atm	Temperature K			
Liquid	1	150.5	50	0.0774	1509
Liquid	1	156.5	75	0.227	2029
Liquid	1	161	100	0.361	2400
Liquid	2	160.5	50	0.155	1508
Liquid	2	167	75	0.456	2030
Liquid	2	172.5	100	0.738	2414
Liquid	10	187.5	50	0.78	1507
Liquid	10	198	75	2.31	2031
Liquid	10	206	100	3.84	2436
Solid	1	20	50	0.0380	1371
Solid	1	63	50	0.0505	1445
Solid	1	20	75	0.147	1894
Solid	1	63	75	0.170	1960
Solid	1	70	75	0.173	1969
Solid	1	20	100	0.274	2287
Solid	1	63	100	0.294	2339
Solid	1	70	100	0.301	2346

Based on data from [225] and [226]

burning. Modeling the burning of solid ozone was much simpler than modeling the burning of RDX. One process modeled was a gas/surface reaction. A detailed analysis was performed on the reaction mechanisms at play in the ozone flame and how they are affected by the heterogeneous reaction [227–229].

The detonation of solid ozone was simulated using a reactive empirical bond order (REBO) potential formality, which described the gas-phase properties of isolated reactant and product molecules and high-density phases generated under shock compression [230]. The model described an ozone molecular solid with the density and velocity of sound within physical norms. The detonation characteristics depended on crystallographic orientation of the crystals.

Even tiny, nanoscale voids and cracks, imperfections in the crystal lattice, can aggravate the shock sensitivity of solid ozone. The initiation characteristics of the model were dependent on the crack width, suggesting that there was also a similar geometry-dependent effect in detonation propagation [231]. A two-dimensional simulation was developed for the detonation of a model crystal consisting of solid ozone [232]. The presence of nanoscale voids lowered the initiation threshold of detonation.

4.2.6 Detonation of Liquid Ozone and Liquid Ozone/Liquid Oxygen Mixtures

4.2.6.1 Detonation of Liquid Ozone

An attempt was made to explain the liquid-phase detonation behavior of liquid ozone by establishing a chain reaction of kinetic events [233]. Measured critical diameters for the propagation of ozone detonations in capillary tubes agreed with those predicted by Khariton's theory about the critical diameter of solid explosives.

4.2.6.2 Detonation of Liquid Ozone/Liquid Oxygen Mixtures

If one plots the temperature required for thermal initiation of LOZ/LOX (15 to 90% O₃) detonations by flash heating, the minimum required energy is an exponential function of the ozone concentration c [234, 235].

A solution of ozone in LOX will not detonate if the initiation energy E is smaller than

$$E_{\min} = 186e^{-\frac{c}{6.9}}$$

where c is the ozone concentration in mass-% and E is the energy in cal. The mechanical shock sensitivity of liquid ozone can be determined using either the drop weight sensitivity test method or the adiabatic compression sensitivity method. The pressure increase that leads to the detonation of LOZ/LOX mixtures can be expressed as an exponential equation of the ozone concentration c and decreases with increasing ozone concentrations [236, 237]:

$$P_{\text{ref}} = 173e^{-0.0382 \times c_{\text{O}_3}}$$

where c is the ozone concentration in mass-% and P is the pressure in atm. The shock sensitivity of these mixtures seems to be proportional to the energy required for thermal initiation. Only mixtures with less than 29.5 mass-% and more than 68.5 mass-% ozone were investigated because mixtures in the interim range would separate into two phases. Glycerin trinitrate, known to be very shock sensitive, was tested in the same apparatus for comparison. It exploded when suddenly compressed from 1 to 96 atm. There appears to be some sort of correlation between the shock (adiabatic compression) and thermal initiation of LOZ/LOX mixtures. The test series used only mixtures with less than 29.5 and more than 68.5 mass-% O₃, because intermediate mixtures have a tendency to separate into two immiscible phases. Glycerin trinitrate (nitroglycerin) was tested for comparison in the same adiabatic compression sensitivity apparatus. It exploded when suddenly compressed from 1 to 96 atm. The experiments from which the two preceding equations were derived were conducted in an apparatus whose basic element was an explosion vessel, a tube 20 mm in diameter and 400 mm in length. A shock tube (diameter 20 mm, length 1080 mm), divided into two unequal sections by a rupture diaphragm, was inserted in the enlarged upper section of the vessel. The results obtained showed that ozone/oxygen solutions possess a very high sensitivity to pressure pulses. The dilution of liquid ozone with oxygen

led to a sharp decrease in the pressure pulse necessary to excite an explosion in the solution.

One of the reports stated that “Solid ozone with solid carbon dioxide, nitrous oxide, and argon present has the same impact sensitivity as solid ozone alone. The use of solid ozone is to be avoided” [238].

The handling of liquid ozone and ozone/oxygen mixtures presents a very difficult challenge because one must maintain a narrow range of temperatures. If the temperature of homogeneous mixtures drops below a critical temperature, phase separation causes an ozone-rich layer to precipitate which has been blamed for many of the explosions observed with ozone/oxygen mixtures [239]. Such mixtures are sensitive to initiation by mechanical shock, flames, or electric sparks. Liquid oxygen at its natural boiling point (90 K = -183°C) dissolves 17.6 mol-% ozone. If the ozone concentration in the mixture exceeds this number, for instance at 18.6 mol-% O_3 , an electric spark causes a weak explosion. Above 21 mol-% it causes a violent detonation. If the ozone content exceeds 23 mol-%, the mixtures begin to become sensitive to shock. Two-phase mixtures with even higher ozone concentrations explode regardless of the type of initiation stimulus (often unintentionally). Table 37 shows that the explosive limit of LOZ/LOX mixtures decreased instead of widened with decreasing temperatures, as one might expect. This was caused by the phase separation happening as the mixture cooled off. Only at very low temperatures does one notice a stabilizing effect from lowering the temperature.

Table 37: Explosion limits of liquid ozone/oxygen mixtures.

Temperature		Composition	
K	$^{\circ}\text{C}$	Mol-% ozone	Mass % ozone
90	-183	17.6	24.3
89	-184	15.0	20.9
87	-186	10.8	15.4
85	-188	8.8	12.6
83	-190	7.7	11.1
81	-192	7.0	10.1
79	-194	6.8	9.9
77	-196	6.9	10.0

Based on data from [239].

The limits of detonability and detonation velocity of LOX/LOZ solutions using a spark ignition were determined at temperatures above the boiling point of LOX [211]. To obtain homogeneous mixtures at temperatures above the boiling point of LOX, samples were held in pressurized vessels. Mixtures containing less than 50 mass-% ozone could be made to detonate by a weak spark.

If a charge of 100% liquid ozone was used as a booster charge, explosions were possible in mixtures containing less than 50 mass-% O_3 . In a mixture containing 35 mass-% O_3 , this mode of initiation triggered only a relatively slow decomposition reaction. The results are summarized in Table 38.

Table 38: Detonation properties of LOZ/LOX mixtures.

Ozone concentration Mass-%	Capillary diameter mm	Initial pressure atm	Ignition method ^a	Tube material	Type of observed detonation	Velocity of detonation m/s
100	4.8	1.0	A	Glass	steady	5730 ± 460
100	4.8	28	A	Glass	delayed	6040 ± 410
100	8	1.5	A	Glass	steady	5800 ± 150
100	8	28	A	Glass	steady	5810 ± 70
85	8	21	A	Glass	steady	5600 ± 60
69.5	8	28	A	Glass	steady	5100 ± 180
65.6	4.8	1.5	A	Glass	brisant	—
54.5	4.8	32	A	Glass	less brisant	—
55.5	8	1.5	A	Glass	steady	4500 ± 80
49.7	8	1.5	A	Glass	none	—
47.6	4.8	28	A	Glass	none	—
39.7	4.8	1.5	A	Glass	none	—
48.4	4.8	1.5	B	Glass	decomposition	5600–6100
48.0	8	21	B	Glass	steady	4160 ± 140
42.0	4.8	1.5	B	Glass	decomposition	4100–5800
41.1	8	28	B	Glass	none	—
37.9	4.8	21	B	Glass	none	—
100	11	1.5	A	Lead	steady	6390 ± 100
100	11	28	A	Steel	steady	6110 ± 210

^a Method of initiation: A = direct electrical spark; B = initiation by a booster charge of 100% ozone
Based on data from [211]

Sometimes a weakly luminescent decomposition front was observed propagating into the mixture, which, after traveling halfway down the tube, suddenly transitioned into an explosion (detonation?) front. The data for 100% ozone in the preceding table agreed well with calculated theoretical data reported earlier [209] ($v = 5070$ m/s, $T = 3140$ K, $P_{\text{expl.}} = 4 \times 10^4$ atm; start conditions: 90 K, 1 atm).

The detonability of LOZ/LOX mixtures was determined in tubes of various diameters and different containment materials [240]. Such data are of practical value if one wants to prevent ozone detonations from propagating from the rocket combustion chamber into the injectors, the feed system, or even the oxidizer supply tank. Samples containing 100, 49, 40 or 30% ozone in LOZ/LOX were confined in steel or lead pipes that were 40 cm long, 12 mm ($\frac{1}{2}$ in.) outer diameter (OD), and having a wall thickness

of 0.8 mm (1/32 in.) and initiated either by an electric spark or by a booster charge of 100% ozone. The detonation of 100% LOZ disintegrated the tubes into tiny splinters. In addition, 49- and 40-% LOZ resulted in coarser splinters and required a LOZ booster, while 30% LOZ was not detonable, not even when a booster charge of 100% LOZ was detonated next to it.

An explosion may transfer from a detonation of gaseous ozone/oxygen mixtures to initiate a detonation of a liquid ozone/oxygen solution [241].

4.2.7 Slow Gas-Phase Decomposition of Ozone

There are thousands of publications on gas-phase decomposition, mostly on photolysis under the conditions of the ozone layer in Earth's upper atmosphere. Most of these operate at very low pressures and relate only remotely to the decomposition of gaseous ozone as it is encountered in a laboratory while preparing ozone for a rocket experiment. The decomposition of ozone as a source of singlet atomic oxygen would be of interest for chemical lasers like COIL, where current technology creates atomic oxygen by the reaction of alkaline hydrogen peroxide with chlorine. If ozone could be brought safely on board, the complicated and messy caustic hydrogen peroxide/hypochlorite combination would no longer be needed.

Publications referenced in this section are limited to those operating at atmospheric pressure and with only minimal dilution by inert gases.

4.2.8 Stabilization and Desensitization of Ozone

While stabilizers have been found for high-concentration hydrogen peroxide as a rocket propellant and dextrin has been used as a desensitizer for lead azide, no stabilizers or desensitizers have been found for ozone. Many patents have been filed, but they must be treated with caution and skepticism. Perfluoroethylamine in amounts of 0.5–15% was claimed to reduce the sensitivity of liquid ozone [242].

The detonability of thin layers of frozen ozone depends on the thickness of the layer deposited. Below a certain thickness (<1 mm) the layer will no longer detonate. Amorphous (as opposed to crystallized) solid ozone in thin layers is much less sensitive than bulk frozen ozone prepared by conventional methods [243]. Amorphous samples of solid ozone that formed at temperatures below 20 K were stable to laser irradiation.

The search for inert solvents capable of separating ozone from a process stream and storing it as a solution in a safe manner has been expanded to halocarbons, mostly of the Freon family [244]. An alternate method to dissolving it in inert solvents is to adsorb ozone from a process stream that contains only 8–9 mass-% ozone onto a silica gel in a cold trap. Ozone can be safely stored in this adsorbed state and desorbed in pure form on an as-needed basis. Until 1960, carbon tetrachloride was the only solvent known to be inert toward ozone. However, the ozone solubility coefficient in CCl_4 was relatively low (4.6 at 261 K = -12°C). Freons have solubility coefficients for ozone at

158 K (–115 °C) that are several orders of magnitude better than those of CCl_4 , on the order of 1500–3500. Ozone can be separated from the process gas at the ozonizer outlet by dissolving it in Freon, whereas unreacted oxygen does not dissolve. A trace of free fluorine in Freons has a stabilizing effect on the ozone. The best stabilizer and solvent for liquid ozone is Freon 14, CF_4 . The best stabilizer and solvent for gaseous ozone is Freon 22, CHClF_2 . Neither complexes nor solvates are formed when ozone dissolves in Freons. The concentration of ozone in Freon-ozone mixtures can reach 50%. Solutions of 10% ozone in Freon 12 at 195 K (–78 °C) are completely safe [245]. See also [246].

4.2.8.1 Photolysis of Gaseous Ozone

Not only does ozone form from oxygen under the influence of UV light, but UV photolysis also effects the decomposition of liquid or gaseous ozone [247, 248]. The quantum yield during the photochemical decomposition of liquid ozone at 90 K (–183 °C) is on the order of 2.0. In the ozone layer on top of the atmosphere, a dynamic equilibrium concentration of ozone is maintained (unless “civilized” inhabitants of Earth release ozone-destroying chemicals from their refrigerators and air conditioning units) where ozone is simultaneously formed by the photolysis of oxygen and ozone is destroyed by UV radiation. There are so many publications on the photolysis of ozone under a wide range of atmospheric conditions and in the absence or presence of artificial and naturally occurring halogen compounds that we’ll not attempt to reference any of those here. Suffice it to say that if ozone is ever used as a rocket propellant, it should be kept in the dark. A flash from a strobe or a laser pulse could be used to initiate the decomposition or combustion of ozone and ozone-fuel mixtures in a controlled way.

Light emitted from decomposing ozone may cause adjacent non-decomposed ozone to be photolyzed, thereby propagating the decomposition front in a flame or a detonation at much higher speed than would be expected by traditional theoretical flame velocity calculations.

4.2.9 Radiolysis of Ozone

The same mechanisms that cause the formation of ozone by the radiolysis of oxygen will also lead to the destruction of ozone by radiolysis. Depending on the concentration of oxygen and the intensity of hard radiation, there is a dynamic equilibrium concentration of ozone in irradiated oxygen, like the effect of UV photolysis. Ozone can be smelled in the proximity of radioactive materials in air. The decomposition of ozone by ionizing radiation has been explained by a negative ion-chain mechanism [249]. The γ -irradiation of liquid or solid oxygen is one method for producing ozone, but the ozone yield is limited by the reverse reaction [60, 61].

5 Construction Materials for Handling Ozone

The main concern in selecting construction materials that come in contact with ozone during ozone preparation, concentration, and storage is the inadvertent catalysis of ozone decomposition that can lead to explosions and detonations. Many metals become passivated by the formation of a thin oxide layer once they are in contact with ozone, but some oxides are just as good catalysts as the bare metal itself. Only very few metals are suitable for ozone equipment. Like precautions taken in the first use of new equipment with fluorine, it is best to passivate the equipment slowly by starting out with inert gas and gradually increasing the ozone concentration to the level the system will be exposed to during its nominal operation. For liquid ozone solutions in liquid oxygen, one starts with equipment that is already qualified for LOX and subjects the list of materials to a secondary screening to see if some materials in contact with ozone have to be replaced before the apparatus can be used.

Referring to the literature, the following metals are supposed to be suitable for handling of liquid ozone: aluminum 2S, 3S, 24S, 52S, and 61S; CRES 302, 304, 316, 410, and 416; and titanium and Stellite [18]. It is known that titanium in liquid oxygen is sensitive to shock and shear and the same problem would be encountered with liquid ozone and titanium.

Few elastomers are compatible with ozone. Rubber (latex rubber, ethylene-propylene-terpolymer (EPT) polymers) becomes rapidly embrittled by ozone, and even a low ozone concentration in air (city smog, high-altitude airplanes) will accelerate rubber deterioration. Perfluorinated and perhalogenated polymers are suitable as flexible hoses and gaskets for ozone systems; this includes polytetrafluoroethylene (PTFE), polychlorotrifluoroethylene (PCTFE), and polyvinylchloride (PVC).

6 Toxic Properties of Ozone

Many publications prior to 1958 contradicted each other about the odor and toxicity of ozone at various concentrations [250, 251]. The possible sources of these contradictions were inaccurate methods of analysis used for transient ozone concentrations and a lack of documentation about the quality of the gas (mixture) used for the production of ozone. The purity of the product differs substantially depending on whether pure oxygen or air was used as the starting reactant. Ozone made by ozonization of air contains a very high concentration of dinitrogen pentoxide, which is more toxic than ozone, and its toxicity rivals that of phosgene [252]. See also [253].

The Committee on Toxicology of the US National Academy of Sciences issued a report on emergency and continuous exposure limits for selected airborne contaminants. The report contains a seven-page summary of ozone toxicity and considerations for setting safe limits of ozone concentrations in ambient air [254].

6.1 Inhalation Toxicity of Ozone

The main concern about ozone toxicity is the lifelong exposure of populations in urban areas due to smog formation. Ozone is not the only irritant in these situations; nitrogen oxides, acetyl peroxide, peroxyacetic acid, and many others contribute to lung problems. It would be difficult to single out ozone as the main irritant and health hazard. The olfactory threshold of ozone is 0.05 ppm by volume. Airplanes flying at high altitudes may contain ozone at up to 0.5 ppm in the cabin. For a long time it was assumed that ozone monitors and alarm systems in ozone-handling laboratories were unnecessary because the odor provided ample warning before dangerous concentrations were reached. This position changed in 1979, when the Threshold Limit Value-Time Weighted Average (TLV-TWA) was again lowered, this time to 0.1 ppm.

A volunteer physiologist who inhaled 8 ppm ozone for 1 h suffered significant lung damage, and his respiratory capacity was reduced by 50%. Even concentrations below 8 ppm and exposures lasting less than 1 h can cause swelling of the mucous membranes and lung tissue.

Figure 22 shows the safe limits and observed symptoms in a concentration-time diagram.

Up to 4 ppm and for exposures not exceeding 100 h, one can assume a non-symptomatic range within which one does not observe permanent adverse effects.

In animal tests, exposure of rats to 2.4 ppm ozone caused pulmonary edema and hemorrhage [255]. After breathing in this atmosphere for 32 h, some of the animals ac-

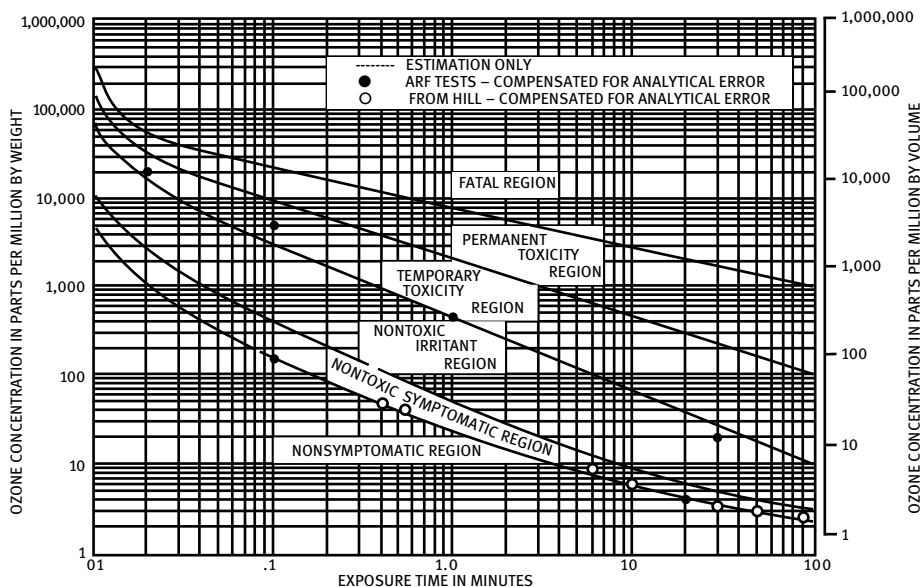


Figure 22: Tolerance and toxicity limits of ozone inhalation in humans. (From [7].)

climatized and suffered no additional effects. In a group of 102 mice exposed to 2 ppm ozone for 24 h, the fatality rate was 20%. The LC 50 after a 4-h exposure was 3.6 to 4.1 ppm for male mice, 3.6 to 6.4 ppm for male rats, and 9.1 to 12.1 ppm for hamsters.

Repeated exposure of rats to 2 ppm ozone for 3 h resulted in rapid (within 3 h) and persistent (up to 72 h) histological changes in the bronchiolar epithelium, including hypercellularity, loss of cilia, and necrotizing bronchiolitis [256].

The American Conference of Governmental Industrial Hygienists (ACGIH) recommendation for inhalation TLV-TWA for ozone in the US was 0.1 ppm in 2010. National Institute for Occupational Safety and Health (NIOSH) recommendations for TLV-TWA (2013) were 0.1 ppm (0.0196 mg/m³) with a **ceiling** notation. The immediately dangerous to life or health (IDLH) concentration was given as 5 ppm, which appears to be quite conservative considering that human volunteers have survived 8 ppm exposure for 1 h (although with significant lung damage). It was recommended to keep the TLV-TWA for humans for the 8-h workday below 0.1 ppm.

7 Handling of Ozone and Ozone/Oxygen Mixtures

Liquid oxygen containing up to 10 mass-% liquid ozone can be handled using essentially the same precautions as for liquid oxygen itself, except for precautions to prevent inadvertent inhalation of boiloff gases vented to the atmosphere. A previous chapter (Section 4.2.6.2) summarized in detail the hazards resulting from the buildup of ozone in residue if oxygen was allowed to evaporate from LOZ/LOX mixtures. To prevent the accumulation of ozone and eventual phase separation of a mixture, either the mixtures must always be cooled externally with liquid nitrogen or the LOX boiloff must be compensated by adding fresh LOX [257]. Storage of LOZ/LOX solutions under pressure narrows the miscibility gap and allows the storage of solutions containing more than 24 mass-% O₃ [258].

Even an experienced experimenter using the proper equipment will occasionally encounter unexpected ozone explosions. Adequate precautions would include bullet-proof plastic shielding and remote manipulation apparatus, like that used for radioactive substances. The various parts of an ozone production and liquefaction apparatus should be separated from each other by blast shields, such that an accidental detonation originating in one part of the system cannot destroy adjacent parts of the system. Detailed instructions for handling liquid ozone can be found in [259, 260].

7.1 Storage of Ozone and Ozone/Oxygen Mixtures

Ozone and ozone/oxygen mixtures can be stored indefinitely at liquid nitrogen temperatures.

It has been suggested that gaseous ozone can be stored safely in cylinders filled with small alumina beads such that the interstitial space is below the critical diameter for ozone detonation propagation [246].

7.2 Transfer of Ozone and Ozone/Oxygen Mixtures

When transferring LOZ/LOX mixtures from one container to another, the receiving vessel and the transfer tubing must be precooled with liquid nitrogen or LOX to prevent changes in the ozone concentration as a result of preferential evaporation of LOX from the mixture. One method would be to immerse the entire apparatus in a bath of liquid nitrogen [240, 261]. Pressurized transfer would best use helium as the pressurant gas.

7.3 Neutralization of Ozone in Boiloff from Storage Tanks

Because the vapor pressure of ozone (<1 mm Hg at $90\text{ K} = -183^\circ\text{C}$) at the storage temperature of liquid oxygen (or liquid nitrogen) (<30 mass-% O_3 in the liquid phase) is very low, the boiloff gases in the storage area contain only a small ozone concentration. This is enough to be irritating, but with proper ventilation this gas would readily disperse in air. If the storage area is not adequately ventilated, the ozone concentration in the room air can reach dangerously toxic or even explosive levels.

It has been proposed to remove small ozone contamination from LOZ/LOX boiloff by passing the gases through a catalyst bed containing manganese(IV) dioxide (Section 4.2.1.2). Manganese oxide acts as a catalyst that will cause ozone to decompose to oxygen. One must be careful that none of the catalyst fines can migrate upstream to the storage container. This method is limited to LOZ/LOX mixtures with less than 30% LOZ, because at higher concentrations the boiloff vapors might reach the explosive limit and the catalyst would trigger an explosion that might propagate upstream to the storage vessel. Finely divided manganese(IV) dioxide is also recommended as a filling for gas masks to protect personnel working in areas with high ozone concentrations. Tests of ozone gas masks were conducted at the Armour Research Foundation at the Illinois Institute of Technology, Chicago, Illinois. The filters and the housing may not contain any gaskets made of rubber or other flammable materials.

Excess ozone that has passed through water treatment plants unreacted must be destroyed before the gases are allowed to vent to the atmosphere. In the water treatment industry, this is done by passing the gases over heated catalyst beds.

Liquid ozone is almost completely stable when kept cold below $161\text{ K} = -112^\circ\text{C}$ [186]. The rate of decomposition in a range of 113 to 161 K (-160 to -112°C) is 0.01 to 0.02% within 24 h . Many materials have been tested for compatibility with ozone, but often the degree of dispersion (particle size of powders) was not reported. Aluminum oxide, manganese(IV) dioxide, and lithium peroxide caused rapid decompo-

sition of gaseous ozone at room temperature, while nickel sponge and activated charcoal caused explosions.

7.4 Lessons Learned in Handling Ozone

Organizations that developed a significant amount of experience in the proper handling of ozone ultimately drew the following conclusions: “It has been the experience of the staff of Armour Research Foundation that highly concentrated ozone, as either a gas or a liquid, can be produced and handled in pilot plant quantities with care and without mishap” and “100% liquid ozone and all liquid ozone/oxygen mixtures, if properly prepared and very carefully handled, are relatively stable” [19, 262].

NASA Lewis Research Center conducted rocket engine tests with LOZ/LOX mixtures as oxidizer in combination with gaseous hydrogen as fuel. During these tests the agency gained substantial and well-documented experience in the handling of LOZ/LOX mixtures at rocket test sites. The experimenters concluded that LOZ/LOX mixtures with up to 30 mass-% O_3 can be handled safely as long as all necessary safety precautions are observed [240, 263]. The handling of more concentrated mixtures is more problematic and was beyond the recommended practice.

7.5 Accident History of Ozone

A paper by Miller [240] contains some impressive images of the damage caused by ozone explosions in rocket test facilities.

8 Ozone Mixtures with Other Oxidizers (Besides Oxygen)

Besides the thoroughly studied LOZ/LOX mixtures, a few more mixtures of LOZ with other oxidizers are of potential interest as rocket propellants. In all these cases the other oxidizer acts as a diluent and reduces the explosive hazards of pure ozone.

For instance, the physical properties of mixtures of ozone/fluorine/oxygen and ozone/fluorine, which represent very energetic oxidizers, have been investigated [264]. It is important to learn that fluorine and ozone, as well as fluorine and oxygen, are miscible in a temperature range from 74 to 79 K in all ratios. This represents a difference from the ozone/oxygen system, which has a well-known miscibility gap that reappears in the ternary diagram of Figure 23. At 77.5 K only mixtures containing less than 10 or more than 89 mass-% ozone are homogeneous solutions. The miscibility gap can be narrowed by the addition of fluorine. Most mixtures with more than 50 mass-% fluorine are homogeneous liquids. In Figure 23, the solid dots indicate homogeneous solutions, and the plus signs indicate the two-phase region.

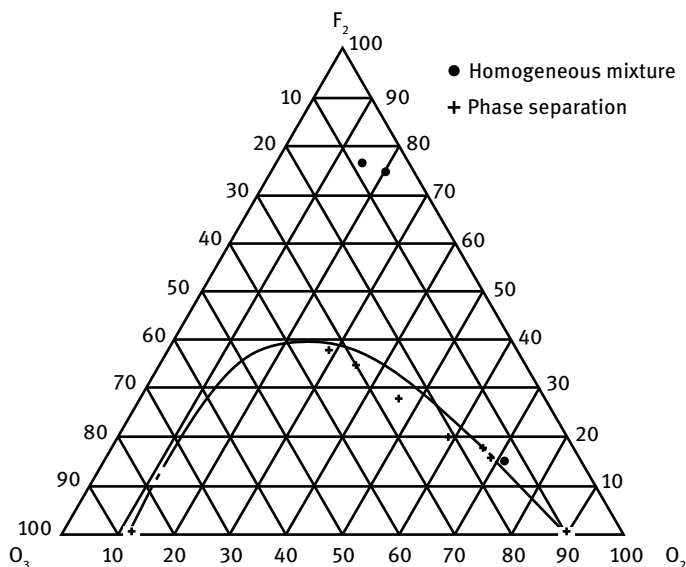


Figure 23: Phase diagram of ternary system $O_2/O_3/F_2$ at 77 K. (Republished and modified from [264], with permission of © 1962 American Institute of Physics; permission conveyed through Copyright Clearance Center Inc.)

The solid line is the approximate miscibility boundary, but its exact location is not known in the area where the line becomes a dashed line.

Fluorine was added to LOZ/LOX mixtures as a means to prevent a dangerous phase separation and to completely solubilize O_3/O_2 solutions [265–267]. Adiabatic U-tube shock tube tests and critical diameters were determined for homogeneous solutions. These data were then used to determine the maximum concentration of ozone that could be safely handled in flow tests. It was concluded that a solution of ozone, oxygen, and fluorine containing about 30 mass-% ozone and at least 14% fluorine, when handled under carefully controlled conditions, should be a feasible rocket-propellant oxidizer.

Other diluents for ozone that have been tested include nitrogen and carbon monoxide [72]. Despite the similarities of CO and N_2 with respect to their physical properties, they show unexpected solubility behavior in liquid ozone. CO is miscible in all proportions at 77.4 K with liquid O_3 , while N_2 in O_3 and vice versa show very limited solubility. A preliminary ternary composition diagram of the system liquid $O_2/O_3/N_2$ at 77.4 K was given as an example.

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Perchlorate Oxidizers

1 Perchlorates in General

Perchlorates are the salts of perchloric acid with metal cations or other nonmetallic cations. Perchlorates are used in numerous industrial applications such as explosives, pyrotechnics, and rocket propellants. The most important perchlorate is ammonium perchlorate (AP), which is the preferred solid propellant oxidizer. With an oxygen balance of +34.04% AP is at the top of the list when comparing solid propellant oxidizers based on their available oxygen content. The second-most important perchlorate is potassium perchlorate, which is used in many igniters and other pyrotechnic formulations due to its thermal stability, which is better than that of AP. Sodium perchlorate is an intermediate in the production of AP. Therefore, its properties are well-known. Lithium perchlorate is often used in mixtures with other perchlorates to improve their properties. Of all the alkali metal perchlorates, lithium perchlorate, LiClO_4 has the highest oxygen content. Metal perchlorates are not used as rocket propellants because the metal oxides formed as a result of combustion add to the non-condensables in the exhaust and result in poor rocket performance. Alkali metal perchlorates are used mostly in pyrotechnic igniter mixtures and in airbag gas generants. This book contains short sections on alkali metal chlorates and perchlorates in Section 11 and earth alkaline metal perchlorates in Section 12. Properties of metal perchlorates have already been sufficiently summarized in other publications such as [1–6].

The 1969 Pearson summary in *Oxidation and Combustion Reviews* was preceded by an earlier version published as a government report and as such is available in the public domain [7]. The first edition of the Schumacher book was even translated into Russian in 1963.

Perchloric acid is of interest for the synthesis of various other perchlorates that are useful as propellant ingredients. Perchloric acid by itself is not used as a rocket propellant, however, its decomposition kinetics have been studied extensively because they play a role in the decomposition and combustion of some perchlorate oxidizers, predominantly that of AP. A section on perchloric acid decomposition is available in the 1968 and 1969 Pearson books and, while we have not devoted an entire section in this book to the decomposition of perchloric acid, a few supplementary references will be provided later in this.

1.1 Environmental Effects of Perchlorates

Perchlorate ions are quite persistent in the environment and perchlorates from AP production wastes and accidental spills have been found to leach into aquifers and drinking water supplies. AP waste streams are generated when cleaning out mixing and

casting equipment where composite propellants have been mixed, cast, and cured. AP waste streams are also generated during the demilitarization of AP-based solid propellants. Careless spillage of perchlorates during decades of propellant processing before its toxic properties were better understood has caused detectable amounts of perchlorates to contaminate some aquifers and drinking water supplies. The environmental effects of perchlorates are discussed in detail in Section 8 of this book.

1.2 Natural Occurrence of Perchlorates

The possibility of naturally occurring perchlorate has only recently received significant attention. In the wake of discovering perchlorate ions in the soil of polar regions on Mars, chemists began to take a closer look at the natural occurrence of perchlorates on Earth and began to realize that solar system-wide perchlorate occurrence is more common than initially assumed. The Phoenix Mars Lander performed aqueous chemical analyses of Martian soil scooped from the northern plains of the *Vastitas Borealis*. The solutions contained ~10 mM of dissolved salts with 0.4 to 0.6 mass-% perchlorates leached from each sample [8]. The remaining anions included small concentrations of chloride, bicarbonate, and sulfate. The strong signal of perchlorate ion overwhelmed the selective ion electrode detector where one would have expected nitrate ion. Saturated solutions of perchlorate salts in water may exist in underground pockets of brine on Mars. These solutions have very low freezing points and very low vapor pressure, such that their existence at certain depths below the surface or even at the surface is possible. It has been speculated that perchlorate ions might be part of a life-supporting extraterrestrial biologic cycle if there are bugs that can thrive on it [9]. If bulk deposits of perchlorates can be found on Mars as mineral deposits, they might be mined and used as rocket propellants for *in-situ* resource utilization (ISRU).

The formation and decomposition of perchlorates have been studied in simulated extraterrestrial ices in laboratory apparatus on Earth. Carbon dioxide-rich chloride-bearing ices were exposed to energetic electrons in laboratory simulation experiments to investigate the formation of chlorine oxides (Cl_xO_y) in the condensed phase on Mars [10]. The radiolysis-induced synthesis of chlorine oxides (Cl_xO_y) was monitored online and *in-situ* via infrared (IR) spectroscopy and quadrupole mass spectrometry (QMS). Three discrete chlorine oxides were identified: chlorine dioxide (OClO), dichlorine monoxide (ClOCl), and chloryl chloride (ClClO_2). Higher irradiation doses supported the facile production of ClO_3^- and ClO_2^- bearing higher chlorine oxides. These can lead to the formation of perchlorates as found on Mars.

Samples of Martian soil scooped from aeolian deposits in Gale Crater and pyrolyzed produced mono-, di-, and tri-chloromethane and oxygen, as identified by evolved gas and gas chromatograph-mass spectrometer analysis equipment on board the Mars Science Laboratory Rover, where the source of the carbon is still in dispute [11]. The temperature at which the first oxygen was observed was similar

to where one would expect it if the soil sample had contained hydrated calcium perchlorate $\text{Ca}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$.

Samples of Martian soil heated to $\sim 1108\text{ K}$ ($\sim 835^\circ\text{C}$) under helium flow released H_2O , SO_2 , CO_2 , and O_2 , where evolved O_2 was coincident with the release of Cl_2 . This suggests that oxygen is produced from the thermal decomposition of an oxygen-chlorine compound [12].

Traces of perchlorates were found in ice and water samples that were collected at remote, pristine locations on Earth where there was very little chance of industrial pollution [13]. Relying primarily on domestic, agricultural, and recreational wells, 326 groundwater samples from across the coterminous United States (US) were sampled and analyzed. Care was taken to avoid known sites of perchlorate use or release, as documented by the Environmental Protection Agency (EPA) in the US. Using IC-ESI-MS and a ClO_4^- internal standard, a method detection limit (MDL) of 40 ng/L perchlorates and a minimum reporting level (MRL) of 120 ng/L was achieved. Of the 326 samples, 147 (45%) were below the MDL and 42 (13%) were between the MDL and MRL. Of the 137 samples that could be quantified, most (109 samples) contained $<1000\text{ ng/L}$ perchlorate. The remaining 28 samples contained between 1000 to 10400 ng/L. It was concluded that perchlorates occur naturally in many groundwaters, but the unusually high perchlorate concentrations ($>10000\text{ ng/L}$) previously reported for the west-central Texas area even in the absence of industrial activity appear to be anomalous. Perchlorate concentrations were positively correlated with nitrate levels ($P < 0.001$) but not with chloride concentrations. A better understanding of the role of atmospheric processes in the formation or transport of perchlorates is needed. Gradually the realization began to emerge that perchlorate ion is more ubiquitous in natural unpolluted environments than earlier generations were aware of [14].

One of the suspect sources of perchlorates in agricultural areas is nitrate fertilizer imported from Chile. Imports of Chilean nitrate fertilizer, which contain perchlorate as a natural component, peaked around 1920 and have dropped significantly since the 1960s. The total amount of Chilean nitrate fertilizer imported into the US between 1930 and 1993 was estimated as being $2.4 \times 10^{10}\text{ kg}$. Assuming an average perchlorate content of approximately 0.2%, the total amount of perchlorates imported over this time was approximately $4.8 \times 10^7\text{ kg}$. Much of that still remains in the soil and some of it has found its way into agricultural products and groundwater. Although the use of Chilean nitrate fertilizer has decreased since its peak in the 1920s, the current amounts of Chilean nitrate fertilizer products being shipped and used in the US are still substantial. According to the Foreign Trade Division, US Census Bureau, the amount of sodium nitrate imported from Chile into US ports in 2001 was 88150 metric tons. Chilean sodium nitrate fertilizers marketed in the US until at least the year 2000 contained about 1–2 mg perchlorate / g fertilizer. Changes made subsequently to the principal manufacturer's refining process have intentionally lowered the perchlorate concentration to less than 0.1 mg/g.

2 Ammonium Perchlorate Production

Beyond any doubt, AP is currently the most important solid rocket propellant oxidizer. Accordingly, this chapter on AP spans several hundred pages.

Ammonium perchlorate, also known as AP, perchloric acid ammoniate, NH_4ClO_4 , and CAS RN [7790-98-9], forms colorless crystals which are not as hygroscopic as ammonium nitrate (AN) or ammonium dinitramide (ADN). AP undergoes a reversible phase change from orthorhombic to cubic crystal structure when it warms from below 513 (240 °C) to above 523 K (250 °C) (see Section 3.1.2). As a solid propellant oxidizer, AP is a topic of much interest in publications, more so than any other solid rocket propellant ingredient. Consequently, trying to assemble and systematically reference this large amount of literature in this chapter of this book has been extremely difficult. In spite of this challenge, we have assembled a chapter that is more complete and more up-to-date than any other publication currently available. Many references had to be omitted because they were either too old or they duplicated work already published by other investigators. Moreover, some publications were written in obscure languages that were difficult to translate.

There are several good summaries on the physical and chemical properties of AP in available literature. A very comprehensive summary containing 320 references is provided by Hall and Pearson [15]. This was supplemented by a publication covering literature published in the subsequent 18 months published in the same periodical [2]. More recent summaries are those by Jacobs and Whitehead [16], which contains 419 references, and Boldyrev [17] which contains 202 references. Both publications discuss the thermal decomposition and combustion of AP, which are important aspects with regard to its use as a rocket propellant. We have attempted to incorporate most of these aforementioned references in the current summary of the available literature and have further expanded the literature search to include more recent publications.

The production of AP, the main ingredient of composite solid rocket propellants, far outpaced that of the other perchlorates. It was not until 1928 that GFS Chemicals began producing magnesium perchlorate for use as a desiccant (“Anhydrone”, “Dehydrite”), which led to perchlorate salts becoming available on the US market. Up until 1940, the total worldwide production of perchlorates had not exceeded 3.6 million pounds. An abrupt change in production was realized with the onset of World War II and the resulting increase in demand for rocket and missile propellants. Annual perchlorate production quickly increased to 36 million pounds because of this demand and remained at a high level thereafter. By 1974, perchlorate production in the US had reached 50 million pounds.

An excellent summary of the history of perchlorate production in the US was written by one of the key contributors to this remarkable development [4]. According to this account, an Air Corps Jet Propulsion Project at the California Institute of Technology contacted the Western Electrochemical Company (WECCO) Inc. in December 1942 to establish a domestic source of perchlorates for use in solid rocket propellants. Up

until this time the production of chlorates was mainly for matches and pyrotechnics. WECCO constructed a perchlorate pilot plant in Los Angeles. Experimental quantities of potassium perchlorate and AP were produced as required by the US Air Corps. In 1943 WECCO designed and built a large-scale plant in Los Angeles to produce potassium perchlorate with a capacity of 100 short tons/month. It expanded its capacity a year later to 200 short tons/month. WECCO designed another potassium perchlorate plant to be constructed in Henderson, NV, with a capacity of 1200 short tons/month, which started operation in 1945 in a converted magnesium electrowinning plant. The KClO_4 was used in jet-assisted take-off (JATO) rockets for heavy airplanes. Four of the principals of the JATO rocket project at Guggenheim Aeronautical Labs at the California Institute of Technology (GALCIT) later went on to found Aerojet. Even today, Aerojet remains one of the key rocket propulsion companies in the US and a consumer of AP.

WECCO began production of AP in a small plant in Henderson, NV, in 1947, and then built a larger plant with a 50 short tons/month capacity that began production of AP in 1953 and became part of American Potash and Chemical Corporation in 1955 and Kerr-McGee in 1967. Other temporary perchlorate producers during WW-II were Cardox in Claremore, OK (KClO_4 , 1941–1945), Vick Chemical in Greensboro, NC (NH_4ClO_4 , 1943–1945), and Electric Reduction Company in Canada. In the post-WW-II era, other AP producers were Hooker & Foote (Columbus, Mississippi) and PennSalt in Portland, OR.

Early in the 1950s, the Solvay Division of Allied Chemical developed a new process for on-site generation of OCIO for the bleaching of paper pulp, starting with sodium chlorate solution. This increased the competing demand for sodium chlorate to a point where the perchlorate production needed to be set up to its own chlorate electrolysis units. In the early 1960s, alternate methods for the production of AP were sought, including the reaction of ammonium sulfate with sodium perchlorate [18].

A new production facility was established by the Pacific Engineering and Production Company (PEPCON) in Henderson, NV, which was operated by WECCO employees. Late in the 1960s with Minuteman, Peacekeeper, Polaris, and Trident in position, it appeared that the AP demand had peaked and was likely to drop. At that moment, NASA (National Aeronautics and Space Administration) decided to design the Space Shuttle with solid propellant boosters instead of liquid propellant boosters. This advanced the AP business for a further 40 years. In 1998 American Pacific Corporation (AMPAC) acquired the AP business of Kerr-McGee Chemical Corporation. As of 2011, the WECCO at Cedar City, UT, became a division of AMPAC. AMPAC still has a PEPCON division but this only deals with water treatment and not in AP production. Since 1998 AMPAC is the only North American producer of AP.

Recent production data for AP as well as for the other perchlorate salts are lacking. In 1994, production of AP in the US was estimated at 22 million pounds or just 36% of capacity. Actual production volumes for AP have been historically dependent on the demand for aerospace and military applications due to its predominant use in rocket

propellants. This use has resulted in defining AP as a strategic chemical. However, current worldwide production figures are not readily available.

Perchlorate ion is recognized as an impurity in the production of electrochemically produced chlorine products, including sodium chlorate. The pulp and paper industry uses most of the sodium chlorate consumed in the US for on-site production of OClO to bleach cellulose fibers. Sodium chlorate has also been used as a non-selective contact herbicide and a defoliant for cotton, sunflowers, Sudan grass, safflower, rice, and chili peppers. Assuming a sodium chlorate consumption rate of approximately 10^9 kg per year and a 0.01% perchlorate content, a source strength of roughly 10^5 kg per year was calculated. However, only a fraction of that would find its way into the environment.

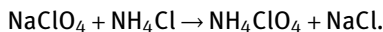
The Census Bureau in the US does not list perchlorates as a separate reportable item on its Schedule B book on imports or exports. Instead, perchlorates are lumped together under the general category of perchlorates, bromates, perbromates, iodates, and periodates. The total amount of imports for this category was 1.867×10^6 , 1.881×10^6 , and 1.281×10^6 kg for 2005, 2006, and 2007, respectively [19]. Exports totaled 1.349×10^6 , 2.067×10^6 , and 1.927×10^6 kg in 2005, 2006, and 2007, respectively (USITC, 2008). Notably, in the wake of the detection of perchlorate contamination in many aquifers and surface waters in the US, the EPA has assembled a database of perchlorate manufacturers and users and is keeping track of perchlorate imports and exports.

In the aftermath of the explosion at AMPAC Henderson and the shutdown of its Kerr McGee facility in Henderson, the authorities have struggled to secure an adequate AP supply for national defense and space program use. It took several steps to restore the industrial base for AP production. The WECCO and Kerr-McGee Chemical Corporation were allowed to add a surcharge to the per-pound price of AP to repay the loan for the rebuilding of the PEPCON plant and for the relocation of and improvements made to the Kerr-McGee plant. The US government guaranteed an annual AP purchase for 7 years to buy 20 million pounds from Western Electrochemical and 30 million pounds from Kerr-McGee. In the event that surcharge payments were not sufficient, US Department of Defense (DoD) and NASA would pay additional AP procurement fees. The surcharge payments to Western Electrochemical were based on amortization of the 92 M\$ cost to build a new AP production facility in Cedar City, UT. Surcharge payments were concluded as of March 1992 after the US government paid 41.7 M\$ surcharges to both producers.

Each launch of the space shuttle consumed about 680 metric tons (1.5 million lb_m) of AP. The AMPAC plant in Cedar City has a capacity in excess of 13600 metric tons (30 million lbs) per year but the production rate as of 2004 was closer to approximately 5000 metric tons (11 million lbs) per year [20].

2.1 Production Methods for Ammonium Perchlorate

The average rocket propellant chemist will rely on a source of AP and would not have to know how it is made. However, stability and performance of AP depends on impurities that are carried over from the manufacturing of this chemical. Therefore, to have full confidence in the adequate quality of the oxidizer and the solid rocket propellants made therefrom, one must know how this chemical is produced. Most of the AP is created by a metathetical reaction of sodium perchlorate (from electrolysis of sodium chlorate) and ammonium chloride:



The process can be carried out continuously by feeding a chlorate-free sodium perchlorate solution to a stirred reactor (A) with anhydrous ammonia and aqueous hydrochloric acid at 363 K (90 °C) [21–23]. As illustrated in Figure 1, the reaction product stream is withdrawn continuously and fed to a crystallizer (B) where the water is removed by lowering the pressure. The AP crystals are withdrawn from the crystallizer as a slurry and the crystals are separated from the liquid in a continuous centrifuge (C). The wet crystals are washed with water and dried. The mother liquor is fed to a second crystallizer (D) where NaCl precipitates and the supernatant liquid from that step is returned to the first reactor.

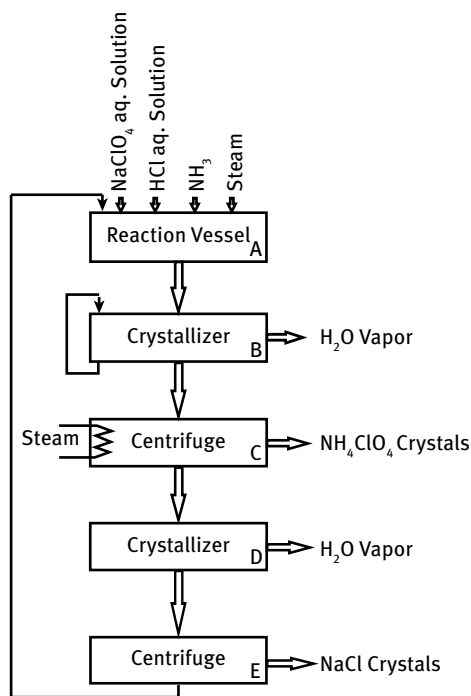


Figure 1: Flow diagram of continuous AP production process. (Reproduced and modified from [21].)

The hazards of producing AP were well-known in the chemical industry when they first started producing it in quantity for fledgling US missile programs [24]. Nonetheless, the disposal of the brine from this process has become a major environmental problem after years of negligence where the brine was allowed to evaporate in unlined ponds. Waste sodium chloride salt crystallized from the brine was even sold as highway deicing material for several decades until the leaching of perchlorates into aquifers and drinking water sources was detected and caused an environmental uproar. Corrective action has been taken since and strict environmental regulations are now in place for the disposal of waste products from AP production. However, it will take several decades until all perchlorate contamination is flushed from the aquifers and streams.

Perchloric acid and AP of high purity can be produced by electrolysis of chloric acid and subsequent reaction with ammonium hydroxide in a proprietary Olin process. The process involves no alkali metals, chlorides, or transition metals, and thus produces propellant and explosive grade AP of high purity and with no associated instability or pollution problems. The products can be recovered by solution crystallization drying or direct spray drying, respectively.

In the process at AMPAC, sodium chlorate is dissolved in DI water and the solution is filtered to remove insoluble residues. The solution is electrolyzed to convert sodium chlorate to sodium perchlorate, which is crystallized and dried for storage. Ammonium chloride solution is made on-site by reacting anhydrous ammonia and aqueous hydrochloric acid. The ammonium chloride solution is then reacted with sodium perchlorate solution. The less soluble AP precipitates in a two-step crystallizer; it is filtered and dried and some of the brine goes back into the NaClO_3 electrolysis cells.

Only two materials can be used as anodes in the industrial production of perchlorates: platinum and lead(IV) dioxide. Platinum is very costly while lead-dioxide, on the other hand, is very cheap. Unfortunately, due to its brittle nature, it requires a suitable substrate over which it has to be coated to form an anode. An AP production plant in India adopted the less expensive lead dioxide as the anode material [25]. The previously used Graphite Substrate Lead-Dioxide Anodes (GSLA) had several disadvantages such as short service lives and low current efficiency. A new anode system based on Titanium Substrate Lead-Dioxide Anodes (TSLA) was developed to overcome these problems. Due to its superior corrosion resistance, the titanium substrate could be re-used after the useful service life of the lead-dioxide coating. The TSLA system was found to be superior to GSLA with respect to the current efficiency, cell voltage, and reusability of the substrate. The TSLA system was only one-tenth as costly as platinum but produced almost the same current efficiency. The AP production plant in India achieved a production rate of 800 tons/y.

2.1.1 First Crystallization of AP

Freshly prepared AP is rarely crystallized in the same shape in which it is used for making rocket propellants. Preparing it in small particle size at the production facility would be futile because the crystals tend to agglomerate during transport and storage. Also, finely ground AP is in a higher transportation hazard category than coarser particle size AP.

Some alternate methods for first crystallization are discussed here. Some of the particle size comminution technology described here for AP could just as well be used for other oxidizers. This more general information on process design for granular materials and other oxidizers belongs into a later volume on Composite Solid Propellants.

2.1.2 Recrystallization of AP

Recrystallizing is the preferred method for purification of AP. This step is encountered when AP is manufactured the first time and also during an important process while recycling AP that has been washed off from demilitarized rocket motors. Recrystallizing under special conditions may also result in smaller crystal size AP that gives a higher burning rate.

AP is recrystallized by batch crystallization. This is done by cooling a saturated aqueous solution. The cooling rate is consistently maintained by using a cooling-rate controller so that the decrease in temperature is linear. The amount of agitation during the cooldown influences the product size distribution. Supersaturation is inevitable and needs to be carefully reviewed. In one process optimization experiment, the supersaturation was observed by means of a refractometer for three different cooling rates [26, 27]. The results showed quantitatively how the rate of cooling determines the supersaturation levels and consequently how the particle size of the product is affected. Supersaturation is very high during primary nucleation and decreases during crystal growth and secondary nucleation. The extent of secondary nucleation is determined by the particle size distribution of the product.

Spherical or near-spherical shapes of oxidizer particles allow for more uniform packing density and lower viscosity of the poured propellant. Rounded AP particles can be obtained by pouring irregularly shaped AP powder with a specific particle size into a saturated solution of AP in water and stirring it vigorously for 0.2 to four hours at 13500 to 3000 RPM at a constant temperature, thus wearing off the sharp edges [28]. An alternate method starts with a saturated solution of AP in water that is stirred vigorously while it cools down. In the latter case the particle size is determined by the rate of cooling.

AP, which is grown as whisker crystals with whisker diameters from one to five μm , offers improved high burning rates in composite propellants. Further accelerated propellant burning rates would require sub-micron diameter material. The same method can also be applied to production of whiskers which are doped with co-crystallized burning rate catalysts [29].

A saturated aqueous solution of AP oozing through the pores of a porous (fritted) glass tube coated with a polymeric silicon evaporates in warm air. This forms long AP whiskers with length-to-diameter ratios of 10 : 1 to 100 : 1 [30]. The crystals continue to grow as long as the tube is fed the AP solution. The crystals fall off under their own weight or can be scraped off with a spatula and dried. The whiskers can be stored under ambient conditions without loss of optimum ballistic performance. This is better than freshly ground AP crystals which require immediate use after grinding as they tend to agglomerate with time and aging. A similar phenomenon of whisker growing can be observed in wet basements of houses when gypsum crystals grow on the surface of porous masonry while ground moisture permeates the foundations.

Most spray drying methods for AP use just plain water to dissolve the salt. However, if very small particle sizes such as ultra-fine AP (UFAP) are needed, adding a volatile solvent to the solution before spraying it will result in droplet breakup by flash evaporation and smaller oxidizer particle sizes.

Acetone, ethanol (15–85 vol.-% in water), or methanol (70–100 vol.-% in water) were tested as potential solvents [31]. The mean diameter of AP particles decreased with increasing concentration of the organic solvent and increasing inlet temperature of hot air, but this bottomed out at 1.3 to 2.2 μm . The finest AP was produced with 100% methanol and a drying air temperature of $>313\text{ K}$. Mixing AP with flammable solvents is a hazardous operation [32].

In order to prepare a crystal-habit-modified AP, a saturated solution of AP at 333 K was poured into butanol cooled to 273–275 K [33]. In one study, crystallization of AP was carried out with two mixture ratios: One was a mixture of butanol and saturated solution [9 : 1 by volume, named as (B-1)], and the other was a 3 : 2 mixture in volume ratio [named as (B-2)]. AP obtained by crystallization from distilled water was ground for ten minutes in a vibration ball mill and was used as a reference AP for comparison. AP obtained by the above three methods was used as an oxidizer for composite propellants and their processability and burning characteristics were compared. The results were as follows: **(1)** Maximum AP contents of propellants using (B-1), (B-2) and reference AP were 63.5, 76.0, and 86.5 mass-%, respectively. Maximum AP solid loadings of propellants using (B-1) AP and (B-2) AP were considerably lower because (B-1) and (B-2) are dendrite-shaped. **(2)** Subsequently, (B-1) AP was ground for five to 30 minutes in a vibration ball mill. (B-1) AP was ground for five minutes, (B-2) AP was ground for three minutes, and the reference AP had approximately the same particles size and specific surface area. Propellants containing 80 mass-% AP were prepared using these three grades of AP. Following measurement of their burning rates it was found that the propellant using (B-1) AP ground for five minutes had the highest burning rate. Propellants using (B-2) AP ground for two minutes had the next highest burning rate. It was suggested that crystal habit modification can have an effect on increasing the burning rate.

An attempt was made to modify the crystal habit of AP by adding *n*-hexane. The particle characteristics of the crystal-habit-modified AP and the burning rate charac-

teristics of the composite propellant using the crystal-habit-modified AP were investigated [34]. It was noted that: **(1)** The crystal shape of the modified AP is dendritic. **(2)** The intensity of the lattice plane (011) of the modified AP is remarkably high. It was found that the crystal habit of AP can indeed be modified by hexane. **(3)** The thermochemical behavior of the modified AP was almost the same as the typical behavior of AP. **(4)** Both the mean particle diameter of the modified AP and the modification degree of crystal habits were decreased by grinding.

Water-soluble polymers as crystal-growth modifiers are gaining more frequent use in the field of morphogenesis of inorganic crystals. AP particles with a particular morphology were crystallized by a polymer-assisted crystal-habit modification route using poly(vinyl alcohol) [35]. AP crystals with a rectangular prism and a rectangular wedge shape were obtained. The X-ray diffraction (XRD) patterns revealed that the phase of AP obtained was the same as that obtained from saturated solutions.

Crystal-habit-modified AP allows one to produce propellants with increased burning rates [36]. The modified AP crystals often have a dendritic shape. However, dendritic AP is not convenient to mix and cast in an AP/binder slurry because of its high viscosity. A crystal-habit-modified AP with polygonal or spherical shapes was prepared by redissolving and precipitating in ethylene glycol such that the intensity of the lattice plane (210) of the modified AP was remarkably high. The shape was almost hexahedral, and the mean particle diameter was approximately 150 μm . The crystals were characterized via scanning electron microscopy (SEM) and XRD and their sensitivity was determined by the drop weight impact test.

A ceramic membrane solvent/anti-solvent crystallization method was tested for the safe and rapid preparation of superfine AP crystals [37]. Acetone and ethyl acetate were chosen as the solvents and anti-solvents. The ceramic membrane with a regular pore structure allowed one to control the feeding rate, size, and morphology of AP. Several types of micron-size AP particles with different morphology were obtained including particles with polyhedral-, quadratic prism-, or rod-like shapes. Higher volume ratios of anti-solvent to solvent, higher feeding pressures, and higher temperatures resulted in smaller particle sizes.

The effect of crystallization parameters such as cooling patterns, agitator rpm, retention of crystals in the mother liquor, and the presence of surfactant on the morphological, thermal, and physical characteristics of AP crystals was examined in a 5-L capacity laboratory glass crystallizer [38]. It was found that spherical, transparent, and smooth-surface crystals can be obtained by crystallization having a slow cooling pattern and an agitator rotation rate of 600 rpm. Irregular-shaped crystals were obtained with fast cooling patterns and/or lower agitator rpm. Crystals made in the presence of a surfactant and examined by SEM, bulk density, and the transparency of crystals had some porosity.

Recrystallized AP has modified crystal habits and different thermal and morphological properties [39]. The morphology of AP crystals is affected by the presence of ethylene glycol during crystallization [40].

2.1.3 Freeze-Drying of AP Solutions

Freeze-drying of a frozen solution of 8–10% AP in water is described in detail in a patent [41]. An aqueous solution of AP is flash-frozen in a dry ice bath and the ice is sublimed at below freezing in a vacuum chamber at $<50\mu\text{m Hg}$ pressure. Water is the preferred solvent because that makes this process safer than other processes that use flammable solvents. Average particle sizes varying between 1.7 to $2.1\mu\text{m}$ have been obtained this way.

The early objective was to establish freeze-dried UFAP manufacturing methods for the economical production of UFAP with a weight median diameter (WMD) ranging from $1.0\mu\text{m}$ to less than $0.5\mu\text{m}$. Emulsion formulation affects product quality and, therefore, a flow viscometer for emulsions was developed, calibrated, and used to characterize the emulsions. With proper emulsion and rapid freezing in a rotary drum freezer, the achievable size range is between 0.3 to $0.6\mu\text{m}$ weight mean diameter. The ultimate goal of this project is the process design for a 1000000 pounds per year UFAP processing facility. Spray freezing with a centrifugal spray device was evaluated as an alternate method.

The freeze-drying process described in US Pat. No. 3685163 [42] involves forming an emulsion of aqueous AP and an organic liquid immiscible with water and a non-solvent for AP, then freeze-drying the emulsion for recovery of the UFAP product. The emulsion can be flash-frozen by pouring it into liquid nitrogen. The frozen material must then be kept at below 233 K (-40°C) while freeze-drying is in progress and at low pressures. The emulsion to be freeze-dried must retain its stability during the entire freeze-drying process in order to preclude separation and coagulation of solution droplets with accompanying formation of unduly large AP product particles. In most instances an emulsifying agent is required for maintenance of the emulsion stability. However, the emulsifying agent does not separate from the AP particle product. Hence, it constitutes a process impurity material, which comes to be incorporated into the propellant. The ratio of aqueous phase: immiscible phase must be optimized to obtain the smallest possible UFAP particle size (Figure 2). Particle sizes of UFAP produced using this method were in the sub-micron range.

The initial AP concentration in the water is 5 to 15% AP. If less than 5% is used, the process is not economical. If more than 15% is used, the difference in density between the aqueous solution and the oil makes it difficult to obtain a stable emulsion.

UFAP handling, storage, and shipping properties were investigated with respect to product coatings, solid propellant formulation processing, and rocket ballistic parameters [43]. Approximately 40 compounds were evaluated and six materials were identified that protect UFAP from particle growth during storage and handling. It was demonstrated that coated UFAP could be stored for several months under low (30%) R.H. humidity conditions and at temperatures up to 333 K (60°C), but not under high humidity and temperature conditions. Ballistic and processing evaluations revealed wide variations in properties with different types and blends of UFAP and different coating materials. A dramatic effect of humidity on the ballistic properties of propel-

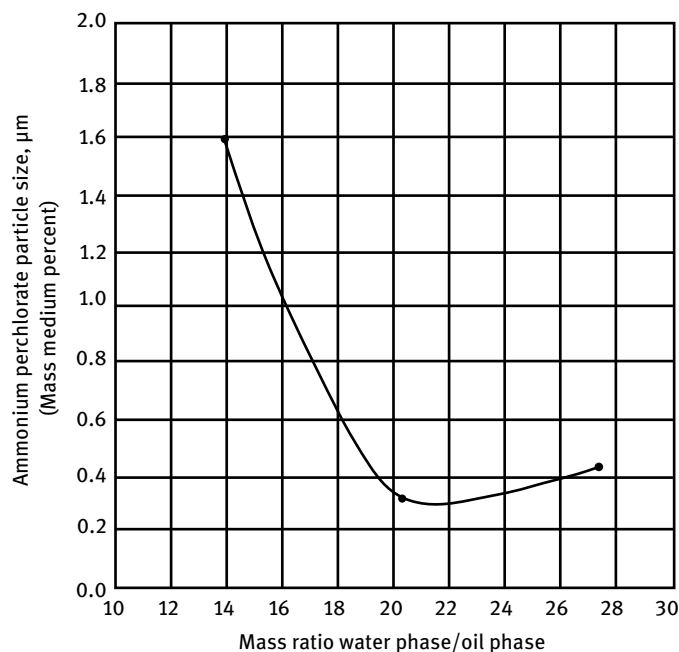


Figure 2: Optimization of water/oil phase ratio. (Reproduced and modified from [42].)

lants made with UFAP was demonstrated by making two identical batches of propellant, one from UFAP stored at 10% R.H. for one week and the other stored at 50% R.H. for one week. Burning rate decreased with increasing storage humidity and the mix was very viscous before it could be poured. Aziridine-coated UFAP prepared from the SWECO Vibro-Energy Mill was more readily processible than samples of freeze-dried or fluid energy milled UFAP. Applying hydrophobic coatings introduces combustible organic compounds into an oxidizer, resulting in an increase in explosive sensitivity of the material. The sensitivity heightened as the content of the coating material was increased.

UFAP particles can be made by spraying an aqueous AP solution containing a surface active agent onto a moving film of a refrigerated organic liquid. This forms fine frozen droplets and, by freeze-drying [44], recovering fine AP particles from the frozen droplets.

Ultra-fine porous AP (PAP) consisting of sub-micron particles can be obtained by flash-freezing the solution in liquid nitrogen and then freeze-drying it [45]. The freeze-dried AP was investigated by SEM and XRD. There was no effect of freezing on the crystallinity of AP.

If a saturated aqueous AP solution is poured into a glass vessel and the pressure in the vessel is lowered to <0.1 mm Hg, the saturated solution will freeze. Most of the

water will be sublimed when the vessel is kept at <0.1 mm Hg for 36 hours at room temperature (293 ± 5 K = 20 ± 5 °C), leaving a residue of fine AP crystals [46]. This product was investigated by SEM, Brunauer–Emmet–Teller (BET) surface area measurement, drop-weight impact sensitivity testers, and XRD. Freeze-dried AP were mostly needle-like shaped crystals (diameter 2–5 μ m and a specific surface area of ~ 2.4 m²/g). When 2 mass-% of a surface-active agent was added to the saturated solution prior to freeze-drying, the shapes and the properties of the product were almost the same as those of freeze-dried AP prepared without the use of surface-active agents. The crystallinity of freeze-dried AP was similar to that of ground AP.

AP/hydroxy-terminated polybutadiene (HTPB) propellants prepared with mixtures of freeze-dried UFAP and ground AP had burning rates that increased with increasing UFAP content [47].

Nano-AP was made using a non-aqueous method by dissolving AP in methanol, followed by adding the dissolved AP to liquid HTPB prepolymer, homogenization, and vacuum distillation of the solvent [48]. The nano-AP thus formed was characterized using a particle size analyzer, transmission electron microscopy (TEM), XRD, and SEM for particle size, purity, and morphology. The data indicated that the particle size of the prepared AP was in the range of 21–52 nm and the thermal decomposition temperature was lower than for coarse AP. Nano-AP composite propellant formulation with 86% solids loading revealed a 14% increase in burning rate in comparison to standard propellant composition, and still had desired mechanical properties.

2.1.4 Precipitation of AP in a Solvent/Non-Solvent System

A process that can potentially operate as a continuous process instead of a batch process is described in a patent [49] where a solution of AP in tetrahydrofuran (THF) is poured into a stirred non-solvent (a high-boiling hydrocarbon). The precipitate is allowed to settle following which the decanted supernatant fluid is fed to a distillation apparatus. The THF is distilled off and more of the precipitate filtered from the hydrocarbon suspension is drained from the pot. The THF vapors are condensed in a cooler above a trickle bed, packed with raw AP, where it saturates itself on the way down and re-enters the process. AP crystals with narrowly controlled particle sizes (1.2, 31, or 61 μ m) were produced by this method.

Another process for making UFAP by freeze-drying emulsion proceeds as follows [50]:

- a. Forming an aqueous solution of AP then mixing this solution with an organic liquid immiscible with water and a non-solvent for AP.
- b. Adding a branched-chain HTPB with a molecular weight not exceeding about 2500 and a diester emulsifier to the resulting mixture, then agitating the resulting mix to form an emulsion of an organic liquid as continuous phase and an aqueous AP solution as dispersed phase.

- c. Flash-freezing the emulsion by pouring it into liquid nitrogen.
- d. Subliming the organic liquid and ice from the frozen emulsion.
- e. Then recovering the residual UFAP particles produced by the process.

The UFAP thus produced had particle sizes of less than $1\mu\text{m}$. The mean diameter of the UFAP depends on the interfacial tension between the organic solvent and the AP solution. Addition of a surfactant will reduce the particle size but foaming may cause problems [51].

The precipitation of AP from methanol solutions of AP by a solvent/non-solvent method using diethyl ether, chloroform, methylene chloride, or isobutanol yields rounded crystals [52]. When ether, chloroform, or methylene chloride were the non-solvent precipitants, the product had a particle size less than $5\mu\text{m}$, but crystals obtained with isobutanol as the precipitant had an orthorhombic shape and the mean crystal size was larger than $10\mu\text{m}$. The precipitation ratio of the four salting-out solvents improved in the sequence isobutanol, methylene chloride, chloroform, diethyl ether. The characteristics of the precipitated AP crystals were investigated by SEM, XRD, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) and were found to be very similar.

Rounded and finely divided oxidizer particles can be obtained by applying high-frequency acoustic vibrations during the cooling of the solution or evaporation of part of the solvent [53]. Thus, a stirred saturated AP solution at 368 K (95°C) was placed in a water bath at 288 K (15°C) and subjected to 20 kHz ultrasound while cooling. After 24 hours the acetone- and diethyl ether-washed and dried precipitate consisted of uniform and round shaped $70\text{--}180\mu\text{m}$ particles. A similar solution treated for five hours at 90 kHz yielded rounded $10\text{--}20\mu\text{m}$ particles. The method can also be applied to hydrazinium nitroform or and nitronium perchlorate.

Another method for production of UFAP uses saturated aqueous solutions and chills them in an emulsion with a heavy, non-miscible solvent like methylene chloride (dichloromethane) and ultrasonic agitation [54]. By using a non-solvent phase, growth of the precipitated crystals is prevented and a large proportion of fine particles become suspended in the non-solvent liquid layer below. In one example, chilled methylene chloride was poured into a saturated solution of AP with ultrasonic agitation. Lecithin may be added as an emulsifying agent. After ceasing the agitation, sub-micron-size particles of AP settled into the lower layer and were separated and dried from the non-solvent. The particle size ranged from about 0.6 to $4.5\mu\text{m}$ with about half the particles in the sub-micron size. Other non-miscible fluids suitable for this process are chloroform, perchloroethylene, carbon tetrachloride, trichloroethylene, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,1,2,2-tetrachloro-1,2-difluoroethane, or 1,1-dichloro-1,1,2,2-tetrafluoroethane.

2.1.5 Grinding of AP

General information on grinding of solid propellant ingredients will be provided in a later volume in this series. Grinding of AP is a hazardous operation as AP can ignite if it overheats during grinding, particularly so if the grinding is pushed to the limit by producing UFAP, which is detonable under certain conditions.

Grinding of AP crystals may leave fractures and residual stresses in the particles. It is typically at these disturbed locations that thermal decomposition of AP starts around the nuclei after the ground material is processed into a propellant and if it becomes exposed to high temperatures. Notably, AP with small particle sizes can be made by mechanical crushing through dry milling in a spiral jet mill (classifier mill) [55].

Aerojet developed a facility which was designed to simultaneously produce five different particle size ranges in bulk or in smaller batches [56]. Raw material arriving in 2265-kg (5000-lb) bins is transported by dry air to one of four grinders from a central location. Grinding is remotely controlled for safety reasons and optimum reproducibility of the particle size of the completed product.

An intermediate grade of fine AP, which is coarser and easier to manufacture than UFAP, is a grade called [special fine AP] (SFAP) which was developed by the Thiokol Chemical Corporation. [57]. Special fine AP is AP in the particle size range 4 to 7 μm . Average particle sizes are often measured as [weight mean diameter] (WMD). WMD is the theoretical diameter of the 50% point by weight of a sample. Three commercially available grinders were evaluated for their ability to produce AP in the desired SFAP particle size range but only one was rated to be able to grind AP this small. The Micro-Pulverizer is a hammer mill but was not able to produce anything smaller than 14 μm WMD. The Micro-Bud hammer mill could not produce anything smaller than 9 μm WMD. The Jet-O-Mizer specification promised particle sizes in the desired range but its throughput was much slower than the other two mills. The Jet-O-Mizer is a vertical elongated torus fluid energy mill. Particle comminution occurs by particle-to-particle impact and the energy is provided by tangential air inlets.

AP can be continuously ground in a jet mill with helium or nitrogen gas [58]. The highest grinding efficiency and sub-micron-sized fractions were achieved when heated helium was used. It was proposed to continuously mix the ground oxidizer with the other granular propellant ingredients dispersed in an inert gas in a specially designed mixing tube.

Grinding equipment is prone to wear down with continued use, and although the grinding tools are much harder than the AP they are grinding, wear on the surfaces will change the clearance between the moving and stationary surfaces and cause the particle size to change during the life of the machine. Continuous particle sizes and particle size distribution measurements are required to assure a reproducible product. Statistical process control can help to identify deviations from normal product properties and trigger corrective action before the ground AP is processed into propellants [59]. The target size is a nominal 16 to 20 μm grind of AP. The reproducibility of a statistically

significant number of grinds made over a two-year period on a production line was analyzed statistically to assure reproducibility. The time period during this process included two mill rebuilds, which introduced an additional variable.

Microfine AP (with particle sizes as small as $5\mu\text{m}$) can be produced by grinding under high-frequency low-amplitude vibration in refrigerant R 113. This method also enhances safety. Solid loadings $>87\%$ in a composite aluminized propellant were attained by using a trimodal particle size distribution of AP (coarse, fine, and microfine) [60]. Even at 90% solids the propellant had good processability with a density of 1.84 g/cm^3 .

AP has been pulverized by an impact mill (air classifier mill) to study the influence of different operating parameters, viz., effect of mill speed, classifier speed, feed rate, and damper opening (suction rate) on the particle size [61]. Further, based on the different grinding parameters, an empirical equation was then developed to predict the size of particles. The experimental results indicated that the values were very close to the predicted ones. In addition, particle size distribution has also been studied by applying different model equations; it has been found that the Rosin-Rammler model is the most suitable model for this operation.

The effects of particle size on propellant slurry viscosity and ballistic parameters are well documented, however, the effect of oxidizer particle shape is not well understood. Therefore, different methods for size and shape characterization were examined and the effects of size and shape of AP on composite propellant properties were studied [62]. The data indicated that as the size of AP decreased, the propellant slurry viscosity and the burn rate increased. An examination of the effect of the size of ground AP particles on their shape revealed that as the size of ground AP decreased, the shape factor decreased and particles became more irregular in shape.

A superfine powder of AP with a particle size of $2\mu\text{m}$ was obtained by crushing in a jet mill under optimized technological conditions [63]. The electrostatic problem during AP crushing is a safety hazard. However, a way to eliminate electrostatic charge build-up was found to ensure the safety of the crushing process.

Sub-micron AP was prepared in a vertical stirring grinding machine by controlling the grinding time, rotating speed, and the feed rate of the materials [64]. The dispersing medium used was *sec*-Butyl alcohol. The final products were obtained by using a vacuum freeze-drying method. Particle size distribution, grain sizes, and crystal structures of these AP particles were characterized by laser particle size analyzer, field emission SEM, and XRD. This showed that the AP had an average particle size of 460 nm. The friction sensitivity, impact sensitivity, and TGA of sub-micron AP was compared with that of coarse AP; it was found that the friction and impact sensitivities had increased (worsened) by 20% and 18.7%, respectively. In the differential thermal analysis (DTA) (with a heating rate of 10°C/minute), the high-temperature decomposition (HTD) peak temperature of sub-micron AP had decreased by 60°C , and the activation energy of decomposition was reduced by 27.3 kJ/mol .

In one study, AP was first ground by a jet mill, and then superfine spherical AP particles were prepared by a planetary ball mill [65]. Their morphologies, particle size, and shape and IR spectra were characterized by SEM, Micron laser particle size analyzer, and FTIR. Bulk density and thermal mechanical properties of superfine spherical AP and non-spherical AP with the same size were characterized. The impact sensitivity and friction sensitivity, hygroscopicity, and caking of superfine spherical AP and non-spherical AP with the same size were studied. The results revealed that superfine spherical AP prepared by the milling method had good sphericity, smooth surface, and fewer defects. The thermal decomposition peak moved to a lower temperature in the DSC. The impact sensitivity and friction sensitivity of superfine spherical AP were lower than those of the non-spherical AP and hygroscopicity and caking were effectively improved.

The relationship between particle size and the impact or friction sensitivity of UFAP has been analyzed [66]. Not all grades of AP produce the same desirable small particle size results upon grinding. The grindability of AP from three different sources revealed some differences [67]. The thermal stability of AP fine particles comminuted by grinding or by recrystallization may be quite different [68].

2.1.6 Agglomeration of UFAP

Once UFAP is produced, problems arise with regards to how to keep the crystals from agglomerating and growing back together ("caking"). Thermodynamically, the agglomeration of small particles is favored because it results in a decrease of entropy. The tendency of AP to cake together even while perfectly dry during long-term storage at ambient temperatures was attributed to ion mobility. This allows ions to spontaneously move around and rearrange themselves. Coatings that can retard the agglomeration of UFAP during storage, between production and formulating it into a propellant, have been evaluated.

The particle growth rate of uncoated fluid energy milled AP (1.7 μm) was determined by exposing samples at two temperatures and three different relative humidities [43]. Particle growth persisted in all six test conditions. It was concluded that simple storage conditions will not prevent particle growth of uncoated UFAP. Most of the growth occurred during the first 24 hours of storage. Coated samples could be stored at 10% R. H. for ten weeks without noticeable particle growth.

Various coatings have been applied to UFAP during the precipitation and crystallization to prevent the small particles from agglomerating during storage and to act as bonding agents to the organic polymer when processed into propellants [69]. Sub-micron particle size AP particles are made by mixing a solution of AP in a volatile liquid with a less volatile liquid which is miscible with the first liquid and is a non-solvent for AP. The resulting mixture is then heated to vaporize the volatile liquid and form a suspension of fine AP particles in the second less volatile liquid. A particle coating agent soluble in the second liquid was used to limit particle growth of the finished

product. The ultra-fine particles were coated with the coating agent and could be recovered from the suspension by vaporization of the second liquid to form a powder or by partial vaporization of the second liquid to form a concentrated slurry or paste in which the AP was the disperse phase.

Surface modification of UFAP (0.5–1 μm diam.) was evaluated to prevent agglomeration during production and storage [70]. Neither single-component anti-static agents nor single-component moisture-proofing materials and friction modifiers prevented coagulation but some surface-active agents can inhibit coagulation. Fresh unmodified UFAP had combustion performance that is similar to modified AP. However, after a few days of storage, the performance of the unmodified samples deteriorated whereas the surface-modified materials did not.

Various surfactants which impose negative or positive charges on the particle surface were evaluated to see if they promote or retard agglomeration of UFAP in colloidal suspensions [71]. The effectiveness of such additives depends on the type and quantity of the media and on the surface-charge characteristics of the additives, dispersity, stability, and coagulation tendency of the particles. When the particles were suspended in trichloromethane, the stability of the particles was better than in other liquids. When the particles were suspended in mixtures of organic liquids and water, some additives had an advantage with maintaining the stability and dispersity of the particles. Such agents included surfactants of the anionic, non-ionic, and cationic types. Mixtures of additives, such as mixtures of two or more surface-agents, and an anti-foaming agent were better for the dispersity and stability of the particles. Usually the total quantities of the additives are ~0.1–0.5 mass-% (based on the weight of the AP).

One of the methods to avoid the agglomeration of superfine AP powder is to coat AP raw material with nitrocellulose (NC) and then crush the coated AP in a jet mill [72]. AP coated by this method had reduced hygroscopicity. After being stored for 30 days in air, it had no aggregation and its particle size remained at about 2.5 μm . Coating AP with NC can prevent the superfine powder of AP from agglomerating and makes it possible for the superfine AP to be used for the propellants with high burning rates, even after extended storage in dry air.

The anti-caking mechanisms due to the use of surfactants in AP crystalline products were examined [73]. The influence of surfactants and impurities in anti-caking matrix-liquor from different manufacturers on anti-caking properties of AP crystals were investigated by storage and sieve analysis tests. The results revealed that surfactants from different manufacturers can have different anti-caking effectiveness. Cl^- and Ca^{2+} contamination in anti-caking matrix-liquor has a remarkable influence on anti-caking properties of AP crystals. Surface modification of the AP not only minimizes the troublesome caking but also reduces the hazards due to build-up of electrostatic charges during processing. Surfactants and inert powders were used as anti-caking, anti-static additives [74].

2.1.7 Porous AP

While it is usually the objective to prepare dense oxidizers without porosity, a special form of PAP has been developed and tested for the sake of higher burning rates. PAP can be prepared using methods very similar to those used for UFAP. A fluidized-bed pilot-scale process was developed to produce PAP in small quantities [75]. The burning rate of propellant prepared with PAP was higher than that of propellant with regular AP. To facilitate mixing with a binder and to further improve the burning rate, PAP can be coated with a solution of the prepolymer adduct of divinylbenzene and ethyleneimine [76].

Another method of preparing AP with ultra-high surface area for propellants with ultra-high burning rates is by thermally shocking AP crystals (mean diam. 180 μm) by heating to ~423 K (~150 °C) followed by rapid cooling then multiple extractions with EtOH and/or BuOH for formation of indentations and/or cavities on the surface, crevasses, and tunnels within the crystals [77]. Thermal shocking produces microcracks which are etched by the solvents to produce indentations and porosity with highly pitted surfaces in which the pits have a rather large length-to-width ratio oriented with their long sides parallel to one another, thus having the appearance of terraced pyramids. Subsequent coating with a hexane solution of divinylbenzene forms a thin coating to prevent agglomeration. This product can be used as a direct replacement for porous NH_4ClO_4 produced by thermal decomposition at 422–478 K (300–400 °F) but has improved burning rate, tensile strength, strain at maximum stress and break, modulus of elongation, and extinguishing properties.

PAP can be produced by fluidized bed technology on a laboratory scale. The burning rate of a composite propellant could be greatly increased by partially substituting PAP for the granular AP while the mechanical properties of the propellant would remain unchanged [78]. The burning rate of a fast-burning composite modified double base propellant with 34–38% PAP was about three times that of an AP propellant with no special catalysts.

Notably, the PAP discussed here must not be confused with the porous residue that is left behind after the first phase of a two-step decomposition has been completed (see Section 4.3.3).

2.1.8 Coatings for AP

AP and other oxidizers for solid propellants may be coated to make them less hygroscopic and to prevent agglomeration. It can also be used to achieve better bonding with an organic polymer in a composite propellant formulation. Several anti-caking agents have been listed in the previous chapter which discussed UFAP.

Tricalcium phosphate (TCP) is used as an anti-caking agent in AP. AP and TCP assay analyses cannot be carried out by estimating the insoluble calcium salt in water because a reaction takes place between TCP and AP in aqueous solutions. This is evident from the release of ammonia. It was concluded that TCP in the presence of AP is

not stable and should not be used in composite rocket propellants which have critical composition [79].

Kinetic studies revealed that, in binders involving epoxy resins and carboxyl groups in polybutadiene-acrylic acid-acrylonitrile terpolymers, the rate of the polymerization reaction is reduced and the epoxy groups in Epon[®] H-825 are consumed faster than carboxyl groups in the presence of AP. Over 200 different coatings were evaluated to prevent or retard the oxidizer-epoxide interaction. The coatings can be adsorbed from solutions of AP and deposited on a fluidized bed of the oxidizer, or merely added to the propellant formulation [80]. Coatings evaluated include polyethyleneimines, linear polyalkylenepolyamines, alkylamines, amides and polyamides, quaternary ammonium compounds, fatty acids and polymerized fatty acids, and a variety of polymers.

Controlled modification of surface characteristics of AP is possible by ions common to AP production, surface coating with metal oxides and salts, and surface coating with various non-ionic, anionic, and cationic surfactants. Tests revealed that surface modification had measurable and significant effects on the viscosity, wettability, and thermal properties of AP in propellant blends. Optimization and control of surface properties can lead to improvements in formulation, storage stability, and ballistic properties of AP-based solid propellants.

Impact sensitivities of AP coated with eight different polymers including bonding agents and binders were much higher (more sensitive) than those of uncoated AP [81]. Coating by encapsulation caused sensitization while simple mixing did not lead to the same results.

Bonding between AP and HTPB, constituting a non-reinforcing filler system, has been studied in the presence of a new bonding agent, a zwitter ion molecule, which is the 2,4-dinitrophenylhydrazone derivative of 1,1'-bisacetylferrocene (DNPHD AF) [82]. Extensive conjugation and a permanent ionic character make the DNPHD AF bond strongly with the ionic oxidizer AP. Through its terminal —OH group, HTPB bonds with the NO₂ groups of DNPHD AF.

AP is often coated with bonding agents to improve the bond between the inorganic oxidizer and the organic binder. It is important to select only bonding agents that are compatible with AP that do not react prematurely or during the curing of the propellant [83]. Fourier transform infrared (FTIR) spectrometric analysis of coated AP revealed that the interfacial bonding force is by hydrogen bonds for aziridine type compounds and ionic bonds for alkylene polyamine derivatives, respectively.

Tepanol[®] (a tetraethylenepentamine acrylonitrile glycidol adduct with polar hydroxyl and nitrile groups attached) has been evaluated as an AP coating. Saturation of the oxidizer surface with ionic Tepanol was intended as a means of inhibiting AP low-temperature decomposition (LTD) reactions. If a coating by Tepanol bonding agent saturated all available ionic sites on AP particles, some lattice energetics would cover external AP surface ions where decomposition usually starts. Expected improvements were: (1) A reduction of one atmosphere burn rate and (2) inhibition of the AP LTD pro-

cess. If one atmosphere burn rate was slowed, higher inputs for electrostatic discharge (ESD), drop weight impact, and friction tests might be needed to obtain propellant ignition.

The alkalinity of polyamine bonding agents such as Tepanol will cause evolution of ammonia when reacted with AP in chloroform. For propellants containing 0.15 mass-% Tepanol, the total weight of ammonia generated per unit weight of propellant was equivalent to 120 ppm [84]. Successful application of these bonding agents is, therefore, dependent on how well the ammonia byproduct can be dissipated from the mix before the isocyanate curing agent is introduced because otherwise the propellant might blister. Ammonia generation by the bifunctional aziridine-based bonding agent system HX-752 was found to be 25 times less severe (on a week-by-week basis) than Tepanol. HX-752 is, therefore, better-suited to applications where removal of ammonia is impractical such as continuous process mixing. Diethylenetriamine (DETA), which is used to reduce the propellant viscosity to processable levels (<25 kPs), generated up to five times as much ammonia (on a week-by-week basis) as Tepanol in chloroform/AP slurries but required less than two hours to react completely.

To avoid ammonia formation other bonding agents based on vinyl ethers have been developed [85]. There is no increase in ammonia liberated above baseline propellant values and no increase in end of mix viscosities with these coatings.

The properties of coated AP were analyzed by a solubility experiment and DSC [86]. The combustion properties of coated AP propellant were tested and the mechanism of reduction of the AP burning rate and pressure index by coating was explained. It was found that coated AP reduced the burning rate and pressure index of AP/HTPB composite solid propellants.

Fluorocarbon polymer coatings can be used to enhance thermal stability and electrostatic protection of composite propellant compositions. A technique has been developed to coat AP with a copolymer of hexafluoropropylene and vinylidene fluoride (HFP-VF) using a solvent-counter solvent precipitation method [87]. The coated AP is then used to prepare AP/HTPB/Al propellants and compared to similar propellant made with uncoated AP. Viscosity build up and visco-elastic behavior as well as mechanical, ballistic, thermal, and sensitivity properties were measured while keeping solids loading at 86%. The data on viscosity build up indicated that as the percentage of coated AP increased, end of mix viscosity and viscosity build up increased accordingly. The burn rate of the composition also increased with a higher percentage of HFP-VF coated AP. The thermal stability of the composition increased as the percentage of HFP-VF coated AP was increased. The data on sensitivity indicated that impact sensitivity decreased on increasing the percentage of HFP-VF coated AP while no change was observed in friction sensitivity value.

Metal oxides like iron(III) oxide serve as oxidizers in thermite-type igniter formulations. The igniter formulations can be improved by replacing the metal oxide particles with AP that have been coated with a metal oxide coating. Coated AP was incorporated

into a nanothermite composite formulation [88]. The perchlorates were encapsulated through a series of thermal decomposition, melting, phase segregation, and recrystallization processes. This occurred within levitated aerosol droplets. Several samples, including $\text{Fe}_2\text{O}_3/\text{KClO}_4$, CuO/KClO_4 , and $\text{Fe}_2\text{O}_3/\text{NH}_4\text{ClO}_4$ composite oxidizer particles were created. The results revealed that these composite systems significantly outperformed the single metal oxide system in both pressurization rate and peak pressure. The ignition temperatures for these mixtures were significantly lower than those of the metal oxides alone.

Thermal stability of AP particles can be improved through micro-encapsulation techniques. A solvent/non-solvent method was used to micro-encapsulate AP particles with polymer films such as Viton A and NC [89]. The thermal stability of coated AP was examined using DSC, TGA, and SEM. Further to this, the heat of decomposition and coating morphology of pure and coated samples was documented. Viton significantly and unfavorably attenuated the heat of AP decomposition. Therefore, NC was chosen as a more appropriate coating material for AP. The thermal analysis of NC-coated samples, prepared at optimized coating conditions, revealed that the first stage decomposition temperature increased by about 12°C with respect to uncoated samples and reached 578 K (305°C). Micro-encapsulation of AP particles with fibrous NC enhanced its heat of decomposition ($\sim 120\text{ J/g}$) with no obvious adverse effects on kinetic parameters and thermal decomposition temperature.

The influence of mineral wax and dioctyl phthalate (DOP) coatings on the impact sensitivity of AP was studied by measuring the impact sensitivity of the coated AP powder and examining the surface with SEM [90]. The results revealed that the effects on impact sensitivity of AP were different for mineral wax and DOP. Due to gas release that occurs in the low temperature stage, the impact sensitivity of coated AP was increased by adding dioctyl phthalate and was decreased by coating AP with mineral wax. The study indicated that the endothermic material was better for reducing the AP impact sensitivity.

To reduce the hygroscopicity of AP, the surface of AP crystals was coated with polystyrene (PS) and fluorosilane (FAS: $\text{C}_{14}\text{F}_{12}\text{H}_{20}\text{SiO}_3$) films [91]. AP/PS/FAS composite particles and AP/PS/FAS composite film were prepared via composite of AP and PS and the processing of FAS. The hygroscopicities of coated AP samples were studied via moisture absorption rates and a water contact angle test and their micromorphology structures were investigated by scanning electron microscope (SEM)-energy dispersive X-ray analysis (EDAX). The moisture absorption rate of AP/PS/FAS film was the lowest of all samples tested and it almost no longer absorbed any moisture. It was found that FAS molecules exist on the surface of AP/PS/FAS films where they form a hydrophobic surface.

The hygroscopicity of AP can be decreased by modifying the surface of AP. In one experiment, AP was coated by graphene oxide (GO), AP/GO mixtures were modified by fluorosilane (FAS: $\text{C}_{14}\text{F}_{12}\text{H}_{20}\text{SiO}_3$), and a binary coating of AP mixtures was applied [92]. Testing of the moisture absorption rate in an atmosphere of 85% rela-

tive humidity (R.H.) at 293 K (20 °C) revealed that the moisture absorption rate was reduced. The moisture absorption rate of AP and AP/GO composites decreased further after they were modified by fluorosilane. The minimum moisture absorption rate was attained by a binary coating method where the concentration of GO was 0.40% and the concentration of fluorosilane was 1%. Thermal analysis revealed that the high peak temperature of the exothermic decomposition of AP/GO/FAS mixtures decreased by 33 °C when the concentration of GO was 0.40% and the concentration of fluorosilane was 1%.

In order to reduce the mechanical sensitivity of AP superfine powder, octadecylamine was used as the coating agent and coated superfine AP particles were prepared by jet milling [93]. The coating effect, thermal decomposition characteristics, and sensitivity characteristics of coated superfine AP particles were studied by particle size analysis, SEM, DSC, and sensitivity testing. Experimental results revealed that the particle size of coated superfine AP particles was 5.8 μm , with a coating layer present on the surface. Compared with the pure AP superfine particles, the impact sensitivity of coated superfine AP particles with 1 mass-% coating was reduced by 31% and friction sensitivity was decreased by 12%. When the mass fraction of coating agent was increased to 3%, the impact sensitivity of coated superfine AP particles was reduced by 34.5% and friction sensitivity was decreased by 22%. However, the coating agent had some negative impacts on the thermal stability of AP. As such, it is recommended that its concentration should be kept below 1 mass-%.

Fumed silica coatings act as desiccant and prevent agglomeration of UFAP [94]. Various other coating materials have been evaluated for preserving the properties of UFAP during storage [95].

Coatings with several inert materials, including some functional carbon materials, paraffin wax, and the well-known insensitive energetic material 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) were evaluated to reduce the undesirable high sensitivity and hygroscopicity of UFAP via polymer modified coating [96]. Structure, sensitivity, thermal and hygroscopicity of the UFAP-based composites were studied by SEM, sensitivity tests, DSC, wetting contact angle, and hygroscopicity analysis. The results revealed that both the impact and friction sensitivity of UFAP can be remarkably reduced with only a small amount of 2 mass-% of desensitization agents, while thermal stability was improved and hygroscopicity was reduced to a large extent at the same time.

Coatings of nanothermites, such as $n\text{CuO}/n\text{Al}$ ($n\text{Al}$), $n\text{MoO}_3/n\text{Al}$, $n\text{Fe}_2\text{O}_3/n\text{Al}$, $n\text{NiO}/n\text{Al}$, and $n\text{MgO}/n\text{Al}$ encapsulated into AP had higher activity in decreasing the decomposition temperature of AP, thus increasing the heat release and ignition and combustion properties than the corresponding physically-mixed mixtures [97]. The lowest decomposition temperature of AP was shown by $n\text{Al}/n\text{CuO}/\text{AP}$, which demonstrated the highest heat release and best ignition and combustion properties among all the composites tested.

3 Physical Properties of Ammonium Perchlorate

The molecular mass of AP is 117.489 g/mol. This number is needed to convert thermochemical properties from a mass basis to a molar basis and vice-versa.

3.1 Melting Point of Ammonium Perchlorate

The melting point of AP at atmospheric pressure is difficult to measure because the material begins to decompose and sublime before it melts. In addition to this, melting is preceded by a solid-solid phase transition at 513 K (240 °C), which further complicates the issue. The melting point of pure AP is unknown since it decomposes or even explodes beforehand.

3.1.1 Melting Point Diagrams of AP Mixtures

AP can be mixed with many other oxidizers to obtain desirable properties, for instance with reduced hydrogen chloride output in the exhaust gas. The main oxidizer candidate for such mixtures is AN. In fact, many AP/AN composite propellants have been formulated and tested. Similar mixtures have been discussed in the AN chapter in *Encyclopedia of Oxidizers*.

3.1.1.1 Melting Points of AP Mixtures With Other Ammonium Salts

The most attractive mixture of ammonium oxidizers is the mixture of AN and AP, possibly combining the advantages of both oxidizers in one propellant ingredient. The mixture would have better performance than AN and emit less environmentally objectionable hydrogen chloride in the exhaust than AP. Before AP/AN mixtures can be used, the physical properties must be known, in particular their tendency to undergo phase transitions with sudden changes in density and crystal shape.

Unfortunately, the complete diagram could not be obtained because the liquidus temperature at 12% AP was high enough to cause rapid decomposition of AN [98]. The freezing point and melting point of AN/AP mixtures in the range from 0–12 mol-% AP are shown in Figure 3. The mixtures tend to undercool before they crystallize. This is why the two lines are not on top of each other.

There appear to be two closely located, incompletely resolved eutectics melting near 427 K (154 °C) with compositions in the range from 6.8 to 8.1 mol-% AP, at which point it was difficult to obtain accurate measurements. XRD data indicated the existence of a peritectic at about 8.2 mol-% AP. The freezing point curve (solid line) shows a minimum whereas the melting curve (dashed line) drops to a low value (close to that of the eutectics) and remains there, regardless of the AP content. The dashed line is erratic and unusable. Both AN and AP undergo phase transitions, which affect their mechanical and thermal stability properties. It was of interest to see how the phase

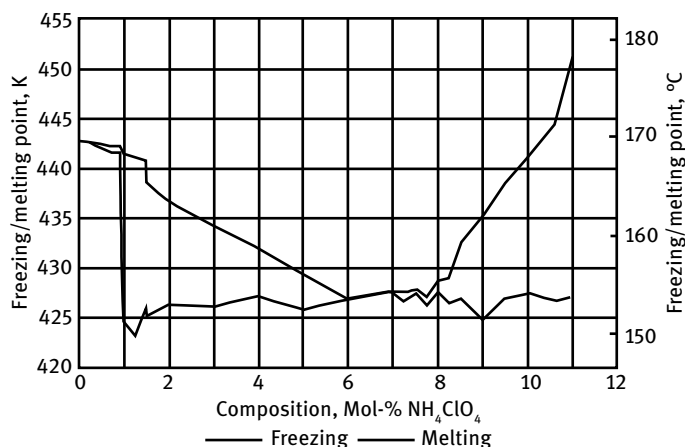


Figure 3: Freezing/melting point diagram of the AN/AP system. (Graph created by Schmidt, 2020, based on data from [98].)

transitions would be affected by adding the other oxidizer. In AN, the transition at 399.6 K (126.5 °C) corresponds to the transition from cubic to rhombohedral. This transition persisted across the entire part of the phase diagram studied. The transition temperature dropped rather sharply (about 2 °C) over the first 0.5 mol-% of AP added. After this, it remained constant within the accuracy of the measurements. This slight drop in the transition temperature corresponded to the region of solid solution formation. On the AN-rich side of the diagram the cooling curves remained at a constant temperature during the transition. As more AP was added, the transition occurred over a temperature range rather than at a particular temperature. This temperature range increased with the AP content.

Another phase diagram revealed that the melting point in the AP/AN system does not drop significantly until the AN concentration reaches 80% AN. Then the melting point drops sharply toward a eutectic containing 90% AN and melting at 419 K (146 °C) [99].

AP is the most popular oxidizer, however, it is not the cleanest. Its environmental impact can be reduced by adding nitrates. Solid propellants containing both AN or phase stabilized ammonium nitrate (PSAN) and AP are called “dual oxidizer” composite propellants. The AN and AP can be dry-mixed as individual powders or the two salts can be co-crystallized from water and then ground to the desired particle size. AN and AP can be co-crystallized by freeze-drying [100]. AN adhered to the less soluble AP particles during the drying process to form combined AP/AN particles. The AN content of the combined AP/AN samples dominated particle properties, including shape, hygroscopicity, thermal decomposition behavior, and ignition sensitivity.

Several propellants were formulated with the co-crystallized oxidizer and compared to conventional AP-based propellants [101] (see [102]).

3.1.1.2 Melting Points of AP Mixtures With Other Perchlorate Salts

Lithium perchlorate is an oxidizer with a very high oxygen content. Mixtures of lithium perchlorate with AP could potentially improve the performance of rocket propellants using mixed oxidizers. Liquidus temperatures for samples containing more than 40 mol-% AP could not be obtained because of rapid decomposition of this salt as the temperature was raised. Decomposition of samples containing less than 40 mol-% AP was negligible. The phase diagram of the binary system $\text{LiClO}_4/\text{NH}_4\text{ClO}_4$ shows that the system has a simple eutectic at 69.5 mol-% LiClO_4 at 455 K = 182 °C (Figure 4) [103].

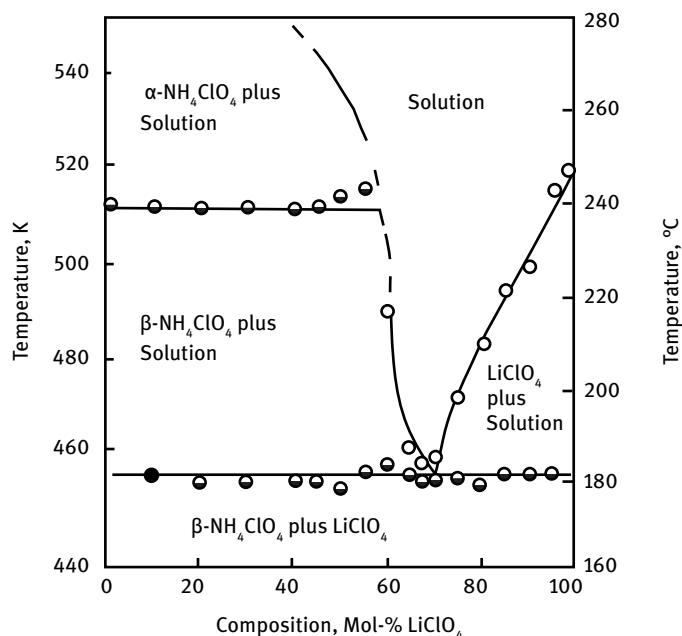


Figure 4: Phase diagram of the $\text{LiClO}_4/\text{NH}_4\text{ClO}_4$ system. (Reprinted and modified from [103], with permission from © 1959 American Chemical Society; permission conveyed through RightsLink.)

AP with 1 mass-% of lithium perchlorate added can survive heating at 543 K (270 °C) for up to 24 hours without any noticeable indication of thermal decomposition. Eutectic formation in the $\text{NH}_4\text{ClO}_4/\text{LiClO}_4$ system has been credited with a stabilizing effect that extends the range of thermal stability of AP [104]. The crystallographic transition characteristic of AP persisted throughout the composition range studied (55-0 mol % LiClO_4).

A eutectic containing 30.5 mol % (32.64 mass-%) AP and 69.5 mol % LiClO_4 has a higher solubility in polymerizable monomers. It is more easily processed into homogeneous dissolved polymer solid propellants than either AP or LiClO_4 [105].

Addition of sodium perchlorate to AP would lower the available oxygen content somewhat but would also reduce the amount of chloride emitted in the objectionable form of hydrogen chloride. Instead, some of the chloride escapes as sodium chloride, which is benign and settles out of the atmosphere and dissolves in the ocean where there is already plenty of it.

3.1.1.3 Melting Points of AP Mixtures With Other Salts

Another oxidizer suitable as an additive to AP is sodium nitrate. Although sodium nitrate does not have a high useable oxygen content, the presence of sodium in the exhaust scavenges some of the chloride and emits it as inert sodium chloride rather than as toxic and corrosive and ozone-depleting hydrogen chloride. Essentially, similar results at a fraction of the cost could be achieved using mixtures of sodium perchlorate with ammonium nitrate. Furthermore, sodium perchlorate is less expensive than AP. The related phase diagram of ammonium nitrate with sodium perchlorate is shown in *Encyclopedia of Oxidizers* (“Nitrate Oxidizers” chapter).

3.1.1.4 Melting Point Diagrams of AP Solutions

The freezing point depression as the result of dissolving AP in water is 0.709° at $0.2135 \text{ mol AP}/1000 \text{ g H}_2\text{O}$, 1.189° at $0.3616 \text{ mol AP}/1000 \text{ g H}_2\text{O}$, 1.755° at $0.535 \text{ mol AP}/1000 \text{ g H}_2\text{O}$, and 2.656° at $0.8069 \text{ mol AP}/1000 \text{ g H}_2\text{O}$. The eutectic point in the system $\text{NH}_4\text{ClO}_4/\text{H}_2\text{O}$ is $270.4 \text{ K} = -2.72^\circ\text{C}$ and contains 9.84 mass-% AP.

3.1.2 Phase Changes of AP

3.1.2.1 Phase Changes of AP at Atmospheric Pressure

At ambient pressure and temperature AP crystallizes in the orthorhombic crystal system. Space group $Pnma$ and the ammonium ions are allowed essentially free rotation. Variable temperature studies indicate that, at least up to 78 K, ammonium ions undergo increasingly large amplitude rotational oscillations about definite equilibrium positions. Under ambient conditions of temperature and pressure, AP exists in an orthorhombic crystal structure ($Pnma$) in which the NH_4 ions freely rotate. Despite numerous reports of anomalies in a variety of physical properties of AP in the temperature range 10–298 K, a definitive study using neutron diffraction, inelastic neutron scattering, and Raman spectroscopy has shown that there is no evidence for any phase transition in this temperature range [106]. On heating to above 511–513 K, AP undergoes an orthorhombic to cubic phase transition in which almost unrestricted rotational orientation of the perchlorate ions is observed [107]. The rotation of the cations, however, begins below room temperature. On heating to above 511–513 K, a reversible phase transition to a cubic structure takes place in which there is almost unrestricted rotational reorientation of the perchlorate ions. AP exists in three solid phases: a low-temperature phase, an orthorhombic crystal structure phase, which is stable from 83 to 513 K, and a high-temperature phase, which is cubic and stable from 513 K to the melting point 723 K.

All alkali metal perchlorates except lithium perchlorate undergo phase changes from (bipyramidal) orthorhombic to cubic when heated and so does AP [108]. The dimorphic transition temperature has been explained as the point where the ClO_4^- anion begins to rotate freely in the crystal structure. AP undergoes a reversible phase change at 513 K (240 °C). This temperature is close to its melting point and point of incipient thermal decomposition. Below 513 K, AP exists in the form of orthorhombic crystals. Above 513 K, AP exists in the form of cubic crystals. The phase transition orthorhombic $\rightarrow$ cubic is endothermic but it is accompanied by incipient thermal decomposition. The rate at which AP converts to the cubic crystal phase from the orthorhombic crystal phase is relatively slow compared to chemical reactions. It is difficult to measure the enthalpy of the phase transition in a DSC or DTA because incipient decomposition of AP releases additional heat. It was possible to suppress the decomposition by heating AP in a stream of ammonia (see Section 4.6.6.3) [109]. The enthalpy of transition measured in this way is +9.6 kJ/mol (2.3 ± 0.2 kcal/mol) (an average of ten determinations). The calculated density of orthorhombic AP is 1.95 g/cm³ whereas the high-temperature form has a density of only 1.76 g/cm³ for a volume difference of 9.7%. Even if a rocket motor is not accidentally igniting if heated above 513 K (240 °C) (a very hazardous condition that should be avoided), the volume expansion of AP which usually makes up 80% of the propellant may rupture the motor casing (in the case of an end burner) or cause the coaxial perforation or cavity to choke for simple mechanical reasons. Choking the perforations may cause excessive pressure build up because the combustion products have no way to escape.

The orthorhombic to cubic transition occurs via slippage of planes moving parallel to each other to create rectangular crystal faces. When cubic AP is cooled to below 513 K (240 °C) the crystal forms many grains, with each grain having an orthorhombic structure. However, the macroscopic appearance of the whole crystal remains cubic. This state has been referred to as “relic cubic”.

Thermal decomposition of AP proceeds differently depending on if one starts out with an orthorhombic or cubic modification. The orthorhombic form of AP decomposes faster than the cubic form. Also, the effect of additives on the dissociation of AP is different depending on which modification exists at the moment when the additive is stepping into action [110]. A third rarely seen modification exists below 83 K. It was suggested that the transition at 83 K is associated with thawing the cation free rotation, whereas the 513 K transition corresponds to the onset of perchlorate ion rotation.

A comparative study of polymorphic transformations in ammonium and the alkali metal perchlorates using DTA developed correlations between the observed trends in the transformation temperatures and available crystallographic and thermodynamic data [111]. Considerable hysteresis was observed in the transformations in ammonium, potassium, rubidium, and cesium perchlorates. Doping of AP with ammonium phosphate caused an upward shift in the transformation temperature and an increase in the thermal hysteresis. Prior mechanical and thermal treatment resulted in a broadening of the hysteresis loops in the case of ammonium and potassium perchlorates.

The enthalpy of phase transformation was measured as $20.3 \pm 0.6 \text{ cal/g} = 2.39 \pm 0.07 \text{ kcal/mol} = 9.99 \text{ kJ/mol}$ [112]. DSC operations were carried out at heating rates of 2, 4, 8, 16, 32, and 64 K/min. The activation energy for the phase change endotherm was measured by scanning methods and was derived from three different equations. The activation energy derived from the equation $\log S/\Delta H$ versus $1/T$ was $667 \text{ kJ/mol} = 159.5 \text{ kcal/mol}$.

When studying polymorphous transitions in AP crystals, it was discovered that there are two mechanisms of the transformation of the rhombic modification into the cubic one [113]. At low temperatures the transition follows an atom-by-atom mechanism. At temperatures above 516 K (243 °C) the transition is of the martensite type. In both cases the polymorphous transition proceeds through the formation and growth of nuclei of the new phase; the growth of martensite nuclei occurs not continuously but incremental. The interface boundary can be coherent during the transition from the rhombic modification into the cubic one.

An ESR study of free radicals in X-irradiated AP single crystals was aimed at resolving the controversy that had arisen over the possible occurrence of low-temperature phase transitions in AP, which at room temperature has an orthorhombic structure (space group *Prma*) [114]. ESR spectra revealed no changes attributable to any phase transitions. It was concluded that AP does not undergo any phase transitions below room temperature.

3.1.2.2 Phase Changes of AP at Very High Pressures

The structural behavior of AP at high pressures is poorly understood. For instance, several studies reported in the literature appear to contradict each other. The pressures where the phase transitions take place are much higher than typical rocket operating pressures but all phase changes need to be understood to make sure they do not take place unexpectedly as with ammonium nitrate.

A strong pressure dependence on the orthorhombic to cubic transition temperature was observed when AP was compressed to 0.4 GPa. The orthorhombic to cubic transition that occurs at 511 K at ambient pressures has been followed as a function of pressure up to 0.4 GPa and a very strong pressure dependence (216 K/GPa) of the transition was observed. However, subsequent optical studies revealed that it was only weakly pressure-dependent [115]. The high-pressure phase diagrams of NH_4ClO_4 and NH_4BF_4 were studied using DTA and volumetric techniques [116]. The usual orthorhombic $\rightarrow$ cubic transition was followed by up to 4 kbar and 573 K. AP exploded violently at 602–623 K and 2–3.6 kbar, although this would only happen above 713 K in atmospheric pressure. The explosion may be due to the large volume change upon phase transition. The high-temperature portions of these diagrams were intermediate between those of the corresponding potassium and rubidium salts. However, at low temperatures, the onset of hydrogen bonding caused the appearance of phases which are unique to the ammonium compounds.

AP demonstrated previously unreported phase transitions when pressurized and heated in a diamond anvil cell at high temperatures (up to 693 K) and high pressures (up to 26 GPa) [115, 117]. These studies also reported the pressure dependence of the solid-liquid transition and claimed that there was no evidence for a high-pressure phase transition up to 26 GPa. Liquid droplets were observed above the well-known orthorhombic to cubic phase transition at 513 K and were interpreted as signs of incipient melting. The melting point decreased with increasing pressure. A phase diagram was constructed showing all the different phases. Preliminary high-pressure DSC data revealed a weak pressure dependence of the orthorhombic to cubic phase transition. Unexpectedly, Foltz and Maienschein [115, 117] found that the temperature of AP phase change was reduced by increasing the pressure. Since increased pressure should resist a volume increase and with small thermodynamic energy forcing the phase change, one would anticipate that increased pressure would instead cause a rise in phase change temperature. Foltz and Maienschein had difficulty taking measurements at low pressures while observing AP phase change behavior. Their lowest pressure at phase change temperatures was about 10 kbar (~ 1.0 GPa, ~ 145000 psi).

Crystal structures have been measured by XRD at pressures up to 5.0 GPa under conditions of shock compression. A change in the powder pattern was reported at 4.70 GPa, and the authors suggested that, on the basis of its complexity, the pattern was characteristic of a monoclinic or triclinic unit cell [118].

Using a combination of XRD and neutron diffraction techniques, augmented by vibrational spectroscopy, structural information of fully deuterated d-AP was measured at pressures up to ~ 8 GPa [119]. Under hydrostatic conditions d-AP undergoes a first order phase transition at 3.98 GPa, which is in agreement with the results of previous studies. The structure of the new orthorhombic phase (*Pnma*), which features a more closely packed structure with more extensive hydrogen bonding, was resolved and an equation of state for this new phase at pressures up to 8.1 GPa was obtained. High-pressure techniques were used to investigate polymorphism in energetic materials and new high-pressure phases of AP were structurally characterized using single-crystal X-ray and powder neutron diffraction [120].

Infrared studies of AP revealed a change in the ν_1 mode of the perchlorate group between 1.0 and 2.4 GPa [121, 122]. This was assigned to the orthorhombic to cubic transition. Single-crystal shock-wave studies revealed no obvious phase transformations but suggested that if any phase transition did occur that it would be accompanied with a negligible change in volume or with very slow kinetics [123, 124].

Calculations of the polymorphic phase stability, structural transition, and lattice dynamics of AP under high pressure revealed that AP attains a global minimum energy structure in *Pnma* symmetry over *Pna2₁* [125]. However, the difference is very small at ~ 1 meV per formula unit. The calculated phonon dispersion curves indicated that AP is dynamically stable in both *Pnma* and *Pna2₁* crystal symmetries at ambient pressures, which unambiguously shows the existence of polymorphism in AP. The *Pnma* phase of AP was found to be mechanically unstable above 4 GPa. AP undergoes a first-order

structural phase transition above 4 GPa. The high-pressure phase crystallizes in orthorhombic crystal symmetry ($P2_12_12_1$) at 6.9 GPa, which is consistent with the recent experimental results.

3.2 Density of Ammonium Perchlorate

3.2.1 Density of Solid AP

The densities of the two crystal modifications of AP are quite different. Particle swelling and shrinkage would cause severe delamination problems similar to those of AN if the phase transition point was at a lower temperature. The density of the orthorhombic phase is 1.957 g/cm^3 and the density of the cubic phase is 1.756 g/cm^3 . After AP transitions from orthorhombic to cubic phase at 513 K (240 °C), crystal volume increases by 10.8%. Older sources give the density of the orthorhombic phase at 298 K (25 °C) as 1.9518 g/cm^3 and the density of the cubic phase above 513 K (240 °C) as 1.732 g/cm^3 .

3.2.2 Density of AP Solutions

The density of AP solutions in water is tabulated in Table 1.

Table 1: Density of AP solutions.

Temperature, °C	Ammonium perchlorate concentration, mass-%						
	2	4	6	8	10	12	14
	Density, g/cm^3						
15	1.0088	1.0186	1.0286	1.0387	1.0490	1.0594	1.0700
25	1.0065	1.0160	1.0257	1.0355	1.0455	1.0557	1.0660

Data source: [126].

Once one has an accurate density chart, the concentration of AP solutions can be determined with a thermometer and a hydrometer [127]. The deviations of this crude method are of the order of 4 g/L. The density of saturated AP solutions containing 20% AP at 298 K is 1.0982 g/cm^3 .

3.3 Vapor Pressure and Sublimation of Ammonium Perchlorate

AP exerts a noticeable vapor pressure when heated. The vapor pressure of AP must be taken into consideration when conducting volumetric studies of the thermal decomposition of AP. The rate of sublimation increases faster with temperature than the rate

of decomposition in vacuums. The vapor pressure can be measured either in static or in dynamic systems. The vapor pressure of AP is caused by partial dissociation of AP into ammonia and perchloric acid. No ion clusters or undissociated AP was found in the vapor phase above heated AP. Sublimation papers are now provided in chronological order.

The dissociation pressure of AP was measured using a dynamic transference method [128, 129]. In a number of runs the following parameters were varied:

1. flow rate of helium gas
2. reaction temperature
3. initial mass of AP
4. initial particle size
5. partial pressure of NH_3 added to carrier gas

The vapor pressure can be expressed using the following equation:

$$\log p = -6283.7/T + 10.56$$

where p is the vapor pressure in mm Hg and T is the temperature in kelvin. The heat of dissociation is 58 ± 2 kcal/mol in the temperature range of 520–620 K.

The vaporization and sublimation products of AP and other volatile perchlorates as studied by a cold matrix isolation technique and identification of products by IR absorption spectra are ammonia and perchloric acid [130]. Other IR bands found in the products were assigned to NH_3 , HCl , and H_2O . Comparing the vaporization temperatures of AP, hydrazinium perchlorate, hydroxylammonium perchlorate, and methylammonium perchlorate (MEAP), the relative vaporization temperatures could be correlated with the pK values of the bases in aqueous solution.

The kinetics of AP sublimation were investigated over a wide range of temperatures and vapor pressures up to 1 atm [131]. A model for AP sublimation takes both surface diffusion and diffusion through the gas phase into consideration. An equation describing the kinetics of sublimation was in strong agreement with the experimental data. The evaporation coefficient β is strongly pressure-dependent, indicating the importance of surface diffusion in the evaporation process. The AP sublimation process commences by the transfer of a proton from an NH_4^+ ion to a ClO_4^- ion at a disturbed surface kink site. The NH_3 and HClO_4 molecules thus formed remain adsorbed at these positions for a finite time. Unless they can diffuse away to become adsorbed on separated sites away from the surface step the proton-transfer process will reverse itself and the ions will recombine. At low pressures, the evaporation process is then completed by the desorption of NH_3 and HClO_4 molecules into the gas phase.

It is difficult to study the sublimation of AP without running into unwanted decomposition problems. There are several studies where sublimation and decomposition of AP have been measured simultaneously. Methods for rapidly heating a solid body of AP include hot wires, hot foils, laser, and hot air convective heating. AP specimens (pellets that are 0.156 inches in diameter and 0.5 to 1 inch in length) were ex-

posed to various levels of convective surface heating from a gas burner at one atmosphere ambient pressure [132, 133]. Previously, linear pyrolysis rates were obtained by pressing specimens against heated plates (solid and porous) and heated wire meshes. Surface regression rates were measured and, simultaneously, surface temperatures were determined by measuring the IR emission near $3.1\text{ }\mu\text{m}$. The results appear to corroborate the previously suggested value of 83.68 kJ/mol (20 kcal/mol) for the apparent activation energy for AP pyrolysis (see [134].)

In the early 1970s the activation energies reported for AP sublimation varied considerably, from 84 to 126 kJ/mol (20 to 30 kcal/mol) depending on the method used. A mass-spectrometric thermal analysis method was used to study the kinetics of the sublimation of AP and attempts were made to consolidate data from different sources [135]. The AP sample was held in a titanium cup and placed in a heated tube close to the Knudsen cell inlet and ionization electrodes of the mass spectrometer.

DTA demonstrated that the addition of inorganic salts to AP, or preheating AP, delays the sublimation process, rendering AP more suitable for solid rocket propellant use [136]. Sublimation was enhanced by precompression of the pellets and by decreasing the particle size from 500 to $200\text{ }\mu\text{m}$. Reducing the particle size further to $100\text{ }\mu\text{m}$ led to a reduction in rates of sublimation. It is assumed that imperfections and residual strain in the crystals caused these effects.

The sublimation of AP was investigated by using simultaneous DTA and TGA [137]. Critical evaluation of the isothermal kinetics of data obtained by a thermobarogravimetric technique indicated that the kinetics are consistent with an expression for a contracting cylinder rather than a contracting sphere model. The activation energy for sublimation obtained experimentally is in strong agreement with that derived from the Schultz-Dekker theory ($75.3 \pm 8.4\text{ kJ/mol} = 18 \pm 2\text{ kcal/mol}$). The sublimation process in AP was compared to that in ammonium halides. It is shown that a previously reported value of 30 kcal/mol for the activation energy was obtained under conditions where decomposition instead of sublimation dominated.

The fact that the activation energy of thermal decomposition of AP turned out to be smaller than the heat of sublimation (88 and 125 kJ/mol , respectively) had been the subject of discussion for some time. It was proposed that a quasi-equilibrium is established on the surface of AP between the crystals and dissociation products, while the limiting stage is desorption of dissociation products (ammonia and perchloric acid). The heat of dissociation of AP into ammonia and perchloric acid has been estimated to be $242\text{--}251\text{ kJ/mol}$ [138].

Time-of-flight (TOF) mass spectrometer measurements of the flux of molecules from the surface of ammonium salts vaporizing into vacuum revealed that, in the case of AP, the vapor subliming from a single crystal surface was comprised of ammonia and perchloric acid [139]. When the source was compressed powder instead of a single crystal, the vapor included a mixture of lower molecular weight species, which may be due to subsurface decomposition. See [140].

The kinetics and mechanisms for the sublimation/decomposition of AP can be represented by first-principles calculations using a generalized gradient approximation with the plane-wave density functional theory (DFT) [141]. The model assumes supercells containing 4, 8, and 16 NH_4ClO_4 units. The predicted enthalpy changes for the reaction of solid NH_4ClO_4 going to gaseous NH_3 and HClO_4 is 188 ± 6 kJ/mol 45.0 ± 1.5 kcal/mol. The calculated desorption activation energies for NH_3 , HClO_4 , and $\text{H}_3\text{N}\cdots\text{HOCLO}_3$ molecular complexes (individually and from the relaxed surface) are 189, 182, and 117.6 kJ/mol (45.3, 43.5, and 28.1 kcal/mol), respectively. The rate constant for the dominant sublimation process desorbing $\text{H}_3\text{N}\cdots\text{HOCLO}_3$ as a pair can be presented by

$$k_{\text{subl}} = A \exp\left(\frac{-E}{RT}\right) = 6.53 \times 10^{12} \exp(-28.8/RT),$$

where k_{subl} is the sublimation constant in s^{-1} (which is in reasonable agreement with available experimental data), E is the activation energy in kcal/mol, and T is the temperature in kelvin. As one would expect, the decomposition of $\text{H}_3\text{N}\cdots\text{HOCLO}_3(\text{G})$ to $\text{NH}_3(\text{G})$ and $\text{HOCLO}_3(\text{G})$ is considerably faster; about 1×10^7 times faster than that for the sublimation process in the same temperature range. The rate constant for the gas-phase dissociation step can be expressed by

$$k_{\text{diss}} = A \exp\left(\frac{-E}{RT}\right) = 1.20 \times 10^{15} \exp(-14.6/RT)$$

where k_{diss} is the dissociation constant in s^{-1} , E is the activation energy in kcal/mol, and T is the temperature in kelvin. This study further confirmed that the activation energy for the sublimation of an ammonium salt is significantly lower than the enthalpic change and that the molecular complex of acid and base sublimates concurrently as a pair.

3.4 Solubility of Ammonium Perchlorate

AP is soluble in polar solvents and is insoluble in non-polar solvents such as diethyl ether or hexane.

3.4.1 Solubility of AP in Water

The solubility of AP in water is summarized in Tables 2 and 3.

The solubility of AP in water can also be expressed as a polynomial function

$$W = 10.696 + 0.3617t + 0.000263t^2$$

where W is the AP concentration in mass-% and t is the temperature in $^{\circ}\text{C}$ (see [142] also).

Table 2: Solubility of AP in water.

Temperature		Solubility, g AP/100 mL saturated solution
K	°C	
273	0	10.8
298	25	20.0
318	45	28.0
333	60	33.6
348	75	39.4
373	100	88

Data source: [3].

Table 3: Solubility of AP in water.

Temperature		Mass % AP in saturated solution
K	°C	
273.1	0.0	10.73
273.1	0.0	10.74
288.3	15.2	15.95
298.1	25.0	19.64
298.1	25.0	19.95
298.1	25.0	20.02
303.1	30.0	21.875
318.1	45.0	28.02
328.3	55.2	31.55
333.1	60.0	33.64
338.2	65.1	35.70
348.1	75.0	39.05
348.1	75.0	39.45
357.8	84.7	42.54

Data source: [126].

3.4.2 Solubility of AP in Anhydrous Ammonia

If dry AP is exposed to ammonia gas at atmospheric pressure it becomes deliquescent. AP forms various amines which may contain AP in association with 4 or 6 mols of ammonia. The phase diagram of AP in ammonia is shown in Figure 5. The tetrammine and hexammine adducts are weakly expressed peritectics (points A and B) on the right side of the curve. The eutectic point (point C) of the $\text{NH}_4\text{ClO}_4/\text{NH}_4\text{ClO}_4 \cdot 6\text{NH}_3$ system is at 176 K (-97°C) and contains 49 mass-% AP. The other eutectic points between $\text{NH}_4\text{ClO}_4 \cdot 6\text{NH}_3$ and $\text{NH}_4\text{ClO}_4 \cdot 4\text{NH}_3$ and between $\text{NH}_4\text{ClO}_4 \cdot 4\text{NH}_3$ and NH_4ClO_4 are less pronounced. A solution that is saturated with AP at 283 K contains 72.4% AP and has a vapor pressure just below atmospheric pressure. These solutions are similar to DIVERS solutions containing AN or ammonium thiocyanate.

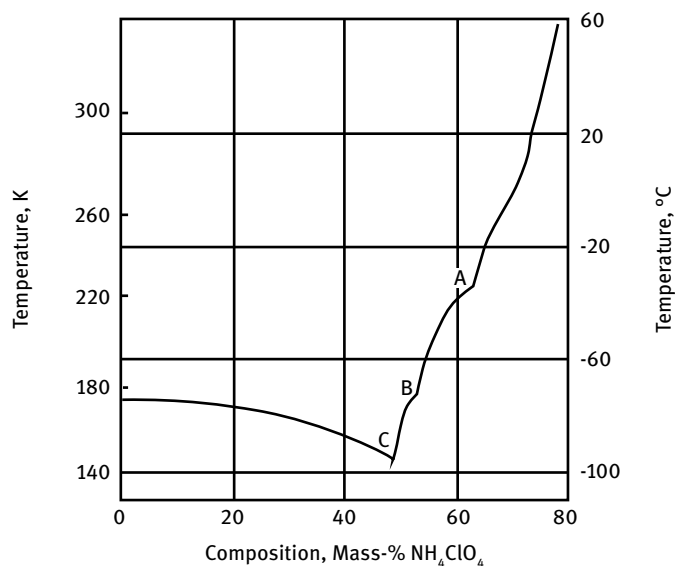
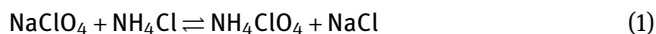


Figure 5: Phase diagram of the AP/ammonia system. (Reproduced and modified from [126].)

The solubilities of ammonium chloride, potassium chloride, sodium chloride, AP, potassium perchlorate, and sodium perchlorate at 240, 273, 298, and 323 K (−33, 0, 25, and 50 °C) in liquid ammonia have been determined as well as the solubilities of the salt pairs and the ternary mixtures necessary to prepare the quaternary phase diagrams for the two chemical processes



and



These equilibrium diagrams demonstrate the possibility of carrying out the above processes in liquid ammonia [143].

3.4.3 Solubility of AP in Organic Solvents

The solubilities of AP and potassium perchlorate in organic solvents are summarized in Table 4.

The solubilities of AP and other inorganic perchlorates are tabulated in a reference work on solubility [144, 145]. The solubility of AP in methanol as a function of temperature is given in Figure 6 [52]. The solubility of AP in methanol can be expressed by the following equation:

$$C^* = 2.4412 - 1.6665 \times 10^{-2}T + 2.9145 \times 10^{-5}T^2$$

Table 4: Solubility of AP and potassium perchlorate in organic solvents.

Solvent	Solubility, g AP/100 mL saturated solution, at 298 K	Solubility, g potassium perchlorate/100 g solvent, saturated solution, at 298 K
Methanol	6.862	0.1051
Ethanol	1.907	0.012
1-Propanol	0.386	0.010
1-Butanol	0.017	0.0045
iso-Butanol	0.1272	0.005
Acetone	2.26	0.155
Ethyl acetate	0.032	0.0015
Diethyl ether	insoluble	insoluble

Data source: [3].

where C^* is the solubility in g AP/100 g solution and T is the temperature in kelvin. The solid line in Figure 6 was calculated using this equation. This solvent is of practical interest for producing AP with smaller particle sizes than would be possible by recrystallizing them using water. Older sources give the density of a saturated solution of AP in MeOH at 298 K as 0.8218 g/cm³ and it contains 6.41 mass-% AP. It is less solu-

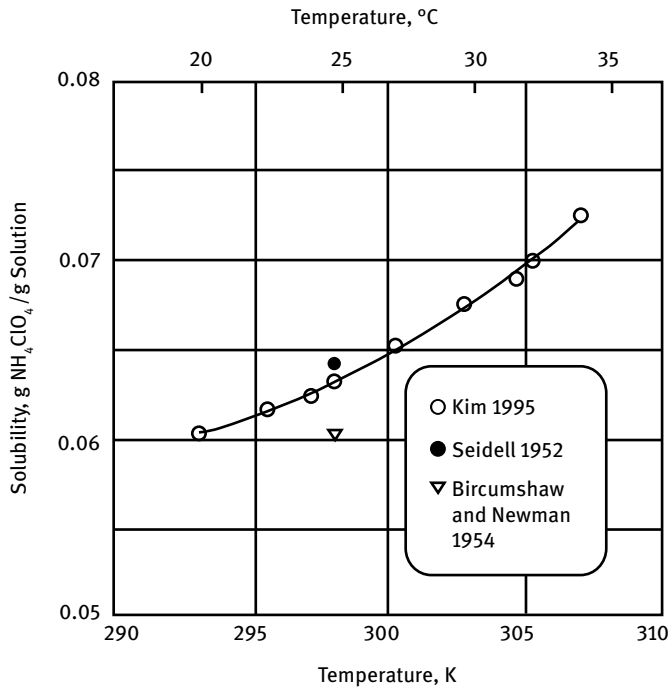


Figure 6: Solubility of AP in methanol. (Reproduced and modified from [52].)

ble in EtOH where a saturated solution at 298 K contains only 1.872 mass-% AP and its density is 0.79505 g/cm³.

AP is insoluble in diethyl ether, methylene chloride, or chloroform but it has a limited solubility in isobutanol (0.1268 g AP/100 g solution).

Most of the solubility work with inorganic oxidizers is done with polar solvents. In the case of AP, however, additional concern has arisen about its solubility in less polar solvents like the hydroxy-terminated polyglycols or polybutadienes it is dispersed in during the processing of composite propellants and prior to the addition of the isocyanate crosslinking agents. The solubility of AP in polyglycols is very small but will affect the oxidizer particle size and thus the burning rate of the final product [146]. AP is sufficiently soluble in polyethylene oxide (polyethylene glycol) to make the polymer electrically conductive.

The solubility of AP in various candidate solvents is of key importance in the selection of solvents for demilitarization of AP-based solid propellants and eventual recycling of the material. The preferred solvent so far has been water but other solvents are evaluated as well.

3.5 Thermal Conductivity and Thermal Diffusivity of Ammonium Perchlorate

Thermal diffusivity measurements on compacted AP powder, pressed pellets of AP, and NaCl (for comparison) from room temperature to 513 K (240 °C) were corrected to extrapolate to solid and non-porous crystal data. The thermal diffusivity of compressed AP powders was measured as a function of porosity, particle size, and temperature. In this temperature range, the thermal diffusivity α of AP can be described by the linear equation

$$\alpha = 2.50 \times 10^{-3} - 4.55 \times 10^{-6} t$$

where α is the thermal diffusivity in cm²/s and t is the temperature in °C [147, 148]. Point data for 323 K are $5.02 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-1}$ with a heat capacity of $1.134 \text{ J g}^{-1} \text{ K}^{-1}$ ($0.271 \text{ cal g}^{-1} \text{ °C}^{-1}$).

Thermal diffusivities and specific heats of AP, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) were measured from room temperature all the way up to the decomposition temperature region by use of a laser flash method [149, 150]. Radiation heat losses were a significant problem and required the application of a new correction technique. Thermal conductivities were calculated from the thermal diffusivity, specific heat, and density of each material. The diffusivity of AP single crystals was measured along three different directions relative to the crystal lattice. The thermal conductivity (see Figure 7) and thermal diffusivity (see Figure 8) of single crystal AP was found to be independent of orientation. However, it drops markedly at the point of phase transition.

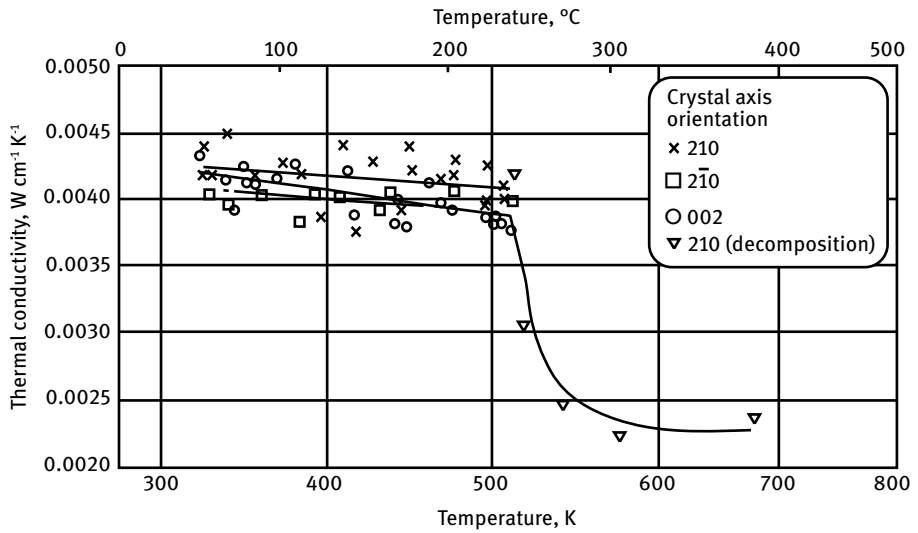


Figure 7: Thermal conductivity of AP single crystals in various directions in relation to crystal planes. (Reprinted and modified from [149], with permission from © 1985 Springer Nature; permission conveyed through Copyright Clearance Center.)

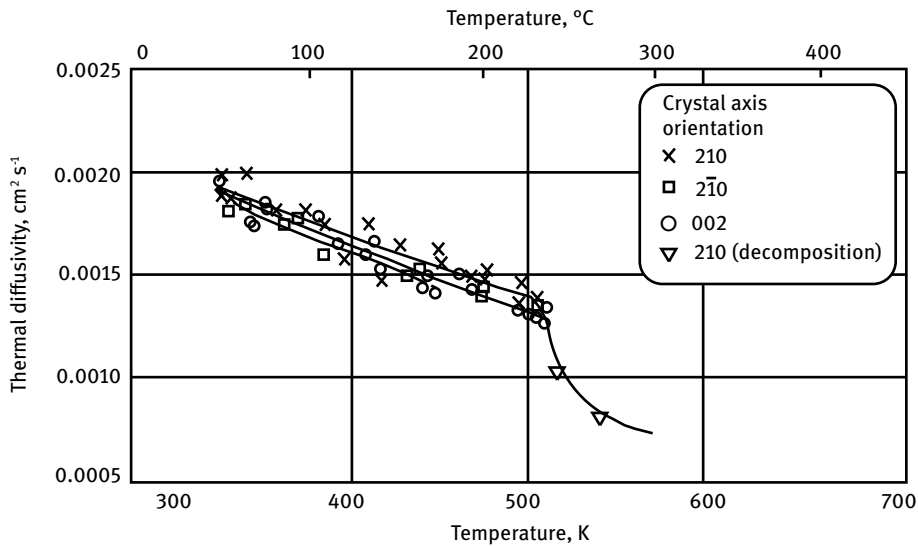


Figure 8: Thermal diffusivity of AP single crystals in various directions in relation to crystal planes. (Reprinted and modified from [149], with permission from © 1985 Springer Nature; permission conveyed through Copyright Clearance Center.)

The conductivities of pressed AP powder pellets were much lower than those of single crystals at $0.0030 \text{ W cm}^{-1} \text{ K}^{-1}$ (compared to $0.0042 \text{ W cm}^{-1} \text{ K}^{-1}$ for single crystals). The thermal diffusivities of AP mixed with a HTPB binder and of HTPB alone were also measured.

Because the thermal conductivity and thermal diffusivity of AP was already well described in existing literature, AP was used as the reference standard for calibrating an apparatus used for the determination of heat capacity, thermal conductivity, and thermal diffusivity of a range of other oxidizers, binders, and rocket propellants [151]. The thermal diffusivity α of AP between the range of 293 to 487 K (20 to 214 °C) can be described by the linear equation

$$\alpha = 2.58 \times 10^{-3} - 4.54 \times 10^{-6} t$$

where α is the thermal diffusivity in cm^2/s and t is the temperature in °C. Likewise, the thermal conductivity λ of AP between the range of 20 to 214 °C can be described by the linear equation

$$\lambda = 1.38 \times 10^{-3} - 9.2 \times 10^{-7} t$$

where λ is the thermal conductivity in $\text{cal cm}^{-1} \text{ s}^{-1} \text{ °C}^{-1}$ and t is the temperature in °C. Similar data is contained in the same publication for a wide range of oxidizers, binders, and solid propellants.

3.6 Electrical Conductivity of Ammonium Perchlorate

AP has an anomalously high value of electrical conductivity. It is two to three orders of magnitude higher than that of alkaline metal perchlorates, which are similar to AP in their crystal structure and other properties. The activation energy of conductivity is well below that of alkaline perchlorates. The effect of oxygen on the electrical conductivity of AP is quite specific, whereas in the case of alkaline perchlorates, no such oxygen dependency has been observed. Some ammonium salts (e.g., ammonium dihydrogenphosphate) are proton conductors.

There are several methods to arrange information on electrical conductivity in a systematic manner. The following sections could be separated by the method of conductivity measurement used, direct current (DC) measurements (with solid state electrolysis at the electrodes), or alternating current (AC) measurements including impedance measurements at high frequencies. Instead, the material is only arranged in chronological order.

One interesting feature of an ionic solid is the possibility of correlating the creation and destruction of charge carriers by measurement of the DC conductance during its thermal decomposition. A study of the effects of temperature and gaseous environment on the electrical conductivity of AP pellets revealed that, at temperatures between 298 and 398 K (25 °C and 125 °C), argon and oxygen depressed the electrical

conductivity of AP approximately by one or two orders of magnitude, respectively. The activation energies determined from the temperature dependence of the conductivity were 106.1, 111.9, and 135.4 kJ/mol (25.36, 26.75, and 32.37 kcal/mol) for vacuum, oxygen, and argon, respectively. At higher temperatures, the measured activation energy was 32 kcal/mol. The conductivity was increased by the presence of ammonia, showing a first order dependence on the partial pressure of ammonia in the nitrogen carrier gas. The activation energy in the presence of ammonia was 83.7 kJ/mol (20 kcal/mol).

The very first measurements of the electrical conductivity of AP under oxygen, argon, and vacuum produced surprising differences between the three atmospheres which are difficult to explain [152] (see Figure 9).

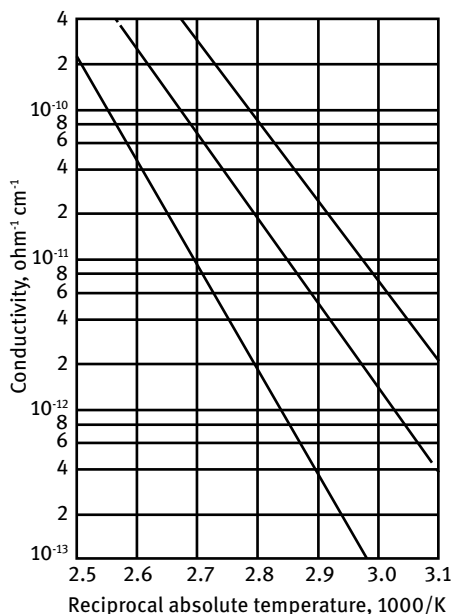


Figure 9: Electrical conductivity of AP. (Republished and modified from [152], with the permission of © 1963 Springer Nature BV; permission conveyed through Copyright Clearance Center.)

Legend:	Pressure (mm Hg)	Atmosphere
—	0.01	Air
- - - -	1.0	Oxygen
- · - · -	1.0	Argon

These measurements were made on pressed AP 12-mm (0.5 inches) diameter grains that had been annealed overnight under vacuum at 383 K (110 °C). Obviously, these data would differ from single crystal data.

Electrical conductivity measurements using an applied DC potential were made on an AP single crystal [153]. An interpretation of the conductivity plot has been tentatively based on the assignment of a Frenkel defect structure to the crystal in the orthorhombic form and a Schottky disorder in the cubic form. The energy of migration of a defect has been calculated to be 0.5 eV and the energies for the formation of an ion defect pair are somewhere around 0.6 and 3.0 eV. A plot of electrical conductivity versus reciprocal absolute temperature contains several linear regions. Changes of the

slopes occur at 365, 444, 528, and 583 K (92, 171, 255, and 310 °C). The break at 528 K is also observed in DTA and is attributed to a phase change.

The electrical conductivity of solid AP was measured over a temperature range from 500 to 600 K [154, 155]. From the variation of the ionic conductivity in an applied electric DC field as a function of temperature, the enthalpy of formation of lattice defects was found to be 100 kJ/mol (24 kcal/mol) and the energy barrier for lattice-defect migration was 83.7 kJ/mol (20 kcal/mol). The relatively high electrical conductivity of AP compared with alkali halides and the marked influence of gaseous ammonia on conductivity are interpreted in terms of a mechanism of charge transfer by proton jump. Most of the electrical conductivity measurements were carried out at temperatures above the polymorphic phase transition temperature (513 K). As shown in Figure 10, the conductivity varied from 10^{-10} to 10^{-7} ohm $^{-1}$ cm $^{-1}$ in temperatures ranges

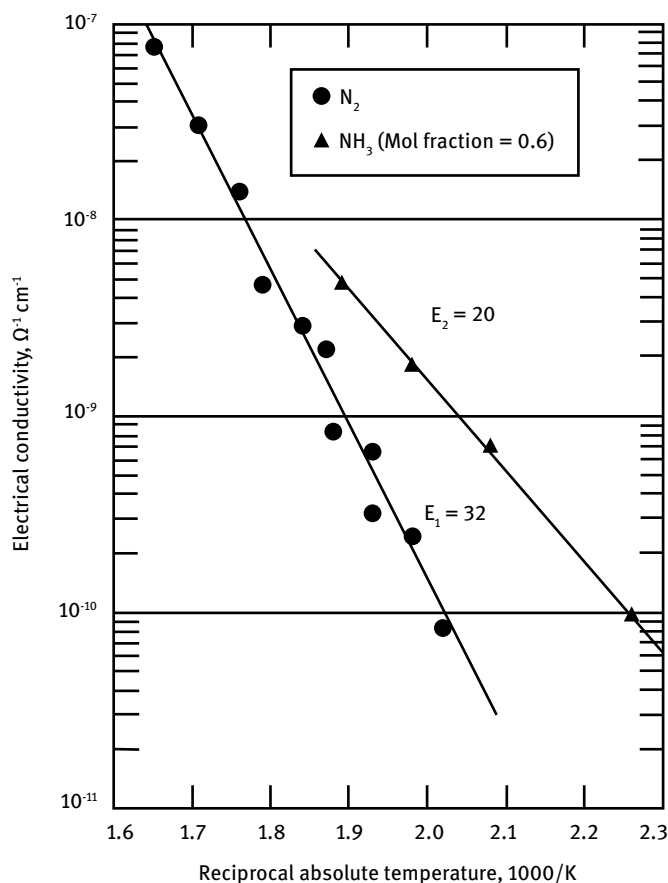


Figure 10: Electrical conductivity of AP as a function of temperature. (Reproduced and modified from [155], in AD-639222.)

between 500 to 600 K. In several experiments, ammonia was added to the carrier gas nitrogen to inhibit sublimation and to explore the influence of ammonia on conductivity. The results indicated that conductivity increased by up to one order of magnitude in the presence of ammonia and depended on the partial pressure of ammonia in the carrier gas (solid line and triangular symbols in Figure 10).

Conductivity data from Wise [155] did not show any discontinuity in going from the orthorhombic to the cubic crystal structure (contrary to observations by other investigators). During the short periods of time required for the measurements, the amount of thermal decomposition and sublimation of AP was found to be small at temperatures less than 575 K, as evaluated from changes in total mass of material.

AP undergoes a phase transformation in the temperature range 513 to 543 K (240 to 270 °C) at atmospheric pressure. The crystal change is from the orthorhombic to the cubic form. Electrical conductivity measurements using an applied d.c. potential, were made on a single crystal of AP. Maycock, Verneker, and Gorzynski [153] studied the electrical conductivity of AP in temperature ranges of 333 to 553 K (60 to 280 °C). An interpretation of the conductivity plot was tentatively based on the assignment of a Frenkel defect structure to the crystal in the orthorhombic form and a Schottky disorder in the cubic form but they did not recognize it as proton conductivity. Their plot of conductivity $\log \sigma$ as a function of reciprocal absolute temperature revealed four distinctly different slopes with breakpoints B, C, D, and E (with the one at 528 K (255 °C) being attributed to the change in crystal structure) (Figure 11).

In the case of AP, the proposed mechanism of protonic charge transport involves movement of a proton from an ammonium ion in the lattice structure to an ammonia molecule located at a lattice vacancy or at an interstitial position [156]. The neutral ammonia molecule thus formed at a lattice site may become the recipient of a proton from an adjacent cation in the lattice as a result, and so on. By this proton transfer charge transport is greatly facilitated compared to that seen with ammonium ion migration via Schottky or Frenkel defects. The measurements carried out with AP single crystals were in satisfactory agreement with those obtained from the pressed pellets of AP. The electrical currents measured for a given applied voltage were not frequency dependent.

Electrical resistance of AP pellets at high pressure with temperature variation revealed no discontinuities [157]. This suggests that no phase transformations occurred. The samples were in the form of disks prepared by compaction of the recrystallized polycrystalline material in a scrupulously cleaned mold at a pressure of 1.238 GPa (180000 psi) at 298 K (25 °C). Hydrostatic pressure on the disk samples was generated with a cubic anvil apparatus. Tantalum foil was the best material for electrical contacts in resistance measurements. This material was found to be inert to AP under the high temperatures and pressures used in this study. Platinum and molybdenum were unsuitable for making resistance measurements. Under the aforementioned conditions, these metals were attacked by AP and produced unreplicable resistance curves.

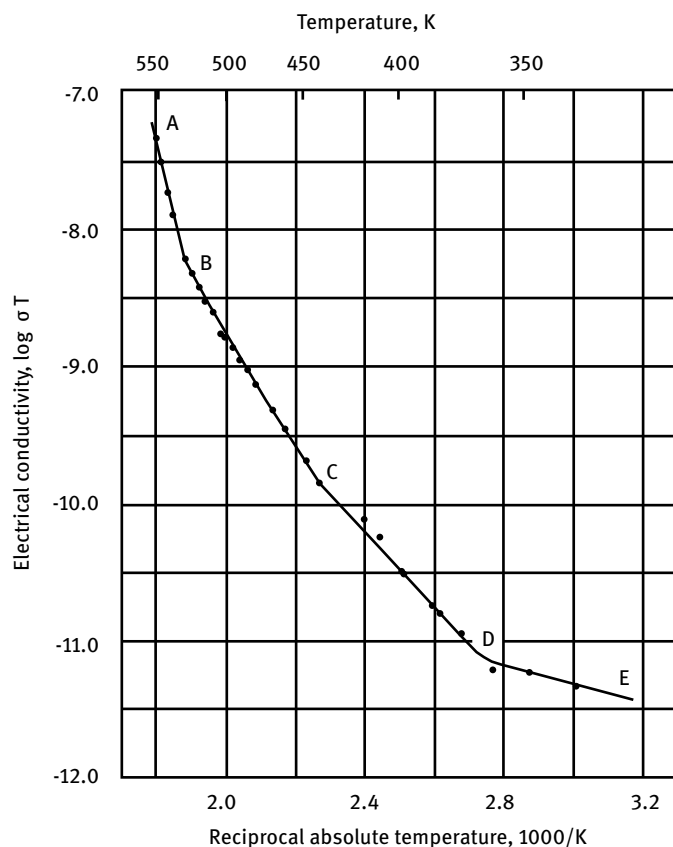


Figure 11: Electrical conductivity of AP as a function of reciprocal absolute temperature. (Reprinted and modified from [153], with permission from © 1967 Elsevier; permission conveyed through RightsLink.)

The plot of electrical resistance against reciprocal temperature at 1, 2, and 3 GPa in Figure 12 shows none of the discontinuities usually associated with phase changes. It is possible that the application of high pressure prevents transformation since there is a 9.7% increase in volume associated with the transition.

The electrical conductivity of AP changed considerably after irradiation by γ -radiation from a ^{60}Co source, 4.5 MeV protons or X-rays (applied doses of radiation were 6.5×10^{-18} to 9.8×10^{-20} eV/g) [158]. The minimum dose that causes a post-radiation change in the conductivity was determined, as was the conductivity versus the dose over a wide range of doses. Charge carriers in NH_4ClO_4 were negative. The post-radiation conductivity was measured at a continuous heating rate of approximately $2^\circ\text{C}/\text{min}$ at 293–443 K (20–170 $^\circ\text{C}$).

The electrical AC conductivity of pressed pellets and single crystal AP was measured over a wide temperature range and the effect of water and ammonia on conduc-

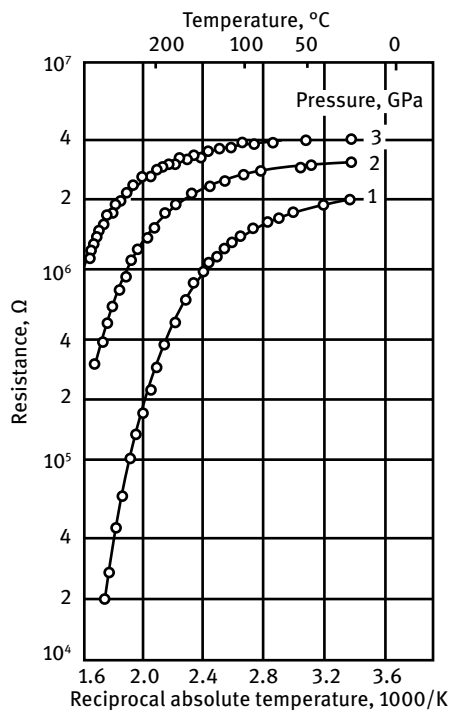


Figure 12: Electrical resistance of AP as function of temperature. (Reproduced and modified from [157], in NASA-TN-D-6013.)

tivity was examined [159]. The results support the theory of a proton transfer mechanism for the electrical conductance over the entire temperature range studied (298 to 443 K). Adsorbed H₂O or NH₃ act as proton traps. Transfer of a proton from an NH₄⁺ ion to H₂O or NH₃ leaves behind a proton hole, which then gets filled from a neighboring NH₄⁺ ion, and so forth. This process requires only a very small activation energy.

The AC electrical conductivity, both of compressed AP pellets and of AP single crystals, was measured at 1591 Hz from room temperature up to incipient decomposition temperatures [160]. The observed effects of annealing and the partial decomposition that follows require considerable caution to be taken when it comes to accepting various defect models for the conductivity that had been previously proposed in the literature.

The electrical conductivity of single crystals of pure AP and of AP doped with Ba²⁺ ions was measured at a frequency of 1591 Hz between room temperature and 533 K (260 °C) [161]. The crystals displayed a marked increase in conductivity at the temperature of the orthorhombic → cubic phase transition. It was suggested that this sudden increase in conductivity is more likely due to secondary effects (specifically, dislocation generation) than to the actual change in crystal structure. The general similarity between the results for pure and doped crystals tends to support a proton transfer mechanism for AC conductivity that does not involve vacancies. However, vacancies may be important in DC conductance mechanisms.

The hypothesis concerning proton conductivity was verified and confirmed experimentally [162] based on measured changes in the conductivity of AP caused by doping with Ba^{2+} and SO_4^{2-} , the effect of water vapor, ammonia, and temperature cycling. The steps of proton conductivity in AP proposed by Jacobs are (i) proton detachment from the ammonium ion, (ii) its transition to a trap, and (iii) transference of thus formed proton vacancy along the cation lattice.

DC electrical conductivity measurements were reported for sulfate-ion-doped and barium-ion-doped AP [163]. The fact that barium-ion-doped AP displayed no marked differences in electrical behavior from that of the pure salt was used as strong justification for the theory (which later was proved to be erroneous) that the conduction process in AP is controlled by interstitial ammonium ions. Measurements of surface conduction revealed no evidence for proton conduction at or near the surface where such a process would be expected to dominate via sublimation. The dominant point defect structure deduced from electrical measurements, i.e., interstitial NH_4^+ ions, would seem to favor electron transfer from ClO_4^- to NH_4^+ ions as the first step in the thermal decomposition of the solid. This is because this mechanism requires the existence of interstitial NH_4^+ ions (notably, however, this mechanism is not accepted by the scientific community).

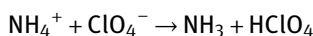
Owen, Thomas, and Williams have made arguments in favor of the ion mechanism of conductivity. DC and AC electrical conductivity measurements were made on AP in compressed disc and single crystal form [164]. The near-identity of the electrical conductivity of AP with that of certain alkali perchlorates was cited as argument against conduction by protons. The non-ohmic behavior of AP single crystals revealed that the [classical] theory of ionic conduction based on the migration and creation of point defects is not adequate to fully describe the observed conduction process. The possibility of various electronic mechanisms, including Schottky emission of electrons from the metallic electrodes with associated carrier injection into the crystal, was also discussed. As none of these mechanisms were entirely satisfactory, the electrical conductivity of AP remained a subject of vigorous discussion for several more years to come in the scientific community.

Owen, Thomas, and Williams [165] argued that the ion mechanism of conductivity in AP can be proven by similarity between the activation energies of conductivity in AP and rubidium perchlorate, with the latter compound exhibiting undoubtedly an ion mechanism of conductivity [165]. The DC conductivity and its variation with temperature of single AP crystals and the crystallographically related RbClO_4 was supposed to prove that detached protons and transient NH_3 species are not involved in the bulk migration of charged carriers in NH_4ClO_4 , contrary to what takes place in NH_4Cl . Simple equality of the data on conductivity activation energies for the two solid salts is evidently insufficient to prove the mechanism of transfer processes. Moreover, the ion mechanism did not explain such features of transfer processes as a strong dependence of conductivity on the composition of gas phases above AP (especially on ammonia enrichment and changes in conductivity during thermal decomposition, etc.). As such,

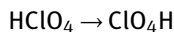
the ion model of conductivity eventually had to be abandoned. This made space for a mechanism based on proton transfer.

On the basis of previous work on the determination of transport numbers, the following mechanism has been proposed for the formation and migration of conducting protons in the AP lattice [166]:

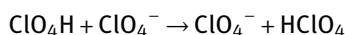
1. Transfer of the proton from cation to anion:



2. Reorientation of the protonated anion:



3. A proton jump to a neighboring anion:



This theory was supported by the fact that the conductivity of AP crystals increased proportionally to the concentration of an added proton donor impurity, such as HSO_4^- ions. At the same time, the activation energy decreased. The mobility of protons in the AP lattice is

$$\mu = 20 \exp\left(-0.81 \frac{\text{eV}}{kT}\right),$$

where μ is the ion mobility in $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and T is the temperature in kelvin. The dielectric relaxation of AP crystals has been investigated. Values of the activation energy for the ion mobility and for the time of dielectric relaxation were very similar. There is a close relationship between electrical conductivity and thermal decomposition of AP. The activation energies for the overall rate of LTD $E_t = 142 \pm 6.7 \text{ kJ/mol}$ ($33.9 \pm 1.6 \text{ kcal/mol}$) and the rate of nucleation growth $E_g = 146 \pm 21 \text{ kJ/mol}$ ($35 \pm 5 \text{ kcal/mol}$) are very similar. Consequently, the processes of nucleation growth determine the total rate of thermal decomposition of AP.

The electrical conductivity of single crystals of AP was measured between 298 and 453 K (25 to 180 °C) [167, 168]. Plots of $\log \sigma T$ versus $1/T$ revealed two linear regions, one from 298 to 373 K (25 to 100 °C) and another from 373 to 453 K (100 to 180 °C). Activation energies for the conduction processes in the low- and high-temperature regions were 0.12 and 1.04 eV, respectively. The electric conduction is a bulk process and not a surface mechanism. Conduction in the low-temperature region is predominantly due to the migration of protons and is sensitive to the concentration of interstitial H_2O molecules which act as proton donor and acceptor sites. In the high-temperature region, conduction is due to migration of NH_4^+ through cation vacancies. The low-temperature activation energy presumably represents the potential barrier for the migration of protons and the high-temperature activation energy the barrier for the migration of NH_4^+ ions. The conductivity is sensitive to the interstitial H_2O concentration in the low-temperature region and to the cation vacancy concentration in the

high-temperature region. Similar measurements were made for doped crystals containing various quantities of Mg^{2+} , Cu^{2+} , Ca^{2+} , Sr^{2+} , or SO_4^{2-} ions. The conductivity of doped crystals was a function of the ion radius of the cation impurity.

The electrical conductivity of AP undergoing thermal decomposition was increased by doping the AP crystals with SO_4^{2-} ions [169]. The enthalpy for migration of defects was 0.8 eV and the enthalpy for formation of defects was 1.2 eV. The defect structure of AP is of the Schottky type and the major charge-carrying ion is ClO_4^- .

A mechanism of proton conductivity was proposed by Hor and Jacobs [170, 171]. The DC electrical conductivity of pure and doped AP single crystals was measured in two different crystal orientations, with the electric field applied perpendicularly to either (001) or (210) planes. The conductivity along the direction of the *c*-axis was found to be lower than that normal to (210) by a factor of five to ten. The DC electrical conductivity of AP was decreased by Pb^{2+} ions but increased by SO_4^{2-} and CrO_4^{2-} ions. The DC conductivity of AP crystals was enhanced by doping with CrO_4^{2-} so that charge transport by defects introduced by the CrO_4^{2-} ions is inferred [172]. Exposure to ammonia enhanced the conductivity of pure AP. A proton conduction mechanism was proposed that takes due regard of the structure of AP. The effect of the various additives on the conductivity are attributed to their influences on the formation of charge-carrying protons.

Electrical conductivity of burning AP pellets with rectangular cross-sections can be used as a diagnostic tool to measure the progression of the flame front. Rectangular slabs (compressed to a density of 1.93 g/cm^3 , dimensions 10×10 , 12×12 , $12 \times L$, $L = 2.7\text{--}8 \text{ mm}$) were mounted between Zn or Pb electrodes attached to opposite faces. The conductivity was recorded as a function of time after the pellet was ignited from one end [173]. For the stable combustion region, an attempt was made to explain the pressure dependence of electrical conductivity in terms of an increase in surface temperature in accordance with the conductivity mechanism of liquid ionic salts.

It was assumed that proton conductivity is realized due to the formation of a complex N_2H_7^+ between the ammonia molecule located in the interstitial space and one of the ammonium ions surrounding it [174].

If the potential across an AP crystal is increased to the point of electrical breakdown, the crystal will ignite and explode [175, 176]. The electric strength of AP depends on the density, the thickness of pressed pellets, the duration (τ) of the pulse front edge of the high voltage, and the dose of γ -pre-irradiation (if any). The electric breakdown of both irradiated and unirradiated pressed AP pellets follows the path of air pores. At $\tau < 2 \mu\text{s}$, the increase in the irradiation dose causes an increase in the electric strength of AP tablets. However, at $\tau > 5 \mu\text{s}$ it causes a decrease in the electric strength of the AP pellets. This may be connected with the AP decomposition during irradiation and the time of the electric pulse action. During the radiation chemical decomposition, the thickness of the near-surface layer and its physical and chemical properties change. This has an effect on the breakdown voltage of AP. With long voltage pulses, the burning out of a through-channel takes place and it ends in electric breakdown of the dielectric.

3.6.1 Other Aspects of Electrical Conductivity

In the preceding sections we were mostly interested in electrical conductivity, how it may be affected by dopants, and how changes in electrical conductivity may relate to changes in crystal structure, thermal stability, and burning rate. A totally different aspect is the use of AP (besides many other ionic salts) as a dopant for proton-conducting solid polymer polyethylene oxide (PEO). The protons in the NH_4^+ ion have sufficient mobility to make polymer films electrically conductive [177–179]. AP is soluble in polyethylene oxide. The NH_4ClO_4 solution in PEO and the solution-cast film made therefrom is sometimes called a [complex] but it is not a complex in the sense of inorganic chemistry. The solubility of NH_4ClO_4 in PEO is limited to a maximum concentration NH_4^+/EO ratio of 0.167 (which is safe because otherwise this would be a rocket propellant). The highest conductivity (approximately $1.05 \times 10^{-5} \text{ S cm}^{-1}$) is for a film with an NH_4^+/EO ratio of 0.02–0.1. Proton-conducting solid polymer electrolytes can be used in novel lightweight ion batteries.

3.7 Permittivity (Dielectric Constant) of Ammonium Perchlorate

The permittivity (dielectric constant) of AP was measured in a frequency range between 100 to 10000 Hz and is equal to 5.1 ± 0.3 [180]. It was shown that the values of conductivity of AP obtained directly from these measurements coincide with those calculated using the tangent of the loss angle.

AP, AN, and organic explosives can be ignited by heating with microwaves at $2450 \pm 50 \text{ MHz}$ [181].

3.8 Magnetic Properties of Ammonium Perchlorate

Nuclear magnetic resonance (NMR) spectra of AP revealed that both the ammonium and perchlorate ions can rotate freely [182]. The second moments of the proton resonance absorption line in polycrystalline NH_4ClO_4 were found to be $1.27 \pm 0.02 \text{ gauss}^2$ at 70 K and $1.18 \pm 0.01 \text{ gauss}^2$ at 298 K. These results were interpreted in terms of reorientation of the ammonium ion using random or nearly random axes. Spin-lattice relaxation times for polycrystalline NH_4ClO_4 have been measured as between 77 and 298 K by a progressive saturation method. These relaxation times are consistent with a barrier hindering reorientation of $2.0 \pm 0.6 \text{ kcal}$. Both ions were found to rotate in the cubic structure while only ammonium does in the orthorhombic one. The molar magnetic susceptibility of AP is 46.3×10^6 .

The proton spin-lattice relaxation, second moment, and magnetization of NH_4ClO_4 were investigated between 1.5 and 100 K using pulse NMR techniques [183]. The data was interpreted with reference to the possible hindered rotor levels of the NH_4^+ ion.

Nuclear magnetic resonance spectra of AP crystals between 1.3 and 50 K and relaxation experiments revealed that an increase in the proton second moment from its high-temperature value of $\sim 1.18 \text{ G}^2$ to the value of 4.30 G^2 below 4.2 K was associated with a characteristic activation energy of $\sim 4 \times 10^{-21} \text{ J/molecule}$ ($\sim 0.6 \text{ kcal/mol}$) [184]. No evidence could be found for nuclear spin conversion between the symmetry species of the ammonium ion from measurements of the static proton magnetic susceptibility above 1.3 K. Measurements of the proton relaxation times T_1 and $T_{1\rho}$ agreed with previous findings from others regarding NH_4ClO_4 and were similar to observations on other ammonium compounds having low reorientation barriers.

The spin-lattice relaxation time of the dipolar energy T_{1D} and the characteristic time T_{SD} for the spin diffusion between NH_4^+ ions of different librational symmetry species were measured as functions of temperature and crystal orientation in NH_4ClO_4 [185]. The graph displaying the T_{1D} versus temperature function showed shoulders around 44 and 28 K related to the librational tunneling frequency and the proton resonance frequency, respectively. A broad minimum around 10 K is believed to correspond to the linewidth transition. The characteristic time T_{SD} is less than 0.5 ms above 4 K, showing that the ammonium protons in different symmetry species have, at least locally, a common spin temperature during the magnetization recovery.

A study of the spin-lattice relaxation of protons in NH_4ClO_4 at low temperatures revealed that the NH_4 librational tunneling determines the spin-librational wave functions, which are derived first [186]. The dominant transition rates related to the magnetic dipolar interaction between the NH_4 protons reproduce the angular dependence of the proton relaxation time well. When all the transition rates were taken into account, both the temperature and frequency dependence of the relaxation rate aligned with existing experimental data for a powder sample of AP.

Measurements of an AP sample in a DC superconducting quantum interference device in zero field at 4.2 K revealed unexpected magnetic moment oscillations at 1.5 kHz [187]. A computation of the magnetic fields suggested that the proton nuclear magnetic resonance may explain the measured resonance (considering reorientation of the ammonium group by quantum tunneling of protons and a magnetic proton dipole-dipole intermolecular interaction model).

3.9 Crystal Morphology and Mechanical Properties of Ammonium Perchlorate Single Crystals

The crystal faces on AP single crystals behave quite differently when it comes to thermal decomposition or etching with a solvent. Some of the etch pits on the cleavage surfaces were found to be distributed randomly while others were clearly aligned in specific crystal directions. Strained crystals exhibited slip bands. Moreover, the various possible systems were deduced by computing from the crystal structure, the most

likely low-index slip planes, and slip directions also, which are consistent with the observed etch pit alignments and slip bands.

Cleavage and growth faces of AP single crystals have been examined by high-power interference-contrast microscopy [188]. From the observed directions of etch-pit arrays on three crystallographically distinct faces of the orthorhombic form of AP, and from the nature of the slip bands on deliberately deformed crystals also, the nature of the dislocations present have been clarified. All the observed alignments and bands on the various faces may be accounted for in terms of dislocation movement on $(20\bar{1})$, (201) , (401) , $(40\bar{1})$, (110) , $(\bar{1}10)$, (010) , and (001) planes. Preferential evaporation occurred from dislocation cores emergent at (001) faces.

The formation of etch pits on the cleavage surfaces of AP single crystals has been studied by optical and electron microscopy [189]. Ethyl and butyl alcohols and their mixtures were the most satisfactory etchants. Well-defined etch pits could not be detected on the c face, which dissolved very rapidly. Numerous round etch pits then appeared followed by elongated and roughly parallel curved channels which finally became connected. This left nearly circular flat-topped 'hills' with clearly delineated terraced sides. However, when the crystals were etched in butyl alcohol, well-defined rectangular pits were formed on the m face, with either a 3:1 or 4:1 length-to-width ratio. They resembled elongated stepped or terraced pyramids and were always orientated with their long sides parallel to the $[001]$ direction.

Surprisingly, co-crystallizing AP whiskers with potassium permanganate additions not only increases the burning rate but also improves mechanical strength and elasticity of such crystals [190]. Such whiskers were grown up to a length of 50 mm in humid conditions promoting creep.

The laser-Brillouin scattering method was used for the determination of the elastic and elasto-optic constants of AP crystals at room temperature [191]. One of its advantages over the ultrasonic technique is that the usual boundary conditions required by the latter are relaxed. However, it is suitable only for transparent crystals. The elastic and elasto-optic constants may be used to predict the dynamical behavior of ions and molecules in a crystal. The polarized Brillouin scattering spectra yielded nine elastic constants as well as the absolute value of nine elasto-optic constants.

The fracturing behavior of AP is of interest for the grinding of AP powder and the friction and impact sensitivity of anything containing AP. Diamond pyramid (Vickers) micro-indentation hardness testing was used to examine the plastic deformation and cracking behaviors of single crystal AP. Using polarized light microscopy, it was determined that the strain field caused by edge dislocations surrounding the hardness impression was rather far-reaching. In a separate series of tests, single crystals placed in a mineral oil bath were shocked by exploding a detonator. High-speed photography was used to observe the crystal response to the shock wave and samples were recovered for quantitative chemical analysis of decomposition products [192–194]. Traces of slip planes and cracks formed at hardness indentations on (210) and (001) surfaces were examined under the microscope. In the vicinity of the diamond impact, residual

strains were found to extend beyond crack tips. Similar residual strains exist in freshly ground AP and may heal with time.

An ultra-high-vacuum (UHV) atomic force microscope (AFM) was used to study AP surfaces at room temperature and atmospheric pressure down to 10^{-9} mm Hg vacuum [195, 196]. Because AP is hygroscopic, special precautions in sample handling were necessary. Atomic force microscopy studies of the (210) plane of AP revealed several interesting surface artifacts induced by the scanning tip, although the applied force was less than 30 nN. Nano-scale surface sensitization may have been caused by the scanning tip during repeated raster scanning while tip-sample contact was maintained. A roughening pattern may have been formed when the surface was exposed to moisture. Identification of features was difficult due to the large unit cell of this salt (40 atoms / unit cell). AP crystals were immersed in mineral oil with the (210) surface 6.0 mm from a detonator. When fired, the detonator delivered a 24.4-kbar shock, corresponding to the reaction threshold for that crystal orientation. High-speed photographs revealed luminosity near some of the hardness impressions. The photographs also revealed the occurrence of the same slip deformation identified previously from hardness testing. The shocked crystal was recovered intact and cleaved twice through Vickers impressions on the (001) and shock-entry (210) surfaces, allowing spatial chemical analysis of the interior regions of the crystal using X-ray photoelectron spectroscopy (XPS). Along these freshly cleaved surfaces, the XPS results revealed enhanced perchlorate decomposition as a result of the impressions. The greatest decomposition was not immediately adjacent to the impressions but near the tips of cracks and along slip planes that extended from these impressions by at least several millimeters [197].

3.10 Thermodynamic Properties of Ammonium Perchlorate

The heat capacity, enthalpy of formation, and entropy of formation can be calculated from the polynomial Shomate equations based on data curve fitted by NIST and posted on the Webbook website:

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + \frac{E}{\tau^2}$$

$$H^\circ - H^\circ_{298.15} = A\tau + B\frac{\tau^2}{2} + C\frac{\tau^3}{3} + D\frac{\tau^4}{4} - \frac{E}{\tau} + F - H$$

$$S^\circ = A \ln(\tau) + B\tau + C\frac{\tau^2}{2} + D\frac{\tau^3}{3} - E/(2\tau^2) + G$$

where A through H are constants, C_p = heat capacity in $\text{J mol}^{-1} \text{K}^{-1}$, H° = standard enthalpy in kJ/mol, S° = standard entropy in $\text{J mol}^{-1} \text{K}^{-1}$, and τ = temperature K/1000. The constants A through H are listed in Table 5 for two temperature regimes below and above the phase change at 513 K.

Table 5: Shomate equation constants for AP.

Temperature range, K	298–513	513–1000
A	49.81390	225.2150
B	297.3000	–203.0560
C	–186.1620	402.2310
D	128.3380	–137.7330
E	0.245965	–7.484290
F	–321.6170	–373.0730
G	164.3460	476.7260
H	–295.7670	–295.7670

Data source: [198].

3.10.1 Heat Capacity of AP

Heat capacity data used by [151] were derived from the thermal diffusivity α of AP for the range from 293 to 487 K (20 to 214 °C) and can be described by the linear equation

$$C_p = 0.251 + 4.076 \times 10^{-4}t,$$

where C_p is the heat capacity in $\text{cal g}^{-1} \text{°C}^{-1}$ and t is the temperature in °C. This calculates into a heat capacity of $1.093 \text{ J g}^{-1} \text{K}^{-1} = 0.261 \text{ cal g}^{-1} \text{°C}^{-1}$ at 298 K. The same authors obtained and listed similar data for a wide range of other oxidizers, binders, and solid propellants. The heat capacity of AP has been measured repeatedly but the measured data does not always agree. Average data in existing research for temperatures below 513 K are $1.29 \text{ J g}^{-1} \text{K}^{-1}$ ($0.309 \text{ cal g}^{-1} \text{°C}^{-1}$) and $1.527 \text{ J g}^{-1} \text{K}^{-1}$ ($0.365 \text{ cal g}^{-1} \text{°C}^{-1}$) for temperatures above 513 K.

The heat capacity of AP was determined by adiabatic calorimetry from 5–350 K and found to be of simple sigmate character without thermal anomalies. The heat capacity (C_p), entropy (S°), enthalpy function $(H^\circ - H^\circ_0)/T$, and Gibbs energy function $(G^\circ - G^\circ_0)/T$ evaluated at 298.15 K from these data were 30.61, 44.02, 20.24, and $-23.78 \text{ cal mol}^{-1} \text{K}^{-1}$, respectively [199]. The heat capacity of AP and two other perchlorates is shown in Figure 13. This figure combines two curves in one chart. The lower right portion of this split chart is an enlarged view of the lower left corner of the chart.

The heat capacity of AP is a function of the degree of freedom of free rotation of the ammonium ion and changes at the point of phase transition. There is a very low rotational barrier of the NH_4 groups in NH_4ClO_4 that shows up in NMR spectra [200].

The specific heats of AP, RDX, and HMX were measured at room temperature all the way up to the decomposition temperature region by use of a laser flash method [149]. The specific heats of AP, RDX, and HMX as a function of temperature are graphed in Figure 14.

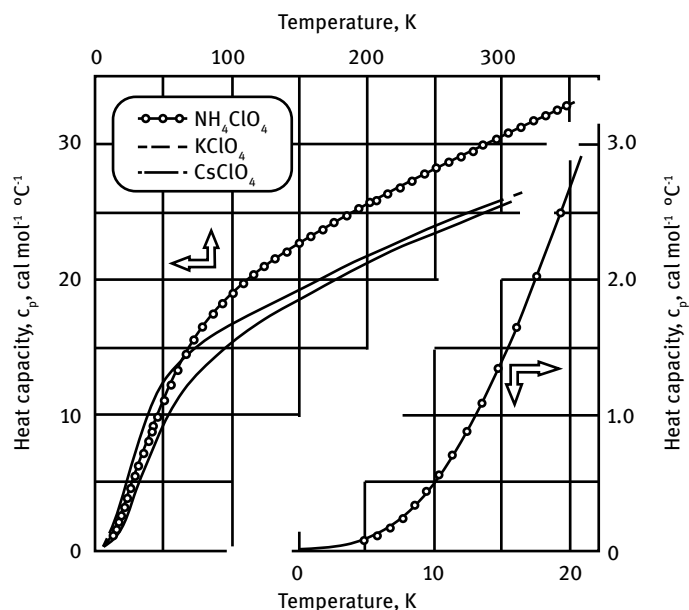


Figure 13: Heat capacities of NH_4ClO_4 , KClO_4 , and CsClO_4 . (Republished and modified from [199], with the permission of © 1969 American Institute of Physics; permission conveyed through Copyright Clearance Center, Inc.)

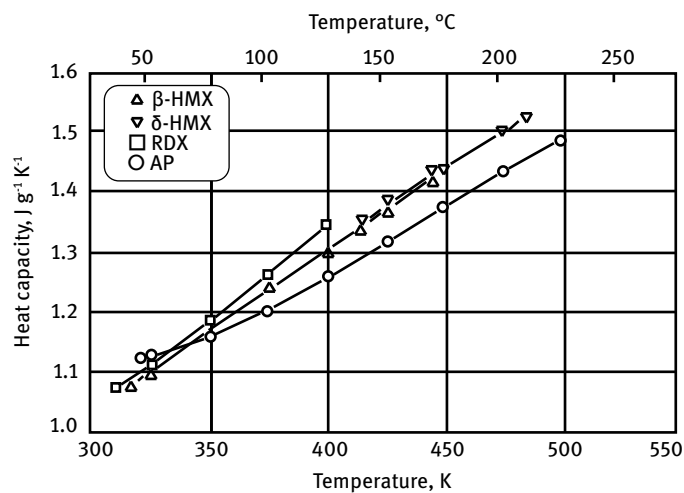


Figure 14: Heat capacities of AP, RDX, and HMX. (Republished and modified from [149], with permission from © 1985 Old City Publishing, granted by Dr. Ian Mellanby 10 May 2021.)

Other sources for heat capacity produced C_p at 298 K = 128.072 J mol⁻¹ K⁻¹ [201]. The equation for AP in the NIST Chemistry WebBook gives a heat capacity of 128.04 J mol⁻¹ K⁻¹ at 298 K [202].

3.10.2 Heat of Fusion and of Sublimation of AP

A heat of melting of 251 J/g (60 cal/g) and a melting point of 820 K were used for calculations of surface burning processes in AP [203]. The heat of sublimation of AP can be calculated from the vapor pressure curve and is estimated to be 243 kJ/mol (58 ± 2 kcal/mol) [128, 129]. The equilibrium gas pressure over the AP solid surface was measured. The temperature dependence of gases over solid AP allows the calculation of a dissociation enthalpy ($H_{\text{diss}} = 240.6 \text{ kJ/mol} = 57.5 \text{ kcal/mol}$). H_{diss} of a salt can also be calculated from the enthalpies of formation from salt and from gaseous bases and acids. This calculation for AP gives 241.8 kJ/mol (57.8 kcal/mol), which is in good agreement with results obtained from the surface temperature-pressure dependence. It also conforms with mechanisms of the gasification of salt through dissociation reactions. Values of enthalpy from 238 to 251 kJ/mol (57–60 kcal/mol) for AP dissociation have been obtained in many other studies. One must remember that one molecule of the salt produces two molecules of gas rather than one. The AP dissociation enthalpy so often has been erroneously taken as the activation energy of AP decomposition, with dissociation processes described as a reaction characterized by kinetic parameters.

3.10.3 Enthalpy of Formation of AP

The enthalpies of formation of the orthorhombic (low temperature) and cubic (high temperature) modification of AP differ by 9.6 kJ/mol (2.3 kcal/mol) [109]. The enthalpy of transition measured in this way is +9.6 kJ/mol (2.3 ± 0.2 kcal/mol). Other sources give the phase change enthalpy as 11.3 kJ/mol (2.7 kcal/mol) [204, 205]. The transition from orthorhombic to cubic is endothermic. The energy required for converting orthorhombic phase AP to cubic phase AP is only 9.6 kJ/mol (2.3 kcal/mol). If the modification is not stated for thermodynamic data at 298 K, one may assume that data is for the orthorhombic modification. Literature data for the enthalpy of formation of AP is summarized in Table 6.

The most reliable thermophysical data are assumed to be those posted at the NIST WebBook website. However, the enthalpy of formation recommended by NIST is $\Delta_f H^\circ_{\text{solid}} = -295.77 \text{ kJ/mol}$ based on fairly old data from Chase [198] that was last reviewed in December 1962. Obviously, these numbers require a thorough re-examination in view of more recent data.

The enthalpy of dissolution of AP was measured on a precise swinging solution calorimeter [210]. The most reliable value of the formation enthalpy of AP was derived on the basis of the selected value of the anion formation enthalpy and measured value of the salt dissolution enthalpy.

Table 6: Literature data for the standard enthalpy of formation of solid AP.

Enthalpy of formation ΔH_{298}^f				References
SI Units		Other units		
kJ/mol	kJ/kg	kcal/mol	cal/g	
−293.7	−2499.8	−70.21	−597.5	[2]
−294.4	−2505.8	−70.36	−598.9	[15]
−295.3	−2513.4	−70.58	−600.7	[199]
−295.767	−2517.4	−70.69	−601.7	[206]
−295.767	−2517.4	−70.69	−601.7	[201]
−295.767	−2517.4	−70.69	−601.7	[198]
−295.77	−2517.4	−70.58	−601.7	[202]
−295.8	−2517.4	−70.70	−601.7	[207]
−295.9	−2518.5	−70.73	−601.9	[208]
−295.98 ± 1.35	−2519.2	−70.74 ± 0.32	−602.1	[209]

AP $M = 117.489 \text{ g/mol} = 8.5114 \text{ mol/kg}$.

Heat capacity, enthalpy of formation and free energy of formation AP and ADN were predicted using DFT calculations but the agreement with experimental data was only very poor, with predicted heat capacity much higher than measured values [211]. The data indicated that ADN decomposes more readily than AP.

The enthalpy of formation of solid NH_4ClO_3 , an unstable chemical and a common contaminant in AP, is $-272 \text{ kJ/mol} = -65.1 \text{ kcal/mol}$.

3.10.4 Entropy of Formation of AP

Literature data for the standard entropy of formation of solid AP are listed in Table 7.

Table 7: Literature data for the standard entropy of formation of solid AP.

Entropy of formation ΔS_{298}^f		References
$\text{J mol}^{-1} \text{K}^{-1}$	$\text{cal mol}^{-1} \text{°C}^{-1}$	
184.18		[202]
184.180		[201]

The ionic entropy of the ClO_4^- ion can be derived from the enthalpy of solution of NH_4ClO_4 (0.80 kcal/mol), the mean activity coefficient of NH_4ClO_4 ($\gamma = 0.394$), the solubility of NH_4ClO_4 ($m = 2.12$), and the ionic entropy of $\{\text{NH}_4\}^+$ ion $S_0^{298}[\text{NH}_4^+(\text{aq})] = 27.1 \text{ cal mol}^{-1} \text{K}^{-1}$. The entropy of solution of NH_4ClO_4 is $26.1 \text{ cal mol}^{-1} \text{K}^{-1}$ from the above data. This leads to a standard ionic entropy for aqueous ClO_4^- ion of $43.0 \pm 0.2 \text{ cal mol}^{-1} \text{K}^{-1}$ [199]. Wagman et al. reported $43.5 \text{ cal mol}^{-1} \text{K}^{-1}$ for this property [212].

3.11 Molecular Structure of Ammonium Perchlorate

It was suggested that, on the basis of qualitative changes in unindexed powder diffractometer patterns, both NH_4ClO_4 and isostructural NH_4BF_4 should undergo polymorphic transitions near 83 K. Neither the heat capacity work of Westrum and Justice [199] on NH_4ClO_4 nor that of others supported this contention.

3.11.1 Crystal Structure of AP

AP crystallizes in an orthorhombic $Pna2_1$ space group and contains four molecules per unit cell. Each perchlorate ion is surrounded by seven ammonium ions and vice-versa.

Early XRD studies suggested an ordered hydrogen-bonded arrangement of the ions but this arrangement was not consistent with the overwhelming evidence from IR [213], electron proton resonance (EPR) [214], NMR [182], slow neutron data [215], and neutron diffraction data [216]. This suggested free rotation of the ammonium ion at room temperature. An IR study by Ibers [182] indicated reorientation of ions in AP at temperatures as low as 77 K with an activation energy of 2.0 ± 0.60 kcal/mol. Ibers predicted a line-width transition between 45 K and 55 K. However, experiments have been performed with temperatures as low as 20 K with no evidence of a line-width transition. A value of 0.55 ± 0.05 kcal/mol was obtained for the potential barrier of reorientation from the hyperfine splitting in the EPR spectrum, based on examining the ion radical $\cdot\text{NH}_3^+$ in single crystals of AP at temperatures of 75 K to 293 K.

A computer simulation of crystal defects in AP was essentially a modification of an earlier crystal defect program [217, 218]. This program had evolved gradually over a period of ten years. It was initially developed for determining defect properties in alkali halides with NaCl type structures. Later, it was extended to include the complex ion cubic crystal modification of AP. Based on the numerical results, a vacancy migration turnstile mechanism was proposed to account for the DC electrical conductivity of AP. By and large, these theoretical calculations agreed with the experimental work of Maycock, i.e., the activation energies for migration of a vacancy and the energy of formation of the Schottky defect were found to be 20% lower than those reported by Maycock.

A neutron diffraction study of AP concluded that orientation of ammonium ion is a highly disordered one, with the ion undergoing a free or nearly free rotation [216]. A rotating ammonium ion is also supported using IR spectra [213], heat capacity studies between five and 350 K [199], cold neutron scattering cross section studies [215, 219, 220], and NMR studies at low temperatures [182]. The second moments of the proton resonance absorption line in polycrystalline NH_4ClO_4 were found to be 1.27 ± 0.02 gauss² at 70 K and 1.18 ± 0.01 gauss² at 298 K. These results were interpreted in terms of reorientation of the ammonium ion around random or nearly random axes. Spin-lattice relaxation times for polycrystalline NH_4ClO_4 were measured between 77 and 298 K by the progressive saturation method. These relaxation times indicated a reorientation barrier of 8.368 ± 2.5 kJ (2.0 ± 0.6 kcal).

The crystal structure of AP was studied at 298, 78, and 10 K by means of neutron diffraction [221]. The NH_4ClO_4 crystal has an orthorhombic unit cell, space group *Pnma*, with four formula units per cell at all three temperatures. The unit cell dimensions at 298 K are $a = 9.20$, $b = 5.82$, $c = 7.45$ Å, as determined previously; at 78 K, $a = 9.02$, $b = 5.85$, $c = 7.39$ Å; and $a = 8.94$, $b = 5.89$, $c = 7.30$ for 10 K. Initial positions of H atoms were determined from a difference Fourier map of the room temperature data. Each ammonium group is surrounded by ten oxygen atoms with short N—O distances ranging from 2.9 to 3.25 Å. The ClO_4^- group and NH_4^+ group each have essentially ideal tetrahedral structure. They are linked together by N—H...O type hydrogen bonds; one for each hydrogen to form a three-dimensional network. Examination of the rms amplitudes for libration and the hydrogen bonding of the NH_4^+ ions indicated that two of the four hydrogens were bound identically, one hydrogen was bound more rigidly, and the fourth more weakly. These results suggested that the rotational motions of the ammoniums are quite complex even at 10 K.

The crystal structure of AP had been assigned to the orthorhombic space group *Pnma*. With the availability of improved instruments and computing capability, the structure of AP has been re-examined several times and earlier discrepancies were resolved. Since only two-dimensional X-ray or neutron diffraction data had been used until 1975 for the crystal structure determination of AP, a redetermination of AP structure by three-dimensional X-ray counter data produced the following cell parameters: $a = 9.227$, $b = 7.454$, $c = 5.819$ Å (24 °C), $Z = 4$, space group *Pna2*₁ [222]. The previously proposed space group, *Pnma* (which was used for the two-dimensional analysis), did not allow a three-dimensional refinement. The ammonium ion does not have a completely free rotation.

The structure of AP at 298 K has been refined, starting with the same XRD data of Peyronel and Pignedoli [222], although it took a different mathematical approach [223]. A satisfactory refinement was achieved in space group *Pnma*, which was in agreement with earlier observations at low temperatures. It clearly demonstrated that *Pnma* is the correct space group for room-temperature NH_4ClO_4 , just as it is at lower temperatures. The observed bond lengths, Cl—O(1) = 1.432, Cl—O(2) = 1.424, Cl—O(3) = 1.442 Å, are (within one standard deviation) the same as those of Peyronel and Pignedoli [222]. This was obtained with the positions of the ammonium ions held fixed.

The orthorhombic phase of AP was investigated by XRD below room temperature [224]. The temperature dependence of lattice constants revealed anomalous behavior around 200 and 100 K. The length of the *b*-axis steeply increased as temperature decreased, especially when below 100 K. The crystal structure in the orthorhombic phase was then refined at 300, 250, 200, 150, 120, 100, and 80 K. The parameters essentially agreed with the results of Choi, Prask, and Prince [221].

The effect of pressure up to 5.6 GPa on the structure of AP was investigated at room temperature using XRD, IR, and Raman spectroscopy [225, 226]. New peaks were also observed in the XRD pattern above 0.9 GPa and could not be indexed to the orthorhombic structure. The intensities of these new peaks increased up to 2.9 GPa. However,

when above 3.0 GPa all of the peaks observed at lower pressures disappeared completely and a new set of peaks appeared that persisted up to 5.6 GPa, which was the limit of the study.

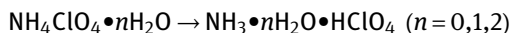
Two phase transitions were observed. Under hydrostatic conditions, the first transition started at about 0.9 GPa, with the appearance of a few new diffraction peaks and a discontinuity in the pressure-induced shifts of certain Raman frequencies. This transition is most likely a molecular change in AP due to the [freezing] of freely rotating NH_4 units, which is similar to effects seen at low temperatures. The second transition started at 2.9 GPa with a drop in diffraction intensity followed by a new pattern of diffraction peaks by 3.0 GPa. This transition was also characterized by another discontinuity in the Raman shifts and the emergence of two new Raman modes. The phase above 3.0 GPa was stable to 5.6 GPa. The P - V data to 0.9 GPa obtained from XRD measurements were used to calculate a bulk modulus of 15.2 ± 0.3 GPa for the ambient-pressure phase of AP (see [227]).

3.11.2 Computational Chemistry of the Molecular Structure of AP

The electronic structure, vibrational properties, absorption spectra, and thermodynamic properties of crystalline AP and ADN were compared using DFT in the local density approximation [211]. The results revealed that the p states for the two solids play a very important role in their chemical reactions. From the low frequency to high frequency region, ADN has more degrees of freedom of motion modes for the vibrational frequencies than AP. The absorption spectra of AP and ADN display a few strong bands in the fundamental absorption region. The thermodynamic properties revealed that ADN is easier to decompose than AP as the temperature increases. Calculated AP crystal lattice parameters were very close to those measured by Peyronel and Pignedoli [222].

AP that is subjected to sudden compression may detonate. The compressibility and phase change behavior of AP crystals at very high pressures are, therefore, important for modeling detonation processes in AP. DFT can be used to predict the hydrostatic compression of crystalline AP and the compressibility of AP crystals at very high pressures [228].

The structures and energy levels of AP and different aggregates formed by AP with one or two water molecules in both gaseous and condensed phases were calculated at the B3LYP/6-311G(3df,2p) level using a polarizable continuum model (PCM) method [229]. The results revealed that, for the gaseous dissociation processes, the main dissociation channel is



with dissociation energies of 61.5, 78.7, and 82 kJ/mol (14.7, 18.8, and 19.6 kcal/mol), respectively. The formation of $n\text{H}_2\text{O} \bullet \text{ClO}_4 \bullet \text{NH}_4$ ($n = 0, 1, 2$) ion pairs is not favored energetically because the dissociation energies are 462, 479, and 489 kJ/mol (110.5, 114.4,

and 116.9 kcal/mol) for $n = 0, 1, 2$, respectively. In aqueous solution, AP and its aggregates mainly dissociate into ion pairs, reflecting the important effect of solvation. The solvation free energy predicted with PCM for the isolated AP (−30.0 kcal/mol) is consistent with the average values determined from the aggregates of AP with one H₂O (−30.2 kcal/mol) and 2H₂O (−30.0 kcal/mol), respectively. These values indicate that the PCM method can accurately predict effects of hydrogen bonding between the solvent (H₂O) and the solvate (NH₄ClO₄) on the solvation energies.

The crystal structure of AP was computed using a DFT method [230]. The energy band structure, density of energy states, electron population, and charge density of AP were analyzed and demonstrated that AP is an insulator with a band gap of 5.517 eV. The conduction bands of AP are mainly composed of O-2p and Cl-3p orbits and the valence bands are composed of atomic (ionic) orbitals in the crystal. The structure of AP is that of a typical ionic crystal. Weak hydrogen bonds N—H···O exist in the crystal.

The optical properties of NH₄ClO₄ crystals, including dielectric function, refractive coefficients, absorption spectra, and reflection spectra were calculated by a first-principle method based on DFT [231]. The relationship between peaks in the dielectric function curves and the inter-bands transitions in the band structures were analyzed. Computational results demonstrated that the static dielectric function should be 1.10, the static reflectivity n_0 should be 1.05, and the maximum absorption coefficient should be $1.91 \times 10^5 \text{ cm}^{-1}$ corresponding to a peak energy of 10.88 eV, in agreement with existing experimental results. The response function explains electron density distribution throughout the AP crystal lattice [232].

3.12 Optical Properties of Ammonium Perchlorate

3.12.1 IR Spectra of AP

An IR, Raman, and XRD study of NH₄ClO₄ was conducted in the temperature ranges 300 to 17 K, 300 to 130 K, and 300 to 120 K, respectively. This was to determine the effects of low temperature on the rotational behavior of the ammonium ion, to search for evidence of hydrogen bonding, and to determine whether low-temperature phase transitions exist between 300 and 120 K [233]. The infrared studies also included the deuterated salt. The ammonium ion rotated with relatively little hindrance in NH₄ClO₄ at room temperature. Changes in the IR spectra, as well as intensity measurements of the vibrational bands indicated anomalous behavior in the region 100 to 110 K as well as 17 to 50 K (see Figure 15).

Infrared, Raman, and XRD data conclusively demonstrated that no phase change occurs in AP from 300 to 120 K. A phase change at 100 to 110 K, corresponding to the 173 K change in the isomorphous NH₄BF₄ salt, was tentatively proposed but could not be proven. Some evidence of distortion of the ammonium tetrahedron at temperatures below 50 K was found. There were strong indications of hydrogen bonding below 20 K and weaker hydrogen bonding between 50 and 20 K.

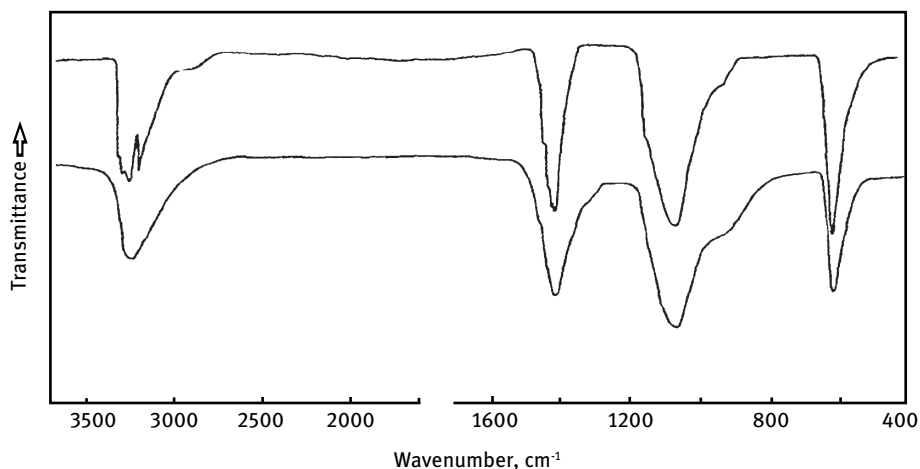


Figure 15: Infrared spectrum of NH_4ClO_4 at room temperature (bottom) and at 17 K (top). (Republished and modified from [233], with the permission of © 1972 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center).

There was no source given for the IR spectrum posted on the NIST Webbook website but we are presenting it here nevertheless in the hope that we can find a better quality spectrum of more recent provenience. This spectrum has contamination due to oil around 2900 and 1380 cm^{-1} and is marked with an asterisk in Figure 16.

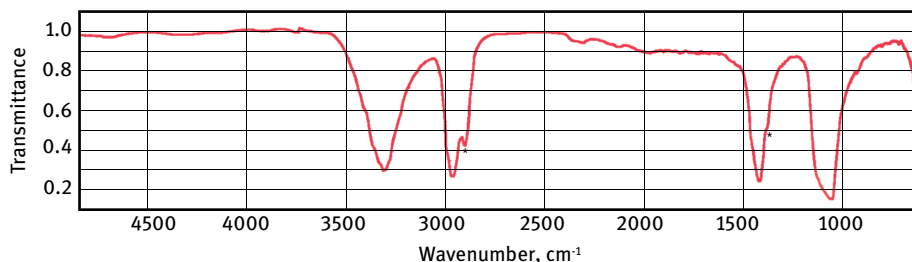


Figure 16: Infrared spectrum of NH_4ClO_4 . (Reproduced and modified with permission from [234].)

The spectral transmittance of large single crystals of normal AP and deuterated AP grown from aqueous solutions has been measured in the ultraviolet (UV), visible, near-IR, and IR regions of the spectrum [235]. The crystals were transparent in the visible region and throughout much of the UV region. The absorption edge of both the deuterated and undeuterated crystals was in the UV region near 200 nm. There were strong absorption bands in the near-IR and IR regions. The absorption was so

strong that the instrument bottomed out and no details of the absorption bands were revealed. From the intensity of an absorption band at $1.55\ \mu\text{m}$, the mol-percent ^1H in the deuterated AP crystals was estimated to be 1.1%.

An infrared study by Brill and Goetz [121] noted the disappearance of the band at $939\ \text{cm}^{-1}$ associated with the ν_1 mode of the ClO_4^- group at pressures between 1.0–2.4 Gpa. They tentatively assigned this to the orthorhombic to cubic transition.

Molecular motion of the ammonium ion has been investigated by IR spectroscopy in a series of ammonium salts which were known to be weakly hydrogen-bonded. Infrared spectra of the isotopically isolated NH_3D^+ ion in NH_4ClO_4 and NH_4BF_4 were recorded as being between 295 and 22 K [236]. The absorption in the N–D stretching region of the NH_3D^+ ion consisted of two broad bands centered at 2425 and $2399\ \text{cm}^{-1}$ with approximate half-widths of 20 and $30\ \text{cm}^{-1}$, respectively, at 22 K. The broadness of the bands has been attributed to rapid reorientation of the NH_3D^+ ammonium ions and the consequent short lifetime of the upper vibrational state. The band broadening persists down to the lowest temperature. No significant lifetime broadening has been found in the spectra of the NH_3D^+ ion in other salts.

The IR spectra of the ND-stretching bands of dilute NH_3D^+ in NH_4ClO_4 measured over the temperature range from 3 K to room temperature revealed that, at low temperatures, the NH_3D^+ is preferentially oriented [237]. The extent of the orientation at a given temperature depends on the deuterium concentration, and thus on the concentration of NH_3D^+ ions. As the temperature is raised, the various N–D stretching bands collapse due to a variety of dephasing processes.

The isotope effect, which is visible if one or more hydrogens are replaced by deuterium, depends on the location of the N–D bond in the crystal lattice. The N–D stretching region of the IR of deuterium-doped NH_4ClO_4 indicates the existence of subtle energy differences [238]. The N–H spectrum in ND_4ClO_4 was also examined. Comparison of the two sets of spectra led to an explanation of the small energy differences as due to tunneling among the distinct positions the NX_3Y^+ ions can assume in the lattice. The distinct orientations of NH_3D^+ and the ND_3H^+ ions have slightly different energies and this, along with the impact of tunneling, accounts for all the eight observed lines.

IR spectra of AP was predicted using DFT calculations in the local density approximation and was compared to experimental spectra as well as those obtained for ADN [211]. The lattice mode spectra of AP and ADN display similar features in the region $28\text{--}220\ \text{cm}^{-1}$. AP has seven frequencies in this region, all of which are in good agreement with existing experimental findings [106]. AP has four frequencies in the region of $400\text{--}700\ \text{cm}^{-1}$. The molecular motion of the first frequency is the symmetric bending of ClO_4 . The associated motions corresponding to the following frequencies are concentrated in the asymmetric bending of ClO_4 . Similarly, ADN also has four frequencies which do not appear in AP. This is due to these corresponding to the asymmetric bending of $\text{N}(\text{NO}_2)_2$. AP has five frequencies in the region of $1000\text{--}1200\ \text{cm}^{-1}$. The molecular motions of the first two frequencies are the symmetric stretching of

ClO_4 , and the motions corresponding to the following frequencies are the asymmetric bending of ClO_4 . Calculated frequencies for AP in this region [211] had large deviations from corresponding existing experimental values. The motions of these frequencies are concentrated in the ClO_4 moieties, thus this discrepancy may be due to intermolecular hydrogen bonding interactions present in the crystal lattice which are not well described by DFT. The motion modes of NH_4 in AP and ADN present similar features in the region of $1400\text{--}3300\text{ cm}^{-1}$. The motion of the first frequency involves the asymmetric bending of NH_4 , whereas those of the next two frequencies are concentrated in the symmetric and asymmetric stretching of NH_4 , respectively.

3.12.2 UV Spectra of AP

Irradiation of AP crystals with UV light produces an effect similar to the effect of X-rays or γ -rays [239]. The action of light, which is similar to the action of ionizing radiation, is mainly restricted to the induction period.

Color centers absorbing at 610, 295, and 360 nm were formed in AP crystals irradiated with UV light of $2537\text{ \AA}$ [240]. Thermal bleaching overnight at room temperature destroyed the 610-nm band with no apparent change in the 295 and 360-nm bands. Further thermal bleaching for two weeks resulted in the formation of a new band at 500 nm and elimination of the 360-nm band. Bleaching of the 610-nm band at room temperature can be prevented by storing the crystals under vacuum conditions. These visible crystal defects can become the nucleus for thermal decomposition.

3.12.3 Raman Spectra of AP

A Raman study of AP was conducted within the temperature range 300 to 17 K to determine the effects of low temperature on the rotational behavior of the ammonium ion, to search for evidence of hydrogen bonding, and to determine whether low-temperature phase transitions exist between 300 and 120 K [233]. The observed Raman frequencies, relative intensities, and scattering assignments are summarized in Table 8.

In the Raman spectrum (at room temperature), three components of ν_4^- , two of ν_3^- , one of ν_2^- , and one of ν_1^- were detected. No bands attributable to ν_3^+ or ν_4^+ could be detected. Upon cooling, a third component of ν_3^- , ν_1^+ , ν_4^+ , and weak components of ν_3^+ were detected. No appreciable frequency shift occurred for any band in the temperature range 300–130 K. Raman spectra revealed that no phase change occurs in AP from 300 to 120 K.

The Raman spectra of oriented single crystals of AP were measured as a function of temperature between 12 and 300 K [241]. The results were consistent with the assignment of NH_4ClO_4 crystal structure to the $D2h$ space group at all temperatures. A weak B1g mode at 180 cm^{-1} was assigned to an NH_4^+ libration. An anomalous temperature dependence was observed for low frequency B1g and B3g lattice modes, which needed further investigation in the range of 18–80 K.

Table 8: Observed Raman frequencies, relative intensities, and scattering assignments of NH_4ClO_4 at room temperature and at 130 K.

Wavenumber, cm^{-1}	Relative intensity	Wavenumber, cm^{-1}	Relative intensity	Assignment
300 K		130 K		
—	—	3320 ^a	3}	$\nu_3^{+?}$
—	—	3220 ^a	3}	$\nu_3^{+?}$
—	—	3201	13	ν_1^{+}
1417	3	1417	3	ν_4^{+}
1137	5	1137	5	ν_3^{-}
1108	10	1108	8	ν_3^{-}
1064	4	1065	10	ν_3^{-}
935	100	936	100	ν_1^{-}
921	18	922	29	$2\nu_2^{-}$
635	33	638	29	ν_4^{-}
630	36	630	16	ν_4^{-}
625	61	624	52	ν_4^{-}
461	70	462	90	ν_2^{-}

^aA series of weak overlapping bands were found in this region. Resolution and interpretation are difficult.

Data source: [233].

The NH_4^{+} ion has four fundamentals in AP at 3350 cm^{-1} (T_2 stretch), 3209 cm^{-1} (A_1 stretch), 1680 cm^{-1} (T_2 bend), and 1420 cm^{-1} (E bend) [242]. All modes become A' or A'' in the Cs sites of NH_4^{+} and ClO_4^{-} . All bands except the A_1 mode are weak and not all have been reported before in the Raman spectra. The A_1 mode was found to broaden slightly with increasing temperature. At 513 K, which is the phase transition temperature, a 10 cm^{-1} decrease in the frequency was noted along with a further increase in the bandwidth. The barrier to rotation of the NH_4^{+} ion in AP was small ($<4\text{ kJ/mol} = <1\text{ kcal/mol}$).

A detailed temperature-dependent study has been conducted to assess the Raman spectra of oriented AP single crystals in the spectral regions of lattice modes and internal vibrations of the ClO_4^{-} and NH_4^{+} ions between 10 and 300 K. This revealed that the internal modes of the ClO_4^{-} ions were splitting into several components due to site and correlation field effects [243]. The line width, frequency shift, and intensities of some of the internal modes of the ClO_4^{-} and NH_4^{+} ions and the frequency shift of a few lattice modes revealed anomalous temperature dependence around 180 and at 40 K. These anomalies have been explained in terms of phase transformations associated with the changes in hydrogen bonding strength and reorientational freedom of the NH_4^{+} ions in the lattice. The low-temperature transition at 40 K exhibits a sharp and discontinuous anomaly in some of the spectral parameters measured in this study. This is associated with order-disorder-type transition. The measured line width of the ν_1' mode in the diagonal scattering configuration can be understood in

terms of vibrational dephasing of the ν_1 excited state due to vibrational-librational coupling. The estimated activation energies in the 50–160 K and 10–40 K temperature ranges are found to be 141 and 51 cm^{-1} , respectively, which correspond to the observed NH_4^+ librational frequencies.

Single-crystal and powder neutron diffraction, coherent neutron inelastic scattering, and Raman spectroscopy have been used to study the low-temperature structure and dynamics of AP [106]. No evidence of a low-temperature phase transition between room temperature and 20 K was found. Based on analysis of thermal motion amplitudes and inelastic neutron-scattering data for ND_4ClO_4 , a Raman-active B_{3g} symmetry zone-center mode at 45 cm^{-1} was identified as a libration. Another Raman-active mode, which was a B_{1g} symmetry at 33 cm^{-1} , and a previously unobserved A_u symmetry mode at 12 cm^{-1} , were inferred to have significant librational character at $q = 0$. Comparison of these results with earlier incoherent neutron scattering results suggested that, because of the low activation energy of ammonium ions, classical jump reorientations strongly influence ammonium-ion sublattice dynamics, even at temperatures as low as 20 K.

A detailed temperature-dependent Raman spectra study of oriented single crystals of NH_4ClO_4 and ND_4ClO_4 in the lattice-mode region from 10 to 300 K allowed an assignment of the Raman bands in the lattice-mode region. This provided deeper insight into the dynamics of ammonium ions in the lattice [244]. Based on the deuterium isotope shift, characteristic changes in bandwidth with temperature, structural information, and temperature-dependent sidebands of $\pm 19 \text{ cm}^{-1}$ (10 K) from the main bands were observed. This is believed to be associated with some of the internal and lattice modes of the NH_4^+ ion below 30 K. These spectral features have been explained in terms of a model in which the NH_4^+ ion rotates almost freely around one of the axes coinciding with the $\text{N}-\text{H}(2)\cdots\text{O}(1)$ bond while it performs librational motions around the two perpendicular axes below 30 K.

The breakdown of the crystal lattice of AP in the 300–625 K range has been followed in real time by laser Raman spectroscopy [245, 246]. Examination of the external and internal modes of the ions revealed that the onset of essentially unhindered tumbling of the ClO_4^- ion seems to be intimately tied to the beginning of decomposition of AP. The effect of K^+ as an isomorphous dopant in the crystal lattice is to permit the ClO_4^- ion to tumble at a lower temperature (0.8% K^+ produces a 60–70 K lowering in the tumbling temperature) and thus decompose at a lower temperature also. All vibrational modes found in AP, including several not previously reported modes, were assigned.

3.12.4 Refractive Index of AP

The indices of refraction in the direction of the three crystal axes a , b , and c , at the wavelength of the sodium D-lines (589 nm) were measured and found to be $n_a = 1.482$, $n_b = 1.487$ and $n_c = 1.483$ [191]. Older sources have reported these as $n_\alpha = 1.4818$, $n_\beta = 1.4833$, and $n_\gamma = 1.4881$ at 589 nm.

3.13 XPS Photoelectron Spectra of Ammonium Perchlorate

XPS was used to identify the first intermediate species produced during AP initiation by varying stimuli and increasing the intensity of stimuli also [247]. Comparing species on the surface of AP damaged below the initiation threshold with that of clean AP allowed the investigators to propose an initiation mechanism. Control XPS spectra were recorded on the surface of freshly cleaved AP single crystals.

The line widths of X-ray photoelectron spectra have been found to correlate with dislocation densities in a shock-damaged crystal of AP [248]. A centimeter-sized AP crystal was loaded at several sites with a diamond pyramid (Vickers) indenter creating localized strain centers. The crystal was non-uniformly damaged by a rapidly decaying shock (peak pressure of 24.4 kbar at the entry surface), was recovered intact, and then cleaved through the indentations. The cleaved planes permitted interior analysis of the crystal by XPS over a pattern of 1 mm by 1 mm areas. The linewidth of the CL ($2p^{3/2}$) spectra ranged from 1.70 eV for the region of greatest visible damage to 1.22 eV for the region with no visible damage. This is the same linewidth as that obtained for unshocked AP (control). An approximate correlation of dislocation density versus XPS linewidth was obtained. The correlation was refined by chemically etching and determining densities on another cleaved plane in the recovered crystal.

4 Chemical Properties of Ammonium Perchlorate

4.1 Reactions with Ammonium Perchlorate

Reactions of perchlorates in general and AP in particular can be subdivided by the medium in which they occur. For rocket propellants, we are mostly interested in reactions of AP with oxidizable substances in a dry state. For the synthesis, purification, environmental fate, and disposal of perchlorates, we are mostly interested in reactions that take place in aqueous solutions. There are several books on the chemistry of perchlorates which give a good introduction into this subject area of chemistry, including [249].

The persistence of perchlorates in the environment once it has been spilled into soil and leached into groundwater is due to the lack of reactivity of perchlorate ions. Perchlorates are so unreactive in aqueous solutions that they often are used as supporting electrolytes in batteries and electrochemical cells. The conditions under which perchlorate becomes reduced in an electrochemical cell or in the presence of strong reductants depend on the galvanic potential and the pH [250].

4.1.1 Reactions of AP with Inorganic Compounds

4.1.1.1 AP Reactions in the Solid State

One of the effects that takes place during the decomposition of AP is the reaction of AP (also known as perchloric acid or perchlorate ion) with ammonia. This reaction has been investigated very thoroughly with the finding that the presence of an excess of ammonia has a distinct effect on the rate of decomposition of pure AP in that it slows it down and inhibits it significantly.

A study of the inhibiting effect of ammonia gas on the kinetics of the thermal decomposition of AP in the temperature range 488–543 K (215–270 °C) revealed that an initial ammonia pressure of about 200 mm Hg will cause full suppression of the decomposition of the orthorhombic crystals at temperatures close to the point of AP polymorphic transformation (513 K = 240 °C) [251, 252]. With the cubic crystals, only 0.5 mm Hg is the corresponding pressure required to achieve full suppression. In the case of complete inhibition of the decomposition in the presence of ammonia, AP crystals become yellowish. The activation energy of decomposition of the orthorhombic modification is 121.3 kJ/mol (29 ± 0.6 kcal/mol) in the absence of ammonia, and 159 kJ/mol (38 ± 1.1 kcal/mol) under ammonia pressure of 6.5 mm Hg. A kinetic analysis of the traditional proton transfer model of AP decomposition revealed that the increase of the activation energy in the presence of ammonia can be explained by this model.

4.1.1.2 AP Reactions in Aqueous Solutions

AP reactions in aqueous solutions are common to all perchlorate salts due to the salts usually being completely dissociated and because the ions are solvated.

While there are many methods that will remove perchlorates from contaminated groundwater there are only a few methods that will effectively destroy them. If regenerable ion exchange resins are used for water treatment the brine obtained during resin regeneration has to be disposed of somewhere. The brine was previously routinely dumped into the ocean, however, there are now restrictions with regards to doing that. Other than bioreduction, inorganic reductants were sought to reduce perchlorates to an innocuous form of chloride which can be safely dumped in surface streams or oceans.

One of the few inorganic reductants capable of reducing ClO_4^- to Cl^- is titanium(III). It is difficult to explain why weak reductants [Ti(III)] reduce perchlorates while strong reductants [Sn(II), Cr(II)] do not. The cause may be that perchlorates have to be complexed in a perchlorato complex where bridged electron transfer (an inner-sphere mechanism) can take place. The highly symmetrical perchlorate ion is a poor electron acceptor that is reluctant to give up oxygen to form chlorate. In complexes forming in ethanolic Ti(III) solutions, the symmetry of the ClO_4^- ion is distorted and it becomes more susceptible to reduction [253]. While this process may be cost-prohibitive as a method for perchlorate destruction, it may point the way to other more economical methods where the Ti^{4+} is electrically reduced back to Ti^{3+} in an electrolytic cell.

4.1.1.3 Reactions of AP with Metals

The reactions of AP with metals are very important for several reasons. While AP is being manufactured it comes into contact with many metals and may leach contaminants out of the process equipment that later adversely affect the thermal stability and the burning rate of the product. Solid propellants have to be mixed in metal containers and with metal stirrers where additional AP/metal contact may take place. Interactions between AP and the metals might cause unexpected reactions and accidental ignitions.

Reactions of Solid AP with Metals

Many AP-based composite propellants have added metal powders to increase the heat of combustion of the propellant and reduce its propensity for chamber pressure oscillations. Premature reactions between AP and the metals (mostly aluminum) might cause unwanted ignitions or limit the storage shelf life of the propellants. In some instances the AP and the metal powder are mixed together before the binder is added. The dry mix is a potentially hazardous operation, which is why the hazard properties of dry AP/metal mixtures have been extensively tested.

The effects of aluminum and nickel powders of various grain sizes on the thermal decomposition of AP were investigated by TGA and DSC in a dynamic nitrogen atmosphere [254]. The TGA results demonstrated that Al powders have no effect on the thermal decomposition of AP which are conventional grain sizes, while the nanometer-sized Ni powders have a great influence on the thermal decomposition of AP with conventional or superfine grain sizes. The results obtained by DSC and *in-situ* FTIR analysis of the solid residues confirmed the catalytic effects of nano-nickel. The burning-rate enhancing activity of nano-nickel may be caused by acceleration of the gas phase reactions during the second step of AP decomposition.

AP mixed with varying amounts of aluminum powder (or any combustible metal) is a powerful and sensitive explosive. AP mixed with aluminum powder ("aluminized AP") or wax is also a powerful explosive [255]. When mixing propellants containing AP and aluminum, one will not want to dry-mix the two ingredients before adding the binder unless taking special precautions.

The onset of thermal decomposition of AP lowers in the presence of ferrosilicon containing 20–25% Fe [256]. Ferrosilicon in an AP:FeSi ratio of 10:3 and serves both as a catalyst and performance enhancer. It is also useful for propellants in which part of the AP has been replaced with NaNO_3 as a chloride scavenger to avoid the formation of HCl in the exhaust.

Reactions of AP Solutions With Metals

Perchlorate ion in a solution is relatively difficult to reduce. Reduction reactions have been studied as a means of perchlorate removal from polluted drinking water (see Section 8.9.10). The reduction of perchlorate ion with iron metal with illumination using UV light has been tested as a method for removing perchlorates from contaminated

groundwater to restore its quality as drinking water [257]. While the reaction of perchlorates using iron in the dark is very slow, it can be accelerated by using UV light of sufficiently short wavelength ($<185\text{ nm}$). The metallic iron provides electrons for the reduction of perchlorates all the way to chloride, while less than 1% stays behind as chlorate. Chlorate is an intermediate in the reduction process. Bacteria will also digest perchlorates and iron(0).

The kinetics of perchlorate reduction using elemental iron has been examined at elevated temperatures using microwave heating and conventional heating [258]. Results from microwave heating study revealed that 98% of aqueous perchlorates can be removed in one hour at 473 K (200 °C). The rapid and complete reduction of perchlorates using elemental iron at elevated temperatures suggests that iron reduction processes at elevated temperature and pressure may be an option for complete removal of perchlorates from polluted water and industrial discharges.

Large quantities of AP/binder/Al propellant have to be removed from outdated rocket motors or as part of demilitarization efforts. One of the safest methods of demilitarization is the removal of propellant from motors using a high-pressure water lance. Slow reactions between dissolved AP and suspended Al may take place while the leached oxidizer and the particulates are waiting to be separated for further processing (and eventual recycling of the AP).

4.1.1.4 Reactions of AP Solutions With Metal Hydrides

Since the majority of composite propellants contain AP, it may react unexpectedly with a variety of solid propellant ingredients. The specific impulse of solid propellants can be improved by addition of metals and/or metal hydrides. One of the metal hydrides with the best I_{sp} improvement is beryllium hydride. Studies of the decomposition of AP revealed the first step to be the dissociation into gaseous ammonia and anhydrous perchloric acid. The subsequent reactions are the combustion of the various hydrogen species, including metal hydrides with perchlorate species. The hydrogen atoms, oxygen atoms, and chlorine atoms also recombine to H_2 , O_2 , and Cl_2 by three-body collisions. The reaction between beryllium hydride and AP produces BeO but does not produce BeCl or $BeCl_2$ [259].

4.1.2 Reactions of AP With Organic Compounds

The primary interest in the reactions of AP with organic compounds is the potential reaction of AP with binders during mixing, curing, storage, and actual burning. AP/binder reactions underneath the flame front determine the temperature of ignition and the burning rates. Reactions with polymeric binders are discussed in Section 4.1.2.4. Because it is sometimes difficult and messy to mix AP with actual binders in small batches, other more easily obtained organic compounds have often been substituted for polymeric binders in laboratory tests of AP combustion. Experimental methods to study reactions of AP with organic compounds (polymeric

or not) include DTA, DSC, TGA, ARC, sandwich burners, T-jump FTIR, T-jump mass spectrometry, Raman spectroscopy, and mass spectrometry.

In an effort to identify where the AP decomposition products attack the weak links in an organic molecule the reactions of AP with aromatic compounds substituted with amino, methyl, and carboxyl groups were studied by measuring the burning rates of pressed pellets in a combustion bomb under nitrogen pressure [260]. The introduction of amino or methyl groups into the benzene ring increased the burning rates in proportion to the number of groups introduced. Such studies can help in developing formulations with higher burning rates. On the other hand, if one avoids amino groups, the propellant can have better thermal stability.

The effects of 5% urea, oxamide, dicyandiamide, poly(vinyl chloride), hexachloroethane, diphenylamine, urethane, anthracene, hexamethylenetetramine, salicylic acid and its derivatives (benzoic acid and its derivatives), and 8-hydroxyquinoline on AP combustion characteristics at pressures up to 10.13 MPa (100 atm) were investigated [261]. The lower pressure limit of stable combustion, combustion rate, and coefficients of inhibition in the exponential equation of combustion (dependence of burning rate on pressure) have been determined. The chemical structure of the additive was related to the combustion characteristics of AP. The effect of the additives on the primary dissociation of NH_4ClO_4 and on the decomposition of HClO_3 was discussed in detail. Reaction of poly(methyl methacrylate) tubes used for sample containment can change the combustion rate at most pressures. The results were compared with the results for similar systems containing RDX instead of AP.

The combustion of AP-based composite propellants has been studied at pressures between 100 kPa and 20.6 MPa (15 and 3000 psi) in order to determine the mechanisms by which the fuel components influence the burning rate of the composites [262–265]. To have flexibility in the choice and concentration of the fuel components, all combustion experiments were performed with pressed powder strands. The fuels studied included those which were expected to affect the combustion mechanism of the composite primarily through their effect on: (1) the oxidizer decomposition mechanism and (2) the composite surface temperature. The combustion of pure and doped AP was studied using both pressed powder strands and pressed end-burning motor grains. The objective was to study the reactions which occur on or immediately adjacent to the surface (“zone of influence”) of burning composite propellants. The fuels included benzoic acid, hydroquinone, isophthalonitrile, triphenylmethane, aluminum, phenolic resins, sucrose, benzamide, acetamide (fuels producing ammonia), succinamide, phthalamide, and phthalamic acid. A composite with a relatively unreactive fuel such as benzoic acid had a lower burning rate than a similar composite with a more reactive aliphatic acid such as stearic acid. At pressures above 6.88 MPa (~1000 psi) the burning rate of the benzoic acid composite was lower than that of pure AP. Composites with fuels which char on decomposition have higher burning rates than composites with similar fuels which volatilize without charring. This has been demonstrated both for a series of fuels in which char occurs due to dehydration and in a series of fuels

where char forms due to dehydrogenation. Fuels (amides, diamides, and acid amides) which decompose thermally at temperatures below the composite surface temperature to form NH_3 or H_2O significantly affect the combustion rate of AP composites at all pressures. Generally, these fuels lower both the burning rate and the burning rate pressure exponent. There are ions which have both the thermodynamic potential and the kinetic reactivity to reduce perchlorate ions in a solid-solid or solid-liquid reaction. Ions such as CNO^- , CN^- , and SCN^- all react with KClO_4 in a DTA to cause deflagration and detonation. Composites containing fuels with functional groups (e.g., nitriles) which have the potential to reduce perchlorate ions generally have relatively large burning rate pressure exponents above 13.76 MPa (~2000 psi).

Urotropine was mixed with AP, then pressed to pellets and burned in a strand burner at varying pellet compression densities, different pellet confinement, and two different chamber pressures [266]. The main objective of the study was to measure the effect of density on the burning rate of pure AP pellets. The urotropine was added only for comparison.

4.1.2.1 Reactions With Nitrate Esters

The unwanted reaction of AP with nitrate esters in composite modified double-base propellants can be retarded with the addition of a stabilizer, resorcinol, which is applied via co-crystallization. This occurs by first dissolving AP in liquid ammonia then adding 1–10 mass-% resorcinol [267]. The solution is evaporated at room temperature following which the crystals are dried at 311–339 K (100–150 °F) for 0.5–1 hours. They are then held in 25 mm Hg vacuums at room temperature for 72 hours.

4.1.2.2 Reactions With Nitramines

Based on the condensed-phase mechanism and thermolysis experimental results, synergistic interactions between AP and HMX in nitrate ester plasticized polyether (NEPE) propellants were studied from the two viewpoints of molecular structure and chemical reaction [268]. Related to bond polarity, formal charges, chain reaction theory, and the systematic comparison of solid monopropellant combustion and modeling, a [linkage-mutualism] mechanism was proposed. AP content and particle size can influence the mechanism. Therefore, they will have significant effects on the ignition and combustion characteristics of AP/NEPE propellants.

4.1.2.3 Reactions With Other Organic Matter

Perchloric acid is sometimes used to destroy organic matter in environmental, biological, petrochemical, and geological samples and to prepare them for the analysis of trace metals by fuming the sample in a crucible under the fume hood (“wet ashing”). This is one of the pathways through which unwanted perchlorate ions find their way into waste streams. Changing the fuming procedure has been proposed so as to capture and trap the perchloric acid fumes instead of allowing them to go up the fume stack [269]. Hot, boiling perchloric acid for this application has to be at least 50%

HClO_4 . The CRC Handbook of Laboratory Safety [270] reports several accidents caused by perchlorate deposits in improperly constructed fume hood systems.

4.1.2.4 Reactions of AP With Organic Polymers

Reactions of AP with organic polymers can potentially occur prematurely during mixing, curing, or storage stages and will definitely occur if burning a solid propellant grain.

PS is not a preferred binder for solid propellants. Nonetheless, it is sometimes used for fundamental studies in laboratories in academic settings because it is readily available. The kinetics of the decomposition of catalyzed AP with and without the presence of PS has been measured over a wide temperature range [271, 272].

A clean-burning polymer that is easily processed and is available as a powder with a wide range of molecular weight and particle sizes is polyethylene (PE). Consequently, it has been used as a model binder instead of the more difficult to cure carboxy-terminated polybutadiene (CTPB) or HTPB binders. AP can be mixed with PE powders and additives and pressed to pellets for subsequent burning rate studies. Another clean burning binder is NEPE. The thermal stability of perchlorate composite propellants was studied at 408 and 443 K (135 and 170 °C) [273]. The objective was to determine the importance of heterogeneous oxidizer-fuel reactions in thermal degradation processes. The experimental approach used to elucidate the mechanisms by which the oxidizer/fuel composites thermally degrade was divided into two parts: (1) keeping the fuel type the same and varying the nature of the oxidizers, and (2) holding the oxidizer constant and varying the fuel components. The fuel component primarily utilized was PE. Oxidizers included KClO_4 , KClO_3 , NH_4ClO_4 , and NH_4ClO_4 doped with chlorate, phosphate or arsenate. In the second phase, the oxidizer used was primarily NH_4ClO_4 while the fuels included saturated and unsaturated polybutadiene prepolymers and a series of bonding agents.

There are many reports on the thermal stability of AP in contact with various polymeric binders such as those used in composite propellants. However, quite often the oxidizer particles are not in direct contact with the binder; they are coated first with a bonding agent. The effect of the bonding agent on aging of composite propellants must also be considered.

Delamination of oxidizer particles can lead to increased burning rates and a loss of mechanical strength. SEM was used to examine the failure sites in thermally degraded AP composite propellant samples [274]. The formulation variables tested were oxidizer purity, oxidizer particle size, and oxidizer to binder bonding agent. The binder, a saturated hydrocarbon, was kept constant throughout the experiments. The oxidizers were: AP, chlorate-doped AP, arsenate-doped AP, and phosphate-doped AP. The oxidizer bimodal particle size distribution was 60% of the large fraction and 40% of the small fraction. The bonding agent, when present, was used at the 0.15% level. The data revealed that both the oxidizer purity and particle size had a strong effect on the thermal degradation process. The effect of the oxidizer particle size was more notice-

able at higher temperatures and stress levels. An examination of the failure sites using SEM of propellants subject to higher temperatures and stress conditions indicated that the fracturing of large oxidizer particles led to propellant cracking.

Kinetic studies revealed that in binders involving epoxy resins and carboxyl groups in polybutadiene-acrylic acid-acrylonitrile terpolymers, the rate of the polymerization reaction is reduced and the epoxy groups are consumed faster than carboxyl groups in the presence of AP. Various coatings were evaluated to prevent or retard the oxidizer-epoxide interaction. The coatings, which can be adsorbed from solution on AP, were deposited on a fluidized bed of the oxidizer or were merely added to the propellant formulation, as described in Section 2.1.8. Since consumption of epoxy groups in AP-epoxy resin mixtures have been shown to be independent of the amounts of AP present, it was concluded that this interaction was related to the solubility of AP in the binder system. The solubility of AP in Epon[®] H-825 was determined. Methods of chemically capturing AP or its ionization or decomposition products as they appear in solution were investigated. K, Rb, and Cs salts, which form perchlorates of very low solubility in organic systems, were effective in reducing the AP-epoxy interaction and precipitating perchlorates from solutions in organic binders [80]. Similar oxidizer-epoxy interactions prevented the curing of polybutadiene acrylonitrile (PBAN) propellants with hydroxylammonium perchlorate. Attempts were made to coat it with toluene diisocyanate (see [275] also).

4.1.3 Electrochemical Reactions of Perchlorates

Perchlorates are produced via the electrochemical oxidation of chlorates. It should be possible to reverse this reaction in an electrolysis cell and reduce perchlorates to chlorate or even lower states of oxidation of chlorine.

The electrochemical reduction of perchlorates is mostly of interest for the decontamination of polluted drinking water (see Section 8.9.7).

The reduction of ClO_4^- ions in acid media was studied at smooth polycrystalline rhodium electrodes using voltammetry, chronoamperometry, and impedance spectroscopy [276]. Based on experimental results, a new mechanism for the electrocatalytic reduction of ClO_4^- ions has been proposed. This is based on the assumption that the reduction process starts with the adsorption of perchlorate ions at free active sites on a metal surface. It was also assumed that the whole process occurs on the surface and the role of desorption of intermediates can be neglected.

4.2 Analysis of Ammonium Perchlorate

Analytical methods are required for quality control of AP and for the detection of traces of AP in the environment. The persistence of perchlorate ions in aquifers made the development of sensitive analysis methods for perchlorate a very high priority item

during the 1990s. A review of various analytical methods for perchlorate analysis in a variety of matrices has been provided within [277]. This publication also compares different methods for specificity, sensitivity, and reliability.

The following chapters on the analysis of perchlorates can be subdivided by the matrix in which perchlorates are to be analyzed or by the methods used (see [278]).

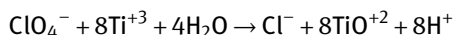
4.2.1 Quality Control of AP

AP from different vendors may meet all military specification (MIL-SPEC) requirements but still produce different burning rate results when formulated into a composite propellant.

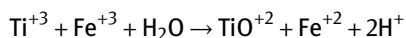
4.2.1.1 Assay of AP

Previously, a procedure set forth in the Military Specification JAS-A-192 specified the reduction of perchlorate to chloride via fusion in a Parr bomb and the subsequent determination of chloride by an argentometric titration. These procedures were time-consuming and subject to errors due to incomplete reduction and the inevitable spattering of the sample.

A more direct method is the reduction of perchlorate ion with a 15 mol % excess of titanium(III) chloride in strongly acidic and boiling hot solutions according to [279, 280]:



The boiling time is 15 minutes but can be reduced to eight minutes if a trace of osmium(VIII) (which acts as a redox catalyst) is added to the solution. The excess Ti(III) is then back titrated with standard ferric ammonium sulfate solution:



using thiocyanate as the indicator.

A round robin exercise was conducted for the purpose of evaluating three assay methods for AP [281]. Eleven government and commercial laboratories submitted quadruplicate analyses for two different samples. These results were subjected to statistical analysis-of-variance to estimate the significance of interlaboratory variation. It was found that the laboratories were unable to reach an agreement, regardless of the methods used.

A comparison of AP assay using the distillation method and the formaldehyde method found that the difference between the two methods can amount to 0.35 to 0.22% [282].

4.2.1.2 Water Content of AP

One of the most common contaminants in AP which has been around for a while is water. The hygroscopicity of AP is not as bad as that of AN [283] Although AP is not very

hygroscopic (and not nearly as bad as AN or ADN), moisture absorption is a serious problem to contend against. Excessive moisture in the presence of isocyanate curing agents could result in bubble formation due to evolved CO_2 . It can also cause irregular mechanical and burning behavior of the cured propellant. This is problematic as moisture in AP affects the nucleation and onset of thermal decomposition.

Water in AP can be determined by a Karl-Fisher titration. The determination of water in AP by Karl Fischer titration is simple and straightforward and it is also accurate. However, the use of automatic titration equipment in this determination has resulted in wide divergence of results [284, 285]. Depending on the operating method used, one can selectively measure the surface water on the particles or the total water of dissolved crystals. The accurate titration of small water contents of AP requires that the commercially available and stabilized Karl Fischer reagent first be diluted so the amount of reagent consumed can be measured more accurately with the 10-mL burette generally employed with the autotitrator. The time required for a complete titration can be considerably reduced in the presence of dissolved salts and by using a 3:1 pyridine-methanol solution as the titration medium. Two samples of AP, one with 0.01 and the other with 0.05% H_2O , were sent to eight laboratories for a round-robin analysis. The improved method was shared with all eight laboratories and the results of the round-robin effort was compared and statistically evaluated. An analysis method using the METTLER Karl-Fischer DL-38 automatic moisture analyzer to determine the water content of UFAP was simple and rapid, and had good repeatability and a small deviation [286].

4.2.1.3 Contaminants in AP

The production of AP using the metathetical reaction of sodium perchlorate and ammonium chloride, with the sodium perchlorate having been prepared via the oxidation of sodium chlorate, leaves detectable amounts of chlorate ion in the product. It is an absolute [VERBOTEN] among propellant and pyrotechnics formulators to have chlorates and ammonium salts in the same composition. Ammonium chlorate, NH_4ClO_3 , even in small quantities, is very unstable [287] and would cause any formulation containing AP and chlorate ion to have reduced thermal stability. The chlorate contaminant concentration in AP can be determined spectrophotometrically, either by using the reaction with brucine [288] or benzidine [289, 290] or by tracing the change of pH as indicated by methyl orange during the reaction of chlorate or bromate with chloride in acidic media [291].

The lattice parameters of six samples of AP and AP/KClO_4 solid solutions were determined by wide angle XRD using fixed count techniques [292]. The results indicated that this technique could be used to monitor the purity of AP with regard to KClO_4 as solute in the AP/KClO_4 solid solution system.

In AP production, chlorate impurities in the raw material will influence the thermostability of the produced AP and any propellants formulated therewith. Four different methods for eliminating chlorate contamination in AP were evaluated [293].

It was discovered that the $\text{HCl} + \text{H}_2\text{O}_2$ process works best. That involves reacting the $\text{V}(\text{NaClO}_4) : \text{V}(\text{HCl}) : \text{V}(\text{H}_2\text{O}_2) = 400 : 4 : 1$ mixture for one to one-and-a-half hours at 363 K (90 °C), and continuing the reaction 15 to 30 minutes after stopping the heating process. This treatment reduces sodium chlorate impurities in the sodium perchlorate solution from which AP is made by metathetical substitution to below 0.014%, which is the maximum allowed per the Chinese national military specification.

4.2.2 AP Military Specifications

AP Military Specifications have evolved over time, reflecting the improvement in manufacturing techniques and the tighter quality control for solid propellants in a wide array of military applications (Table 9).

As of 1963, one of the applicable AP specifications has been MIL-A-192A, Amendment 2, which described two grades on the basis of moisture content plus a modification which contains the conditioning agent TCP. Each grade may have seven classes of particle size distribution. Despite the seemingly large number of grades and classes, propellant manufactures have found this specification to be inadequate for their needs and company specifications, or their purchase descriptions were used instead. Standardization is completely lacking and this undoubtedly contributed to confusion and increased costs. Another revision of MIL-A-192A was made in an attempt to overcome this situation [294]. It did not accomplish its purpose, however. This was mainly because it failed to include certain details regarding newer tests and requirements. In addition to this, the specification was inadequate with regard to the particle size requirements. The latter was difficult to specify because the particle size distribution required for optimal performance was still in flux.

4.2.3 Emission Spectrographic Methods

Emission spectrographic methods can be used for analysis of metallic contaminants in AP and other ammonium salts. Inductively coupled plasma-atomic emission spectrography can be used for simultaneous multi-element determinations of various suspect metals in AP.

One of the methods of working with solid samples that is widely used for the identification of small samples of energetic materials (which is often a task in forensic investigations) is nanosecond Laser Induced Breakdown Spectroscopy (LIBS). LIBS is a new technique used for the detection and identification of very small samples of chemical, biological, explosive, and hazardous materials. LIBS vaporizes a target with an intense laser pulse, which generates a very hot plasma. The spectral emission from the plasma contains a specific signature of atoms relating to the material, including nitrogen and oxygen.

Laser-induced breakdown spectroscopy analysis of AN and AP revealed characteristic lines corresponding to O, N, H, C, and K [295]. The oxygen line at 777.38 nm and three nitrogen lines (N1, N2, N3) at 742.54, 744.64, and 747.12 nm were used for evalu-

Table 9: Military specifications for AP.

Document ID	Document status	Date	No. of pages	Title
JAN-A-192	Canceled	1 Mar 1945	8	Ammonium Perchlorate
MIL-A-192B	Active	2 Sep 1965	25	Ammonium Perchlorate, Technical
MIL-A-192B Notice 2 Validation	Active	18 Aug 1999	1	Ammonium Perchlorate
MIL-A-23442A	Active	3 Mar 1965	16	Ammonium Perchlorate
MIL-A-23442A(1) Notice 2 Reactivation	Active	7 Jun 2006	1	Ammonium Perchlorate
MIL-A-23946(1) Notice 2	Canceled 28 Aug 1996	19 Aug 1964	13	Ammonium Perchlorate for Solid Propellant Grains (No superseding document)
MIL-A-23948(1) Notice 2	Canceled 28 Aug 1996	19 Aug 1964	14	Ammonium Perchlorate special Coarse Grade for Solid Propellant Grains (No superseding document)
MIL-A-82667 Base Document	Superseded	31 Jan 1977	17	Ammonium Perchlorate, General Specification for
MIL-A-82667A(1)	Active	22 Sep 1978	13	Ammonium Perchlorate, General Specification for
MIL-A-82667/2(Amendment 3) Notice 2	Active Re-activated 11-APR-2001	15 Nov 1993	4	Ammonium Perchlorate, Conditioned ^a
MIL-A-82830 Base Document	Canceled	5 Feb 1990	24	Ammonium Perchlorate, Conditioned ^a (with Reduced Alkali Metal Content) (No superseding document)
MIL-STD-1322-20 Notice 1	Inactive	14 Aug 1969	6	Palletizing Domestic Unit Load, Ammonium Perchlorate (In 30-Gal. Steel Drum)
STANAG-4299 ED.1	Active	27 Jan 1993	25	Specification, Ammonium Perchlorate (NH ₄ ClO ₄) for Deliveries from one NATO Nation to Another; Limited distribution

^aThis specification gives detailed requirements for two types of AP with an anti-caking agent added.

Data source: <https://assist.daps.dla.mil/quicksearch/>.

ating the O/N atomic ratios. The intensities were calculated using the area under the peaks and were normalized to their respective transition probabilities and statistical weights. The O/N ratios estimated from the LIBS spectra were ~4.94 and ~5.11 for AP and ~1.64 and ~1.47 for AN, which is quite different from the actual stoichiometric ratios (four for AP and one for AN).

4.2.4 Quantitative Analysis of AP in Environmental Samples

The quantitative analysis of perchlorate ion in environmental samples (soil, water, fertilizer, vegetation) must be done very accurately because the results may have legal implications if a polluted site near an industrial source of contamination is examined. There are numerous potential interferences that need to be considered. An excellent survey of analytical methods for perchlorate is provided by Urbansky [296].

A chapter in the book *Perchlorate: Environmental Problems and Solutions* by Sellers et al., [297] contains a section on analytical methods. This provides an excellent summary of sample preparation and analytical methods available.

While a rapid degradation of perchlorates in aquifers and polluted waters would be desirable, degradation of perchlorate in water samples during transit from the sampling site to the analytical laboratory may alter the results depending on how long the sample has been sitting around before it was analyzed. The determination of perchlorate cannot normally be carried out in the field. Water samples for perchlorate analysis are often shipped to a central laboratory where they may be stored for a significant (this is variable and depends on the workload) period before analysis. The effect of such storage was not known until the long-term stability of perchlorate ion in deionized water, tap water, groundwater, and surface water was actually examined under carefully controlled conditions [298]. Sample sets containing 1000, 100, 1.0, and 0.5 µg/L perchlorate ion in deionized water and also in local tap water were formulated. These samples were analyzed using ion chromatography for perchlorate ion concentrations against freshly prepared standards every 24 hours for the first seven days, biweekly for the next four weeks, and periodically after that for a total of 400 or 610 days for the two lowest concentrations and a total of 428 or 638 days for high concentrations. All samples except for the surface water samples were found to be stable for the duration of the study, allowing for holding times of at least 300 days for groundwater samples and at least 90 days for surface water samples.

4.2.4.1 Gravimetric Methods

Most perchlorates are very soluble in water and there are only very few insoluble perchlorates.

Gravimetric methods for analysis of perchlorates are used mostly for the assay of samples with high perchlorate content (AP, composite propellants). Reagents that can precipitate perchlorate are nitron (3,5,6-triphenyl-2,3,5,6-tetraazabicyclo-[2.1.1]hex-1-ene; 1,4-diphenyl-3-phenylamino-1,2,4-triazolium hydroxide inner salt; 4,5-dihydro-2,4-diphenyl-5-(phenylimino)-1H-1,2,4-triazolium hydroxide inner salt), tetraphenylarsonium chloride [299], or 2,4,6-triphenylpyrylium chloride [300].

Nitron precipitation suffers from many interferences because all large ions (bromate, iodide, nitrate) are also precipitated.

4.2.4.2 Detection of AP in Water

Before 1997, perchlorate could not be readily detected in groundwater at concentrations below 100 µg/L, until the California Department of Health Services developed an acceptable analytical method that lowered the detection limit to 4 µg/L. Subsequently, groundwater samples containing perchlorate were soon encountered in several western states and gross contamination became apparent in the Colorado River. The discovery of perchlorate in the aquifers feeding municipal drinking water sources has resulted in extensive investigations about the source of the contamination, the rate of its dispersal, and the possible consequences of perchlorate ingestion (if consumed with drinking water). All these studies depend on the availability of a reliable method of analysis for perchlorate ion in water.

Because perchlorate ion in water is not very reactive there are not many reagents that can be used for the determination and identification of AP in water. Water contamination studies over the past two decades have proposed methods for analysis of perchlorate in water, thus allowing this area to improve substantially.

The EPA has issued three recommended analytical methods for the analysis of perchlorate in drinking water:

EPA, Method 314.1, Determination of perchlorate in drinking water using inline column concentration/matrix elimination ion chromatography with suppressed conductivity detection. US Environmental Protection Agency, Office of Ground Water and Drinking Water. EPA815R05009 (2005)

EPA, Method 331.0, Determination of perchlorate in drinking water by liquid chromatography electrospray ionization mass spectrometry. US Environmental Protection Agency, Office of Ground Water and Drinking Water. EPA815R05007 (2005)

EPA, Method 332.0, Determination of perchlorate in drinking water by ion chromatography with suppressed conductivity and electrospray ionization mass spectrometry. US Environmental Protection Agency, Office of Research and Development. EPA600R05049 (2005)

A very good summary of analytical methods for perchlorates is contained in [301].

A ClO_4^- reductase-based biosensor for rapid determination of ClO_4^- in water was developed using a ClO_4^- -sensing bio-electrode made by coating *Dechlorosoma sp.* ClO_4^- reductase on a Nafion (ion-exchange matrix) layer pre-coated on the polished surface of the glassy carbon electrode [302]. The response time was $\sim 111 \pm 28$ s. A linear correlation was established between biosensor response (measured in nA) and ion-chromatography conductivity readings (measured in µS). Biosensor response to ClO_4^- was optimum at an applied potential of -0.6 to -1.0 V. ClO_4^- reduction was maximal in the pH range from 7.6 to 8.0. The ClO_4^- biosensor was stable even after repeated use (24 analyses were conducted on day one over a ten-hour period at room temperature).

A microchip capillary electrophoresis system using contact conductivity detection has been developed for the determination of perchlorates in water. This is an inexpensive and portable system for routine online monitoring of perchlorates in drinking

water [303]. The method has several advantages including reduced analysis times relative to IC, inherent portability, high selectivity, and minimal sample pre-treatment. The system is capable of detection limits of 3.4 ± 1.8 ppb ($n = 6$) in standards and 5.6 ± 1.7 ppb ($n = 6$) in drinking water.

Trace levels of perchlorate can be determined using total reflection X-ray fluorescence (TXRF) [304]. Perchlorate anions were concentrated on anion-selective membranes that had been prepared on the surface of quartz reflectors. The reflectors were immersed in water solutions containing nanogram per milliliter (ppb) concentrations of perchlorate. After this step, the reflectors were taken out of the solution and were analyzed using TXRF. Minimum detection limits lower than 1 ng/mL and good linearity at the concentration range of 1–50 ng/mL were achieved.

4.2.4.3 Electrochemical Methods

Perchlorate ions can be analyzed using ion-selective electrodes, although other ions may interfere with the process [305]. Two types of electrodes, without an inner reference solution, were constructed using octylammonium chloride as the sensor, a mixture of dibutyl phthalate and *o*-nitrophenyloctyl ether as the solvent mediators, and polyvinylchloride (PVC) as the plastic matrix. The membranes were obtained via direct application onto a conductive epoxy resin support. The limit of detection of the direct potentiometric method developed was found to be 0.01% and the precision and accuracy of the method expressed in terms of mean relative standard deviation (RSD) and average percentage of spike recovery were 0.4% and 100.5%, respectively.

4.2.4.4 Ion Chromatographic Methods

EPA method 314.1 relies on ion chromatography with conductivity detection. If a pre-concentration column is used, the detection limit can be as low as 0.14 µg/L (Table 10). But this method also requires a second analysis on a different column to verify all peak assignments and reduce the chance of false-positive reports.

Table 10: Perchlorate ion chromatographic analytical method performance.

EPA Method	Operating mode	LCMRL ^a
331.0	Direct injection (200 µL) with matrix diversion, LC-MS or LC-MS-MS detection	0.02 ppb
330.0	Direct injection (200 µL) with matrix diversion, IC-MS or IC-MS-MS detection	0.04 ppb
314.1	Preconcentration (3 mL) with matrix rinse, suppressed conductivity detection	0.1 ppb

^aLowest Concentration Method Reporting Limit (LCMRL).

There are several ion chromatographic methods for the analysis of perchlorates in solutions [306, 307]. Most of these use conductivity detection and some work even in the presence of a high degree of salinity [308].

An electrospray ionization mass spectrometry method was used to check for trace concentrations of perchlorate in drinking water samples from southern Nevada at 8–9 µg/L [309].

Perchlorates in the low µg/L range can be analyzed using ion chromatography, either with pre-concentrations [310] or without [311–316]. These methods are linear over the range of 2–100 µg/L. Quantitative perchlorate recovery was demonstrated in spiked drinking water and groundwater samples.

An ion chromatographic method that reduces the amount of interference of other total dissolved solids (TDS) ions used a silver-saturated ion exchange resin in a Dionex AS16 separation column [317]. This sample preparation method was based on the unusually high solubility of silver perchlorate. It was found that the silver perchlorate would remain in a solution while most of the other interfering anions would precipitate out at the surface of the ion exchange resin in the form of their silver salts. This way background conductivity was dramatically reduced and any excess silver would remain on the resin. The calibration curve was linear over five orders of magnitude. The MDL for perchlorate was 0.19 µg/L.

Perchlorate was generally not detected in surface water samples collected from 50 sites across the Great Lakes Basin [318]. Concentrations of only six samples were near the MDL of 0.2 µg/L.

A new method was developed for the analysis of perchlorate in water by using reversed-phase liquid chromatography/electrospray ionization-mass spectrometry/mass spectrometry (LC/ESI-MS/MS) in the negative ESI mode [319]. Selective and sensitive perchlorate detection was obtained by monitoring the $^{35}\text{ClO}_4^- \rightarrow ^{35}\text{ClO}_3^-$ and $^{37}\text{ClO}_4^- \rightarrow ^{37}\text{ClO}_3^-$ mass transitions. The $^{35}\text{ClO}_4^- \rightarrow ^{35}\text{ClO}_3^-$ transition was quantitated against the internal standard ^{18}O -labeled sodium perchlorate ($\text{NaCl}^{18}\text{O}_4$). $^{37}\text{ClO}_4^- \rightarrow ^{37}\text{ClO}_3^-$ transition was examined to provide additional specificity. The method sensitivity, accuracy, and precision were investigated by analyzing fortified blank samples, field samples, and performance evaluation samples. The results (1.01–13.5 µg/L) for the proficiency evaluation samples differed from the certified values (1.04–14.1 µg/L) by 3–18%. This new reversed-phase LC/ESI-MS/MS method is rapid, accurate, and reproducible. The calculated MDLs were 0.007 µg/L for deionized reagent water and 0.009 µg/L for synthesized reagent water, respectively. The minimum reporting limit was 0.05 µg/L.

An alternative, rapid, and reproducible method of analysis of perchlorate in food products makes use of a rugged and inexpensive C18 column, a multi-mode OASIS HLB solid-phase extraction cartridge for sample clean-up, and acetic acid for pH adjustment and protein precipitation [320]. Detectable perchlorate levels in selected commercial food samples were <1.0–2.1 ng/g (fruit and vegetable juices), <1.0–5.0 ng/g (milk), and <1.0 ng/g (bottled water).

A method for the analysis of perchlorates in human saliva samples, using a dilution and ultrafiltration technique, isotopically labeled standards (Cl^{18}O_4), and liquid chromatography-tandem mass spectrometry (LC-MS/MS) offers great selectivity and sensitivity [321]. The LC-MS/MS calibration was found to be linear over the range of 0.01 to 50 ng/mL and for 100 μL injections (i.e., 1–5000 pg injection). The method quantitation limit (LOQ) was 0.4 ng/mL, which includes a sample dilution factor. Salivary concentrations of a convenience sample of 83 persons working and/or living in Albany County, New York, ranged from 0.4 to 37 ng/mL with a mean concentration of 5.3 ng/mL. Analysis of perchlorate in saliva from a population ($n = 86$) with no major sources of exposures, using the method developed in this study, suggests the ubiquitous occurrence of perchlorate in saliva.

4.2.4.5 UV-Vis Absorption Spectroscopic Methods

A spectrophotometric method first precipitates all perchlorates with an excess of nitron then determines the unused nitron in the supernatant solution [322]. Because nitron itself has no absorption suitable for UV-Vis spectrophotometry, it is converted to a red dye ($\lambda_{\text{max}} 490 \text{ nm}$) by reaction with NaOH. The detection limit is about 100 $\mu\text{g/mL}$ within the original sample.

4.2.4.6 Raman Spectroscopic Methods

Surface-enhanced (SERS) and normal Raman spectroscopy can be used for detecting ClO_4^- at low concentrations. The use of selective sorbents greatly enhanced the reproducibility and sensitivity of ClO_4^- detection when using a normal Raman spectroscopy. It was found that ClO_4^- is SERS active and it is possible to detect ClO_4^- at concentrations initially as low as 10^{-6} – 10^{-7} M (or 10–100 $\mu\text{g/L}$) [323]. Later, measurements as low as 10^{-9} M were seen [324]. Quantitative analysis of ClO_4^- was validated with good reproducibility by using both simulated and contaminated groundwater samples. When coupled with a portable Raman spectrometer, this technique has the potential to be used as an *in-situ* rapid screening tool for perchlorates in the environment.

Raman spectroscopy can determine perchlorate loading on a non-selective ion exchange resin such as Purolite A850 acrylic gel [325]. This method was tested using laboratory water samples and actual California groundwater samples with the complexities of competing ions, dissolved organics, and other potential interfering agents. The detection limit for this method of measuring perchlorates on resin was found to be 0.014 meq/g. A linear correlation between resin loading with perchlorates and the intensity of the Raman perchlorate signal was quantitatively verified.

4.2.4.7 Mass Spectrometric Methods

Mass spectrometry is most often used after pre-separating the samples using ion chromatography but it can also be used as a method by itself. EPA methods 331.0 and 332.0 are more sensitive as well as more definitive for perchlorates than EPA method 314.1.

Both EPA methods 331.0 and 332.0 incorporate an internal standard to minimize bias from interferences or instrument variability. A known amount of perchlorate with $^{35}\text{Cl}^{18}\text{O}_4^-$, which reaches a peak at 107 atomic mass units, was added as an internal standard. In addition to monitoring amu 99, 101, and 107 in the effluents, one can also monitor daughter ions that have lost one oxygen and show up at 83, 85, and 89 amu. This technique has been called [multiple reaction monitoring] and greatly enhances the specificity of the method.

An electrospray ionization mass spectrometry/mass spectrometry (ESI/MS/MS) method was developed to measure part-per-billion ($\mu\text{g/L}$) concentrations of perchlorates in groundwater [326]. Selective and sensitive perchlorate detection was achieved by operating the mass spectrometer in a negative ionization mode and by using MS/MS to monitor the ClO_4^- to ClO_3^- transition. The method of standard additions was used to address the considerable signal suppression caused by anions that are typically present in groundwater such as bicarbonate and sulfate. ESI-MS/MS analysis was rapid, accurate, reproducible, and provided a detection limit of $0.5\mu\text{g/L}$ perchlorates in groundwater.

The electrospray mass spectrometer method was found to have a perchlorate detection limit of 0.38 ppb, whereas ion chromatographic methods in use at that time had a detection limit of only 4 ppb [327]. The minimum reporting limit was 1 ppb. The mobile phase for the analysis consisted of 0.5% acetic acid in acetonitrile. Chlorine-containing peaks were detected at m/e of 99.1 (ClO_4^-), 140.1 (the $\text{H}_3\text{CCN}\cdot\text{ClO}_4^-$ adduct), and 159.12 (the $\text{H}_3\text{CCOOH}\cdot\text{ClO}_4^-$ adduct). A linear correlation was found between the peak areas of the $m/e = 99.1$ peak and the perchlorate standard concentrations from 0.5 to 100 ppb.

Because it is a small inorganic anion, perchlorate quantitative analysis is most amenable to electrospray atomization/ionization in the inlet of a mass spectrometer. Low detection limits of the order of 5 ng/L have been demonstrated in the absence of interfering ions. However, in the presence of other chlorine-containing anions, this method is less reliable. If the perchlorate ion could be selectively paired with a host molecule that will raise its m/e by a few hundred units above the noise level of the other water-dissolved solids, the selectivity and sensitivity for perchlorate would be greatly improved. Five organic bases and a cationic surfactant were tested as complexants/extractants and the best results (limit of detection 10 ng/L) were obtained with chlorhexidine [328]. Multiple perchlorate ions can associate with a single chlorhexidine molecule.

In electrospray liquid chromatography/mass spectrometry/mass spectrometry, perchlorate is quantitated by monitoring the ion signal from mass 83, which is formed by a loss of an oxygen atom from the perchlorate molecular ion. The aqueous MDL is $0.05\mu\text{g/L}$ and was determined using an actual groundwater matrix [329]. The soil MDL is $0.5\mu\text{g/kg}$ and was determined using Ottawa sand. A stability study was performed by spiking water samples at 0.25, 10, and $20\mu\text{g/L}$ and analyzing them 50 days later. Acceptable recoveries were obtained for all samples. The RSD for the

replicate analyses in the stability study indicated that the method is capable of RSD values less than 5% in a relatively clean groundwater matrix. Chlorine isotope ratios can be used to define statistical process control limits for use as an additional analyte identification tool.

The origin of perchlorate in the environment can be determined by measuring the isotope ratios of ^{35}Cl : ^{37}Cl . This ratio is different for human-made perchlorate and naturally occurring perchlorate and can be used to trace the source of the pollution. This may be important if legal and liability aspects are involved [330].

4.2.4.8 Detection of AP in Urine

Perchlorate ion that is ingested with food or water is quickly excreted in the urine. Several studies have been conducted studying perchlorate retention in the body and perchlorate excretion in urine. Analytical methods for the analysis of perchlorate in urine include ion chromatography coupled with electrospray tandem mass spectrometry [331] and electrospray ionization mass spectrometry [332].

Because perchlorate competitively inhibits iodide uptake, the presence of larger quantities of iodide may minimize the impact of perchlorate on thyroid function. A method to quantify perchlorate, nitrate, and iodide in human urine, milk, serum, blood spots, amniotic fluid, and infant formula using IC-ES-MSMS has been published [333].

4.2.4.9 Detection of AP in Food Stuff

For the latest findings regarding the determination of perchlorate anion in vegetable foods by ion chromatography-tandem mass spectrometry see [334].

A simple, selective, and sensitive method for quantifying perchlorate in milk powder and milk used hydrophilic interaction chromatography combined with tandem mass spectrometry (HILIC-MS/MS). This method used an Inertsil HILIC column (150 mm $\times$ 3.0 mm, 3.5 μm) with a mobile phase consisting of methanol and 0.1% formic acid (ratio of 60:40 by volume) [335]. The detection was performed by MS/MS via electrospray ionization. Linear calibration curves were obtained in the concentration range of 2.00×10^{-2} to 8.00 $\mu\text{g/g}$ and 4.00×10^{-1} to 20.0 $\mu\text{g/L}$ for perchlorate in milk powder and milk, respectively. The MDL was 4.00×10^{-3} $\mu\text{g/g}$ for milk powder and 8.00×10^{-2} $\mu\text{g/L}$ for milk. The recoveries of perchlorate in spiked milk powder and milk were all >90%. This method can be applied to the quantitative determination of perchlorate in milk powder and milk.

4.2.4.10 Detection of AP in Biological Samples

A method for measuring perchlorate in biological samples that uses ion chromatography (IC) coupled with conductivity detection has a detection limit for perchlorate in the fluids and tissues of rats of 3–6 ng/mL and 0.007–0.7 mg/kg, respectively [336].

4.2.4.11 Analysis of AP in Other Non-Biological Matrices

EPA method EPA/600/R-01/026 was used for an interlaboratory validation of methods for the determination of perchlorate in fertilizers [337]. The ground fertilizer material was either leached with deionized water to dissolve any perchlorate salt (in the case of minimally soluble fertilizers, e.g., supertriplephosphate or timed-release products) or simply dissolved in the case of highly soluble fertilizers (e.g., urea, NaNO_3 , or KCl). The resulting aqueous solution was then subjected to IC with suppressed conductivity detection. Four laboratories applied the method to field samples using 48 different fertilizer products and to seven quality control samples prepared by the EPA. Recovery (81–111%) was demonstrated on spikes of known concentration and a preliminary assured reporting level was determined for each fertilizer matrix by each laboratory. All the laboratories used Dionex IonPac AG16 guard and AS16 separation columns with NaOH or KOH as eluent. The results indicated that perchlorate was not detectable in any real-world fertilizer products (including synthetic fertilizers) that were not derived from Chilean caliche. Perchlorate was detected in only five of the products (concentrations ranging from 1800 to 4200 $\mu\text{g/g}$).

Perchlorate in fertilizer can be analyzed using an IC with gel columns [338] and with other methods. In addition to IC, the fertilizer was analyzed for perchlorate using complexation electrospray ionization mass spectrometry and high field asymmetric waveform mass spectrometry [339].

4.2.4.12 Analysis of AP in Composite Propellants

A potentiometric method that is applicable to the analysis of casting powders and propellants first reduces all perchlorate to chloride via combustion in a Parr bomb, with subsequent titration of chloride ion taking place with a Beckman model K automatic titrator [340]. It was claimed that this procedure reduces the operator variability experienced in the traditional Mohr titration method.

AP in solid propellant slurries can be analyzed using a simple and rapid non-aqueous potentiometric titration method [341].

4.3 Thermal Stability and Decomposition of Ammonium Perchlorate

The thermal stability and the decomposition of AP is important for the storability of AP-based solid propellants under a wide range of environmental conditions and for the maximum temperature tolerated when curing freshly cast grains in an autoclave. The thermal stability also determines the burning rate of AP-based propellants. Catastrophic fires in the vicinity of AP storage areas or rocket motors containing AP-based propellants subject the propellant to cook-off conditions and the thermal stability of AP determines if this condition is survivable. The transition from controlled, slow thermal decomposition to uncontrolled, rapid deflagration is a critical point of no return.

It depends on a variety of factors that must be completely known in order to safely manufacture, store, transport, and use this oxidizer.

One peculiar feature of the thermal decomposition of AP is that a solid residue is formed, which is chemically equivalent to the original material. Attempts to explain this phenomenon, which is of inherent chemical and practical interest, have caused many investigators to concentrate their examinations to the low-temperature region below 523 K (250 °C). AP is stable at room temperatures but decomposes at about 423 K (150 °C). The residue, however, remains quite stable below 523 K (250 °C) unless it is rejuvenated by recrystallization, grinding, or sublimation. In line with these decomposition reactions, AP undergoes dissociative sublimation. The chemical analysis of gaseous products is rather complex and is dependent on many factors including temperature. Freshly sublimed AP has a shorter induction period for decomposition compared to ordinary AP. It may contain some decomposition products that catalyze the decomposition.

Several summary publications regarding the thermal stability of AP are available. The best summary published to date is one by Boldyrev, who has been working on AP decomposition for over 30 years [17]. Boldyrev's review, containing 202 literature references, is the most comprehensive summary of literature data on thermal decomposition of AP that has been published in several decades. It is a very valuable source of information for further in-depth study of the thermal decomposition of AP. The mechanism of thermal decomposition and various factors which influence the thermal decomposition of AP are discussed in detail with numerous references to published literature.

Boldyrev's [17] summary updates and supersedes an earlier excellent summary by Jacobs and Whitehead [16]. This contained a fantastically high number of useful citations (419 references) and remains an excellent source for the interested reader and researchers alike. It also supersedes the summary published by Keenan and Siegmund in the same year [342].

Other summaries on AP decomposition are in book chapters [343, 344]. Two additional very detailed reviews discuss the effect of particle size in coarse AP on decomposition mechanisms and burning rates [345, 346].

The thermal decomposition of AP goes through two stages. The LTD at 420 to 600 K is an autocatalytic nucleation and growth process. In this regime, a crystallographic phase transition at 513 K complicates matters further. Reaction rates just above 513 K are noticeably slower than rates immediately below this temperature. The solid product of this low-temperature reaction makes up about 70% of the initial mass and is chemically identical with the initial reactant but has an increased surface area. The HTD above 600 K does not leave any residue. This reaction may be accompanied by sublimation if the pressure is low enough.

In addition to a comprehensive summary of the thermal decomposition of AP, NH_4ClO_4 , this section of the book also contains a sub-section on the thermal decomposition of the much less stable ammonium chlorate, NH_4ClO_3 . This compound can

be found as a contaminant in AP and has been the cause of numerous accidents in fireworks.

4.3.1 Stoichiometry and Thermodynamics of AP Thermal Decomposition

The decomposition of AP is characterized by two parallel processes: an irreversible and destructive reaction and dissociative sublimation in a reversible equilibrium situation. At moderate temperatures, the dissociative sublimation can be neglected due to the low vapor pressure of perchloric acid, which is one of the dissociation products. At high temperatures (523–773 K = 350–500 °C), and without trapping the dissociation products, the role of sublimation becomes more significant.

The auto-decomposition of AP results in a mixture of reaction products, the exact composition of which depends on the reaction conditions (adiabatic versus isothermal, pressure) and on the absence or presence of contaminants and potential catalysts. Chemical analysis of the reaction products does not always agree with thermodynamic equilibrium predictions.

Figure 17 shows the theoretical adiabatic temperature of complete AP decomposition under equilibrium conditions and constant volume as a function of loading density.

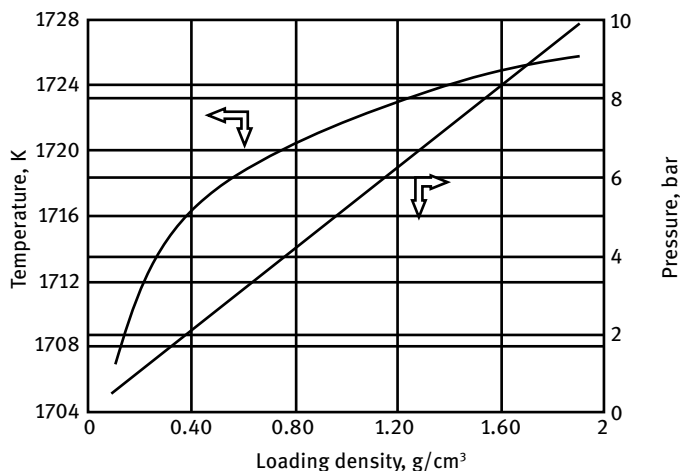
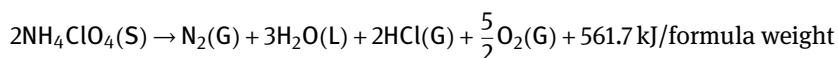


Figure 17: Adiabatic flame temperature of AP decomposition.

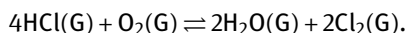
The simplest decomposition equation would be:



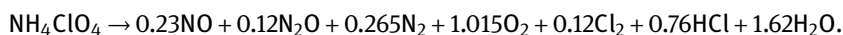
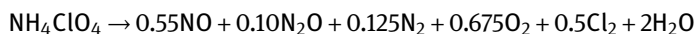
$$\begin{aligned}
 280.9 \frac{\text{kJ}}{\text{mol}} \text{NH}_4\text{ClO}_4 &= 2390 \frac{\text{kJ}}{\text{kg}} \text{NH}_4\text{ClO}_4 \\
 2 \times -295.767 &= 3 \times -285.830 + 2 \times -92.31 + \Delta H_{\text{react}} \\
 -480.387 &= -857.49 - 184.62 + \Delta H_{\text{react}} = -1042.11 + \Delta H_{\text{react}} \\
 \Delta H_{\text{react}} &= 1042.11 - 480.387 = 561.723 \frac{\text{kJ}}{\text{FW}} = 280.86 \frac{\text{kJ}}{\text{mol}} = 2390 \frac{\text{kJ}}{\text{kg}} \\
 \text{AP } M &= 117.489 \frac{\text{g}}{\text{mol}} = 8.5114 \frac{\text{mol}}{\text{kg}}
 \end{aligned}$$

but that is not always what the chemical analysis of the reaction products shows. HCl can dissolve in water as soon as the water condenses in the combustion bomb. This forms a saturated aqueous solution of hydrochloric acid. Room-temperature reagent-grade aqueous HCl typically contains 37 mass-% HCl.

The theoretical adiabatic flame temperature at atmospheric pressure is 1385 K (1112 °C). HCl and O₂ form a pressure-dependent equilibrium



Other measurements suggest that the decomposition of AP at 101 and 6895 kPa (14.7 and 1000 psia) proceeds according to the following equations:



4.3.2 Experimental Studies of AP Thermal Stability and Decomposition

There are many experimental methods to study the thermal stability of AP and AP-based propellants including DTA, TGA, DSC, volumetric gas evolution, Raman spectroscopy, and mass spectrometry. The volatile pyrolysis products can be analyzed using rapid-response analytical instruments such as FTIR or mass spectrometers to detect and identify intermediates of the decomposition reaction. The rate of heating is one of the test variables. Heating rates in DTA, DSC, and TGA are generally slow (1–10 °C/min.). Unfortunately, when looking at existing literature, information on heating rates is not always provided when summarizing the onset of exotherms or other endo/exothermic phenomena. More rapid heating for flash pyrolysis studies can be achieved by heating the sample with a laser or placing a thin film on a resistance-heated metal foil (T-jump pyrolysis).

The thermal decomposition of AP is sensitive to catalysis by contact with container materials in which it is contained during the DTA or DSC test. A common DSC crucible material is pure (soft) aluminum. Pure aluminum has little or no catalytic effect on AP decomposition, but some aluminum alloys (“Duralumin” similar to AA2024, which contains 4.4% copper) and stainless steel cause accelerated decomposition [347]. Comparing results obtained in aluminum and with a mica dish, the DTA thermograms obtained with ‘as received’ and doubly recrystallized AP were essentially the same.

4.3.3 Slow AP Decomposition

There are many techniques available to study the slow decomposition of AP and similar ammonium salt oxidizers. The methods used for the study of AP decomposition include:

- DTA
- DSC
- TGA
- Gas evolution measurements
- IR spectrometry
- Raman spectrometry

To organize the literature on AP decomposition we have subdivided the material by the rate of decomposition, slow decomposition at temperatures below and near the melting point, and rapid decomposition at temperatures that are closer to those encountered in rocket motors.

Other subdivisions can be created, such as by the purity of the AP sample and the presence or absence of catalysts or inhibitors. There are many AP decomposition studies that used single crystals with direct observation, where the progression of decomposition sometimes documents itself by the initially clear crystal turning opaque as the crystal lattice changes and with the evolution of embedded bubbles. The decomposition often spreads visually, which is evident from crystal defects that act as nuclei for the start of the reaction.

Bircumshaw and Newman [348, 349] observed that when AP thermal decomposition occurs in the orthorhombic crystal phase, the mass conversion rate in the orthorhombic crystal phase was faster than in the cubic crystal phase. At temperatures below the normal AP phase transition temperature, the orthorhombic crystal phase decomposition process had a variable induction period before decomposition started.

The low-temperature orthorhombic crystal phase decomposition process produces AP particle porosity, leading to a mechanism for an increased rate of mass conversion to gaseous products [350]. High-speed cinematography of burning coarse AP crystals demonstrated that the pore formation and the pores became the source of decomposition gaseous products. Microscopic observation of heated crystals could see clouds of small (about one micron) particles, which are described as nuclei. These nuclei were non-uniformly distributed but moved and joined up to form reactive centers. Reactive centers grew to a maximum size of about 2 microns and then ceased to grow. Microscopic amounts of liquid containing water were contained in the reactive centers. The maximum size for reactive centers was assumed to be inhibited by local rising water content from AP decomposition. At 507 K (234 °C) nuclei had maximum linear velocity along the main orthorhombic crystal axis in the range of 7 to 10 microns per minute. Smaller nuclei moved faster than larger ones. Activation energies for nuclei movement were determined as being 130 kJ/mol (31 kcal/mol) along the orthorhombic crystal longitudinal axes and 138 kJ/mol (33 kcal/mol) in the

transverse direction. The transverse velocity of nuclei was roughly about one-tenth that along the main orthorhombic crystal axis. Natural and acquired trace impurities are most likely present at the nuclei responsible for porosity formation. Rates of porosity production in coarse oxidizer during solid propellant combustion influences burn rates, burn rate pressure exponents, the violence of slow cookoff trials, and even erosion rates under high-velocity erosive burn recession conditions.

Phase changes and decomposition of AP take place simultaneously. Most investigators have identified only one polymorphic phase change in the range between 503 and 523 K. One investigator suggested that an irreversible second-order phase transition takes place at 513 K and the reversible orthorhombic-cubic transition takes place at 523–543 K [351]. The irreversible second-order transition was said to be the real cause for the change in the decomposition rate at 513 K. Visual observation of the orthorhombic to cubic transition in a single crystal revealed that the transition was accompanied by the appearance of a large number of surface cracks and an apparent sudden increase in surface reaction (i.e., growth of reaction nuclei). One needs to determine whether the amorphous layer, which first appears to form on the large crystal surface, is transformed into crystallites or decomposes (or sublimes), leaving behind the observed structures.

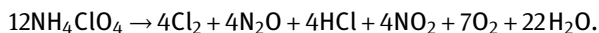
Over the course of six years, from 1962 through 1967, and under the sponsorship of AFOSR with two consecutive contracts, Atlantic Research Corp. has conducted a detailed investigation on the deflagration of high-energy solid oxidizers containing the perchlorate anion [352, 353]. This included AP, hydrazinium(2+) diperchlorate (see *Encyclopedia of Oxidizers*, chapter *Hydrazinium Salts*), and hydroxylammonium perchlorate (see *Encyclopedia of Oxidizers*, chapter *Hydroxylammonium Salts*).

AP is stable at room temperature but decomposes at measurable rates over a wide temperature range from 473 to 713 K (200 to 440 °C). It undergoes an autocatalytic decomposition between 473 and 573 K (200 °C and 300 °C), which is limited to about 30% decomposition and is often called LTD. At 573 to 703 K (300 to 430 °C), the HTD takes over. This reaction is not autocatalytic. Concurrently with these decomposition reactions, AP also undergoes dissociative sublimation both in the LTD and HTD regions and ions can be detected in the vapor phase. At about 673 K (400 °C), AP decomposes very rapidly and suddenly explodes after a short induction period.

A mass-spectrometric investigation of the products of thermal decomposition of AP placed the furnace with the decomposing AP near the ion source of a mass spectrometer [354]. At 384–393 K (111–120 °C), the main products were NH_3 , HCl , Cl_2 , O_2 , and small amounts of nitrogen oxides among the products of decomposition. The molecular complex NH_3HClO_4 was not found. Its existence was postulated in previous investigations of the thermal decomposition of AP. Analyzing the results obtained, Heath and Majer concluded that the primary products of the thermal decomposition of AP are ammonia and perchloric acid. It is not clear why they excluded the possibility of secondary reactions in the gas phase. The presence of HClO_4 , NO , NO_2 , O_2 , and Cl_2 among the products under high vacuum conditions indicate the occurrence

of a parallel reaction proceeding in the condensed phase. However, the high vacuum decomposition products may have contained significant quantities of NO_2 and HCl in addition to the usual major products given as Cl_2 , N_2O , O_2 , and H_2O . The reported product distributions were semi-quantitative, however, because only uncorrected ion intensities were given. Since each AP sample was pyrolyzed in a sequence of increasing temperature steps, the respective effects of time and temperature were uncertain. The appearance of somewhat higher decomposition rates under high vacuum, however, was apparent since their sample was entirely consumed by decomposition and sublimation below 200°C . An additional contribution of their study involved determinations of the 70 eV HClO_4 fragmentation pattern and the effects of a hot platinum filament on the heterogeneous decomposition of HClO_4 .

The decomposition of AP at low pressures and constant temperatures was measured using a TOF mass spectrometer [355]. Chlorine concentration was measured as a function of time and sample temperature. The pyrolysis was conducted under high vacuum conditions where secondary reaction effects are minimized. Perchloric acid and argon were used as internal standards to calibrate the ion intensity, but of course, HClO_4 was also an intermediate decomposition product. The activation energy for sublimation was 89.96 kJ/mol (21.5 kcal/mol). Only small amounts of nitrogen and OClO were detected. Ions that were expected but not found were NH_4^+ , ClO_4^+ , $\text{NH}_4\text{ClO}_4^+$, $\text{HClO}_4\text{HClO}_4^+$, NOCl^+ , N_2O_4^+ , and Cl_2O_3^+ . The intensities of peaks attributed to HClO_3^+ , HClO_2^+ , HClO^+ , and ClO^+ were approximately proportional to HClO_4^+ and agreed with data reported by other investigators. The data indicated that the decomposition stoichiometry can be described by



The same authors later studied the rapid thermolysis of AP using a laser as the heat source. The acidity that develops during AP decomposition can be used as an indication of changes occurring in the material [356, 357]. AP becomes acidic at about 493 K (220°C) and reaches a maximum of acidity at 513 K (240°C). The acidity was not caused by HCl , HNO_3 , or HNO_2 . Therefore it was most likely caused by free HClO_4 . The effects of particle size, ambient atmosphere, additives, and prior irradiations by X-rays or UV on AP decomposition were studied using acidity as an indicator. Metal chlorides, chromic oxide, potassium chromate, or potassium bichromate added as contaminants accelerated the decomposition of AP.

TGA, DTA, XRD, gas chromatography (GC), and MS were used to study the decomposition of AP crystals which were recrystallized from acidic solutions or water and were found to have a number of defects [358, 359]. Surprisingly, the rate of thermal decomposition of AP with a normal structure is faster than that of AP with a defective structure. HClO_4 accelerates the thermal decomposition of AP. When AP was pulverized, its defective structure changed to a normal structure and a small amount of HClO_4 was formed. When AP was heated the defective crystal structure gradually changed to a normal one, its volume increased, and the formation of HClO_4

became noticeable. At temperatures beyond the transition point, a first exotherm occurs, but following this step, the residual AP decomposed exothermally at higher temperatures. NiO accelerated the thermal decomposition of AP and the burning velocity of AP/polybutadiene propellants.

The influence of various parameters on the thermal decomposition of AP at low temperatures revealed that there is a critical value for the particle size on either side of which the reaction rate decreases [360]. An electron transfer mechanism (involving point defects) is supposed to account for decomposition. A proton transfer mechanism leads to sublimation. The effect of aging the crystals at room temperature in vacuo or at 383 K in air resulted in a marked decrease in the rate of gas release. This was attributed to healing of crystal defects by annealing, thus giving fewer nuclei where decomposition starts.

The slow isothermal decomposition of AP single-crystal sections at a relatively low temperature of 483 K (210 °C) was studied using cleaved sections of large single crystals grown from a water solution [361]. Crystals heated isothermally for several hours at 483 K (210 °C) (without igniting) turned optically opaque. This information was later used in the interpretation of the crystal appearance near the flame front in quenched and partially burned crystals.

When heating AP in a constant volume apparatus at a varying mass of AP : volume ratios and measuring the pressure at a constant temperature, AP decomposes each time to a point corresponding to a constant pressure at a particular temperature (e.g., 212 kPa at 423 K) [362]. This indicates an inhibition of thermal decomposition of AP by the products. The extent of decomposition varied from 73% to 1% depending on the mass of AP : volume ratio. Water was found to have a pronounced retarding effect, increasing the induction period and decreasing the pressure at which decomposition ceases. It was theorized that chlorine oxides such as Cl_2O_6 and Cl_2O_7 play a role in the decomposition mechanism. The latter is the anhydride of HClO_4 .

The kinetic constants of AP decomposition in the range from 469 to 553 K (196 to 280 °C) were measured [363]. At the phase transition temperature, only k_2 (the constant connected with the acceleration of the process) changed, whereas k_1 continued to increase with the temperature. As a by-product of the decomposition at both 20 mm Hg and at atmospheric pressure, a condensate was obtained on a cool (about 50 °C) quartz plate and identified as pure (sublimed) AP.

Large single crystals of AP thermally treated for 40 minutes at 499 K (226 °C) at 20 mm Hg pressure and then examined under the SEM revealed rectangular holes which make up the decomposition nucleus [364]. The holes have the shape of the *m*-face with edges running parallel to the edges of the *m*-face. They are arranged in a disk-like pattern and eventually develop into a porous residue. Furthermore, the decomposition seems to occur in layers with the size of the holes becoming smaller and smaller with increasing depth. When the decomposition is stopped after different lengths of time, it could be seen that, in the case of pure AP, the

decomposition interface advanced linearly with time into the crystal. Similar tests were then performed with AP that had been doped with MnO_4^- ions.

An investigation of the thermal decomposition kinetics of AP in terms of weight loss and gas release in the 593–726 K (320–453 °C) range measured total decomposition kinetics up to 663 K (390 °C) and kinetics of the initial fast stage from 668–726 K (395–453 °C) [365, 366]. In the first stage, the initial reaction rate increased more rapidly than the autocatalytic effect. The reaction time at temperatures above 573 K (300 °C) was comparable with the time of heating and thus the kinetics measurements were not reliable enough. The reaction rate in the second stage also increased and was almost independent of the degree of conversion. The velocity may be expressed by the kinetic equation of zero-order $da/dt = k_3$. The value of k_3 depends on temperature according to the equation

$$k_3 = 5.8 \times 10^6 \exp(-32,500/RT) \text{ s}^{-1}$$

in the temperature range between 533 and 663 K (260 and 390 °C). The decomposition kinetics of AP at 668–726 K (395–453 °C) were studied by placing 10 mg AP on an electrically heated Ni-Cr plate under nitrogen at 26.58 kPa (200 mm Hg) pressure. The course of the initial stage could be described with 1st order kinetics. The temperature dependence can be expressed by the equation

$$k_1 = 10^9 \exp(-32000/RT) \text{ s}^{-1}.$$

This equation is identical with that obtained for the temperature range 573–553 K (200–280 °C). The linear pyrolysis method using rectangular molded specimens of AP pressed against a hot bar evaluates the dependence between the temperature T_0 and the rate of decomposition u . The plots of $\log u$ versus $1/T_0$ revealed two different regions; at $T_0 > 773$ –823 K (>500–550 °C), the pressure on the specimen exerts no remarkable influence; the material of the hot bar may accelerate the decomposition (such as several metals or their oxides). The flame appeared only when the specimen was pulled back from the bar so that a small gap was formed between them. The rate of regression at 553–773 K (280–500 °C) on a mica plate under atmospheric pressure can be expressed by the equation

$$u = 2.5 \times 10^6 \exp(-30,200/RT) \frac{\text{mm}}{\text{s}}.$$

This corresponds to $k_0 = 5.9 \times 10^6 \text{ s}^{-1}$. The decrease of decomposition rates >573 K (>300 °C) was explained in terms of structural changes such as dislocations and defects of the crystal lattice. The results revealed that the kinetic reaction parameters (k_0 and E) remained constant over a wide temperature interval (473–723 K = 200–450 °C). However, above 573 K (300 °C), the fraction of material decomposing during the first fast stage of the reaction decreased.

The slow rate of decomposition of AP depends strongly on the conditions under which the AP was recrystallized and on the age of the crystals. The reactivity of AP as

a function of the method of preparation and the age of the material was studied using constant volume isothermal decomposition [367]. Samples were prepared by:

- (1) dissolving analytical grade AP in H_2O at 333–343 K (60–70 °C) and allowing it to recrystallize by cooling to room temperature;
- (2) recrystallizing AP from a saturated aqueous solution cooled to 278 K (5 °C); and
- (3) growing single crystals from a saturated aqueous solution at 318 K (45 °C), then cooling at a rate of 0.1–0.01°/d.

The slow decomposition of AP was studied at 503, 573, and 673 K (230, 300, and 400 °C). Sample (2) was more reactive than sample (1) at all temperatures studied. Sample (2) and sample (3) sublime more readily than sample (1), which was corroborated by DTA measurements. Isothermal decomposition of freshly prepared and aged samples of (1) at the three temperatures indicated that during the first seven days after growth definite desensitization occurs followed by a marked increase in reactivity after 15 days.

AP sometimes needs to be modified to prevent or reduce the risk of inadvertent reignition of extinguishable solid rocket motors. Two methods were found that could eliminate or reduce the exothermicity of propellant grade AP exposed to temperatures of 350–390 °C during soakback [368]. One was a thermal pre-treatment and the other involved an additive. Prebaking AP eliminates the first exotherm and facilitates AP to be used in extinguishable rocket motors without the potential of unintentional reignition of the propellant grain. It was found that AP (in which this first exothermic peak was eliminated) could be prepared by heating the propellant grade AP to 638–663 K (365–390 °C) for several minutes and then allowing it to cool. Furthermore, this exothermic peak was eliminated via the pre-heating technique, even when the fluorocarbon polymer binder was in contact with the AP. This technique for preventing the first exotherm was successful in all samples of AP tested; the samples varied in particle sizes and were from several sources. Another method to prevent reignition was to add several percent of an inert ammonium salt to the AP.

The decomposition of AP in the gas phase at elevated temperatures was studied by allowing the vapor from a sample of subliming AP to pass through a secondary furnace maintained at a higher temperature than that of the subliming AP [369]. The reaction occurring in the secondary furnace was monitored using a pin-hole leak connected to a mass spectrometer. The effects of temperature and the addition of diluent gases were studied and the major products were identified, such as H_2O , O_2 , HCl , N_2O , NO_2 , Cl_2 , NH_2Cl , and NH_3 . Ammonia addition reduced the concentrations of all products except NH_2Cl , which increased. The early literature discussing with AP thermal decomposition up until 1968 was summarized in a review article [342, 370] (see [371, 372]).

In order to avoid secondary reactions and to analyze primary decomposition products, the AP crystal and the analyzing mass spectrometer have to be close-coupled. This is possible with an experimental gas sampling system that approximates a collision-free molecular beam [373]. Results with this system indicate

the occurrence of an exothermic surface reaction with ClO_2 as a major product resulting from the pyrolysis of AP between 473 and 673 K. Analyzing the off-gassing during AP decomposition with a mass spectrometer helps to identify the first and intermediate steps of the decomposition reaction [374].

The kinetics of AP solid state thermal decompositions between 473 and 573 K (200 and 300 °C) were measured using both single crystals and pressed pellets [159]. Kinetic analysis of the TGA decomposition curve by a non-linear least-squares computer program revealed that **(1)** the decomposition consists of four distinct stages, **(2)** the major part of the entire reaction ($0.01 < \alpha < 1.00$, where α is the decomposition fraction) can be described by an Avrami equation, **(3)** the so-called [induction period] involves a linear process plus an exponential process and involves only the first 1% of the total decomposition, and **(4)** the induction period is usually preceded by desorption of previously adsorbed species. The inward growth of surface nuclei is a linear process. Branching of surface nuclei along preferred crystallographic directions leads to exponential growth. This was confirmed by the microscopic observation of decomposing AP crystals under a hot stage microscope. In addition to this, the electrical conductivity of crystals was measured while the decomposition was in progress.

If FTIR is used, ordinarily the decomposition products of AP and other oxidizers are analyzed using their IR absorption when the beam transits the sample. A different IR technique uses the surface reflection of a decomposing AP crystal to observe solid-solid phase changes or decomposition products that accumulate on the surface [375]. The infrared spectra of the surfaces of AP crystals while being heated up to 250 °C have been obtained using internal reflectance spectroscopy. The crystal transformation from rhombic to cubic can be observed in this manner.

Using a TOF mass spectrometer and a probe that sucks species off the surface of decomposing AP crystals, it was attempted to identify the first products that leave the crystal surface at the very beginning of the decomposition process [376]. The species of most concern, HNO ($m/e = 31$), was found as a minor constituent by both high and low-resolution measurements at temperatures above 353 K (80 °C). This was confirmed by the strong reduction of $m/e = 31$ when deuterated AP instead of regular AP was decomposed because DNO occurs at $m/e = 32$. It is considered highly improbable that HNO could have occurred due to reactions other than surface thermal reactions. High-resolution spectra were used to separate the atomic oxygen (or doubly charged O_2) and NH_2 peaks at $m/e = 16$. Other hydrides of nitrogen were also found: NH_4 , NH_2 , and NH . No condensed-phase decomposition species were found at 80 °C or below. Perchloric acid, atomic chlorine, and all the simple chlorine oxides were found, but Cl_2 , HClO , HClO_2 , HClO_3 , or ClO_4 were not detected. Also not detected in the condensed phase were N_2 , N_2O , and NO_2 . The mass range monitored was from m/e 12 to 200. No parent $\text{NH}_4\text{ClO}_4^+$ ion was detected in any of the experiments.

The composition of chlorine-containing thermolysis products during TGA in the temperature range 160–220 °C at atmospheric pressure was measured under conditions of equilibrium of the decomposing AP with the decay products in the

gaseous phase [377]. Products were analyzed using potentiometric titration and UV spectrophotometry to determine the concentration of free chlorine, chloride-ions, and the sum of oxychloro-anions and perchloric acid.

The heat effect of the first exotherm of AP decomposition was $84.3 \text{ cal/g} = 9.9 \text{ kcal/mol} = 41.4 \text{ kJ/mol}$ as determined by isothermal methods and $87.5 \text{ cal/g} = 10.3 \text{ kcal/mol}$ by programmed constant heating rate scanning methods [112]. The heat effect for the second high-temperature exotherm was $190 \text{ cal/g} = 20.3 \text{ kcal/mol} = 84.9 \text{ kJ/mol}$ as determined by DSC. Scanning operations were carried out at heating rates of 2, 4, 8, 16, 32, and 64 K/min . The activation energy derived from the equation $\log S/\Delta H$ versus $1/T$ was $94.6 \text{ kJ/mol} = 22.6 \text{ kcal/mol}$ for the first exotherm and $253 \text{ kJ/mol} = 60.5 \text{ kcal/mol}$ for the second exotherm. Isothermal decomposition of AP produced activation energy of 88.7 to 109.6 kJ/mol (21.2 to 26.2 kcal/mol). The values of the activation energy for the low-temperature and high-temperature exotherms were in close agreement with reported literature values.

During the decomposition of AP powder at 733 K (460°C) the following ions were observed using mass spectrometry: N_2^+ , NO^+ , O_2^+ , HCl^+ , N_2O^+ , and Cl_2^+ [378]. The rate of decomposition depends on the crucible material. Some crucible metals catalyze the reaction.

In addition to the study of isolated AP decomposition, some investigators looked at slow heating rates and isothermal AP decomposition in the presence and absence of a binder (PS) [379]. Thermal changes and activation energies associated with thermal decomposition of PS and AP and propellants were derived from DSC thermograms of PS, AP, and a PS/AP propellant. The AP endotherm started at $517 \pm 2 \text{ K}$ (244°C). The endothermic enthalpy change was calculated to be $10 \pm 0.3 \text{ kJ/mol}$ ($2.39 \pm 0.07 \text{ kcal/mol}$), which agreed well with other reported literature values. About 30% decomposition had already occurred in the low-temperature exotherm (LTE) during both scanning and isothermal operations, which was in accordance with TGA measurements. The total exothermic heat release of both LTE and HTE was estimated to be $1163 \pm 40 \text{ J/g}$ ($278 \pm 10 \text{ cal/g}$). The E_{act} for LTE and HTE in scanning operations were 94 kJ/mol (22.5 kcal/mol) and 253 kJ/mol (60.5 kcal/mol), respectively, which agreed fairly well with values using other techniques. The AP/PS propellant exotherm starts at a later stage than the first exotherm of pure AP.

TOF and high-resolution mass spectrometry of AP and its deuterated derivative were examined in an effort to identify some of the key decomposition species [246]. HNO (mass 31) was found as a minor component at temperatures above 353 K (80°C). It is considered highly improbable that HNO could have occurred by reactions other than surface thermal reactions. High-resolution spectra were used to separate O_2^{2+} and O^+ from NH_2 at mass 16. The presence of NH_2^+ was confirmed along with NH_4^+ , NH_3^+ , and NH^+ . HClO_4^+ , Cl^+ , and all the simple oxides of chlorine were found but Cl_2^+ , HClO^+ , HClO_2^+ , HClO_3^+ , and ClO_4^+ were not detected. Also not detected were N_2^+ , N_2O^+ , and NO_2^+ in the condensed phase. No undissociated parent $\text{NH}_4\text{ClO}_4^+$ was present.

The breakdown of the crystal lattice of AP in the 300–625 K range has been studied by laser Raman spectroscopy [121, 122]. A thorough study was then conducted to examine the decomposition of AP crystals as a function of temperature in the 300–625 K range, as a function of pressure in the 0–40 kbar range, and as a function of isomorphously incorporated K^+ ions in the catalytic level concentration. These results helped one to understand how the oxidizer lattice is destabilized and begins to decompose. Detailed examination of the external and internal modes of the perchlorate ion revealed that the onset of essentially unhindered tumbling of the ClO_4^- ion may be intimately tied to the decomposition of AP. The frequency and linewidth of the ClO_4^- bending modes can be used as a crystal [thermometer]. The effect of K^+ as an isomorphous dopant in the crystal lattice is to permit the ClO_4^- ion to tumble at a lower temperature (addition of 0.8% K^+ produced a 10–15 K lowering in the tumbling temperature) and thus decompose at a lower temperature. Pressure effects on AP decomposition at 300 K show normal behavior. Pressure does not play a significant role in AP crystal decomposition. All vibrational modes found in AP from 40 cm^{-1} to 3500 cm^{-1} (including several not previously reported ones) were assigned, insofar as possible.

A non-confined AP single crystal was placed in a flow of heated N_2 gas and the temperature was regulated to $\pm 2\text{ K}$ using the flow rate. Repetitive Raman spectra were recorded [242]. Notable decomposition was observed beginning at 475 K. The broadening of the ClO_4^- bending modes without broadening of the A_1 stretch may have resulted from the onset of essentially unhindered rotational motion of the ClO_4^- ion. Two very weak previously unreported bands appeared in the orthorhombic phase at 715 and 543 cm^{-1} .

Hydrochloric and nitric acids accumulate during the thermal decomposition of orthorhombic AP in the solid. The concentrations of the acids increase up to a point where 15% degree of the AP has decomposed, after which they decrease again [380].

Samples of AP were aged at 373 and 523 K (100 and 150 °C) prior to heating them in a DTA-TGA. Depending on the aging time, AP revealed different decomposition characteristics [381]. The competing effects of sublimation and thermal decomposition could be separated using a special experimental arrangement. IR spectral investigations of decomposing AP produced information on intermediates formed during the decomposition of AP [382].

The thermal decomposition of solid, molten, and dissolved AP was examined over a wide temperature range from 488 to 658 K (215 to 385 °C) [383]. Over the entire temperature range, the decomposition appeared to proceed on a first-order reaction up to a point where 70% of the original AP was decomposed. In methanol solution, the rate of AP decomposition was similar to that of neat AP, but in aqueous solution, it was substantially slower than that of neat AP. Activation energies and frequency factors were listed for each condition. There may be some chemical interaction between methanol and AP.

Two different techniques, isothermal cook-off of small samples and gas evolution measurements with analysis using a chemiluminescence technique were used to

study the thermal decomposition kinetics of AP [384]. Most of the work was done on commercial propellant-grade AP powder in the 200 μm diameter particle size range. The cook-off tests were used to derive the critical temperatures (i.e., the minimum thermal runaway temperatures) for four sample sizes: 40 mg, 100 mg, 30 g, and 1200 g. The first-order decomposition rate coefficients at 438–603 K (165–330 °C) were between 1×10^{-6} and $3 \times 10^{-2} \text{ s}^{-1}$. Gas evolution rate measurements at 343–383 K (70–110 °C) produced rate coefficients that were several orders of magnitude smaller than any previous kinetic measurements. The activation energies for the two methods were almost identical. The cook-off rate data were fitted to the expression

$$k = A \exp\left[\frac{-E}{RT}\right] = 2.1 \times 10^9 \exp[-126400/RT]$$

where E is the activation energy in kJ/mol. The high-temperature rates obtained with commercial-grade AP at 513–603 K (240–330 °C) were several orders of magnitude higher than previous academic data for very pure AP. These data are, therefore, more applicable to industrial hazard analyses like those conducted in the aftermath of the Henderson explosion. The activation energy did not change at the temperature where AP undergoes a phase change of crystal structure at 513 K.

The decomposition of propellant-grade AP was studied under isothermal conditions in Argon at atmospheric pressure [385]. The weight loss of small samples was determined as a function of time, particle size, temperature, and crystal structure. The weight loss versus time curves has a low rate (slope) branch for the sublimation of highly porous residue which is generated during particle decomposition. The rate of partial decomposition depended on temperature, particle size, and crystal phase, whereas its extent changed with particle size and crystal phase. Sublimation appeared to be particle size independent. The interpretation of weight loss data was supported by optical and SEM of AP samples before and after thermal treatment. These data are needed in predicting the cook-off hazard of AP-based propellants.

The weight loss of small AP samples was measured as a function of time, temperature, and particle size [386]. The rate constants for two size fractions were obtained at six different temperatures. Activation energies for the decomposition of the fine and coarse size fractions were $133 \pm 4 \text{ kJ/mol}$ ($31.78 \pm 0.96 \text{ kcal/mol}$) and $110 \pm 1.7 \text{ kJ/mol}$ ($26.27 \pm 0.42 \text{ kcal/mol}$), respectively. The activation energy for the initiation period was $124 \pm 4.6 \text{ kJ/mol}$ ($29.62 \pm 1.1 \text{ kcal/mol}$).

The thermal decomposition of AP and AP-based composite propellants was studied using the simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) technique [387]. The main objective was to evaluate whether STMBMS can provide new data on AP decomposition that will provide sufficient detail on the reaction mechanisms and associated reaction kinetics to permit the creation of a detailed model of the thermal decomposition process with and without the presence of a binder. Such a model is a necessary ingredient to engineering models of ignition and for a slow-cookoff for these AP-based composite propellants. Results revealed

that the decomposition of pure AP is controlled by two processes: One occurs at lower temperatures ($513\text{--}543\text{ K} = 240\text{--}270\text{ }^{\circ}\text{C}$), produces mainly H_2O , O_2 , Cl_2 , N_2O , and HCl , and is shown to occur in the solid phase within the AP particles. Two-hundred μm diameter AP particles undergo decomposition in the solid phase, whereas $20\text{ }\mu\text{m}$ diameter AP particles react differently. The second process is dissociative sublimation of AP to NH_3 and HClO_4 , followed by the decomposition of, and reaction between, these two products in the gas phase. The dissociative sublimation process occurs over the entire temperature range of AP decomposition but only becomes dominant at temperatures above those for the solid-phase decomposition.

STMBMS was used to give a 3-D plot of z = peak intensity, x = mass, and y = temperature for slow AP decomposition [388, 389]. The data revealed that the overall decomposition is characterized by three distinguishing features: an induction period, an acceleratory period, and a deceleratory period. The major decomposition event occurs in the subsurface of the AP particles and propagates towards the center of the particle with time. The amount of total decomposition is dependent upon particle size and increases from 23% for $\sim 50\text{ }\mu\text{m}$ -diameter AP to 33% for $\sim 200\text{ }\mu\text{m}$ -diameter AP. This is one of the few methods that can separate the chemical and physical decomposition processes from one another.

Based on SEM results of the thermal decomposition of AP in the orthorhombic phase, the overall decomposition is characterized by three distinguishing features: an induction period, an accelerator period, and a deceleratory period [390]. The major decomposition event occurs in the subsurface of the AP particles and propagates towards the center of the particle with time. The amount of total decomposition is dependent upon particle size and increases from 23% for $\sim 50\text{ }\mu\text{m}$ -diameter AP to 33% for $\sim 200\text{ }\mu\text{m}$ -diameter AP. Gas formation rates were measured for the gaseous products and correlated with the visual observations.

AP decomposition is characterized by the occurrence of one major event that consumes up to 35% of the AP, depending upon particle size, and leaves behind a porous agglomerate of AP [391, 392]. The major gaseous products released during this event include H_2O , O_2 , Cl_2 , N_2O , and HCl . The major decomposition event follows three chemical pathways: The first and third channels are affected by the pressure in the reaction cell and occur at the surface or in the gas phase above the surface of the AP particles. The second channel is not affected by pressure and accounts for the solid-phase reactions characteristics of *o*-AP. The third channel involves the interactions of the decomposition products with the surface of the AP.

The decomposition of production-grade AP was studied under isothermal conditions in Argon at atmospheric pressure [393]. The weight loss of small AP samples was determined as a function of time, particle size, temperature, and crystal structure. The weight loss versus time curve had a characteristics sigmoidal shape for the irreversible partial decomposition of AP, which was followed by a low rate (slope) branch for the sublimation of the highly porous residue generated during partial decomposition. The rate of partial decomposition depended on temperature, particle size, and crystal phase, whereas its extent changed with particle size and crystal phase.

The thermal decomposition characteristics of AP and an AP-based composite propellant were measured at temperatures less than 543 K (270 °C) [394]. The studies utilized various techniques to evaluate the thermal decomposition of neat AP as a function of time, particle size, temperature, and crystal structure.

Kinetic measurements for the fine, medium and coarse size fractions of AP revealed that the kinetic parameters changed with particle size [395]. The correlation between particle size and kinetics may be one of the reasons for the scatter in the kinetic data as reported in the literature. In addition to particle size, temperature, and time, there also was an effect of the TCP coating on weight loss during decomposition.

The thermal decomposition of AN and AP was investigated using an accelerating rate calorimeter (ARC). The curves of the thermal decomposition temperature and pressure versus time for the two systems are obviously different. The kinetic parameters such as apparent activation energy and pre-exponential factor of the thermal decomposition of AN and AP were calculated and compared [396].

The isothermal decomposition and sublimation of large TCP-coated AP particles were studied in the temperature range 419–449 K (146–176 °C), where AP is in the cubic phase [397, 398]. The course of the reaction was followed by TGA by measuring the weight loss as a function of temperature and time. Upon phase transition, AP became more stable. The analysis of the weight loss curves yielded activation energies E_a of 85.0 and 146.2 kJ/mol (20.31 kcal/mol and 34.94 kcal/mol) and pre-exponential factors A of $5.48 \times 10^6 \text{ min}^{-1}$ and $1.20 \times 10^{13} \text{ min}^{-1}$ for the decomposition and initiation time, respectively, of cubic AP. Sublimation, in contrast to decomposition, did not show a break upon transition to the cubic phase. Weight loss data was analyzed using the same equation that was used for orthorhombic AP. The analysis yielded $E_a = 130.7 \text{ kJ/mol} = 31.25 \text{ kcal/mol}$ and $A = 5.95 \times 10^{10} \text{ h}^{-1}$ for the kinetic parameters. Sublimation rates were considerably smaller than decomposition rates allowing analysis of decomposition data without correction for weight loss due to sublimation. Decomposition and sublimation kinetics for cubic AP were used to calculate the decomposition and sublimation rates of cubic AP that was heated at constant rates. The TGA results were compared to those of DSC tests and applied to determine the time to cookoff of larger samples of AP-based propellants.

FTIR analysis identified species involved in the solid decomposition step and pointed toward the importance of the diffusion of species in the solid [399] (see [400] also).

Most of the work on the slow decomposition of AP was done in the 1960s and 1970s. However, this was not always with unequivocal results; some questions remained unanswered. It was, therefore, very welcome when a fresh approach to the study of AP decomposition was undertaken by Longuet and Gillard in 2009. The researchers repeated some of the earlier tests but used modern equipment [401] such as TGA/MS, SEM, and FTIR. The objective of this work was to clarify the differences observed in the literature in order to understand the detailed decomposition kinetic process of AP and to establish analytical laws to facilitate the prediction of the thermal behavior of AP.

They re-measured the influence of particle size, the nature of gaseous decomposition products, and the morphologic evolution of crystals during decomposition in the temperature range of 459 to 529 K (186–256 °C). Gaseous species produced during thermal decomposition were quantified and analyzed using TGA coupled with a mass spectrometer. The surface state of AP crystals was analyzed using FTIR in the diffuse reflection mode (instead of transmission). Reflectance IR analysis is an optically simpler technique (particularly for pulverized solids) compared to transmission IR and involves reflected IR coming from the surface of the sample, showing the evolution of species in the solid decomposition stage and the importance of the diffusion of species in the crystals from the core to the surface. The crystals were also examined by SEM after mounting them in a casting resin matrix (Araldite) and cutting them with a microtome in order to observe the cross-section of the crystals at various stages of decomposition.

The TGA mass loss curves of AP heated from 459 to 529 K over a period from 30 minutes to six hours show three typical periods, as demonstrated in Figure 18 and as already observed by earlier investigators:

- an induction period (I)
- an acceleration period (A)
- a deceleration period (D)

The time-temperature surface in the 3-D graph shows a dimple (valley) in the area of the phase change from orthorhombic to cubic phases around 518 K (245 °C).

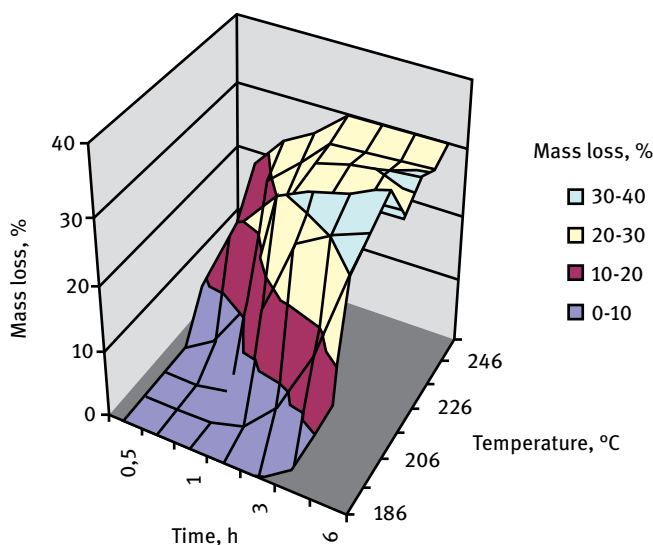


Figure 18: 3-D representation of the influence of temperature and time on the decomposition of AP 160 μm . (Reproduced and modified from [399], with permission granted by P.Gillard, 28 June 2021.)

In Figure 19, the rate of conversion measured by weight loss versus the degree of conversion of AP orthorhombic and cubic phases are illustrated in two separate graphs (top and bottom) for different isothermal experiments.

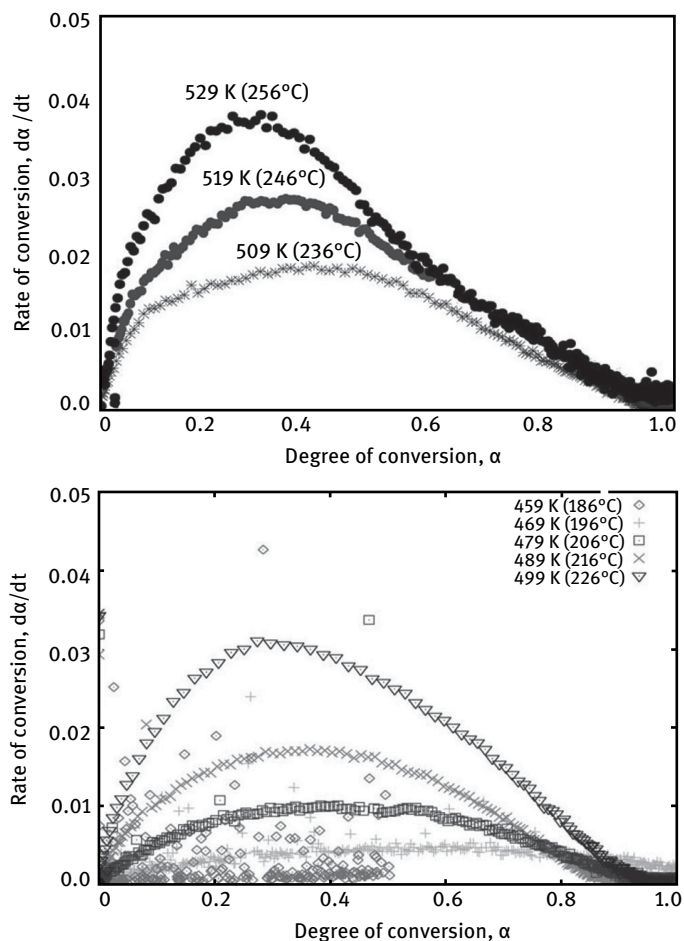


Figure 19: Rate of conversion as a function of the degree of conversion of AP. (Republished and modified from [401], with the permission of © 2009 John Wiley & Sons – Books; permission conveyed through Copyright Clearance Center.)

The sigmoidal forms of the TGA curves suggest that kinetic models like Prout-Tompkins (Eq. 1), Avramii-Erofeev (Eq. 2), or a generalized expression of Prout-Tompkins equation (Eq. 3) should be good candidates for modeling the decomposition process [402].

$$\frac{d\alpha}{dt} = Z \times \exp\left(\frac{-E_a}{RT}\right) \times \alpha \times (1 - \alpha) \quad (1)$$

$$\frac{d\alpha}{dt} = Z \times \exp\left(\frac{-E_a}{RT}\right) \times (1 - \alpha) \left[-\ln(1 - \alpha)\right]^{\frac{n-1}{n}} \quad (2)$$

$$\frac{d\alpha}{dt} = Z \times \exp\left(\frac{-E_a}{RT}\right) \times \alpha^b \times (1 - \alpha)^c \quad (3)$$

Figure 20 shows a comparison of the closeness of fit of predicted rates of conversion to the measured data (shown in green diamonds). As can be seen, the rate predicted from Eq. 3 gives the best fit to the data:

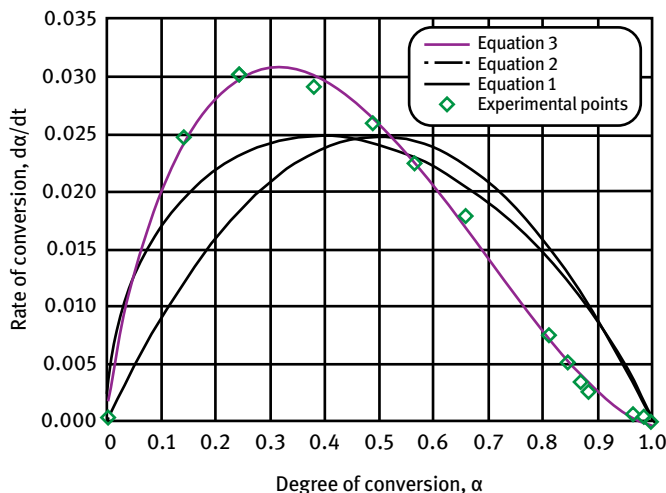


Figure 20: Fit of the rate of conversion as a function of the degree of conversion based on three kinetic descriptions. (Reproduced and modified from [399], with permission granted by P. Gillard on 28 June 2021.)

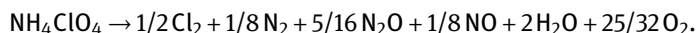
Legend: Eq. (1): Prout-Tompkins; Eq. (2): Avramii-Erofeev; Eq. (3): generalized Prout-Tompkins equation

The Arrhenius parameters were calculated for the two temperature regimes and were within the range of values found in the literature (80–150 kJ/mol).

Using SEM images of heated and cooled individual crystals it was possible to determine the propagation rate of the decomposition front for each temperature

of the orthorhombic phase. These rates were comparable with those observed by Kraeutle [403] on very large crystals in the temperature range of 494 to 504 K (221 to 231 °C).

The overall stoichiometry between 459 and 529 K (186 and 256 °C) can be represented by the equation



Based on FTIR in the diffuse reflectance mode, the following species were identified on the surface of AP crystals: NH_4^+ , ClO_4^- , ClO_3^- , and Cl^- . This result is consistent with observations by Peroni [404]. ClO_3^- and Cl^- were present as contaminants in the undecomposed commercial-grade AP. One of the intermediates of AP decomposition was identified as the ClO_4 free radical. The FTIR reflectance spectra of AP in the process of decomposing at 499 K (226 °C) were measured repeatedly over a period from 30 minutes to three hours and the spectra were superimposed, highlighting the IR absorption bands where the most pronounced changes were taking place (Figure 21).

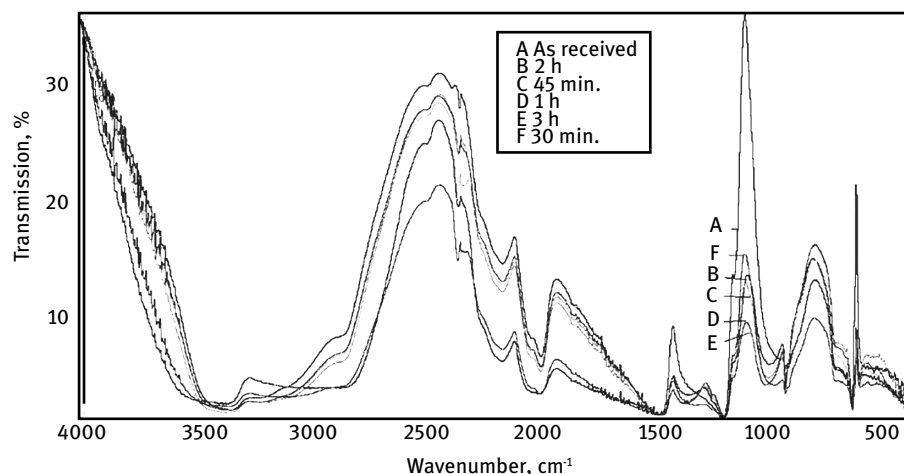


Figure 21: Evolution of reflectance FTIR spectra of AP at different times during heating at 499 K (226 °C). (Reproduced and modified from [399], with permission granted by P. Gillard on 28 June 2021.)

The thermal decomposition characteristics of AP at 443 K (170 °C) were studied using a dry heating method at constant temperature and TGA with relatively large (gram level) sample sizes [405]. The results revealed that with increasing heating time, the mass loss of AP increased, and the maximum mass loss was reached in the second hour. The thermal decomposition processes of AP can be divided into three steps. The maximum mass loss was 32.19% and the maximum rate of reaction was 1.125 s^{-1} .

AP crystals that had been heated for a while at 443 K (170 °C) had an increased impact sensitivity.

The slow thermal decomposition of AP was studied by TGA/DSC/MS/FTIR simultaneous analysis [406]. The MS-FTIR spectra demonstrated that N_2O and NO_2 were the main gaseous products of the thermal decomposition of AP. There was also a competition between the formation reaction of N_2O and that of NO_2 during the process with an iso-concentration point of N_2O and NO_2 . The dependence of the activation energy on the degree of conversion indicated that the AP decomposition process can be divided into three stages, which are (1) autocatalytic, (2) low-temperature diffusion, and (3) high-temperature stable-phase reaction. The corresponding kinetic parameters were determined by multivariate non-linear regression and an updated mechanism of the AP decomposition process was proposed. The abstract did not mention the occurrence of HCl, which one would expect as a decomposition product of AP.

The slow thermal decomposition of AP was investigated by thermo-analytical techniques including TGA, differential thermogravimetry (DTG), and DSC in an inert atmosphere of pure nitrogen at heating rates of 5, 10, 15, 20, and 50 °C/min. [407]. As expected, the reaction front moved forward towards higher temperatures with an increase in sample heating rate. The maximum heat release of 623 J/g occurred at a sample heating rate of 10 °C/min. The decomposition of AP proceeded in two phases, with the LTD maximum decomposition rate peak appearing at 561 K (288 °C), and the HTD maximum rate of decomposition occurring at 703 K (430 °C). During the LTD temperature regime, only 28.2% of the material decomposed and the decomposition ceased for a while. In the HTD temperature regime, the remaining AP decomposes leaving no residue.

4.3.4 Rapid AP Decomposition

Rapid heating of AP more closely represents conditions experienced by AP crystals in a solid rocket motor. Rapid heating can be achieved with lasers or by placing a thin film of AP on a metal foil with low thermal mass that is very rapidly heated by passing an electrical current through it. Prior to the advent of lasers, AP and propellant samples were flash-heated with the focused light from an electric arc.

The orthorhombic phase of AP decomposes faster than the cubic phase. The overall rate of decomposition is dependent on the heating rate. In a rapidly increasing temperature environment, AP may not undergo thermal decomposition until temperatures reach considerably above the 513 K (240 °C) phase transition temperature. This is because the induction period for the AP LTD process had not yet lapsed during the period while the AP was at temperatures below the normal crystal phase transition temperature. With rapid heating, AP could decompose directly from the orthorhombic phase.

4.3.4.1 Flash Pyrolysis Studies of AP

The flash pyrolysis of AP was studied by kinetic time-resolved IR spectroscopy [408]. The absorption spectra of OH, ClO₂, ClO, NO, and NH were observed in the decomposition products. The relative concentration of each was provided for the period of 1000 μs following the initial photoflash. Absorption bands of ClO₂ and OH were the principal bands observed at 20 μs after the flash. NH₃ and ClO₂ appeared very rapidly but after 10 μs the ClO₂ completely disappeared and was replaced by ClO, which then slowly decayed and Cl₂ and HCl go on to form. Flash-heating of ClO₂/NH₃ mixtures produced similar results. The flash pyrolysis data support the theory that the initial step in the decomposition of AP leads to the formation of ammonia and anhydrous perchloric acid. Subsequent reactions consist of the high-temperature oxidation of ammonia by perchloric acid.

4.3.4.2 Laser Pyrolysis Studies of AP

Sudden heating of AP crystals by laser may actually split the crystals by local heating before they ignite. AP crystals are transparent to the 694.3 nm radiation of a ruby laser. Therefore, to absorb more of the light when studying laser ignition of AP, one has to mix in absorbent material such as charcoal or metal oxides. Because the opaque substrate heats faster than the AP, ignition occurs at the substrate-AP interface and it is a heterogeneous reaction. The gases evolved during laser pyrolysis of opacified AP contained within the mass spectrometer were analyzed by mass spectrometer [409, 410]. The opacifiers were carbon black, copper chromite, iron(III) oxide, and manganese(IV) oxide. Shortly after zapping the propellant with a millisecond laser pulse, all the major decomposition products appeared at the same time. Perchloric acid and ammonia had short lifetimes. Relative ion intensities indicated that there was always a stoichiometric deficiency of HClO₄ compared to the amount of ammonia present. Chlorine is a major product when HClO₄ adsorbed on AP crystal surface decomposes, and OClO is a product that then decomposes on a catalyst.

AP and other solid propellant ingredients were pyrolyzed within the low-pressure ion source of a Bendix TOF mass spectrometer [411]. Pure AP is strongly absorbed at 10.6 μm. Input power densities applied were between 5 and 250 cal cm⁻² s⁻¹ = 21 and 1046 W/cm² for 0.1–5 s square pulses. The dissociative evaporation produced NH₃ and HClO₄ which appeared within 2 ms. The •ClO₃ radical was also observed in significant quantities [412]. It can also become trapped in AP crystals [114].

Mass-spectrometric and linear regression rates derived from CO₂-laser pyrolysis of pressed AP pellets at incident fluxes Q ranging from 105 to 16736 W/cm² (25 to 4000 cal cm⁻² sec⁻¹) and pyrolysis product evolution-rate histories were obtained in vacuo by time-resolved (5 ms) mass spectrometry during (a) transient heat-up and (b) subsequent quasi-steady vaporization (QSV) [413]. Vaporization induction times were obtained for (a); these, coupled with heat-transfer approximations neglecting thermochemical heat release, indicated that optical absorption at 10.6 μm dominated over conduction for $Q \gg 300$ cal cm⁻² sec⁻¹. Depending on the flux density, the AP under-

went (a) exothermic high-temperature condensed-phase decomposition (CPD) yielding H_2O , HCl , Cl_2 , O_2 , N_2O , NO_2 , and N_2 in variable proportions, or (b) endothermic dissociative-evaporation (DE) yielding NH_3 and HClO_4 . It was concluded that preferential desorption of NH_3 *in vacuo*, with net accumulation of adsorbed HClO_4 , occurred during transient heat-up and onset of CPD. However, preferential decomposition of adsorbed HClO_4 occurred during QSV when CPD was significant. CPD was the dominant mode of QSV at moderate Q for $200 < Q < 400 \text{ cal cm}^{-2}\text{sec}^{-1}$.

The decomposition of AP was initiated with a pulsed excimer laser at very low pressures (0.00001 mm Hg) [414]. Transient emission spectra from nascent products were identified as OH, NH, ClO, and other free radicals. From a detailed analysis of the temporal behavior of these emission bands, a decomposition mechanism via high-temperature oxidation pathways was inferred. The first stage of pyrolysis occurred at the crystal surface and, simultaneously, AP dissociated to form gaseous ammonia and perchloric acid. Experimental results revealed that the further decomposition of perchloric acid should be a three-body dissociation, i.e., $\text{HClO}_4 \rightarrow \text{OH} + \text{ClO} + \text{O}_2$.

Nanosecond and picosecond duration laser pulses were used to thermally shock AP crystals and study their response to rapid heating, simulating conditions that might occur in a rocket engine [415]. AP decomposition products were analyzed by XPS. Decomposition was initiated amid complex mechanical deformation and micro-cracking processes at the laser impact site but did not propagate at atmospheric pressure. Optical microscopy, SEM, and atomic force microscopy were used to examine the laser-damaged zones and revealed a micro-structure of ultra-fine cracks. It could be seen that despite the very short heating duration, some of the orthorhombic-cubic phase transitions had already occurred.

One advantage of laser pyrolysis is that the beam can be focused through the window in a high-pressure bomb and the reactions on the surface of the AP sample can be studied at very high pressures [416, 417]. The measurement of chemical and physical processes was demonstrated for AP decomposition at static high pressures (up to 2.0 GPa) and with pulsed-laser heating ($3\text{--}22 \text{ J cm}^{-2}$). Time-resolved UV-Vis absorption spectra collected during and after laser-pulse heating revealed the global reactions during ignition and combustion. The time evolution of the absorption $A(t)$ was used to model the global reaction kinetics. The dependence of $A(t)$ on pressure and laser fluence was consistent with a two-phase reaction. This reaction consists of initiation from hot spots and diffusion-limited reaction growth. A change in the contribution of initiation relative to growth in the overall reaction was observed between 1.3 and 1.6 GPa and was ascribed to structural changes in AP. Lasers can also be used for ignition studies of AP/aluminum mixtures [418].

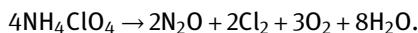
4.3.4.3 T-Jump Pyrolysis Studies of AP With Electric Heaters

An AP sample was confined in a hypodermic needle capillary tube closed on one end with the other end feeding directly into the ionization chamber of a mass spectrometer [354]. When evacuating and heating the sample holder, vaporization started at

393 K (120 °C) and all AP had sublimed by the time the sample reached 473 K (200 °C). The undissociated parent ion $\text{NH}_4\text{ClO}_4^+$ could not be detected, indicating that the first step in AP decomposition is a proton transfer.

The major products of natural and isotopically labeled AP pyrolysis at low temperature at 10^{-3} mm Hg were analyzed in a constant-volume system connected by a molecular leak to a TOF mass spectrometer, which operated at an ionizing voltage of 70 eV [419]. NH_3 and HClO_4 did not evaporate directly into the ion beam but were eliminated by recombination on cold glass surfaces. $^{14}\text{NH}_4\text{ClO}_4$ decomposed at 503 K (230 °C) and produced products with masses 14–74. Parent peaks were at masses of 18, 28, 32, 36, 44, 70, 72, and 74, thus corresponding to H_2O , N_2O , Cl_2 , O_2 , HCl , and N_2 . Nearly all the NO produced came from N_2O . Not all of the N_2 came from N_2O .

Isotope labeling can help to identify the rate-determining steps in a sequence of decomposition reactions. The thermal decomposition products of $^{14}\text{NH}_4\text{ClO}_4$, $^{15}\text{NH}_4\text{ClO}_4$, and deuterated AP were analyzed by mass spectrometer [420]. By investigating the decomposition at approximately 10^{-4} mm Hg and also at 10^{-7} mm Hg in the mass spectrometer inlet system, it was possible to clarify some of the previously conflicting data. This investigation has shown that NH_4ClO_4 decomposes into O_2 , Cl_2 , and N_2O in the molar ratio of 3:2:2 at <573 K (<300 °C). Perchloric acid was not detected. The activation energies for the formation of O_2 and Cl_2 were the same (117 kJ/mol = 28 kcal/mol). This agrees quite well with those calculated in conventional constant-volume experiments. The ratio of O_2 : N_2O : Cl_2 in the decomposition products at 473–503 K (200–230 °C) was 3:2:2, which matches a stoichiometry similar to



A Knudsen-cell mass-spectrometric method yielded reproducible results only after the AP had been pre-dried under vacuum at 473 K (200 °C) for 48 hours [421]. Ion intensity was measured from 413 to 523 K (140 to 250 °C). Activation energies were derived from the slope of $\log IT/\sigma$ versus $1/T$ plots where I is the peak height of the ion, T is the crucible temperature in kelvin, and σ is the ionization cross-section of the specific ion analyzed. It is strange that this method did not show any perchloric acid. It is suspected that HClO_4 decomposed before it could be analyzed. Three energy steps were determined for the decomposition mechanisms of AP in the temperature range 418 K to 525 K. The activation energies obtained from the slopes of observed ion intensities versus cell temperatures for each of the three steps were 22.2 ± 1.1 kcal/mol, 29.9 ± 1.5 kcal/mol, and 44.0 ± 2.2 kcal/mol.

A sample of AP was deposited on a 0.04-mm tungsten filament and heated rapidly by discharging a capacitor through the filament, close to the inlet of a time-of-flight mass spectrometer [422]. Similar TOF mass spectrometer experiments were repeated with AP samples with or without the addition of 4% Fe_2O_3 as a catalyst. The sample was heated to 673 K under a partial vacuum of 10–200 mm Hg [423].

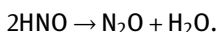
The pyrolysis products of AP were analyzed by TOF mass spectrometry [424]. The primary products of the breakdown reaction in the temperature range studied were ammonia and perchloric acid. The peaks at $m/e = 35, 51, 67, 83$, and 100 correspond to Cl, ClO, ClO₂, ClO₃, and HClO₄ [425]. Because ClO₂ is paramagnetic, it can also be analyzed by the intensity of its ESR signal after freezing out the condensables on an LN₂-cooled cold finger. The ratio of ClO₂/AP is an indicator of the degree of conversion and can be plotted as a function of time, resulting in S-shaped curves. The addition of various copper compounds acting as catalysts cause a shift of these conversion curves to lower temperatures. The concentration and the ratio of NH₃ to HClO₄ in the gas phase were close to what one would expect from a dissociation equilibrium. This is also viewed as a supporting argument for the proton transfer mechanism of AP decomposition.

In spite of the fact that the pyrolysis of AP has been exhaustively studied, two fairly important questions with respect to the decomposition process still remain: What are the exothermic reactions, if any, occurring in or on the surface of the solid and what are the rates and nature of gasification and subsequent gaseous reactions above the solid? A rapidly electrically heated stage holding AP crystals was connected to an evacuated chamber from which Knudsen flow carried decomposition products into a TOF mass spectrometer [373]. The results indicated the occurrence of an exothermic surface reaction with ClO₂ as a major product resulting from the pyrolysis of AP between 473 and 673 K (200 and 400 °C).

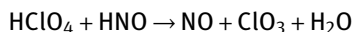
Measurements of the cold surface deposition rates from subliming AP as a function of sublimation temperature and the comparison of the mass spectra of subliming reagent grade AP with that of already sublimed AP reinforced the previously reported observations that decomposition competes with sublimation in the temperature range of 373 to 473 K (100 to 200 °C) [426]. Furthermore, the results also indicated that the sublimed AP is less stable than reagent grade AP.

A series of pyrolysis experiments of AP ranging from low-temperature solid-phase decomposition to high heating rate (10 °C/s) flash evaporation using skimming transient mass spectroscopy [427] was able to identify the gas-phase species. The aim of these experiments was to study the effects of gas-phase reactions and to determine the nature of AP pyrolysis at heating rates that are representative of actual propellant systems.

T-Jump/FTIR spectroscopy of pyrolysis that occurs in a thin layer of AP representative of a burning surface provides the sequence of appearance of the intermediate species and gaseous products [428]. A thin layer of AP was heated at 2000 °C/s to 713 K (440 °C) under 1.3 Mpa = 13 atm Ar. Some HClO₄, but no NH₃, escaped the reaction zone before significant heat was released. NH₃ was quickly oxidized to NO₂, N₂O, and H₂O. At least some of the N₂O may result from



As the decomposition rapidly accelerated and became strongly exothermic NO and H₂O were formed in large amounts and no more HClO₄ was evolved. These observations are consistent with the large influence of the reaction



in the overall rate. The acceleration of the process may result from growth in the HNO concentration. The final product concentrations qualitatively resemble the product profiles determined by microprobe-mass spectrometry of the AP flame.

Probing mass spectrometry (PMS) is a very useful method based on microprobe and molecular beam mass spectrometric probing for the study of solid propellant flame structures at high (10 atm) and low (< or = 1 atm) pressures. PMS has been utilized to study AP and ADN decomposition flames [429] using an installation for studying the thermal decomposition of AP at the high heating rate of the specimen up to 20–100 °/s and under conditions very similar to those present in the condensed phase in the vicinity of a burning surface. Flame structure studies of a sandwich based on AP allowed a confirmation of multi-zone structure and step-by-step mechanism of reactions in AP flame.

The fast thermolysis of AP and its decomposition mechanism under certain simulated conditions of combustion were studied by T-Jump/FTIR [430]. AP was flash-pyrolyzed under a nitrogen atmosphere at different pressures, with a heating rate of 1000 K · s⁻¹ at 874 and 1274 K. It was found that the main gaseous products of AP thermolysis were NO₂, N₂O, NO, HCl, and NClO. Interestingly, the N₂O/NO₂, NO/NO₂, and NO/NClO ratios increased with increasing temperature or pressure.

4.3.5 Other AP Decomposition Studies

A study of the decomposition behavior of pure single crystals of AP in a vacuum has been carried out. This took place during high heating rate decomposition at atmospheric pressure, and through self-deflagration in nitrogen atmospheres 2.06 < *p* < 34.4 Mpa (300 < *p* < 5000 psia) and deflagration in methane atmospheres 0.103 < *p* < 1.376 Mpa (15 < *p* < 200 psia). This helped to identify the rate-determining steps of the process [431].

The thermal decomposition of large single crystals of pure AP and AP doped with Ba²⁺ or SO₄²⁻ ions were investigated over the temperature range 493–563 K (220–290 °C) [432]. The study also included a comparison with compressed pellets of the pure powder and with small single crystals containing macroscopic flaws. The data revealed that the induction period is very complex and comprises a desorption step, a linear process, an exponential process, and the beginnings of an Avrami process. The latter three processes were identified with (1) the inward growth of rapidly formed surface nuclei, (2) branching of surface nuclei and (3) nucleation in the bulk crystal. Kinetic parameters were obtained for these three processes and

also for the growth of nuclei in the bulk crystal. This model matched the kinetic data over the entire range of degree of decomposition α (0 to 1), or $1 \times 10^{-5} < \alpha < 1$ if the desorption step is not included.

4.4 Ammonium Perchlorate Autoignition Temperature and Ignition Delay

Above a certain temperature, the rate of decomposition of AP becomes so fast that a runaway condition leads to autoignition and the production of flames. This event is also called [thermal explosion], depending on how vigorous the reaction is. The reaction may be powerful enough to destroy the sample holder or even the apparatus and its onset is dependent on the sample size. The time delay between arriving at the isothermal hold and the start of flames is often measured; it can be shown that it obeys an Arrhenius-type relationship if its logarithm is plotted against the reciprocal absolute temperature. Contaminants or catalysts will shorten the delay time and lower the activation energy. The time spent in transit from room temperature to the test temperature is usually ignored and is kept as short as possible.

Table 11 is a summary of autoignition temperatures reported by various sources in the literature. This table contains only data for pure AP. A similar table for AP with various additives is provided in Table 17, Section 4.7. The autoignition temperature depends on the gas and the pressure in the surrounding atmosphere.

The ignition delay time for AP heated to and kept at 753 K (480 °C) was ~90 s.

Table 11: Autoignition temperatures and activation energy of pure AP.

Author(s)	Year	Minimum autoignition temperature		Activation energy		Atmosphere	Pressure mm Hg
		K	°C	kJ/mol	kcal/mol		
Galwey and Jacobs [433]	1960	700	427	173.6	41.5	air	760
Osada and Sakamoto [357]	1966	<723	<450	284	68		
		>723	>450	96.2	23		

4.5 Ammonium Perchlorate Decomposition at Elevated Pressures

The majority of laboratory experiments on the decomposition of AP have been conducted at atmospheric pressure. However, this is not the pressure condition under which AP is actually used in rocket motors. There is a lot of academic discussion about AP decomposition mechanisms and the effect of various additives but very little information about how these mechanisms differ when they take place at elevated pressures.

The ignition delay of AP was determined in an electric furnace by measuring the time lag [434, 435]. The ignition delay for AP doped with Cr_2O_3 at 613 K (340 °C) was 135–140 s at 10^{-3} mmHg, whereas it was 56–81 s in the air at atmospheric pressure. The duration of preheating AP adversely affected the delay. The increase in particle size of AP was inversely proportional to the ignition delay. With large surface areas, the evaporation of HClO_4 was significant compared with the sublimation of crystals with small surface areas where evaporation is the rate-determining factor.

The linear pyrolysis rate of AP between 623 and 973 K (350 and 700 °C) at pressures between 101 kPa and 2.62 Mpa (1 and 26 atm) was measured in an apparatus where the substance to be tested is heated using a metal tape energized by a high-current-density and low-voltage transformer in an inert atmosphere within a pressure bomb equipped with an observation port [436]. The results of experimental measurements of the velocity of AP pyrolysis were then curve-fitted for data interpretation. It was shown that there are two pyrolytic domains. The first involves a process of pure pyrolysis and the second relates to the superposition of surface and exothermic reactions. An exothermic reaction took place in the higher temperature (pre-combustion) domain of pyrolysis, presumably similar to that which occurs during combustion. There was no sign of that heat release in the lower temperature region. The heat release began at temperatures in the transition zone between the two domains.

AP decomposition in a closed bomb ceased after the pressure of decomposition products had reached a limiting pressure [362, 437]. The limiting pressures were 147 kPa (1100 mmHg) at 403 K (130 °C), 200 kPa (1500 mmHg) at 423 K (150 °C), and 293 kPa (2200 mmHg) at 443 K (170 °C). Decomposition resumed immediately after the gas was vented and without an induction period. The mechanisms of AP and alkali metal or alkaline earth metal perchlorate decomposition are quite different. They depend on the strength of the base from which the salts are derived.

Extending decomposition studies of AP to extremely high pressures required a special anvil press with a cube-shaped pyrophyllite sample holder and tungsten carbide pistons. The pre-explosion rates of decomposition of AP and an AP-based propellant between 539 and 610 K (266 and 337 °C) were measured at 1.5, 2.5, and 5 Gpa (15, 25, and 50 kbar) [157]. The data were fitted to a first-order rate equation. Arrhenius plots of reaction-rate constants at different decomposition temperatures allowed the calculation of activation energies. For AP, the energies ranged from 169 kJ/mol (40.4 kcal/mol) at 1.5 Gpa to 239 kJ/mol (57.2 kcal/mol) at 5 Gpa. Activation energies for the AP propellant were calculated to be 127 kJ/mol (30.3 kcal/mol) at 1.5 Gpa and 203 kJ/mol (48.5 kcal/mol) at 5 Gpa. At high heating rates, decompositions of AP were explosive.

The thermal decomposition of AP in different gaseous atmospheres was investigated using DTA at pressures up to 5.15 Mpa (51 atm) [438]. It was found that the rates of the first and second stage of AP decomposition in an atmosphere of oxygen or nitrogen increases with pressure. Platinum, which may be used as a sample holder material or in thermocouples, has a catalytic effect on the HTD of AP. The heat of reaction of the

HTD of AP in a platinum cell was calculated from the peak temperatures of DTA curves at various pressures and found to be 326 kJ/mol (77.9 kcal/mol). The activation energy of AP sublimation in helium at 101 kPa (1 atm) is 96–105 kJ/mol (23–25 kcal/mol). The activation energy of the HTD in the platinum cell at various pressures of helium is very similar to that number.

The kinetics of the thermal decomposition of AP at high pressure were investigated by pressure differential thermal analysis (PDTA) [439]. It was found that the peak temperature of HTD moves up. In contrast, LTD on DTA curves of AP moves down with increasing pressure. The apparent activation energy E_{act} for the HTD increased but no changes in the kinetic parameters at LTD occurred as the pressure was raised. The results fit into a model for the mechanism and the rate-controlling process in AP decomposition [439].

4.5.1 Effects of Water on AP Decomposition

Although AP is not very hygroscopic (not nearly as bad as AN or ADN), its various properties are strongly affected by moisture. Water inclusions may become trapped in the crystals during manufacturing and recrystallization processes. Moisture may leak into storage containers during transportation and storage. Propellant processing is not always done in climate-controlled rooms. Many studies on the thermal decomposition and strand burning rates of AP were done without even the slightest effort to measure the water content of chemicals or control humidity in the test chamber. These studies suffer from a lack of reproducibility, and moisture is one of the likely causes for this problem.

The rate of thermal decomposition of AP is affected by moisture [348]. Cleaved single crystals with well-developed rhombic faces were mounted in a climate-controlled chamber under a microscope. These were photographed periodically during the experiment to follow the changes taking place throughout the slow thermal decomposition at 503 K (230 °C) [440, 441]. The air purging through the chamber was saturated to known levels of R.H. by passing it through dilute sulfuric acid in a hygrometer with specific water partial pressures. AP thermal decomposition below the phase transition temperature initially formed cigar-shaped nuclei. The number of nuclei was very small and depended on the purity and the history of the crystal. It remained constant while the decomposition was in progress and the dark zones grew until they overlapped. The results revealed that the water vapor primarily affects the rate of growth of the nucleation. The change of the nucleus growth rate with water vapor concentration is complex. At first, it decreased to a minimum at 15 g H₂O/m³, then reached a maximum and finally declined again. The effect of water vapor pressure on the growth rate of nuclei during thermal decomposition of AP revealed that the rate of nuclei formation is not affected by water vapor concentration. However, the nucleus growth rate was affected by changes in water vapor concentration. At the same time, the character of anisotropy of the nucleus development remained unaffected. Simultaneous changes

occurred in the growth rate of nuclei, both in the direction parallel to the principal axis of symmetry and perpendicular to it. Changes in nucleus growth rate occurred in sync with the changes in the total rate of thermal decomposition. This process was determined gravimetrically. Results were similar to results from experiments on dehydration of crystal hydrates.

In addition to the water carried in with the purge gas, some water is formed as the result of progressing decomposition of AP and may remain trapped in the crystal. The presence of water may enhance the proton exchange between decomposing AP and the ammonia and perchloric acid formed in its dissociation that remains adsorbed to the crystal instead of desorbing. Enhanced proton exchange accelerates the rate of decomposition. Perchloric acid also forms a hydrate that is more stable than the acid itself. Similar tests were performed with ammonia instead of water vapor in the purge gas.

Gas-phase reactions were simulated by computational chemistry methods at various levels of complexity using a generalized gradient approximation with a plane-wave DFT [442–444]. This was conducted in an effort to explain how water affects proton transfer on the surface and in solid AP. This method allowed exploration of the dissociation mechanism and the role that water molecules play in the surface decomposition process compared to those in the gas phase and in solution. For reactions inside or on the solid phase, a Vienna *ab-initio* Simulation Package was used to evaluate the total energies of periodically repeating geometries based on DFT with a pseudo-potential approximation. The energy-distance profile for water molecule(s) approaching or leaving the AP crystal surface was displayed graphically to illustrate the affinity of AP crystals for water. The predicted AP sublimation rate constants were calculated for different amounts of water in the vapor space. Calculations revealed that water molecules can readily desorb from the surface. The desorption energies of $(\text{H}_2\text{O})_1$, $(\text{H}_2\text{O})_2$, and $(\text{H}_2\text{O})_3$ clusters from the surface were 5.2, 12.8, and 9.5 kcal/mol, respectively. These results, together with the fact that H_2O desorbs readily from the AP surface with relatively low energies, suggest that the formation of a solution layer on a decomposing AP surface is not likely at high temperatures where AP sublimates. Water molecules do not affect the proton transfer process between $\text{NH}_4^+/\text{ClO}_4^-$ ion pair on the surface but they can significantly reduce the sublimation energy of AP by co-desorbing with the $\text{NH}_4^+/\text{ClO}_4^-$ ion pair. The sublimation energies of AP with $n\text{H}_2\text{O}$ ($n = 0, 1, 2, 3$) were predicted to be 117.5, 89.5, 77.8, and 59.4 kJ/mol (28.1, 21.4, 18.6, and 14.2 kcal/mol), respectively (see [445]).

The hygroscopicity and moisture sensitivity of the thermal decomposition of fresh and irradiated AP is different [446].

4.5.2 The Effect of Confinement and Pressure on AP Decomposition

The thermal decomposition of AP has been extensively studied in the past. Nevertheless, the various results published illustrate conflicting findings. On the one hand,

significant differences regarding the influence of different parameters on the decomposition can be seen. On the other hand, a lack of useful quantitative laws to predict the thermal behavior of this crystal under a range of operating conditions (temperature, duration of exposure, type of confinement) has been reported.

Kinetic curves were measured for the thermal decomposition of AP at 503 and 533 K (230 and 260 °C) [447]. An inert gas pressure of 10.1 Mpa (100 atm) failed to alter the kinetics of this reaction.

The course of AP decomposition proceeds through different paths if the decomposition products are trapped and in contact with the crystal surface. The same occurs if the decomposition products are carried away by vacuum or a purge gas [399, 401, 448].

In addition to the effect of confinement, the type of purge gas may also have an affect on the rate of decomposition of AP. It was observed that AP decomposition under nitrogen proceeded more slowly than under air [449]. Nitrogen is a decomposition product of AP and its presence may retard the decomposition by the law of mass action (but only if this is a reversible equilibrium reaction!).

4.5.3 The Effect of Thermal Pre-Treatment (Aging) on AP Decomposition

The effects of accelerated aging at 348 K (75 °C) on the thermal decomposition of AP were studied using DSC, TGA/DTG, and FTIR [450]. DSC thermogram of fresh AP showed the endothermic peak to be 520 K (246.9 °C), which was attributed to the phase transition of AP from orthorhombic to cubic form and two exothermic peaks, the first at 561.6 K (288.5 °C) (weak) and the second at 697 K (423.9 °C) (sharp). This was caused by the decomposition of AP. Samples were taken after 80, 120, and 140 days of aging. These were analyzed using DSC and FTIR and compared to the fresh sample. After 120 days of aging, the DSC thermogram showed two distinguished endothermic peaks at 595.8 K (322.7 °C) and at 704.3 K (431.2 °C), which was attributed to the decomposition of AP in two stages. Also, FTIR spectra showed a new peak at wave number 800 cm^{-1} , which was assigned to chlorate ions. The activation energies of aged AP decomposition calculated from TG/DTG isothermal data and a first-order rate equation method is summarized in Table 12

Activation energy goes through a minimum of 40 to 80 days of aging. Any samples exposed for >120 days were severely decomposed and the E_a numbers were unreliable.

In another aging test series, AP samples with four different particle sizes were aged, i.e., subjected to a thermal stress test in a closed sample holder consisting of an isothermal hold for ten minutes at 298 K (25 °C), a ramp at 10 °C/min. to 498 K (225 °C), and isotherm holds at 498 K (225 °C) for three hours [449]. To determine the fraction of unreacted product remaining following experiments in **closed** cells, the residues of AP were collected and subjected to thermal decomposition via TGA **open** cell for two hours at 498 K (225 °C). The weight loss rate was recorded. The decomposition topographic phenomena were illustrated by a series of very good SEM images which showed the evolution of porosity at different stages of the decomposition process.

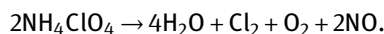
Table 12: Activation energies of aged AP decomposition.

Aging duration, <i>d</i> , at 348 K (75 °C)	Activation energy, <i>E_a</i>	
	kJ/mol	kcal/mol
Zero	69.9	16.708
20	52.7	12.6
40	30.6	7.32
80	29.7	7.1
120	90.7	21.68
140	54.7	13.085

Data source: [450].

4.6 Kinetics of Ammonium Perchlorate Thermal Decomposition

The stoichiometry of AP decomposition depends on the rate of heating, the operating pressure, and the presence or absence of catalysts. Several stoichiometries were already presented in Section 4.3.1. A general equation can be written as



Authors of various comprehensive studies on the thermal decomposition of AP considered the following four possible pathways:

1. An electron transfer process from the perchlorate anion to the ammonium cation;
2. A proton transfer reaction from the cation to the anion (similar to the decomposition of all ammonium salts), accompanied by the formation of perchloric acid and ammonia;
3. The thermal breakdown of the perchlorate anion breaking a Cl—O bond similar to the thermal decomposition of perchlorates of alkaline metals; and/or
4. Formation of NO_2ClO_4 as an intermediate.

Before one can study the kinetics of AP decomposition, one must have a complete understanding of the dynamics of AP sublimation. Therefore, several studies were conducted to measure the sublimation vapor pressure of AP below the onset of thermal decomposition (see Section 3.3).

A transition-state decomposition rate theory for intermosaic orthorhombic AP decomposition looked at the electron exchange in adjacent NH_4^+ and ClO_4^- ions [451]. This theory was based on observations and measurements by Bircumshaw and Newman [348, 349]. They had observed that slow decomposition at 503 K (230 °C) proceeds by the formation of opaque spots (nuclei) on the crystal surface. Schultz and Dekker [451] developed a single consistent treatment of the kinetic data in terms of the linear rate of progression of the interface between the partially decomposed and undecomposed crystalline material.

Over the past century, many investigations have been performed to study the decomposition kinetics of AP. The principal results of these studies have shown that AP decomposes in two stages: At low temperatures ($T < 573 \text{ K} = T < 300^\circ \text{C}$) 30% of the AP is decomposed and the rest of the material is left as a structured, porous residue, and at temperatures above 623 K (350 °C) this residue is subjected to a second stage, exothermic decomposition until all the material is consumed. The justification most frequently used for studying the decomposition of AP is that the behavior of AP in the combustion zone of composite propellants greatly influences the overall combustion and the burning rate of the propellant. Because isothermal decomposition tests possess the desirable attribute of controlling experimental variables with relative ease and are less time-consuming, many studies of the kinetics of AP decomposition have been performed and the results extrapolated to speculations about the burning rate. The question of the relevance of these decomposition results in relation to the behavior of AP particles in a burning propellant has been the subject of extended discussions. A thesis by Siegmund [452] provides a good introduction to this topic due to how it contains an excellent summary of the literature on AP decomposition up to 1969.

The precise nature of the reaction mechanism was a subject of discussion for a long time. Thus, some authors expressed the opinion that the limiting stage in the thermal decomposition of AP is the transfer of an electron from the ClO_4^- ion to the NH_4^+ ion. An investigation of the catalytic activity of the oxides of metals of variable valence in the thermal decomposition of NH_4ClO_4 has revealed the existence of a relationship between the electrical properties of the oxides and their catalytic activity. It has also served to confirm electron transfer assumptions. Other investigators arrived at the conclusion that the stage controlling the reaction rate involves the transfer of a proton from the ammonium ion to the ClO_4^- ion. It was also suggested that both mechanisms co-exist: at relatively low temperatures electron transfer is the dominant mechanism, and in the high-temperature region proton transfer is the dominant mechanism. Other theories of the mechanism of perchlorate and nitrate decomposition reactions have been proposed but they have been less widely accepted than the aforementioned mechanisms. The extensive experimental data now makes it possible to construct a general picture of the decomposition of inorganic nitrates and perchlorates [453]. Particularly noteworthy is the fact that ammonium salts are more easily decomposed than salts of the alkali and alkali earth metals. This is typical, not only of perchlorates and nitrates but also of permanganates, bichromates, carbonates, etc. The basic difference between the NH_4^+ ion and the metal ions is its ability to transfer a proton to an anion. The principal objection to proton transfer is that, for AP, the heat of sublimation is approximately 251 kJ/mol (60 kcal/mol), i.e., much higher than the observed activation energy. Owing to the high values of the N—H or Cl—O bond energies, it is difficult to find an energetically favorable elementary event without assuming yet unseen intermediate states. The idea of electron transfer from anion to cation through the forbidden band, though widely held, has not yet been experimentally confirmed. The direct spectral investigation of AP crystals has shown that the

forbidden gap is greater than 4 eV, which exceeds the observed activation energy of the reaction. In order to explain the relatively low values of the activation energy of decomposition of NH_4ClO_4 (125 kJ/mol = 30 kcal/mol) it may be necessary to introduce the idea of electron transfer, although not to the conduction band but to various kinds of electron traps (see [454–458] also).

4.6.1 Experiments in Support of Electron Transfer Processes

The thermal decomposition of AP in vacuo and under small initial pressures of nitrogen, to suppress sublimation, was investigated in the temperature ranges 493 to 553 K (220 to 280 °C) and 653 to 723 K (380 to 450 °C) [348]. In the low-temperature range, only 30% decomposition occurred and much of the residue consisted of AP. In vacuo, sublimation occurred all of the time, including once decomposition had ceased. This indicated that the reaction did not take place in the vapor phase. The sublimed material and the ‘residue’ were analyzed. Surprisingly, it was found that the residue which was porous in texture (the decomposition had occurred throughout the crystal) could be ‘rejuvenated’ via exposure to a solvent vapor and the decomposition could begin anew. The crystals undergo a transformation at 513 K (240 °C) from orthorhombic to cubic crystal structures. During the AP LTD process at temperatures ranging from about 473 to 553 K (200 to 280 °C), a time delay of a few minutes to more than half an hour was observed. Such time delays before AP gaseous products emissions are called induction periods. Once started, AP LTD gassing rate was much faster at 503 K (230 °C) than at 518 K (245 °C). Since the AP phase change temperature is 513 K (240 °C), decomposition kinetics close to that temperature was faster in the lower-temperature stable orthorhombic crystal phase than in the upper-temperature stable cubic phase. Within decomposing coarse AP particles, one can observe microscopic cloudy particles that could coalesce into larger, but still quite small, reaction centers. Holes in coarse AP particles started to appear at subsurface reaction centers that were observed as cloudy spots under microscope observation. Such holes or pores were sources of AP decomposition products. Additives from both co-crystallized and external vapor exposures changed AP LTD rates or induction periods. The addition of impurities, which might be intermediate decomposition products, and the addition of metal oxides affected the rate of decomposition. The energy of activation of the thermal decomposition over the temperature range 488 to 548 K (215 to 275 °C) was 116 kJ/mol (27.8 kcal/mol) for the orthorhombic form and 79 kJ/mol (18.9 kcal/mol) for the cubic form [349]. The rate of decomposition was found to increase to a maximum with decreasing particle size and then to decrease again. An electron transfer mechanism was proposed, which explains some of the observed decomposition results.

In the early rocket age, there were some authors [360, 459] who believed that thermal decomposition, at least under some special conditions (e.g., low temperature and in the presence of a catalyst), occurred due to electron transfer from perchlorate ion to ammonium ion. This provided fodder for many lengthy disputes and the problem of

the real mechanism of AP thermal decomposition was not quite solved for many years. It took several decades to sort out the experimental evidence and arrive at a conclusive agreement. A better understanding of AP decomposition was only possible after the decomposition of HClO_4 , which was formed following the thorough investigation of the decomposition of AP.

It was argued that because manganese salts, manganese dioxide [460], and potassium permanganate catalyze the AP decomposition at low temperatures, it will point to an electron-transfer mechanism because the manganese ion can assume many different states of oxidation. Others suggested that p-type semiconductor metal oxides (CuO or Cr_2O_3) enhance catalytic decomposition of AP on account of their increased electron-hole density [461, 462]. The doping of semiconductor oxides supported this theory. In semiconductor oxides, electron and electron defect concentrations can be increased by incorporating ions of different valencies. Catalytic effects observed with CdO or ZnO must be explained using different mechanisms, however.

Another reaction mechanism proposed by [459] for the uncatalyzed decomposition involves the adsorbed dissociation products NH_3 and HClO_4 , self-protonation of HClO_4 to yield the intermediate ClO_3^+ , and oxidation of NH_3 by ClO_3^+ . The reaction mechanism proposed for the catalyzed decomposition involved the formation of the free radicals $\cdot\text{NH}_4$ and $\cdot\text{ClO}_4$, decomposition of the radicals to NH_3 and chlorine oxides, and subsequent oxidation of NH_3 . The experiments in the temperature range from 523 to 598 K (250 °C to 325 °C) also studied the effect of copper chromite and atmosphere composition on the rate of AP decomposition.

If the AP decomposition proceeds as an electron transfer process, then the reaction should be affected by conducting it in an electrostatic field. This is because electrically charged particles will travel between the electrodes. A novel method for detecting the charge-carrying species in decomposing inorganic salts was applied to AP decomposition [463]. It was observed that the charge-carrying species at two different temperatures (423 and 503 K = 150 and 230 °C) are oppositely charged, i.e., they are negatively charged (ClO_4^- ions) at 423 K and positively charged (NH_4^+) at 503 K.

The effect of aliovalent ion substitution on the decomposition rates of AP has been interpreted as supporting an electron transfer mechanism. In this case, the rate of isothermal decomposition of cubic AP as a function of the concentration of barium dopant concentration was measured by using TGA within the temperature range of 530 to 550 K [464]. The rate of decomposition first passed through a minimum and then a maximum. The dopant showed opposite effects in the two temperature ranges. The decomposition kinetics of both pure and doped AP were best described by a first-order rate law equation with an activation energy of ~138 kJ/mol.

It was proposed that a complex can be formed between a metal ion perchlorate and an $\text{NH}_4\cdot$ radical, which stabilizes the electron transfer process [465].

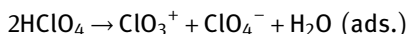
Most experimenters will hesitate to place a sample of AP inside an expensive scanning electron microscope and heat it to decomposition to observe topographical

changes. However, when this was attempted, it was noted that decomposing AP emits exo-electrons [466]. The rate of exo-electron emission was measured at constant temperatures. Different emission peaks were obtained with isothermal samples at low and high temperatures and in transient temperature experiments with different heating rates. SEM images of the surface of crystals at different stages of decomposition provided additional information on the decomposition phenomena.

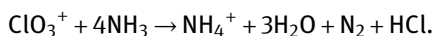
4.6.2 Experiments in Support of Proton Transfer Processes

Galwey and Jacobs [467] concluded from their HTD data that the rate-controlling step was either due to the evaporation of an ion pair ($\text{NH}_4^+ + \text{ClO}_4^-$) followed by gas-phase reaction or because of proton transfer on the surface, which produced ammonia and perchloric acid. Since they assumed that the activation energies for sublimation and for the HTD were different, it was inferred that the HTD takes place via proton transfer.

The thermal decomposition of AP at low temperatures shows several unusual characteristics. The most striking of these is that at low temperatures it decomposes only to the extent of about 20 to 30%, leaving a residue that is chemically identical to the original salt [468]. The experimental results for the rate of decomposition of whole crystals, powder, and pellets could be well-fitted by a kinetic equation. This is in accordance with a detailed model for decomposing salt. It was possible to account in terms of this model (which involved the decomposition of intergranular material only) for the observed dependence of the activation energy on the extent of cold-working to which the solid is subjected, leaving residual strain in the crystal lattice. The cessation of reaction after about 30% conversion was attributed to the presumed ease of ammonia desorption relative to that of perchloric acid, which builds up on the surface. Other authors have suggested that the build-up of HClO_4 on the surface leads to HClO_4 decomposition on the surface



followed by a reaction with ammonia



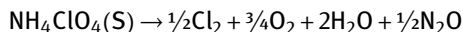
Early experimenters revealed that the activation energy of AP thermal decomposition was practically the same at both low and high temperatures [469]. This mechanism involves a proton transfer from NH_4^+ to ClO_4^- ions on the AP surface as the initial step. Subsequent steps depend on the temperature and the ambient pressure and may involve one or more of: desorption, heterogeneous decomposition on the surface of AP, and homogeneous decomposition in the gas phase. The main nitrogen-containing products of decomposition are N_2O and HNO_3 at low temperatures and NO at high temperatures. IR and mass spectrometric investigations have not been able to detect a molecular NH_4ClO_4 species in the gas phase above decomposing AP. The rate of

decomposition is faster than the rate of sublimation. Both sublimation and thermal decomposition proceed by proton transfer. Measurements of the weight loss or pressure increase at low temperatures revealed that the rates were independent of the experimental method used (with or without removal of the decomposition products). Gas-phase reactions are not rate-determining.

The thermal decomposition of AP starts not over the whole crystal volume or on the whole surface at the same time but in specific nucleation sites near the outer and inner surfaces of a crystal. Having started at these active centers of a crystal, the reaction propagates near the place where it has already started and spreads. That is, the formation and growth of reaction nuclei occur. Reaction nuclei grow and merge with each other, thus forming the reaction region. The propagation is well seen with a microscope. Some sites on the crystals are preferred sites for the onset of decomposition (nucleation sites). These sites are linked to impurities or crystal defects and one would expect to obtain different results for highly purified AP. Based on weight-loss measurements, the activation energy of AP decomposition was the same in the low- and in the high-temperature regime, ~ 125 kJ/mol (~ 30 kcal/mol) in either case. From these data, Jacobs [469] and Russell-Jones [470] concluded that AP thermal decomposition usually occurs by the second of the aforementioned mechanisms where ammonia and perchloric acid are the initial products of decomposition. A similar viewpoint was proposed by Markovitz and Boryta [109].

Kinetics of AP decomposition can be derived from experiments run under isothermal or isoconversional conditions. Another alternative is to allow the reaction to proceed under adiabatic conditions by compensating for heat losses to the environment. An adiabatic method for studying exothermic solid reactions has been developed at Stanford Research Institute (SRI) [471]. Adiabatic conditions can be maintained with this apparatus in samples of a few grams weight for rates of temperature rise from 2–150 °C/min. The adiabatic decomposition of AP has been studied in this apparatus in a temperature ranging between 513–598 K (240–325 °C). The slab-shaped sample was clamped between two heater plates and held in position by spring-loaded bolts. As the sample began to decompose, the temperature of the sample rose above that of the plates. Electrical power was then supplied to the heater plates, which was manually controlled using a variable transformer, at a rate sufficient to maintain a uniform temperature in the plates and sample. As the reaction rate increased, the rate of power supply was correspondingly increased. Under these conditions, the temperature of the sample increased at a rate that depended ideally only on the rate of decomposition. The temperature difference between the plate and sample was kept to less than 0.2 °C up to a rate of temperature rise of about 100 °C/min., the maximum rate at which it was possible to supply sufficient power to maintain isothermal conditions in the assembly. The apparent activation energy derived from an Arrhenius plot was 129.7 kJ/mol (31 kcal/mol). This was higher than activation energies for isothermal decomposition reported by others in existing

literature ($96.2 \text{ kJ/mol} = 23 \text{ kcal/mol}$; $113 \text{ kJ/mol} = 27 \text{ kcal/mol}$). The heat release was compared to that expected from the equation



and matched the predictions.

Other methods to study the decomposition of AP are either based on weight loss in a TGA apparatus or on pressure increase in a closed bomb. TGA measurements are complicated by the concurrent sublimation of the salt. Measurements of the sublimation rate have, therefore, been made over a wide temperature range and kinetic parameters both for sublimation and for thermal decomposition have been established [472]. The activation energy for the low-temperature thermal decomposition was measured as $111.4 \pm 3.64 \text{ kJ/mol}$ ($26.63 \pm 0.87 \text{ kcal/mol}$) from Avrami-Erofeev rate constants and $125.8 \pm 8.28 \text{ kJ/mol}$ ($30.08 \pm 1.98 \text{ kcal/mol}$) from induction periods. The activation energy for sublimation is $117.32 \pm 1.8 \text{ kJ/mol}$ ($28.04 \pm 0.43 \text{ kcal/mol}$) from contracting volume rate constants. It was not clear whether the activation energy for decomposition changes at the phase transition point. The least mean squares values were $141.88 \pm 6.86 \text{ kJ/mol}$ ($33.91 \pm 1.64 \text{ kcal/mol}$) below the transition point and $112.8 \pm 9.87 \text{ kJ/mol}$ ($26.97 \pm 2.36 \text{ kcal/mol}$) above the transition point. The catalytic effects of ammonia (negative) and of perchloric acid (positive) have led to the formulation of a unified mechanism for sublimation and decomposition, which involved proton transfer from NH_4^+ to ClO_4^- ions as the basic step.

While it is generally accepted that the principal initial step in the decomposition of AP is proton transfer, details of the subsequent reactions had not been resolved for several years after this mechanism was first proposed. Data on HClO_4 and ClO_2 flames, on the oxidation of NH_3 , on reactions of nitroxyl, and on the reactions of chlorine oxides published in the 1960s were used to deduce a detailed mechanism for the decomposition of AP [473]. While attention has been focused primarily on the so-called HTD, the basic mechanism is adaptable to a wide range of conditions: to the LTD, to combustion, to the catalyzed decomposition, and to decomposition in the presence of various reactive gases. The central point of the proposed theory is that in the decomposition of AP, NH_3 is oxidized principally by the ClO radical.

The initial step in the thermal decomposition of AP is a proton transfer, based on electrical conductivity measurements and solid-state electrolysis of AP single crystals [474].

Exposure to an ammonia-rich atmosphere allows ammonia molecules to be absorbed into AP crystals at interstitial sites. It has been proposed that these neutral ammonia molecules can form short-lived N_2H_7^+ complexes with the NH_4^+ ions allowing proton transfer between them, thereby enhancing the electrical conductivity considerably. To date, however, there has been no direct evidence of this proposed mechanism. There are only theoretical calculations of an anomalous charge transport mechanism in AP crystals in ammonia-rich atmospheres [174]. The charge-transport mechanism in solid AP crystals exposed to an ammonia-rich environment was studied using *ab ini-*

tio molecular dynamics [475]. In this paper, *ab initio* molecular dynamics techniques were employed to explore a proton transfer mechanism. Computed infrared spectra of the pure and ammonia-doped crystals showed a significant broadening of the NH stretch peak into a lower frequency region. This indicated, through an experimentally verifiable observable, the formation of hydrogen bonds between NH_3 and NH_4^+ units. Comparison of the diffusion constants of NH_4^+ in the pure and doped crystals produced a ratio that was comparable to the experimentally measured conductivity ratio. It clearly showed enhanced positive charge mobility. The possibility of an ammonia umbrella inversion following proton transfer from NH_4^+ and NH_3 adds to the flexibility of this process.

Many of the experimental and theoretical studies mentioned favor the proton transfer hypothesis. However, *ab initio* MD simulation calculations [174, 475] indicated no proton transfer in the ideal crystal.

4.6.3 Experiments in Support of Formation of Nitryl Perchlorate as an Intermediate

The low-temperature (<570K) decomposition is incomplete (approximately 30%), yielding a residual solid with a composition and crystal structure very similar to those of the original reactant. The formation of NO_2ClO_4 as an intermediate during the LTD of AP has been postulated [476–478]. Analytical evidence has been obtained with the finding that an oxidized nitrogenous species is formed during the low-temperature thermal decomposition (ca. 500 K) of AP. The estimated reaction rate of NO_2ClO_4 closely accounts for the observed rate of AP breakdown. Nitryl perchlorate was proposed as a reaction intermediate. This proposed mechanism is quite different from either the electron transfer or the proton transfer mechanisms.

It is interesting to note that nitryl perchlorate also has been patented as a burning-rate increasing additive for AP. However, attempts to introduce synthetic NO_2ClO_4 directly onto the AP reactant resulted in no marked acceleration of reaction. This observation was readily explained by the instability of the additive at the reaction temperature (giving it a lifetime of only 5 s) and its sensitivity to hydrolysis [479]. In addition, the reaction rate of AP prepared with a low water content was greater than that of salt recrystallized from water, which can be explained by a lessening of the extent of hydrolysis of NO_2ClO_4 .

4.6.4 Other AP Decomposition Experiments

Free-radical, thermal, and photolytic decomposition products of AP were compared to those of cyclic nitramines and ADN [480]. The kinetics of the thermal decomposition of AP at temperatures between 488 and 533 K (215 and 260 °C) was studied by measuring the sample mass loss as a function of time applying the isothermal thermogravimetric method [481]. From the temperature dependence of the maximum decomposition rate, two different decomposition stages, corresponding to two different structural phases of AP, were identified. For the first region (488–508 K = 215–235 °C),

corresponding to the orthorhombic phase, the mean value of the activation energy was 146.3 kJ/mol, and the pre-exponential factor was $3.43 \times 10^{14} \text{ min}^{-1}$. For the second region (513–533 K = 240–260 °C), corresponding to the cubic phase, a mean value of the activation energy of 153.3 kJ/mol and a pre-exponential factor of $4.11 \times 10^{14} \text{ min}^{-1}$ were obtained. In an earlier publication the same authors had cited $E_{\text{act}} = 134.5 \text{ kJ/mol}$ and a pre-exponential factor of $1.05 \times 10^{11} \text{ s}^{-1}$ for a temperature range of 513–523 K (240–250 °C).

A combination of TGA, DSC, MS, and FTIR simultaneous analysis was used to study the thermal decomposition of AP [406]. The MS-FTIR spectra showed that N_2O and NO_2 were the main gaseous products of the thermal decomposition of AP, and there was a competition between the formation reaction of N_2O and that of NO_2 during the process with an iso-concentration point of N_2O and NO_2 . The dependence of the activation energy calculated by an iso-conversional method on the degree of conversion indicated that the AP decomposition process can be divided into three stages. These are autocatalytic, low-temperature diffusion, and a high-temperature stable-phase reaction.

The kinetic parameters for rapid pyrolysis of AP were determined by TGA [482].

4.6.5 Isotope Effects on AP Decomposition

If proton transfer is a key step of AP decomposition, then replacing hydrogen with deuterium should have a measurable effect on decomposition kinetics. The thermal decomposition of NH_4ClO_4 and ND_4ClO_4 single crystals was measured by DTA, TGA, and SEM. The volatile products that evolved were analyzed using mass spectrometry in real time [483]. Exothermic decomposition of the deuterated sample was slower but the phase change occurred at the same temperature (513 K = 240 °C), as can be seen from the thermograms in Figure 22.

Contrary to reports from other investigators who stated that decomposition starts at edges and imperfections on the surface of crystals, it was observed that thermal decomposition of NH_4ClO_4 and ND_4ClO_4 always started in the bulk of the crystals. In both cases, decomposition stopped when the degree of conversion was about 30%. Porous products were produced which underwent the same phase transition as the parent single crystals. If pre-decomposed porous samples were temperature-cycled just above 513 K, but below the upper onset of exothermic decomposition, the phase changes of both deuterated and non-deuterated AP are reversible and occur at the same temperature (Figure 23).

Examining partially (30% mass loss) isothermally decomposed NH_4ClO_4 and ND_4ClO_4 under the SEM revealed that the pores of ND_4ClO_4 were smaller and the volume fraction of pores appeared to be lower than that of NH_4ClO_4 (Figure 24). These effects were interpreted as caused by proton transfer at the intersections of dislocations in the bulk of the crystals.

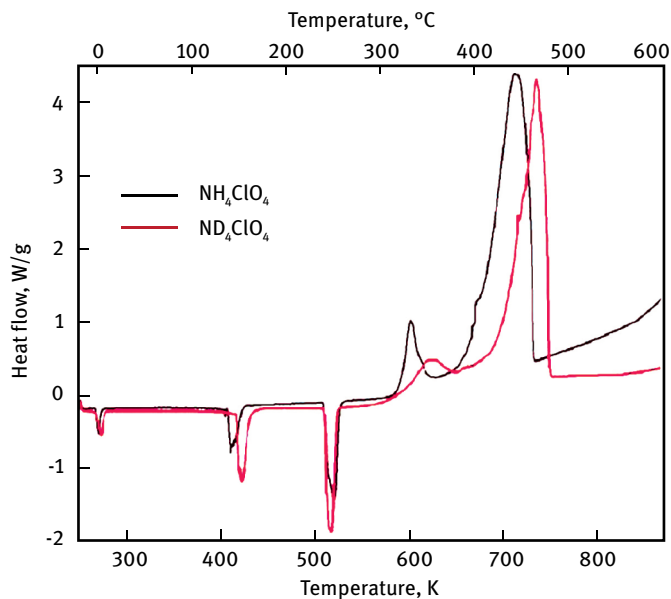


Figure 22: DSC thermogram of NH_4ClO_4 and ND_4ClO_4 decomposition, linear heating rate. (Reprinted and modified from [483], with permission from Elsevier; permission conveyed through RightsLink.)

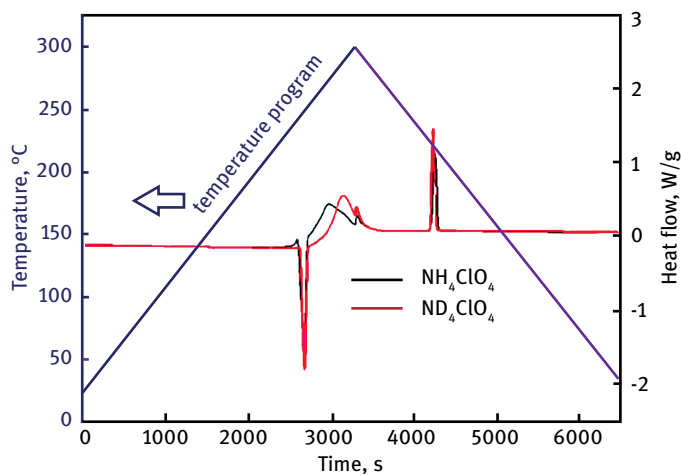


Figure 23: Linear heating and cooling of NH_4ClO_4 and ND_4ClO_4 without decomposition. (Reprinted and modified from [483], with permission from Elsevier; permission conveyed through RightsLink.)

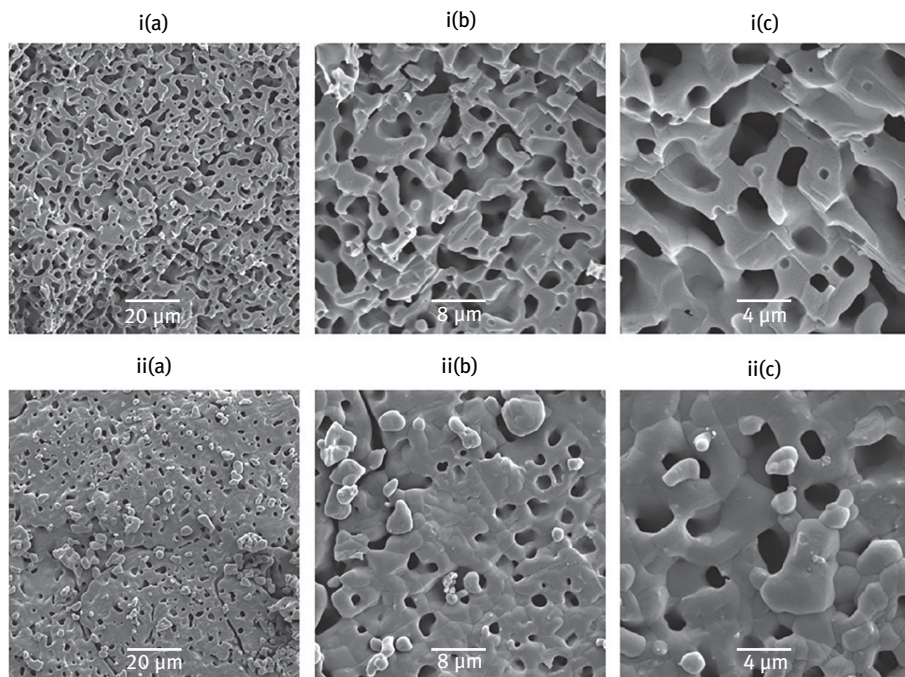


Figure 24: Comparison of SEM images of porous NH_4ClO_4 (top) and ND_4ClO_4 (bottom) at three different magnifications. (Reprinted and modified from [483], with permission from Elsevier; permission conveyed through RightsLink.)

An examination of the thermal behavior of large single crystals of partly and completely deuterated AP by DSC, SEM, TGA, and QMS revealed that the rates of thermal decomposition depend on the degree of deuteration and decreased in the sequence $\text{N}[\text{H}/\text{D}]_4\text{ClO}_4 > \text{NH}_4\text{ClO}_4 > \text{ND}_4\text{ClO}_4$ [484].

4.6.6 The Effect of Perchloric Acid on AP Decomposition

4.6.6.1 Decomposition of Perchloric Acid

One of the many reactions taking place during the decomposition of AP is the decomposition of perchloric acid. One would not consider perchloric acid as an oxidizer in liquid bipropellant combinations or as a monopropellant. We presume the main reason why people investigate the decomposition of HClO_4 is the role it plays in the decomposition of AP [485]. Perchloric acid is so much less volatile than ammonia that it stays behind on the surface of decomposing AP crystals, is adsorbed onto the crystals, and strongly influences the decomposition processes taking place on the surface. The higher decomposition rate of HClO_4 in the presence of AP can be explained by the heterogenic nature of the process [486]. In these nuclei, the oxidation of AP occurs, as

does the formation of an additional amount of HClO_4 . This acid causes the formation of new reaction nuclei on the adjacent defects and so on.

One of the decomposition products of perchloric acid is OCIO . The rate of OCIO formation can be taken as an indication of the rate of AP decomposition. The presence of ClO_2 in the products was believed to have special importance for explaining the behavior of AP under heating. ClO_2 was thought to initiate the combustion process in perchlorate. It should also be noted that ClO_2 , which is a stable paramagnetic molecule, can be detected with the help of electron paramagnetic resonance among the products of low-temperature thermal decomposition of AP [487]. The rate of ClO_2 formation can be modified by heterogeneous catalysts, while the amount of ClO_2 formed during AP decomposition remains unchanged. The addition of homogeneous additives by cocrystallization into AP crystals, for example the incorporation of SO_4^{2-} ions, changes both the rate of ClO_2 formation and its yield.

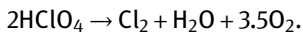
The decomposition of perchloric acid may be catalyzed using the same substances that catalyze the decomposition of AP. As a matter of fact, if one can show a good correlation between the relative reactivity of a series of catalysts for the decomposition of AP and HClO_4 , this may be in support of theories that postulate HClO_4 decomposition as a rate-determining step in AP decomposition.

A close relation had been observed between the catalytic effect of the metal oxides on the decomposition of HClO_4 and the thermal stabilities of the corresponding perchlorates. Namely, that is, that the most active oxides produce the most unstable perchlorates. An attempt was made to compare the catalytic effect of the oxides on the decomposition of perchloric acid and on that of AP. Using the same catalyst in both cases, it was concluded that there is no direct correlation between the relative activity of the oxides in the two reactions.

The effect of chromium(III) oxide on the vapor-phase decomposition of perchloric acid was studied in a flow system [488]. Chromium oxide showed a catalytic effect even at 383 K (110 °C). It was observed that perchloric acid oxidized the chromium oxide, especially above 443 K (170°). As a result, the activity of the catalyst decreased with time. The rate of the catalytic decomposition was practically independent of the perchloric acid concentration. The activation energy was 129.7 kJ/mol (31 kcal/mol).

The vapor-phase decomposition of perchloric acid has been investigated for all the oxides previously studied in connection with the decomposition and combustion of AP [489]. The experiments were carried out in a flow system, using N_2 as carrier gas. The interaction between the catalysts and the substratum was studied using electric conductivity measurements, IR spectroscopy, and chemical and thermal analysis. The oxides catalyze the composition of perchloric acid in the temperature range between 403–673 K (130–400 °C), depending on the metal ion. For 0.5% to 8% conversion per minute, the catalytic decomposition followed first-order kinetics. An exception was chromium oxide, for which the reaction was found to be of zero order. The activation energies determined for the different catalysts ranged from 83.7 to 188 kJ/mol (20 to 45 kcal/mol).

A flow system with nitrogen as carrier gas was used to study the vapor phase decomposition of HClO_4 on propellant catalysts (CuCr_2O_4 , CuCrO_4 , and CuO and a Harshaw Cu-0202 catalyst) [490]. The most effective compound, CuCr_2O_4 , catalyzed the decomposition at $\sim 393\text{ K}$ ($\sim 120^\circ\text{C}$). The reaction equation was



CuO had some catalytic effect above 543 K (270°C), while CuCrO_4 decomposed HClO_4 only above 603 K (330°C). Different types of deactivating side reactions occurred between the catalysts and HClO_4 and were strongly temperature-dependent. The interaction between the catalysts and perchloric acid was studied by IR, kinetic, gravimetric, electric conductivity, chemical, and thermal analytical methods. IR spectroscopy revealed the formation of a surface perchlorate ion on all the catalysts. Simultaneously, oxidation of catalysts containing CuCr_2O_4 occurred. The extent of oxidation increased at higher temperatures when the surface ClO_4^- decomposed. The HClO_4 decomposition was first-order except on CuCrO_4 , where it was zeroth order. The activation energies were $71.1\text{--}175.7\text{ kJ/mol}$ ($17\text{--}42\text{ kcal/mol}$). The effects of the same catalysts on the $\text{NH}_3\text{--HClO}_4$ reaction at $573\text{--}673\text{ K}$ ($300\text{--}400^\circ\text{C}$) were also investigated with perchloric acid and ammonia at different temperatures.

A difference in the effects exerted by metal oxides under different experimental conditions can be attributed to the additional heat release due to the decomposition of perchloric acid on the catalyst. Thus, by comparing the activity for AP and HClO_4 decomposition, the following series of decreasing activity of catalysts for AP decomposition at $T = 360^\circ\text{C}$ was produced: $\text{Co}_2\text{O}_3 > \text{CuO} > \text{Fe}_2\text{O}_3 > \text{MnO}_2 > \text{CuCrO}_3 > \text{Al}_2\text{O}_3 > \text{SiO}_2$ and for catalyst of the decomposition of HClO_4 : $\text{Co}_2\text{O}_3 > \text{MnO}_2 > \text{CuO} > \text{Fe}_2\text{O}_3 > \text{CuCrO}_4 > \text{Al}_2\text{O}_3 > \text{SiO}_2$ [491] (see [492, 493] also).

4.6.6.2 The Decomposition of AP in the Presence of Excess Perchloric Acid

When 5% HClO_4 was added to AP, and the sample heated in a DTA, an exothermic reaction began at 413 K (140°C) and peaked at $\sim 468\text{ K}$ ($\sim 195^\circ\text{C}$), which was much lower than with pure AP. After the AP phase-transition there was a sharp exotherm peaking at 588 K (315°C) [263]. The addition of HClO_4 to AP produced some interesting DTA results. At a temperature slightly higher than its boiling point, there was an exotherm that would appear to be a heterogeneous reaction between gaseous HClO_4 and undissociated AP. A large exotherm occurs around 300°C , the temperature at which exotherms appear in transition metal and ClO_3^- catalyzed AP. Since this temperature is lower than the temperature at which homogeneous decomposition of HClO_4 would be significant, the reaction is most likely either the direct reaction of HClO_4 with AP or due to catalysis byproducts forming in the reaction occurring at 473 K (200°C). When the system is subject to pressure, the LTE disappeared (the higher pressure requires a higher temperature for HClO_4 to boil). However, the sample deflagrated at $\sim 593\text{ K}$ ($\sim 320^\circ\text{C}$), which is lower than the temperature at which pure AP deflagrates at 1.72 Mpa ($17\text{ atm} = 250\text{ psia}$). It appears that below $\sim 573\text{ K}$ ($\sim 300^\circ\text{C}$)

the direct reaction of HClO_4 with AP (both reactants in the condensed phase) is not particularly rapid.

It has been shown that the rate of nuclei formation and the rate of nuclei growth is proportional to the partial pressure of perchloric acid in the atmosphere above decomposing AP crystals at 503 K (230 °C) [425, 17]. Figure 25 illustrates the effect of excess perchloric acid partial pressure on the maximum number of nuclei per surface area of AP decomposition at 503 K (230 °C). Perchloric acid and ammonia counteract each other in this process. Ammonia has the opposite effect on nuclei growth.

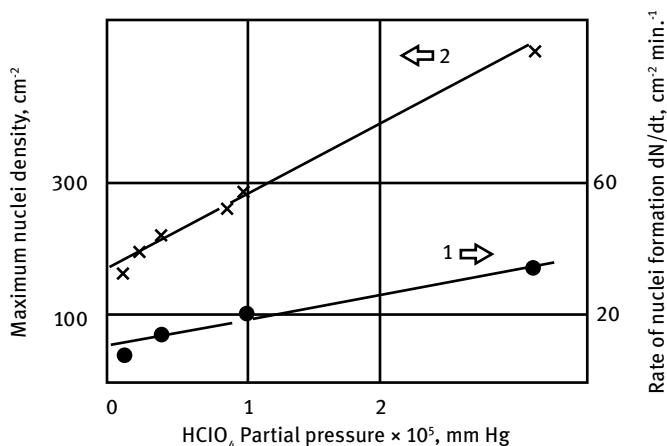


Figure 25: Effect of perchloric acid partial pressure on (1) the rate dN/dt of nuclei formation and (2) the maximum number of nuclei per surface area during AP decomposition at 503 K. (Republished and modified from [17], with the permission of © 2006 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center).

Legend: Left ordinate scale: rate dN/dt of the number of nuclei formation; right ordinate scale: rate of nuclei formation per unit area.

Perchloric acid vapor flowing over decomposing AP in a TGA apparatus reduced the time lag and significantly increased the rate constant of the acceleration period of AP decomposition [494]. The activation energy and the extent of decomposition was hardly influenced. Microscopic examination revealed that the formation of nuclei was greatly enhanced by the presence of HClO_4 . TGA experiments of this type were conducted in the temperature range 473–513 K (200–240 °C), 533–573 K (260–300 °C), and >613 K (340 °C) [495]. At <513 K (<240 °C), the HClO_4 vapor significantly reduced the induction period but the activation energy (125 kJ/mol = 30 kcal/mol) remained unchanged. At higher temperatures, the HClO_4 vapor had a similar effect but the activation energy was 12–20 kJ/mol (3–5 kcal/mol) lower than in a baseline experiment under inert gas (nitrogen). Even at very low HClO_4 partial pressures and flow rates

(5×10^{-8} mol/min) the HClO_4 vapor exerted a clearly observable effect on the decomposition of orthorhombic AP. When the introduction of HClO_4 was delayed until after the normal time lag, only very slight or hardly any acceleration occurred. The extent of AP decomposition was hardly influenced by the presence of HClO_4 vapor. It was found that decomposition usually stopped at 25–28% conversion [496].

Excess perchloric acid accelerates the decomposition of AP, while excess free ammonia retards it. Bircumshaw and Newman [348, 349] have suggested that the formation of centers of decomposition on the AP crystal surface may be associated with the formation of adsorbed perchloric acid. The induction period is shortened by crystallizing an AP sample with 2% excess perchloric acid. Conversely, the induction period is lengthened by passing some ammonia over the salt.

4.6.6.3 The Effect of Excess Ammonia on AP Decomposition

AP recrystallized from a solution containing excess ammonia at pH 12 then washed and dried carefully was found to have fewer crystal defects than AP recrystallized from water, based on XRD examination [359]. If the crystals were pulverized extensively, the thermal stability of the NH_3 -doped crystals decreased. At all pressures, AP is more stable in an atmosphere containing NH_3 than under pure N_2 [263].

Excess perchloric acid and excess ammonia have exactly the opposite effects on the rate of decomposition of AP. Ammonia forms as the result of proton transfer during the first step of decomposition of AP in the condensed phase. Part of the ammonia remains adsorbed to the crystals and the rest is released into the gas phase. At very high pressures, both perchloric acid and ammonia cannot desorb. They will remain and react in the condensed phase. The rate of subsequent reactions depends on the rates of reaction of ammonia with oxidizers in the gas phase. If excess ammonia is provided during a laboratory experiment, the release of ammonia is retarded and more ammonia accumulates in the condensed phase.

Figure 26 shows the effect of the partial pressure of ammonia above decomposing AP crystals at 503 K (230 °C) on the maximum number of nuclei per surface area (n_{max}).

Both the nucleus formation rate and the maximum number of nuclei per surface area decrease when ammonia partial pressure is increased. It is assumed that the reaction nuclei forms as a result of AP dissociation. Indeed, the number of nuclei rises when perchloric acid partial pressure is increased in the atmosphere above the crystal. A similar chart (Figure 25) illustrates the effect of excess perchloric acid partial pressure on the maximum number of nuclei per surface area of AP decomposition at 503 K (230 °C). The two additives work contrary to each other. Increasing ammonia concentration extends the induction period and stabilizes AP against decomposition. The presence of ammonia influences not only the number of nuclei formed at any given time (as demonstrated in Figure 26) but also the rate at which individual nuclei grow in diameter. The nuclei diameter growth rate decreases linearly as ammonia concentration increases (Figure 27).

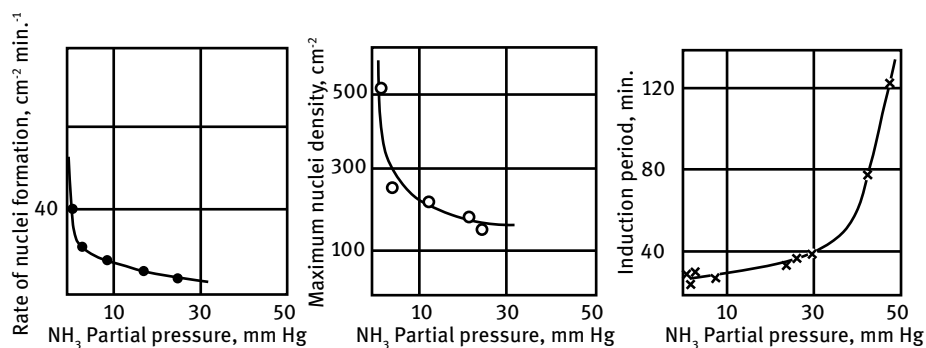


Figure 26: Effect of ammonia partial pressure on (1) the rate dN/dt of nucleus formation, (2) the maximum number of nuclei per surface area, (3) and the induction period of AP decomposition at 503 K. (Republished and modified from [17], with the permission of © 2006 Elsevier Science and Technology Journals; permission conveyed through Copyright Clearance Center).

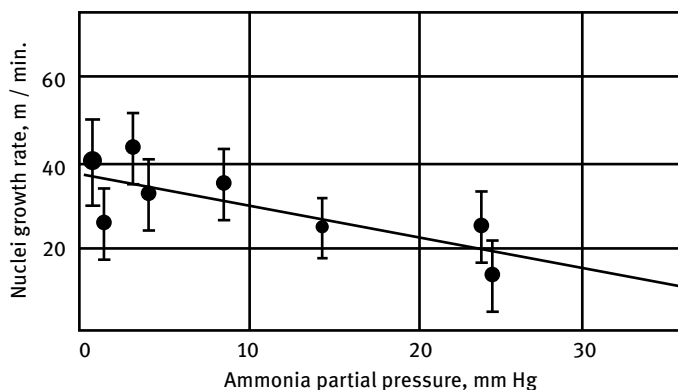


Figure 27: The effect of ammonia partial pressure on the rate of reaction nucleus growth during thermal decomposition of AP. (Republished and modified from [17], with the permission of © 2006 Elsevier Science and Technology Journals; permission conveyed through Copyright Clearance Center).

Heating AP in a stream of ammonia to 515 K (242°C) for 24 hours resulted in only minimal mass loss, while a sample heated under the same conditions in air lost 25.7 mass-%. The stabilization of AP by keeping it under ammonia has been used to measure the enthalpy of transition between the two polymorphic phases of AP [109].

The decomposition of AP is retarded significantly if the process is carried out in an atmosphere of ammonia [497]. The decomposition of AP was studied by DTA and isothermal TGA in the presence of air, nitrogen, perchloric acid, and ammonia. The rate of sublimation of AP was higher than the decomposition in a vacuum. In the pres-

ence of HClO_4 , the decomposition of AP was 100% complete at 623 K (350 °C) but in air, it was only 40% complete at that temperature. In the presence of NH_3 , the decomposition of AP was inhibited up to 613 K (340 °C). The addition of decomposition catalysts at the 1% level influenced mainly the second exothermic maximum at 653 K (380 °C). Catalysts had the same activities in homogeneous and heterogeneous mixtures of AP.

4.6.7 The effect of Stabilizers and Inhibitors on AP Thermal Decomposition

AP is one of the most thermally stable rocket propellant oxidizers. As such, it is not as dependent on stabilizers as some of the oxidizers (e.g., ADN, hydrazinium nitroformate (HNF)) that are trying to replace it. Other than increasing the thermal stability, some additives also reduce the burning rate of AP and prevent it from reigniting accidentally in extinguishable rocket motors.

It is regrettable that with many DTA, DSC, or TGA experiments on catalysts and stabilizers for AP, the rate of heating has not always been stated. Typical rates of heating are in the range of 5 to 10 °C/min.

AP needs to be modified to prevent or reduce the risk of inadvertent reignition of extinguishable solid rocket motors. Two methods were found that could eliminate or reduce the exothermicity of propellant grade AP exposed to temperatures of 623–663 K (350–390 °C) during soakback [368]. One was a thermal pre-treatment (see Section 4.5.3) and the other involved an additive. It was found that the temperature at which the first exotherm occurred could be raised as much as 45 °C by adding several percent of an ammonium salt (e.g., ammonium tetrafluoroborate) to the AP. The delayed exotherm was stronger than that found in AP to which no ammonium salt was added. This technique was also effective when fluorocarbon binder was in contact with the AP. Neither technique appeared to reduce the heat liberated by the deflagration of AP at 743–773 K (470–500 °C). Co-crystallized ammonium salts were also tested as AP additives. In another sample that had been catalyzed by 0.04% of a copper compound, the catalytic acceleration was suppressed via the addition of ammonium tetrafluoroborate [498, 499]. Another very effective inhibitor is ammonium hexafluorophosphate NH_4PF_6 . It was found that the temperature at which the first AP exotherm occurred could be raised 85 °C by adding 1.5% NH_4PF_6 [500]. A series of tests were conducted of the catalytic effect of traces of impurities in AP on this exotherm. Although the first AP exotherm was strongly catalyzed by as little as 0.04% of copper(II) nitrate, the catalysis was suppressed by the NH_4PF_6 additive. The burning rate was increased by adding 0.1% Cu or Zn salts. Independent tests in a combustion bomb and in a rocket motor have demonstrated the increased extinguishment reliability achieved by the NH_4PF_6 additive.

4.6.7.1 Phosphate Stabilizers

Trisodium phosphate Na_3PO_4 is a very alkaline compound (better known for its use in cleaning paintbrushes). When first mixed with AP it may cause the release of am-

monia. The isothermal decomposition of AP, with and without Na_3PO_4 , was followed thermogravimetrically at two temperatures, 541 K (268 °C = low-temperature region) and 655 K (382 °C high-temperature region). Three different samples were run at each temperature: (1) pure AP, (2) 0.1% Na_3PO_4 occluded, and (3) pure AP mechanically mixed with 10% Na_3PO_4 . Na_3PO_4 in both concentrations significantly retarded decomposition of AP at 541 K (268 °C) but not at 655 K (382 °C) [263]. DTA traces of pure AP and AP mixed with Na_3PO_4 looked essentially at the same, except that in the presence of Na_3PO_4 the LTE (at $\sim 598\text{ K} = \sim 325\text{ }^\circ\text{C}$) did not occur until 673 K (400 °C).

Various types of phosphates have been patented as stabilizers for AP and MEAP [501]. The stabilizers in amounts of 0.1 to 3% are added by co-crystallizing them with AP from concentrated solutions. Examples for phosphates for this purpose are $(\text{NH}_4)_4\text{P}_4\text{O}_{12}$, $\text{Na}_3\text{P}_3\text{O}_9$, and $\text{Na}_4\text{P}_4\text{O}_{12}$. Doubly recrystallized MEAP has a beginning exotherm at 563 K (554 °F) while stabilized MEAP with 0.5% $(\text{NH}_4)_4\text{P}_4\text{O}_{12}$ had an exotherm at 612 K (642 °F). A propellant prepared with these MEAP samples and CTPB and Al had a first exotherm at 583 K (590 °F) for the unstabilized and at 650 K (710 °F) for the stabilized oxidizer.

4.6.7.2 Carbonate Stabilizers

The burning rates of AP and AP/PS propellants are lowered in the presence of CaCO_3 and CaO . A contracting-cube equation was proposed that fits the isothermal TGA data for AP decomposition [502]. The inhibition of the LTD of AP controls the burning rates of AP/PS propellants at atmospheric pressure (see [503]).

Calcium oxide and carbonates of calcium, barium, and strontium act as burning rate inhibitors. They also delay the thermal decomposition of AP, as measured by TGA [504].

4.6.8 The Effect of Catalysts on AP Thermal Decomposition

Many inorganic and metal-organic substances catalyze the thermal decomposition of AP and accelerate its burning rate, either of AP by itself or of AP-based solid propellants. Metals can be catalytic as such or in the form of their salts or oxides [465]. Most of the burning rate catalysts currently used for AP are metal oxides. Metal-organic compounds will usually combust and release the metal oxides in a finely divided and highly reactive form.

The studies of the effect of catalysts on the rate of thermal decomposition of AP (in the absence of fuels) often run in parallel with studies on the effect of catalysts on the burning rate of AP either by itself or in combination with fuels (binders) (see Section 5.15.1). However, the catalyst activity for thermal decomposition of AP must not necessarily correlate linearly with the activity for enhancing the rate of deflagration of AP by itself or the burning rate in formulated AP-based propellants. The question remains of whether results of thermal decomposition of catalyst-AP systems or catalyst-propellant systems could be related to the burning rate of formulated composite pro-

pellants. Such a correlation would allow the use of thermal decomposition techniques (a fast technique) to screen prospective burning rate modifiers (a tedious technique) (see [505, 506] also).

4.6.8.1 The Effect of Metal Oxides on AP Thermal Decomposition

Many transition metal oxides (binary and ternary) have been evaluated as either stabilizers or burning rate catalysts for AP. In trying to decide the sequence in which the numerous references should be discussed, discussing the various metal oxides in the same sequence in which they appear in the periodic table of elements was first considered. Then we switched to a different ordering scheme and sorted the data by the number of different metal atoms in the oxide (binary and ternary oxides) and then listed them in alphabetical order.

The catalytic effect of metal oxides on the thermal decomposition of AP at temperatures below the polymorphic transition temperature has been studied extensively (typically trying to rank a series of candidate catalysts in a series of increasing activity). Testing the effects of 1 mass-% of various metal oxides added to pure AP in an isothermal decomposition apparatus [507], measuring the pressure rise in a constant volume glass apparatus, has revealed that:

1. Cu_2O , CuO , CuCl , and ZnO promote both low- and high-temperature reactions;
2. NiO and Cr_2O_3 mainly promote low-temperature reactions;
3. MnO_2 and Cu-chromite mainly promote high-temperature reactions;
4. Al_2O_3 , TiO_2 , Fe_2O_3 , and V_2O_5 are ineffective for both types of reactions.

An electron transfer theory was proposed for the [low-temperature reaction] thermal decomposition of AP and a proton transfer model was promoted for the [high-temperature reaction]. It was concluded that only p-type semiconductors of transition metal oxides are effective for the [low-temperature reaction] of AP and n-type transition metal oxide semiconductors are ineffective since Cu_2O , CuO , and NiO belong to p-type semiconductors and greatly promote the [low-temperature reaction]. On the other hand, ineffective additives such as Fe_2O_3 , TiO_2 , and Al_2O_3 , belong to the n-type. But ZnO is an exception that belongs to the n-type semiconductors. In spite of this, it had the highest catalytic activity to the AP pyrolysis, having the lowest activation energy for AP explosion ($123 \text{ kJ/mol} = 29.5 \text{ kcal/mol}$), compared to 172 kJ/mol (41 kcal/mol) for AP by itself without any catalysts. In separate tests, it was shown that MnO_2 and Cr_2O_3 promote the oxidation of NH_3 gas (a high-temperature reaction) most efficiently. In a subsequent study, the composition of the gases evolved during non-flaming decomposition of AP. This was analyzed and it was found that the presence or absence of catalysts and the type of catalysts affect the gas composition [508]. It was concluded that catalysts that produce higher concentrations of oxygen and lower concentrations of nitric oxide during the combustion of AP may increase the burning rate of AP-based propellants. The presence of nitrosyl chloride made the gas analysis more difficult. At

the same time, some catalysts were very effective in decreasing the mean molecular weight of the combustion products of AP.

A study of the kinetic laws of AP decomposition in the presence and absence of metal oxides must also take into consideration the sublimation (without decomposition) from the kinetic point of view [509]. Based on DSC thermograms, MnO_2 and CoO had a strong effect on AP decomposition, Fe_2O_3 had a weak effect, and moderately effective oxides ranked as follows: $\text{CuO} > \text{Cr}_2\text{O}_3 > \text{Co}_3\text{O}_4$.

A very good summary on the effect of metal oxides on the thermal decomposition and the burning rate of AP by itself and AP in combination with various combustible binders was published by Komarov, containing 84 references from research literature [510].

4.6.8.2 Binary Oxides

There are several dozens of publications dealing with the effect of transition metal oxides on the rate of decomposition of AP and the burning rate of propellants formulated with doped AP. It is difficult to organize this mass of technical information because most papers deal not only with one metal oxide at a time but with a group of metal oxides in a comparative study in an effort to identify the most active metal oxides. The question is if the metal oxides change the overall rate of decomposition or if they catalyze specific steps (the rate-determining steps) of the multi-step decomposition process. The other question is whether the catalytic effect is restricted to the condensed phase or if it extends to the vapor phase in the combustion zone. There is also some overlap between the following sections because some papers discuss binary oxides as well as ternary oxides and other additives. A *binary* compound is a compound that consists of a combination of two elements. There is some inconsistency; where some authors call oxides containing **two** metals [binary oxides], we call them *ternary* oxides. Table 13 gives a summary of metal oxides tested as burning rate catalysts for AP. Some of these references may be listed only in this table and nowhere else in this book. In those instances the reference is given as a footnote. For other references the field in the column under Reference may be blank; in these instances, the case reference is cited in other parts of this chapter. A good summary of the catalytic effects of a large number of metal oxides was compiled by [511]. This data is summarized in Table 14.

In a detailed study of the thermal decomposition of AP, Bircumshaw and Newman [348, 349] noted that MnO_2 exerted a pronounced catalytic effect on the decomposition. The kinetic characteristics and the products of the reaction were altered by the added oxide. The catalytic reaction occurred without concurrent sublimation, which was observed during the low-temperature 473 to 523 K (200 to 250 °C) decomposition of AP at low ambient pressure. Pure AP, when heated in a vacuum in the temperature range 473 to 513 K (200 to 240 °C) undergoes about 30% decomposition, leaving a residue that is chemically identical with the starting material. In contrast, decomposition of AP at 503 K (230 °C) in the presence of 10 mass-% MnO_2 was found to go to

completion. It was also observed that NH_3 and the basic oxide CaO inhibited the AP decomposition reaction.

The kinetics of the thermal decomposition of the mixtures of AP and MnO_2 , compressed to form a rigid pellet, were investigated in the temperature range 410 to 485 K (137 to 212 °C) [460]. It was found that the reaction occurs in two distinct stages, the first of which was the catalyzed decomposition of AP. Two kinetic equations described the process over different ranges of reactant compositions, but both produced energy of activation close to 134 kJ/mol (32 kcal/mol). A reaction mechanism was proposed in which positive hole formation comprises the initial step. The catalytic action of the oxide was ascribed to an extension of the average lifetime of a positive hole by the manganese ions of the oxide. The second stage of the reaction was shown to be the decomposition of pure AP, which was independent of the presence of a catalytic oxide.

In the temperature range of 170 to 200 °C the rate of decomposition was measured gravimetrically by determining the loss of weight of the mixture AP-catalyst as a function of the time [434]. At temperatures above 200 °C, the rate of decomposition was followed gasometrically, condensing out all the gaseous products other than oxygen and nitrogen and measuring the rate of increase of pressure in an apparatus of constant volume. The catalytic activity of several oxides tested increased in the order $\text{MgO} < \text{Cr}_2\text{O}_3 < \text{MnO}_2 < \text{Ni}_2\text{O}_3 < (\text{Co}_2\text{O}_3 + \text{Co}_3\text{O}_4)$. Based on TGA data, it was suggested that Cr_2O_3 catalyzes AP decomposition only in the gas phase. MgO was so inactive that sublimation of AP occurred before it decomposed. The time lag before ignition (under atmospheric pressure) of powdered AP in the presence of manganese dioxide and a mixture of cobalt oxides was found to depend upon the reciprocal absolute temperature by an Arrhenius type equation from which activation energies could be determined.

In the presence of copper(II) oxide, the decomposition of AP takes place at much lower temperatures than the decomposition of pure AP [461]. An increase in the defect electron concentration of copper(II) oxide catalyst (by doping with lithium oxide) accelerated the reaction rate and shortened the induction period. The opposite effect was experienced when CuO was doped with Cr_2O_3 . The effect of the defect electron concentration on the activity of the catalyst was supposed to support the theory of electron transfer in the AP decomposition mechanism. The activation energy of the decomposition between 453–473 K (180–200 °C) was 129 kJ/mol (31 kcal/mol). A similar value of 127 kJ/mol (30.5 kcal/mol) was obtained from the dependence of the time necessary to reach explosion as a function of temperature. The LTD of AP was also studied between 473–503 K (200–230 °C) and the activation energy of 171 kJ/mol (41 kcal/mol) was obtained.

Copper(II) oxide was a superior catalyst in comparison to both copper(I) oxide and copper chromite [529].

A simple theory of self-heating and its application to the system AP and Cu_2O was developed by Jacobs and Kureishy [530]. Approximations usually made using theories

Table 13: Summary of binary metal oxides tested as catalysts for AP decomposition.

Oxide ^a	Author	Year	References
Ag ₂ O	Galwey, Mohamed, and Cromie	1986	[512]
CaO	Bircumshaw and Newman	1954, 1955	[348, 349]
CdO	Solymosi and Fonagy	1967	[513]
Mix of Co ₂ O ₃ and Co ₃ O ₄ .	Hermoni and Salmon	1961	[434]
Co ₃ O ₄	Chen et al.	2005	[514]
Co ₃ O ₄	Alizadeh-Gheshlaghi et al.	2012	[515]
Co ₃ O ₄	Li and Bai	2018	[516]
Co ₃ O ₄	Zhou et al.	2020	[517]
Co ₃ O ₄	Zhang and Meng	2016	[518]
Cr ₂ O ₃	Solymosi	1965	[462]
Cr ₂ O ₃	Burcat et al.	1968	[519]
Cr ₂ O ₃	Hermoni and Salmon	1961	[434]
Cr ₂ O ₃	Wang et al.	2019	[520]
CuO	Singh and Ojha	2002	[521]
CuO	Heng et al.	2009	[522]
CuO	Patil, Krishnamurthy, and Joshi	2008	[523]
CuO	Boldyreva, Bezrukov, and Boldyrev	1967	[524]
CuO	Chen, Li, and Li	2008a, 2008b	[525]
CuO	Apitha et al.	2003	[526]
CuO	Sharma et al.	2015	[527]
CuO	Alizadeh-Gheshlaghi et al.	2012	[515]
CuO	Hu et al.	2019	[528]
Cu ₂ O	Jacobs and Kureishy	1962	[529]
Cu ₂ O	Jacobs and Kureishy	1963	[530]
Cu ₂ O	Zhu et al.	2004	[531]
Dy ₂ O ₃	Dedgaonkar and Sarwade	1990	[532]
Fe ₂ O ₃	Solymosi and Revesz	1963	[533]
Fe ₂ O ₃	Furuichi and Ishii	1974	[534]
Fe ₂ O ₃	Xu, Wang, and Zhang	2008	[535]
Fe ₂ O ₃	Yuan et al.	2014	[536]
Fe ₃ O ₄	Zhang and Meng	2016	[518]
Gd ₂ O ₃	Dedgaonkar and Sarwade	1990	[532]
La ₂ O ₃	Dedgaonkar and Sarwade	1990	[532]
La ₂ O ₃	Raha, Ramamurthy, and Patil	1989	[537]
La ₂ O ₃	Survase, Sarwade, and Kurian	2001	[538]
MgO	Hermoni and Salmon	1961	[434]
MgO	Babar and Qadeer-Malik	2014	[539]
MnO ₂	Bircumshaw and Newman	1954, 1955	[348, 349]
MnO ₂	Hermoni and Salmon	1961	[434]
MnO ₂	Galwey and Jacobs	1959	[540]
MnO ₂	Kishore, Verneker, and Sunitha	1977	[541]
MnO ₂	Kishore, Verneker, and Pitchaiah	1980	[542]
MnO ₂	Dedgaonkar and Sarwade	1990	[532]
MnO ₂	Fu et al.	2008	[543]

^a Table sorted by metal oxide in alphabetical order, then by year.

Table 13: (continued)

Oxide ^a	Author	Year	References
MnO ₂	Galwey and Jacobs	1959	[460]
MnO ₂	Chandru, Patra, and Oommen	2012	[544]
MnO ₂	Chen and Zhu	2015	[545]
MnO ₂	Zhu et al.	2020	[546]
Mn ₃ O ₄	Li et al.	2013	[547]
Nd ₂ O ₃	Dedgaonkar and Sarwade	1990	[532]
Nd ₂ O ₃	Survase, Sarwade, and Kurian	2001	[538]
Nd ₂ O ₃	Zhang et al.	2005	[548]
Nd ₂ O ₃	Survase, Gupta, and Asthana	2002	[549]
Nd ₂ O ₃	Zou et al.	2014	[550]
NiO	Chen et al.	2008b	[551]
NiO	Boldyreva, Bezrukov, and Boldyrev	1967	[524]
NiO	Wang et al.	2005	[552]
Ni ₂ O ₃	Hermoni and Salmon	1961	[434]
PdO ₂	Said	1992	[553]
Pr ₂ O ₃	Dedgaonkar and Sarwade	1990	[532]
Pr ₂ O ₃	Survase, Sarwade, and Kurian	2001	[538]
SnO ₂	Solymosi and Bansagi	1970	[554]
Y ₂ O ₃	Dedgaonkar and Sarwade	1990	[532]
V ₃ O ₇ •H ₂ O	Zhang et al.	2011	[555]
Y ₂ O ₃	Raha, Ramamurthy, and Patil	1989	[537]
ZnO	Zheng et al.	2010	[556]
ZnO	Chai et al.	2019	[557]
ZnO	Li et al.	2017	[558]

^a Table sorted by metal oxide in alphabetical order, then by year.

Table 14: Activation energies of catalyzed AP decomposition.

Catalyst (5 mass-%)	Temperature range		<i>n</i>	Activation energy		Pre-exponential factor
	K	°C		kJ/mol	kcal/mol	
MnO ₂ (active)	481–502	208–229	1.6	201	48.2	2.4×10^{17}
MnO ₂ (pyrolusite)	487–518	214–245	1.4	141	33.7	5.0×10^{12}
Co ₂ O ₃	487–518	214–245	1.4	160	38.3	7.4×10^{14}
CuO	512–543	239–270	2.2	224	53.5	5.0×10^{20}
Cu ₂ O	523–543	250–270	1.6	190	45.5	1.4×10^{17}
Fe ₂ O ₃	523–569	250–296	1.2	171	41.0	2.6×10^{14}
NiO	543–569	270–296	1.2	206	49.2	6.3×10^{17}
V ₂ O ₅	523–576	250–303	1.2	183	43.7	1.6×10^{15}
Cr ₂ O ₃	533–582	260–309	1.1	126	30.1	8.0×10^9
CoCO ₃	481–497	208–224	1.4	195	46.7	1.4×10^{19}
CoC ₂ O ₄	483–502	210–229	1.7	183	43.7	5.4×10^{17}
Co ₂ O ₃	487–518	214–245	1.4	160	38.3	7.4×10^{14}
CoCl ₂ × 6H ₂ O	487–523	214–250	1.1	151	36.0	6.3×10^{13}

Data source: [511].

of self-heating are often erroneous. It is important to point out that kinetic experiments close to the critical ignition state yield results for the fractional decomposition α as a function of time t which deviate from the kinetic law applicable at lower temperatures. Nevertheless, these $\alpha(t)$ curves can be analyzed to yield effective global rate constants which depend on the temperature of the surroundings (T_0) rather than on the temperature of the reactant (which is a function of time). A theory of self-heating using these effective rate constants was applied to the calculation of autoignition times and self-heating curves. The results were in good agreement with the experiments.

The effectiveness of Fe_2O_3 as a catalyst for the decomposition of AP depends on the quality of the Fe_2O_3 powder and the experimental conditions. Contradictory statements about the effectiveness of Fe_2O_3 as a catalyst for the decomposition of AP can be found in the existing literature. The addition of Fe_2O_3 had little effect on the rate of decomposition of AP at 483–513 K (210–240 °C), but at 518–543 K (245–270 °C) the catalytic activity was enhanced significantly [533]. However, a few years following the research conducted by Jacobs and Kureishy (1963), the same group published data showing that in the range of 473–513 K (210–240 °C), the addition of Fe_2O_3 shortened the induction period and increased the rate of decomposition of AP. Above 533 K (260 °C) the reaction became very rapid and resulted in an explosion.

Different metal oxides with different semiconductor properties were used in an attempt to prove the electron-transfer nature of AP decomposition. During a study of the effect of p-type chromium(III) oxide and n-type titanium dioxide on the initiation of the deflagration of AP, it was found that the addition of chromium(III) oxide lowers the onset of the deflagration temperature of AP by about 160° to 180 °C [462]. It was suggested that the defect electron concentration of Cr_2O_3 is key to this mechanism. The electron conductor TiO_2 is an inert substance, even when doped with WO_3 , Al_2O_3 , or BeO . The onset of deflagration temperature was, however, decreased by ~150 °C when TiO_2 was doped with a small amount of Cr_2O_3 . This was attributed to the formation of chromium ions of higher valency on the surface of titanium dioxide (a defect conducting layer). The onset of deflagration temperature for AP has been determined in the presence of both substances as well as the activation energy of the process which leads to the deflagration. The activation energy agreed with that expected for an electron transfer mechanism.

In trying to explain the mechanism of metal oxide catalysis on AP decomposition, questions have arisen about whether the metal oxides just provide a catalytic surface area (true catalysts) or if they come under attack by the perchloric acid and form metal perchlorates that may remain dispersed in the AP crystal just shortly before the flame front reaches this part of the crystal. AP powder was mixed with ZnO , PbO , or CdO in a ball mill and pelletized [559, 560]. In later studies, the decomposition of the pellets was observed under a hot stage microscope and indicated partial melting of the pellets and color changes when heated to 423–453 K (150–180 °C). When pellets were heated to 513–523 K (240–250 °C) and then cooled, they dissolved completely in water without

residue. This indicates a chemical reaction between the metal oxide and the AP. IR spectra of the AP/CdO reaction product were similar to those of $\text{Cd}(\text{ClO}_4)_2$.

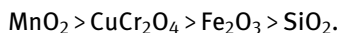
Many investigators have limited their examination of the effect of metal oxide catalysts to experiments in the condensed phase. Only a few have extended their effort to look at the effect of metal oxide surface area (particle size) on the condensed-phase reaction. Similarly, very few have looked at the catalytic effects of metal oxide particles that get carried out of the burning mass into the flame front, remain suspended in the turbulent flow, and possibly catalyze reactions in the gas phase. In one set of experiments with NiO of three different particle sizes (specific surface area 2 to $36 \text{ m}^2/\text{g}$ by krypton BET), the catalyst was suspended on a fritted glass filter held in the vicinity of the subliming AP pellet such that the vapors would have to pass through the catalyst layer [524]. In a parallel test, 1% of the nickel oxide was dispersed uniformly throughout the pressed AP pellet and no catalyst was on the glass filter. In both cases, the rate of decomposition as measured by the pressure increase in a closed bomb at 523 K (250 °C) increased with the specific surface area of the particles. Similar results were obtained with copper(II) oxide. The porosity of the metal oxide particles had a significant impact on the rate of decomposition, more so than the geometrical surface area. If different weights of NiO or CuO are taken and matched in such a way that the surface areas are equal, the effect of the metal oxide impurities on the rate of AP decomposition remains the same. One per-cent of NiO powder with a surface area of $36 \text{ m}^2/\text{g}$ had the same effect as 51% of NiO with a surface area of $0.7 \text{ m}^2/\text{g}$. While many investigators have concentrated on the effects of metal oxides on the solid/molten phase AP decomposition, these experiments showed that processes in the gas phase are also affected by suspended metal oxide particles.

Transition metal oxides that can change the state of oxidation of the core metal are thought to be better catalysts than those of metals that retain the same oxidation state. Using Cr_2O_3 labeled with ^{51}Cr isotope it was attempted to determine whether the action of the additive on thermal decomposition of AP involves oxidation of chromium(III) to chromate or if the additive remains untransformed acting as a catalyst [519]. Results of experiments showed that no traces of hexavalent chromium could be detected after thermal decomposition of AP with the catalyst were added in the ratio 1:1. Moreover, it was demonstrated that if Cr_2O_3 is heated to 573–583 K (300–310 °C) in air for three hours, up to 4% of Cr_2O_3 is transformed into chromate.

The effect of a combination of metal oxide catalysts and X-ray radiation (used for diagnostics to image the progress of the flame front or coming from cosmic radiation) was studied [561]. It was noted that irradiation at the moment of decomposition accelerates the decomposition of AP containing the additives of NiO, Ni_2O_3 , and Co_3O_4 . However, this has no effect on the kinetics of the decomposition of pure AP and of AP containing additives of CdO, CdS, Fe_2O_3 , PbO, WO_3 , or MoO_2 . Existing theories on the mechanism of the effect of preceding irradiation on the subsequent thermal decomposition of AP do not explain the observed effect. X-ray irradiation may induce free radicals in the salt.

Some additives do not catalyze AP thermal decomposition by themselves. Instead, they form the active catalysts during thermal decomposition of the precursor or during its interaction with AP. As an example, a comparison of the effects of different copper salts as additives on the thermal decomposition of AP showed that the efficiency of an additive depends on the ease of its thermal decomposition [562]. The rate of thermal decomposition of AP is strongly affected by the additives which themselves can easily be decomposed or give rise to decomposition products accelerating thermal decomposition (for example, copper(II) nitrate which forms nitrogen oxides during decomposition). A comparison of 1% of copper(II) sulfate, bichromate, benzoate, oxalate, lactate, and nitrate added to AP and heated to 523 K (250 °C) showed that copper(II) nitrate had the highest catalytic effect on AP decomposition while copper(II) sulfate had the lowest.

The activity of catalysts in the thermal decomposition of AP decreased in the order of:



There is evidence that the effect of catalytic additives on the decomposition of AP is connected mainly with other reactions which may occur in this system, rather than with the catalysis of decomposition of perchloric acid (as it was initially assumed); e.g., the oxidation of ammonia using the products of decomposition of perchloric acid. The most active catalyst should be considered to be the catalyst capable of accelerating both the decomposition of the acid and the oxidation of ammonia [492].

A model of the catalysis of the burning of sublimable solid single-component propellants was developed on the basis of a study of combustion in the system $\text{HClO}_4\text{-NH}_3\text{-Fe}_2\text{O}_3$ [563]. If AP is burned without catalysts, the decomposition rate is proportional to the surface area and pressure. The model of heterogeneous catalysis of AP burning predicts an increase in burning rate with a decrease of the radius of the catalyst grains. The increase in the burning rate was very distinct when the radius decreased to $<0.2\mu\text{m}$. The maximum increase in the reaction rate occurred at a catalyst concentration of 4 mass-%. The methods and models of calculation are general in nature and can just as well be used to calculate the burning rate of other perchlorates with other catalysts.

The question that is often asked is whether the addition of catalysts catalyzes the decomposition of ammonia or the decomposition of perchloric acid once the AP salt dissociates into its constituents in the flame front. In order to answer such questions, experiments have been conducted with catalysts applied to HClO_4 -supported flames and with catalysts applied to NH_3 -supported flames [564].

AP decomposition in the presence of various metal oxides (MnO , Cu_2O , CuO , Cr_2O_3 , Fe_2O_3 , CoO , and Co_3O_4) at 1, 5, and 10% was studied by DSC [565, 566]. A general kinetic law was used in interpreting the results from experimental runs. It was observed that in the catalytic decomposition of AP, several reactions occur and contribute to the overall kinetic law. The relative contributions of these reactions

and the actual kinetic parameters (apparent order of reaction, Arrhenius factors, activation energies) were evaluated.

The effect of the addition of 0.1–5% CaO on the combustion and thermal decomposition of AP was studied in a strand burner closed bomb and by DTA [567]. Pressed pellets were burned in plexiglass tubes at 5.05–101 MPa (50–1000 atm). The particle size of the AP powder was $<250\text{ }\mu\text{m}$ and that of the CaO additive was $<100\text{ }\mu\text{m}$.

Comparison of the activation energies for uncatalyzed thermal decomposition of AP with that of powdered AP catalyzed by low concentrations of MnO_2 showed that the rate-determining step for the catalyzed reaction is electron transfer from NH_4^+ to ClO_4^- [541]. The effectiveness of the catalyst is increased by baking the mixture for two weeks at 323 K (50 °C) during which Mn^{2+} or Mn^{4+} ions enter the NH_4ClO_4 lattice.

Vacuum pyrolysis of AP and AP/PS propellants was studied by DTA to measure the effects of transition metal oxides on decomposition and sublimation [542]. Being competitive processes, sublimation and decomposition proportions depend mostly on the pressure of the pyrolysis chamber and also on particle size and the presence or absence of contaminants. Literature data on the enthalpies for complete decomposition and complete sublimation were compared to the results of DTA peak area measurements to calculate the relative extents of sublimation and decomposition for AP by itself and the propellant mixture. For AP by itself and in the absence of catalysts, the extent of sublimation increased with a decrease in particle size. For propellants, the powder sublimed more readily than the bulk material. However, in the presence of metal ions, the bulk material sublimed more readily than the powder. To substantiate this finding, the effect of MnO_2 on NH_4ClO_4 sublimation as a function of particle size was examined. Surprisingly, the extent of sublimation decreased as the MnO_2 particle size decreased.

The kinetics of the thermal decomposition of AP were studied in the presence and absence of rare earth oxide catalysts, yttrium oxide (Y_2O_3), and lanthanum oxide (La_2O_3) [537]. The Prout-Tompkins and contracting-cube ($n = 3$) equations were found to fit the TGA data for the catalyzed thermal decomposition of AP. An attempt was made to use matrix isolation techniques and IR spectroscopy to identify the gases that evolved at different temperatures during the decomposition in the presence and absence of catalysts. The mechanism of the catalyzed thermal decomposition of AP has also been discussed in [537] in terms of an electron transfer process.

IR spectral investigations of AP were conducted over the temperature range of 298–563 K (25–290 °C). This was done in the absence [382] and the presence [532] of varying amounts of ammonium permanganate and using 2% by weight of different rare earth oxide additives. Heating and spectral scanning were done simultaneously, and the peak intensity was presumed to be proportional to the amount of undecomposed AP. The presence of 10% ammonium permanganate lowered the temperature of AP decomposition from 473 to 383 K (200 to 110 °C) and increased the rate by several times. It was theorized that mixed oxides produced as a result of deflagration of ammonium permanganate were catalyzing the process. In the presence of rare earth oxides

additives, the NH_4^+ stretching peak intensity decreased considerably. The extent followed the trend $\text{Gd}_2\text{O}_3 > \text{MnO}_2 > \text{Nd}_2\text{O}_3 > \text{Pr}_2\text{O}_3 > \text{Dy}_2\text{O}_3 > \text{Y}_2\text{O}_3 > \text{La}_2\text{O}_3 > \text{virgin AP}$. An electron transfer mechanism was proposed to explain these results.

The catalytic activity of nanocrystalline transition metal oxides on the decomposition of AP was investigated using thermal analysis [568]. Results indicated that nanocrystalline CuO powders have a strong catalytic activity compared to other metal oxides. The catalytic activity of nanocrystalline CuO powders during the decomposition of AP depended on the methods of preparation and the micro-structure of the resultant nanocrystalline CuO powders. Among them, the catalytic effect of spherical shape finely dispersed nanocrystal CuO powders on AP decomposition was the strongest, and it was able to reduce the onset of the higher temperature peak of AP decomposition down to 366 K (93°C). At the same time, the exotherm increased by 590 J/g to 1420 J/g. Nanocrystalline Fe_2O_3 doped with 5% Cu₂O has an even greater catalytic activity during the decomposition of AP. It reduced the onset temperature of the higher exothermic peak of AP decomposition by 35°C down to as low as 351 K (78°C) and the exotherm increased by 980 J/g to reach 1230 J/g. Compared to binary metal oxides, some new ternary metal oxides have the best catalytic activities.

The catalytic effects of superfine transition metal oxides on the thermal decomposition of AP were studied by DTA [569]. Results showed that both the single transition metal oxides (Co_2O_3 , CuO, Fe_2O_3) and the composite oxides ($\text{Fe}_2\text{O}_3/\text{Co}_2\text{O}_3$, CuO/ Co_2O_3 , $\text{Fe}_2\text{O}_3/\text{CuO}$) have catalytic effects on the thermal decomposition of AP. From the curves of the temperature change of the higher exothermic peak of AP decomposition which is a function of the content of one of the composite transition metal oxides, an optimum mixture ratio ($\text{Fe}_2\text{O}_3 : \text{Co}_2\text{O}_3 = 1 : 3$) was found.

NiO nanoparticles with an average particle size of 10 nm were characterized by XRD, FTIR, and TEM [552]. The catalytic effect of the NiO nanoparticles on the thermal decomposition of AP was measured by DTA and TGA. The catalytic activity of nano-size NiO was superior to that of bulk NiO powder. Adding 2% of nano-NiO to AP decreased the decomposition temperature by 93°C and increased the heat of decomposition from 590 to 1490 J/g.

The crystal phase, morphology, and particle size of Co_3O_4 nano-powders with different average crystallite sizes (23, 30, 35, and 150 nm) were characterized by XRD and TEM [514]. The catalytic activity of nano-size Co_3O_4 in the decomposition of AP was investigated using DTA to make comparisons with micron-size Co_3O_4 . It was found that the nano-size Co_3O_4 made the temperature of the lower-temperature exothermic peak of AP disappear. It also decreased the onset temperature of the higher-temperature exothermic peak by 128°C. The exothermicity increased from 515 to 1265 J/g. Nano-size Co_3O_4 produced better catalytic activity for the thermal decomposition of AP than micron-size Co_3O_4 .

Nano-size Fe_2O_3 as a catalyst has been tested before in solid propellants. However, the problem is that nanoparticles of Fe_2O_3 prepared using the traditional wet method aggregates in water and cannot be distributed homogeneously in the solid propellant,

which leads to a decrease in the catalytic activity. To solve the aggregation problem, nanoparticles of Fe_2O_3 were prepared in an oil/water two-phase system and characterized by XRD and FTIR [570, 571]. Amorphous nanoparticles with a narrow particle size distribution (12 nm) were obtained using this method. DTA showed that the two exothermic peaks of AP decomposition with micrometer-sized Fe_2O_3 shifted to temperatures 110 and 62 °C lower than those of pure AP, respectively. The temperatures of the two peaks of AP with nanometer-sized Fe_2O_3 decreased by 89 and 118 °C, respectively. This means the catalytic performance of nanometer-size Fe_2O_3 is superior to that of micrometer-sized Fe_2O_3 . With the increasing content of nanometer-size Fe_2O_3 , the temperature of the second exothermic peak of AP decreased even more. The temperature of the first exothermic peak of AP did not change too much when the content of nanometer-size Fe_2O_3 was 1% or 2.5%. However, it decreased significantly when the Fe_2O_3 content was close to 5%.

Cu_2O nanocrystals were prepared using precipitation from $\text{Cu}(\text{NO}_3)_2$ and NaOH and tested as catalysts for the AP thermal decomposition [531]. Hydrazine hydrate was used as the reducing agent. The as-prepared Cu_2O nanocrystals were characterized by XRD, TEM, and XPS. The catalytic activity of the Cu_2O nanocrystals of different morphology for the AP decomposition was measured using DTA. Cu_2O nanocrystals with different morphology revealed different catalytic effects on the AP decomposition. The addition of 2% polygonal Cu_2O nanocrystals to AP decreased the upper onset temperature of AP decomposition by 103 °C and increased the exothermicity of decomposition from 590 to 1350 J/g.

CuO nanocrystals and nanorods were explored as catalysts for the decomposition of AP [525, 572]. AP typically undergoes a two-stage decomposition process. The addition of CuO nanocrystals led to a downshift of the high-temperature stage of AP decomposition towards lower temperatures.

In a similar way, the thermal decomposition of AP can be accelerated to varying degrees by adding NiO nanocrystals with different surface areas [551]. With increasing annealing temperatures, the BET surface areas of NiO samples were reduced from 108.6 to 0.9 m²/g. The catalytic activities of NiO nanocrystals on the thermal decomposition of AP were investigated using TGA/DTA. With the addition of NiO nanocrystals, the onset temperature of the thermal decomposition of AP decreased greatly. Larger surface areas of NiO nanocrystals promoted the thermal decomposition of AP more actively than coarse, low-surface area materials.

Nanorods and micro-octahedrons of $\alpha\text{-Fe}_2\text{O}_3$ were selectively synthesized through a one-step hydrothermal treatment of iron(III) chloride [535]. The resulting samples were characterized using XRD, SEM, TEM, and FTIR. It was found that monodispersed nanorods were 10–25 nm in diameter and 50–100 nm in length, while the octahedrons were 100–400 nm in size. These $\alpha\text{-Fe}_2\text{O}_3$ nanorods and micro-octahedrons exhibited quite different catalytic activity on the thermal decomposition of AP. The nanorods significantly reduced the decomposition temperature of AP, but the micro-octahedrons did not.

The catalytic effect of two different sizes of α -Fe₂O₃ nanoparticles on the thermal decomposition of AP was investigated using DSC [573]. The nano-sized Fe₂O₃ particles exhibited more of a catalytic effect on the thermal decomposition of AP than commercial Fe₂O₃ particles. The addition of 2 mass-% of α -Fe₂O₃ particles with a very fine size of 3.5 nm lowered the HTD of AP by 59 °C. The enthalpy of the reaction was 4.574 kJ/g compared to 0.834 kJ/g of uncatalyzed AP and the activation energy was reduced.

Using 1,2-epoxypropane (propylene oxide) as the agent for accelerating the hydrolysis of Fe(III) ions or Fe(III) alkoxylates, an AP/Fe₂O₃ wet gel was prepared using a sol-gel method, and an AP/Fe₂O₃ aerogel was obtained using a supercritical extraction of the solvent [574]. Both pH and NMR studies suggest that the added epoxide acts as an irreversible proton scavenger that induces the Fe(III) species to undergo hydrolysis and condensation to form an inorganic iron oxide framework. This method can be extended to prepare other transition- and main-group metal oxide nanomaterials. The samples were characterized using TEM, SEM, energy dispersive spectroscopy (EDS), and DSC. The results indicated that the aerogels are nanocomposites, in which the particle size of AP is 50–90 nm and the particle size of Fe₂O₃ is about 20 nm. The impact sensitivity of AP/Fe₂O₃ is higher and the friction sensitivity is lower than that of pure AP. The peak temperature for thermal decomposition of AP/Fe₂O₃ is much lower, and the rate of heat release is much faster. For example, in AP/Fe₂O₃ containing 90% of AP, the high and low decomposition peaks are shifted downward by 125 °C and 113 °C, respectively, compared to those of pure AP, and the rate of heat release is four times faster.

Different shapes of CuO nanocrystals were synthesized and tested for their activity in AP decomposition [575–577]. CuO in its various crystalline shapes lowered the onset of decomposition temperature of AP in all cases.

Nanoparticles of CuO, Mn₂O₃, Cr₂O₃, and Fe₂O₃ have been characterized using XRD which indicated an average particle diameter of 35–54 nm [578]. Their catalytic activity in the thermal decomposition of AP was then measured using DTA. AP undergoes a two-step decomposition process where the addition of metal oxide nanocrystals causes a shift of the HTD exothermic peak toward lower temperatures.

Nano-size iron(III) oxide in the shape of nanotubes is a particularly effective catalyst for the decomposition of AP [579]. The highly crystalline α -Fe₂O₃ nanotubes were about 200–1000 nm long, 100–150 nm wide, and the wall thickness was 25–30 nm. A detailed reaction mechanism for AP decomposition over α -Fe₂O₃ nanotubes was proposed.

The effect of the specific surface area of TiO₂ catalysts on the thermal decomposition characteristics of AP was examined with a series of thermal analysis experiments [580]. It was evident that the thermal decomposition temperature of AP decreased when the specific surface area of TiO₂ increased. It might also be possible that TiO₂ influences the frequency factor of AP decomposition because there was no observable effect on the activation energy.

Nano-size NiO/MgO particles were prepared via an impregnation method [581]. The phase and morphology of NiO/MgO catalysts were characterized using XRD, TEM, and energy dispersive X-ray analysis (EDAX) spectroscopy. The catalytic effect of nanometer particles (NiO, MgO alone), NiO+MgO dry mixture particles, and NiO/MgO composite particles on the thermal decomposition of AP was investigated using DSC. The results revealed that NiO particles are highly dispersed on the MgO support. Catalytic performance of the nano-size NiO/MgO composite particles was superior to that of corresponding single ingredients or NiO+MgO dry mixture particles. Nano-size NiO/MgO can make the HTD peak value of AP decrease by 92°C. The temperature difference between the low- and HTD peak shrinks by up to 10.6°C, which indicates good catalytic performance. The MgO support can effectively prevent the aggregation of NiO particles and increase the number of active sites.

Iron(III) oxide, Fe_2O_3 , is a well-known catalyst for the thermal decomposition of AP and is extensively used as a burning rate modifier for AP-based composite solid propellants. The particle size of conventional propellant grade iron(III) oxide was reduced to nano levels via continuous ball milling using a planetary ball mill employing zircon balls in isopropyl alcohol [582]. The batches of nano ferric oxide prepared by varying the ball milling parameters, viz., time and sample mass were characterized using a particle size analyzer, surface area analyzer, and XRD. Lewis acid sites present in the catalyst were determined using a butylamine desorption technique. The catalytic activity of nano ferric oxide samples was evaluated from the thermal decomposition of AP mixed with iron(III) oxide using TG-DTA. The catalytic activity of different batches of Fe_2O_3 was correlated with their surface properties. It was found that continuous ball milling reduced the particle size of Fe_2O_3 to nano levels and the particle size of conventional Fe_2O_3 was reduced from 138 nm to 72 nm after 40 hours of wet ball milling in isopropyl alcohol. The onset of thermal decomposition of AP was reduced from 406 K (133°C) to 339 K (66°C) with the addition of nano- Fe_2O_3 .

The effect of metal oxides, mixed oxides, binary and ternary ferrites, and rare earth metal oxides in the shape of nano-oxides on the thermal decomposition AP has been studied in detail, including assessing the influence of the size of oxides on the thermal decomposition of AP and a comparison of bulk and nano-sized oxides [583]. The size distribution, morphology, and nanostructure of metal oxide nanoparticles are very important characteristics and they do affect the kinetics of the decomposition of AP. Due to the small size and the large surface area, nano-sized metal oxides are more active catalysts on the thermal decomposition of AP compared to their bulk size oxides with the same chemical composition.

Iron oxides which are often used as a burning rate catalyst for all types of composite propellants are polymorphous crystalline minerals, including hematite ($\alpha\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4), and maghemite ($\gamma\text{-Fe}_2\text{O}_3$). Nanoparticulate materials such as hematite and maghemite exhibit high catalytic activity during the thermal decomposition of AP. The catalytic effect of iron oxide nanoparticles was attributed

to their small particle size, more active sites, and high surface area which enable gas adsorption of released products during the thermal reactions. Methods for obtaining nanoparticulate iron oxides and the advantages of the different techniques for characterizing these nanomaterials have been summarized [584]. The morphologies and structures as well as the textural properties created by physical adsorption can be characterized using TEM, SEM, XRD, and FTIR.

4.6.8.3 Ternary Oxides

A *ternary* compound is a compound that consists of a combination of three elements, one of them being oxygen. There is some inconsistency in existing literature; sometimes oxides containing **two** different metals and oxygen are called [binary oxides] but here we call them *ternary* oxides. Table 15 is a summary of ternary metal oxides tested as catalysts for AP decomposition.

Table 15: Summary of ternary metal oxides tested for AP decomposition.

Oxide	Author	Year	References
CdFe ₂ O ₄	Singh et al.	2010	[585]
CoFe ₂ O ₄	Zhao and Ma	2010	[586]
CoNiFe ₂ O ₄	Singh et al.	2008	[587]
CoZnFe ₂ O ₄	Singh et al.	2008	[587]
Cr(OH) ₃ •Al(OH) ₃	Zhang et al.	2014	[588]
CuCo ₂ O ₄	Alizadeh-Gheshlaghi et al.	2012	[515]
CuCoFe ₂ O ₄	Singh et al.	2008	[587]
CuCr _{0.25} Fe _{1.75} O ₄	Boldyreva et al.	1975	[589]
CuCr _{0.5} Fe _{1.5} O ₄	Boldyreva et al.	1975	[589]
CuCr _{1.75} Fe _{3.25} O ₄	Boldyreva et al.	1975	[589]
CuCr ₂ O ₄	Boldyreva et al.	1975	[589]
CuCr ₂ O ₄	Patil, Krishnamurthy, and Joshi	2008	[523]
CuFe ₂ O ₄	Boldyreva et al.	1975	[589]
CuFe ₂ O ₄	Liu et al.	2008	[590]
Cu _x Co _{3-x} O ₄	Said and Al-Qasmi	1996	[591]
CuZnFe ₂ O ₄	Singh et al.	2008	[587]
LaCoO ₃ , La ₂ CuO ₄ , LaMnO ₃ and LaNiO ₃	Hu et al.	2020	[592]
MnCo ₂ O _{4.5}	Zheng et al.	2019	[593]
NdCoO ₃	Weifan et al.	2008	[594]
NdCrO ₃	Yu et al.	2009	[595]
NiCr ₂ O ₄	Boldyreva et al.	1975	[589]
NiCuFe ₂ O ₄	Singh et al.	2008	[587]
NiZnFe ₂ O ₄	Singh et al.	2008	[587]
PbK ₂ [Co(NO ₂) ₆]	Guo et al.	2013	[596]

Sorted alphabetically by metal oxide formula, then by year.

At low temperatures between 489 to 550 K (216–277°C), carbon had no effect on the rate of decomposition of AP. However, copper chromite, either alone or with carbon, exerted a slightly positive catalytic effect, the rate constants for mixtures being about 50% greater than those for the pure salt at corresponding temperatures [597]. The activation energy was unchanged at 129.7 kJ/mol (31 kcal/mol). When copper chromite, cupric oxide, or potassium dichromate was mixed with AP, the rate of the high-temperature reaction was considerably enhanced. The activation energy was the same for all the catalysts tried, viz., 200.8 kJ/mol (48 kcal/mol).

Under government contracts, SRI conducted a series of experiments to study the effect of copper chromite and other mixed metal oxides on the decomposition of AP and AP/fuel mixtures. Among others, they also separated the effects of the catalyst on the decomposition of AP and the subsequent combustion of ammonia in an atmosphere containing HClO_4 . At first, the kinetics of decomposition of AP was studied in detail by itself (without the addition of catalysts). Following that, the addition of copper chromite as a catalyst was studied and reaction mechanisms for both uncatalyzed and catalyzed decomposition was proposed [598].

The rate of heat release during AP decomposition is controlled via the absence or presence of catalysts. The rate of heat release of AP-fuel or AP-catalyst mixtures (both under adiabatic conditions) was studied as a function of temperature [599, 600]. In the presence of catalysts, the autocatalytic feature associated with the nucleation of pure AP disappeared and the adiabatic reaction kinetics followed an Arrhenius-type behavior. Experiments with AP-fuel mixtures showed that measurable heat release occurred at temperatures below the phase transition temperature of AP and that the rate of heat generation per mass of material is greater than that of pure AP, but the data were less reproducible than for pure AP. The rate of exothermic decomposition of pure AP was unaffected by an increase in pressure. This observation suggested that the heat release is controlled using homogeneous or heterogeneous reactions in the condensed phase.

Therefore, the role of condensed-phase reactions in the ignition and deflagration of AP propellants was examined in more detail [601, 602]. A thermal runaway in the condensed phase can account for the ignition phenomena observed. Also, at low steady-state deflagration rates, the contribution of the solid-phase reactions can be illustrated. Some of the propellants quenched during deflagration revealed the existence of a subsurface layer, which was located in a zone at which the temperature had reached a level characteristic of the polymorphic crystal transition of AP.

The action of copper chromite catalyst in contact with solid AP differs markedly from that of the catalyst in contact with the gaseous dissociation products of AP [603]. On exposure to ammonia and perchloric acid at 675 K, the catalyst loses its activity rapidly. This may be due to the oxidation of chromium cation from the plus 3 oxidation state to a higher oxidation state.

The oxidation of ammonia using HClO_4 catalyzed by copper(II) chromite (CuCr_2O_4) and copper(I) chromite ($\text{Cu}_2\text{O} \cdot \text{Cr}_2\text{O}_3$) was studied in order to examine

the role of the copper ion valence state [604]. The results at 673 K (400 °C) indicated that Cu^{2+} is a much better catalyst than Cu^{1+} for this reaction. Similar considerations apply to the complete oxidation of olefinic hydrocarbons such as those in polymeric binders. It was suggested that cupric chromite plays a dual function of catalyzing the decomposition of AP and the oxidation of ammonia and other fuel molecules. Additional experiments spanning the temperature range of 250 °C to 325 °C also studied the effect of copper chromite on the rate of AP decomposition [459].

The kinetics of AP/hydrocarbon fuel and AP/ammonia reactions were studied by passing the fuel gas over granular AP (with and without a copper chromite catalyst) in a reactor at low pressures (17 mm Hg), while slowly raising the reactor temperature and analyzing the exhaust gases (after the removal of corrosive HCl) in a mass spectrometer [605]. They have concentrated on a quantitative examination of the potential contribution of surface-catalyzed reactions between AP, catalyst, and gaseous organic molecules, representative of the fuel binder in an operational propellant. Propylene gas was used as a simulant for hydrocarbon binders. Tests were performed without and with 2.9 or 4.8 mass-% catalyst in the AP. In an uncatalyzed system, reactions between NH_3 and HClO_4 in the gas phase determined some of the kinetics, but in the presence of the catalyst, the role of these reactions diminishes. Both the CuO and CuCr_2O_4 catalysts catalyzed the complete oxidation of hydrocarbons and the oxidation of ammonia, reactions which would be encountered in a propellant composed of AP/ CuCr_2O_4 /binder. Surface-catalyzed reactions would be expected to play an important part in both ignition and combustion of such propellants. One application of the results may be with regards to the evaluation of the surface temperature of an AP/ CuCr_2O_4 propellant on the basis of the kinetic information. For a specified regression rate, the surface temperature of the solid may be estimated by examining the data for the mass consumption rate of solid AP/ CuCr_2O_4 as a function of temperature. For AP/4.8 CuCr_2O_4 , it was found that for the linear regression rate of 0.04 cm/sec (corresponding to a mass consumption rate of 0.0012 mol/sec), the surface temperature would be between 640 and 660 K (depending on the stoichiometry employed). These values were in good agreement with experimental observations.

A different experimental setup was used in an opposing flow burner, where a flow of combustible gas (e.g., methane) impinges on a solid surface of AP (with or without a catalyst embedded in the solid oxidizer) [606]. This is similar to the process in an inversed hybrid rocket where a gaseous (or liquid) fuel passes over a solid oxidizer. A diffusion flame is established in the stagnation region formed by the two counter-current flows of reactants. The solid AP cylinder can be slowly advanced toward the source of the fuel. The trick is to match the rate of advance of the propellant strand to its consumption rate so that the distance between the gaseous fuel outlet and the propellant surface remains constant. With increasing mass flux of gaseous fuel, the mass flux of solid AP (with or without a catalyst embedded in the solid oxidizer) grows until a limiting condition is reached that is governed by the kinetics of the reaction and the mass transfer to/from the surface. Further enhancement in fuel flow does not result

in an increase in the mass consumption rate of the solid oxidizer. One of the variables studied was the catalyst concentration in the oxidizer. The critical mass flux m^* corresponding to the limiting rate of propellant consumption increased significantly as the catalyst concentration in the solid phase was increased from 0 to 5 mass-% (see [607] also).

The most effective catalysts from a group of spinels and ferrites were CuCr_2O_4 and CuFe_2O_4 , indicating that the copper entity is the active part of the molecule [589]. These catalysts were tested with AP by themselves, as well as in a composite propellant containing 20% butyl rubber. Catalyst additions were at 1%. Testing was done at 2.02, 4.04, and 6.06 MPa (20, 40, and 60 atm). The best catalyst was CuCr_2O_4 at any pressure, followed by NiCr_2O_4 and CuFe_2O_4 for the high-pressure tests.

The addition of dichromate ions introduced into the lattice of AP is likely to play a dual role. At the point where the dichromate has not yet decomposed (which occurs at the initial stages of the process), it is an active proton acceptor and so inhibits the formation of reaction nuclei [608]. While the degree of AP decomposition increases, especially at high temperatures, the dichromate ion decomposes. The product of this reaction chromium(III) oxide can cause heterogeneous catalytic action on the rate of thermolysis of AP.

DTA of powdered AP, PS, and AP/PS propellant, catalyzed using small amounts (1 mass-%) of freshly-prepared CuCr_2O_4 and mixtures of CuCr_2O_4 and CuO revealed that decomposition is increased due to heterogeneous catalysis [609]. The kinetics of thermal decomposition of AP in the orthorhombic region of AP by itself with and without CuCr_2O_4 were studied as baseline.

Variable temperature (303–553 K) IR spectroscopic studies were conducted during the thermal decomposition of pure and γ -treated AP [382]. Decomposition was enhanced using γ -radiation or when in the presence of an additive such as Gd_2O_3 . The intensity of the stretching $\sim 1100\text{ cm}^{-1}$ and bending $\sim 625\text{ cm}^{-1}$ frequencies of ClO_4^- decreased upon heating the KBr matrix even below 360 K. Above this temperature, a broad band developed over a band of $480\text{--}510\text{ cm}^{-1}$ in the pure and γ -treated AP, which was attributed to the $\text{ClO}_3^- \nu_4$ vibration.

The catalytic activity of mixed $\text{CuO-Cr}_2\text{O}_3$ oxides on the thermal decomposition of AP was investigated using DTA, electrical conductivity measurements, and XRD techniques [610]. The results indicated that the decrease in the defect electron sites of a CuO catalyst doped with 1 atom-% Cr^{3+} inhibited its activity, while the opposite effect was observed when Cr_2O_3 was doped with 1 atom-% Cu^{2+} . A catalyst containing 70 atom-% Cr^{3+} was found to be the most active during the decomposition of AP. At this Cu:Cr ratio, CuCr_2O_4 formation was demonstrated by XRD. The activity of this spinel was explained on the basis of a hopping electron mechanism between $\text{Cr}^{3+}/\text{Cr}^{4+}$ active sites.

Six metal oxides (CdO , Cr_2O_3 , Co_3O_4 , NiO , CuO , and MoO_3) were prepared using calcination of the corresponding precursors at 773 K (500 °C) for five hours in air and were tested as catalysts for AP decomposition [611]. The acidities and basicities

of these metal oxides were estimated using the adsorption of pyridine or formic acid vapor. The pyrolysis of pure AP and AP mixed with 10 mass-% metal oxide was studied in a dynamic atmosphere with GN_2 purge using TGA (heating rate $5^\circ\text{C}/\text{min.}$) and also by using derivative thermogravimetric analysis. Based on the TGA trace, the low-temperature pyrolysis (LTP) of pure AP started at 568 K (295°C) and high-temperature pyrolysis (HTP) was completed at $\sim 603\text{ K}$ ($\sim 330^\circ\text{C}$). The second step followed in the range of 608 to 638 K ($335\text{--}365^\circ\text{C}$). The differential TGA revealed two peaks; one at 580 K (307°C) and one at 622 K (349°C). The addition of Cr_2O_3 , Co_3O_4 , CuO , and MoO_3 reduced the two pyrolysis stages to one step, which started at 533–558 K ($260\text{--}285^\circ\text{C}$) and finished at 603 to 643 K ($330\text{ to }370^\circ\text{C}$). The lowest completion temperature was with Cr_2O_3 . CdO and NiO retained the two-step decomposition. The oxides can be divided into acidic and basic oxides. A correlation was found between the catalytic activities of the metal oxides during the pyrolysis of AP and their acid-base characters. The higher the ratio of basicity to acidity, the more active the oxide is during the pyrolysis of AP. Cr_2O_3 was the most active and NiO was the least active in this group of basic oxides. The activation energies of the non-catalyzed and catalyzed pyrolysis of AP were calculated from the TGA results. The activation energy of pure AP decomposition was 170 kJ/mol for LTP and 145 kJ/mol for HTP. In all cases, the activation energy of pure AP decomposition was lowered by adding metal oxide catalysts.

Thermal analysis of LaCoO_3 nanocrystals with pure perovskite structure showed a strong catalytic effect on the AP decomposition [612]. The catalytic effect was more pronounced with the increased content of LaCoO_3 nanocrystals in the AP. Adding 2% of LaCoO_3 nanocrystals decreased the upper temperature of AP decomposition by 108°C and increased the exothermic enthalpy of decomposition from 590 to 1390 J/g. When the content of LaCoO_3 was increased to 5%, the upper temperature of AP decomposition decreased by 116°C , and the enthalpy of decomposition increased to 1600 J/g.

The catalytic effect of CuCr_2O_4 on the thermal decomposition of AP as a function of catalyst concentration was investigated using DSC [523]. Addition of a small amount, only 2 mass-% of the nano- CuCr_2O_4 showed the best catalytic effects as compared to nano- CuO in lowering the upper decomposition temperature by 118°C . High heat releases of 5.4 and 3.9 kJ/g were observed in the presence of nano- CuO and CuCr_2O_4 , respectively. A mechanism based on an electron transfer process was proposed for AP decomposition in the presence of nano-metal oxides.

Nanocrystallites of six mixed ternary transition metal ferrites (MTTMF) were prepared using co-precipitation and characterized using XRD and BET [587]. XRD patterns produced average particle sizes of 3 to 7 nm. Catalytic activities of MTTMF's on the thermal decomposition of AP were investigated using TGA, DSC, DTA, and ignition delay measurements. The catalytic activity was found to decrease in the following order: $\text{CoZnFe}_2\text{O}_4 > \text{CoNiFe}_2\text{O}_4 > \text{CuZnFe}_2\text{O}_4 > \text{CuCoFe}_2\text{O}_4 > \text{NiCuFe}_2\text{O}_4 > \text{NiZnFe}_2\text{O}_4$.

Adding 2% of NdCrO_3 nanoparticles to AP decreased the onset temperature of thermal decomposition by 87°C and increased the heat of decomposition from 590 to 1073 J/g [595].

Binary transition metal ferrite nanocrystals MFe_2O_4 ($M = Cu, Co, Ni$) were prepared using a co-precipitation method and were characterized using XRD, which produced average particle sizes ranging from 27 to 44 nm. The catalytic activity for AP decomposition measured using TGA, DTA, and ignition delay were used to evaluate kinetic parameters by model fitting as well as an isoconversional method [613].

Since both zinc oxide and titanium oxide were said to be good catalysts for AP decomposition, it was logical to test a ternary oxide containing both. Nano-size $ZnTiO_3$ powders were prepared by means of a precipitation method using $TiCl_4$, $Zn(NO_3)_2 \cdot 6H_2O$, and $(NH_4)_2CO_3$ as starting materials [614]. The $ZnTiO_3$ nanocrystals were characterized using XRD, FTIR, and TEM. The catalytic performance of $ZnTiO_3$ nanocrystals for AP decomposition was investigated using DTA. The $ZnTiO_3$ powder had a spheroidal shape with particle sizes of about 100 nm. The low- and HTD peaks of AP were decreased by 18.3 and 25.1 °C respectively when adding 5% nano- $ZnTiO_3$ powder. With increasing nano- $ZnTiO_3$ content in AP, the catalytic effects of $ZnTiO_3$ powders on the HTD of AP were enhanced and the catalytic effects of the LTD of AP were reduced.

Cu/Fe mixed oxides were prepared via calcination of Cu/Fe hydrotalcite precursors and tested as catalysts for the thermal decomposition of AP by measuring their catalytic activity using TGA and DTA [615]. The onset of exotherm of AP decomposition was lowered by the addition of 4 mass-% Cu/Fe-mixed oxides at a temperature of 104 °C. Higher catalyst concentrations favored the further decomposition of AP. The proposed catalytic mechanism is the presence of O_2^- on the surface of Cu/Fe mixed oxides, which can accelerate the thermal decomposition of AP.

Nano-size $CoFe_2O_4$ was synthesized by a polyol-medium solvothermal method and characterized using XRD, TEM, and selected area electron diffraction. The catalytic activity and kinetic parameters of $CoFe_2O_4$ nanocrystallites on the thermal decomposition of AP were investigated using TGA-DSC [586]. The decrease in the activation energy and the increase in the rate constant for AP decomposition are a measure for the catalytic activity of these $CoFe_2O_4$ nanocrystallites. The catalytic effect of $CoFe_2O_4$ is noticeable, not only during the HTD process but also during the LTD process. The addition of 5% $CoFe_2O_4$ lowered the activation energy of AP decomposition from 178 to 106.5 kJ/mol and the maximum of the high-temperature exotherm was shifted from 706 K (433 °C) down to 580 K (307 °C).

The catalytic activity of nanometer-size CuO, Fe_2O_3 , and CuO/ Fe_2O_3 on AP thermal decomposition was investigated using TGA-DTA and burning rate measurements [616]. The order of the decreasing catalytic activity was $CuO/Fe_2O_3 > CuO > Fe_2O_3$. The catalytic activity of CuO/ Fe_2O_3 was better than that of CuO or Fe_2O_3 alone, which was attributed to a synergistic effect of the mixed oxides.

Nanocrystalline $Co_xZn_{1-x}Cr_2O_4$ ($x = 0.7, 0.8, 0.9, 0.95$, and 1) was synthesized via a low-temperature combustion synthesis method using citric acid as reductant and metal nitrates as oxidants. It was characterized using XRD, TEM, FTIR, DSC, and catalytic performance for AP decomposition [617]. Results revealed that the

cubic spinel-type solid solution of 30 nm $\text{Co}_x\text{Zn}_{1-x}\text{Cr}_2\text{O}_4$ particles can be obtained at 1073 K (800 °C). Compared with the thermal decomposition of pure AP, adding $\text{Co}_x\text{Zn}_{1-x}\text{Cr}_2\text{O}_4$ nanoparticles to AP decreased its decomposition temperature by 58–68 °C and increased its apparent decomposition heat to 1049–740 J/g, exhibiting a significant catalytic effect.

The effect of ferrite nanoparticles on the thermal decomposition of AP was studied using TGA and DSC [618]. Nanoferrite nanoparticles such as Zn, Mn, Ni, Co, and Cu ferrite had been prepared using a co-precipitation method. All nanoparticles were characterized using XRD and SEM. The average particle sizes were 6.8 to 1.1 nm. Activation energies of HTDs of different mixed oxide nanoparticles were calculated using the Kissinger equation. The catalytic activity of nanoferrites is very sensitive to oxygen and may be effective to improve the thermal decomposition and burning rate of AP-based propellants.

A copper chromite-based burning rate catalyst for composite solid propellants was synthesized using the thermal decomposition of basic copper ethylammino chromate [619]. The course of thermal decomposition of the precursor to copper chromite was examined using DSC-TGA and the volatile products formed were analyzed using TGA-MS. Copper content, surface area, and Lewis acid sites of the catalyst were higher than those in standard copper chromite. XRD analysis showed the presence of CuCrO_2 phases along with CuO and CuCr_2O_4 . The improved surface properties, as well as the synergetic action of three phases of oxides (CuO , CuCr_2O_4 , and CuCrO_2) in the system, increased the catalytic activity of this catalyst, resulting in a reduction of 60 °C in the onset of the decomposition temperature of AP.

Copper chromite in intimate contact with AP may undergo slow chemical changes during aging. Aging is an irreversible process during which the material undergoes a series of slow chemical degradation/oxidation reactions. AP-copper chromite (AP-CC) pellets were aged by subjecting them to temperature cycling and the effect of aging on the linear burn rate was measured [620]. Aging of individual ingredients had no effect on the burn rate, but the burn rate of AP-CC pellets was reduced when AP+CC were aged together. Changes in the properties of copper chromite during aging were identified using XRD and EDS analysis.

Four different perovskites, namely LaCoO_3 , La_2CuO_4 , LaMnO_3 , and LaNiO_3 , were prepared using a co-precipitation method and then used to catalyze the decomposition of AP [592]. LaCoO_3 exhibited the best catalytic performance among all the perovskites tested. The decomposition temperature of AP lowered to 574 K (301 °C) (115 °C lower than pure AP) and the heat release increased from 768 to 1428 J/g.

4.6.8.4 The Effect of Metal Chlorides on AP Thermal Decomposition

The low-temperature thermal decomposition of AP can be initiated using a single-stage nucleation process at a lattice defect site on the surface of the crystal. If the crystals are allowed to age for several days after inducing the lattice defect, an aging and healing effect in the form of a decrease in the decomposition rate with storage

time at room temperature is observed [102, 621]. Sample impurities, and as little as 0.04 mass-% copper(II) chloride, significantly accelerated the decomposition but did not alter the nucleation process or the rate-determining step. It was suggested that catalysis occurs through the formation of ammino complexes which tie up the ammonia on the crystal surface and thereby prevent the reversal of the proton transfer reaction.

In reviewing the Keenan and Siegmund [621] data, it was again concluded that proton transfer leads to the formation of a copper ammino complex and that the reaction of this complex with HClO_4 is the driving force of the reaction. Measurements of the catalyzed AP decomposition using small amounts of copper (0.013 to 0.2 mass-% copper (II) chloride) showed that the rate of reaction doubled with the addition of 0.04 mass-% CuCl_2 . However, the addition of further CuCl_2 caused little further catalysis [622]. These results could not be explained by previous mechanisms. It was suggested that the catalysis results from the formation of a copper-ammine complex, which is more reactive than the uncomplexed ammonia. The complexed ammonia reacts three times faster than the uncomplexed ammonia.

4.6.8.5 The Effect of Metal Chlorates and Chlorate Ion on AP Thermal Decomposition

Chlorate ions are potential contaminants invariably introduced during the production of AP. Chlorates may also form during partial decomposition of AP. They have a strong influence on the thermal stability of AP. As such, the allowable chlorate content is controlled using material specifications (see Section 4.2.2). Chlorates must never be mixed with ammonium salts in propellant or pyrotechnic formulations. Chlorate contamination in AP have been the cause of numerous accidents with pyrotechnic devices in display fireworks.

The impact of adding potassium chlorate on the thermal stability of AP is evident from a rapidly decreasing onset of the first exotherm of AP decomposition (see Table 16) [623]. The phase change endotherm remained unchanged at 517 K throughout this experiment series.

It is very dangerous to mix ammonium salts with chlorates because ammonium chlorate is very unstable and may render the mixture more sensitive to accidental ignition.

There is no practical application for ammonium chlorate and there is no interest in it other than the nuisance of it showing up as a contaminant or intermediate in AP. Nevertheless, samples of ammonium chlorate have been prepared and tested for stability [624]. Ammonium chlorate was prepared via a metathetical reaction of barium chlorate and ammonium sulfate. The barium sulfate precipitate was removed. The slow evaporation of water under vacuum and recrystallization from ethanol was not stable at room temperature but decomposed to form chlorine, nitrogen, water, and ammonium nitrate. It could be stored at 268 K (-5°C) for a longer time. Two decomposition processes were identified when performing the decomposition under carefully

Table 16: Impact of potassium chlorate addition on the thermal stability of AP.

Potassium chlorate, Mass-%	Onset of exotherms	
	K	°C
0	673	400
0.001	593, 673	320, 400
0.009	583, 673	310, 400
0.040	573, 673	300, 400
0.082	543, 673	270, 400
0.370	533	260
0.870	523	250

Data source: [623].

controlled conditions in the range of 348 and 393 K. One leads to OClO and ammonia and the other one leads to chlorine, nitrogen, water, and ammonium nitrate.

The decomposition of ammonium chlorate was studied by measuring the pressure of non-condensable gases formed and by measuring the weight lost during TGA [625]. Both methods resulted in almost identical decomposition/time curves. A measurable decomposition started at 323 K (50 °C) but some samples decomposed at 268 K (−5 °C). Explosions of fresh samples occurred at 363 K (90 °C). The reaction was autocatalytic in character and the activation energy, calculated from the slopes of time lag and rate constant against $1/T$, was 92 to 105 kJ/mol (22 to 25 kcal/mol). A similar value for the activation energy was found from the temperature dependence of the induction period before explosion. It was observed that the addition of chloric acid to ammonium chlorate considerably increased the rate of decomposition whilst the addition of ammonia had a stabilizing effect.

The topokinetical aspects of the LTD of AP crystals, i.e., the nucleation rate (V_n), the rate of nuclei growth (V_g) and their dependence on the concentration of some contaminants and temperature, have been investigated [626]. On the basis of experimental data obtained, it was inferred that the nucleation rate of the LTD for chemically pure AP is determined by the content of free protons and unavoidable ClO_3^- ion impurity

$$V_n = k[\text{H}^+][\text{ClO}_3^-]$$

and has an activation energy of $E_n = 293 \pm 16.7$ kJ/mol (70 ± 4 kcal/mol). The length of the induction period of nucleation (τ_n) is a function of the ClO_3^- contamination:

$$\tau_n = \tau_0 - A \log[\text{ClO}_3^-]$$

The corresponding value of the effective activation energy is $E_\tau = 92 \pm 20.9$ kJ/mol (22 ± 5 kcal/mol). The addition of proton donors catalyzed the nucleation process; proton acceptors inhibited it but all the proton active additives insignificantly influenced the value of V_g . The active centers were found to contain ammonium

chlorate and some amounts of AP degradation products. Several centers joined into larger centers. The activation energy for nucleation was determined as being about 293 kJ/mol (70 kcal/mol) for high purity AP and about 209 kJ/mol (50 kcal/mol) for chemically doped AP. The rate of AP decomposition products formation increased as active centers grew to larger sizes. Increased concentration of chlorate ion in AP produced a proliferation of active centers and decreased induction time before the AP LTD process started. Changes in induction time reduction and increases in the rate of AP LTD reactions were chlorate ion concentration-dependent. As chlorate content was increased, decomposition reaction rates were much greater. After recrystallizing high purity AP five times, the investigators came to the conclusion that consolidated crystalline AP is fundamentally unstable with respect to always producing a minute amount of ammonium chlorate impurity. At the lowest chlorate content in the recrystallized AP, migrating nuclei and active center growth at low concentrations could still be observed even though chemical analysis methods were unable to detect any chlorate content. During UV irradiation of AP crystals through an opaque stencil, a latent photographic image of the stencil was imprinted into the AP crystal. In the early stages of the LTD, this image may be developed and become visible. It is supposed that the latent image arises due to the generation of photo-induced ClO_3^- ions in the course of UV irradiation.

Nobody intends on using ammonium chlorate or ammonium nitrite as rocket propellants, but because of their presence as contaminants in AP and AN, their combustion mechanism and kinetics of thermal decomposition have been investigated [627]. The leading reactions of combustion of both NH_4ClO_3 and NH_4NO_2 at low pressures have been shown to proceed in the condensed phase, with the burning rate defined by the decomposition kinetics at the surface temperature. The kinetics of NH_4ClO_3 and NH_4NO_2 decomposition can be calculated using a condensed-phase combustion model. The heat effect of the decomposition reaction of solid NH_4ClO_3 to oxygen, water vapor, and HCl (or chlorine) averages 42.5–49 kcal/mol or 419–482 cal/g, depending on product composition. The enthalpy of formation of solid NH_4ClO_3 is -272.4 kJ/mol (-65.1 kcal/mol).

4.6.8.6 The Effect of Metal Perchlorates on AP Thermal Decomposition

If one wants to study the effect of metal cations on AP decomposition, the metals have to be added in the form of their perchlorates in order to eliminate interfering effects caused by the accompanying anions other than perchlorate. AP with 1 mass-% of lithium perchlorate added can survive being heated at 544 K (270 °C) for up to 24 hours without any noticeable indication of thermal decomposition. Eutectic formation in the AP/ LiClO_4 system has been credited with a stabilizing effect that extends the range of thermal stability of AP [104].

Cadmium perchlorate and silver perchlorate [628] accelerate the decomposition of AP. These are not transition metals and do not change their valency as readily as manganese or chromium. It was suggested that their activity is due to their ability to

form ammino complexes, thus removing ammonia from the AP dissociation equilibrium.

The DTA of AP/metal perchlorate samples of AP mixed with metal perchlorates in either 95/5 or 99/1 molar ratio was used in search of catalysts that did not introduce another anion [629, 630]. AP and doped AP samples were heated at various rates over a given temperature range. The perchlorates used for doping the AP were those of copper, lead, potassium, cadmium, zinc, manganese, silver, barium, magnesium (magnesium perchlorate has a very high affinity to water and is often used as a desiccating agent [Anhydron] instead of phosphorus pentoxide), sodium, and iron.

The addition of CdO to AP increased the rate and extent of its slow decomposition and lowered its ignition temperature by about 453 K (180 °C) [513]. The activation energy of the catalytic decomposition was about 121 kJ/mol (29 kcal/mol), corresponding to the activation energy expected for an electron-transfer mechanism. The rate-accelerating effect of CdO can be explained by its reaction with AP to form cadmium perchlorate, which proved to be a very active additive. In the presence of $\text{Cd}(\text{ClO}_4)_2$, AP decomposed completely below 513 K (240 °C) and it exploded at 530 K (257 °C). The activation energy of the slow decomposition and of the reaction leading to the explosion was about 123 kJ/mol (29.5 kcal/mol). The observed rate acceleration was attributed to the fusion of the AP and to the high polarizing (complex-forming) power of the cadmium ion in comparison to the effect of the less active perchlorates of magnesium, zinc, and lithium.

Doping with divalent cations of calcium does not inhibit the thermal decomposition of AP. Rather, it accelerates it [455].

Perchlorates of iron, nickel, and cobalt at 0.1 to 0.9 mass-% additive were co-crystallized with AP, dried, pulverized, and tested in the DTA and TGA [631]. Cobalt perchlorate was the most active additive of the three salts. Incorporating additives in the AP crystal lattice promotes AP decomposition more effectively than if the same compound was mechanically mixed with the AP. Metal chelates are more effective than the same metal in their oxide form. It was suggested that the metal APs decompose to the metal oxides, which then become the catalytically active part. This was supposed to be supported by the observation that when 1% metal oxides instead of the metal perchlorates were added to AP, the catalytic effects were very similar. However, other investigators showed that metal oxides become converted to metal perchlorates in the AP condensed phase. If any metal oxides form as the result of metal perchlorate decomposition, this would only be possible in the flame front where they are suspended in a gas phase.

Zinc perchlorate has only a modest effect on the thermal decomposition and ignition of AP [632].

DSC measurements of the thermal decomposition of magnesium perchlorate, AP, and a mixture of AP with magnesium perchlorate, revealed that the addition of magnesium perchlorate lowers the onset of exotherms of AP decomposition significantly and that the decomposition proceeds in a molten phase [633, 634].

DSC thermograms of the pure perchlorates by themselves under 1 atm nitrogen atmosphere prior to mixing showed the usual phase change endotherm for pure AP, followed by a low-temperature and a high-temperature exotherm for AP decomposition. The thermogram of magnesium perchlorate hydrate revealed a succession of endotherms due to the removal of water. However, it does not decompose until the temperature reaches 683 K (410 °C). The tests should have been conducted with anhydrous magnesium perchlorate instead of the hydrate.

Co-crystallization of AP with KClO_4 , and maybe a small amount of KMnO_4 , was expected to improve the thermal stability of AP [635]. The benefit of adding AN seems very dubious and would be expected to have the opposite effect.

The thermal stability and autoignition temperature of ammino complexes of transition metal perchlorates of Co, Cu, Mn, Ni, and Fe and their mixtures with AP in a 1:10 ratio were studied using DTA at 12°/min. [636]. The ignition temperatures were compared with literature values for the corresponding 1:10 metal oxide-AP mixtures. Close agreement was found between the ammino metal perchlorate complex-AP and metal oxide-AP ignition temperatures, but those of the metal ammino perchlorates alone were lower. All the ammino complexes seem to catalyze the decomposition of AP at ≤ 300 °C. The catalytic activity of the oxides may be due to the formation of metal- NH_3 complexes that facilitate proton transfer and/or explosive decomposition of the complexes, liberating heat that catalyzes the AP decomposition. Although the ignition temperatures are similar, the metal oxide-containing mixtures decomposed with greater violence than the other mixtures, indicating that both factors play a role in the catalysis.

The preparation and thermal decomposition of lithium perchlorate ammoniate $\text{LiClO}_4 \cdot 3\text{NH}_3$ and magnesium perchlorate ammoniate $\text{Mg}(\text{ClO}_4)_2 \cdot 7\text{NH}_3$ and the catalytic effect of these compounds on AP decomposition have been investigated [637]. One hesitates to call these compounds [ammino complexes]. Ammino complexes are typically formed by transition metals and the ligands are firmly held in the complex sphere. In the case of lithium and magnesium perchlorate, these compounds should be called ammoniates in analogy to hydrates. The catalytic effect of metal perchlorates on AP decomposition has been attributed to the intermediate formation of metal perchlorate ammino complexes. In the case of a Mg salt-AP mixture, the melting of the Mg perchlorate ammoniate intermediate seems to play an important role in catalyzing the decomposition.

Thermal decomposition and combustion of lithium perchlorate ammoniate/AP ($\text{LiClO}_4 \cdot 3\text{NH}_3 = \text{LPA}$) and magnesium perchlorate ammoniate/AP ($\text{MPA} = \text{Mg}(\text{ClO}_4)_2 \cdot 7\text{NH}_3$) pellets was studied using DTA, TGA, and strand burner techniques at 7.09 MPa (70 atm) [638]. The DTA results of the ammoniate/AP pellets showed that the addition of some ammoniates lowers the ignition temperature of AP. However, isothermal TG of the ammoniate/AP pellets showed that in the case of LPA/AP pellets, the extent of decomposition increased with the increase in the concentration of LPA, whereas in the case of MPA/AP pellets the extent of decomposition decreased with

the increase in the concentration of MPA. Only two LPA/AP pellets (1:10 and 1:20) had higher burning rates compared to plain AP pellets. On the other hand, MPA/AP pellets had lower burning rates compared to AP pellets and some extinguished. Increasing the concentration of MPA in MPA:AP pellets completely suppressed combustion. MgO suppressed AP combustion once its concentration exceeded 5%.

As evident from DTA and TGA data, the addition of Cu^{2+} , Mn^{2+} , Co^{2+} , or Fe^{3+} affects the rate of decomposition due to lattice modification and the formation of catalytically active oxides during decomposition [639]. Small concentrations of these ions inhibited the decomposition by eliminating the first exothermic peak. At higher concentrations, a catalyzed decomposition was observed. Either the influence of the doping ions on the mechanism of the thermal decomposition is different from that of added oxides or a modification of the electron transfer mechanism is taking place.

Doping of AP with Ba^{2+} ions instead of Mg^{2+} ions can have opposite effects depending on the temperature range [464]. The catalytic effectiveness of metal perchlorates is related to the polarizing power of the cation. Also, lowering the melting point will accelerate decomposition because the addition of other salts of the same cation (but with higher melting points) does not show any catalytic effects.

4.6.8.7 The Effect of Metal Fluorides on AP Thermal Decomposition

While the addition of fluorides to metallized solid propellants can potentially increase burning rates, only minute effects were observed when various fluorides were added to uncatalyzed, non-metallized AP [640]. DTA and isothermal TGA were used to study the effect of the addition of ~10% LiF, NaF, MgF_2 , and NH_4F on AP thermal decomposition. With LiF, the DTA of AP remained unchanged. However, isothermal TGA at >543 K (>270 °C) showed some decomposition to ~25% weight loss. With NaF and MgF_2 , the isothermal TGA showed no change but at 578 K (305 °C) NH_4F appears to have some catalytic effect. The lack of effect of LiF at 543 K (270 °C) may be due to the formation of NH_4F and its volatilization. Other observers claimed that LiF can stabilize AP similar to LiClO_4 . Interacting with AP, it forms lithium perchlorate, which inhibits subsequent decomposition [104].

Fluorides of transition metals act as catalysts in the thermal decomposition of AP at 503 K (230 °C). The catalytic activity of fluorides decreased in the order of: $\text{Co}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$. When all other conditions were kept the same, it was always lower than the catalytic activity of the corresponding oxides [641].

4.6.8.8 The Effect of Other Anions on AP Thermal Decomposition

Many investigators studied the catalytic activity of other metal salts (other than oxides) in comparison to that of the metal oxides. It was generally found that the anion does not nearly have as much of an effect on AP decomposition as the cation.

Metal salts of anions that are readily decomposing at the temperature of AP decomposition, such as oxalates or carbonates, are likely to result in the formation of finely divided metal oxides. These are freshly formed and had higher activities than metal oxides that were added as bulk powders.

Effects of Oxalates on AP Thermal Decomposition

When ClO_4^- was partially replaced by $(\text{COO})_2^-$ in a 10^{-1} mol ratio and tested in the TGA, pure AP showed 50% decomposition at 681 K (408 °C) and 100% at 720 K (447 °C). However, the doped sample showed 50% decomposition at lower temperatures (50% at 677 K/404 °C) and 100% at 712 K (439 °C) [642].

The effect of CoC_2O_4 on the catalytic thermal decomposition of AP was measured by DSC and TG-MS. It was found that freshly formed nano-cobalt oxides exhibited better catalytic performance in the thermal decomposition of AP than bulk CoO [643, 644]. Adding 2% of CoC_2O_4 to AP decreased the decomposition temperature by 104 °C and increased the heat of decomposition from 655 J/g to 1469 J/g. Some oxidation of adsorbed ammonia by cobalt oxides via the superoxide active centers took place on the surface of the cobalt oxide. The presence of oxygen can accelerate the oxidation thermal decomposition process of AP, with a distinct increase in the DSC rate of heat release being seen.

The effect of cobalt oxalate nanocrystal morphology on the thermal decomposition of AP was examined using DSC [645]. No direct relationship between the morphologies of catalysts and their activities was observed.

Effects of Carbonates on AP Thermal Decomposition

The kinetics of thermal decomposition of AP in the presence of basic Cu carbonate and Cr carbonate catalysts were studied by isothermal TGA [646]. Prout-Tompkins and contracting-cube equations were found to fit the isothermal TGA data of the catalyzed decomposition. The reaction mechanism was discussed in light of the postulated electron transfer process [647].

Effects of Anions Other Than Oxalate or Carbonate on AP Thermal Decomposition

The addition of 1 mol-% of $\text{Cu}(\text{ClO}_4)_2$, AgClO_4 , or NH_4I prior to irradiation using X-rays or γ -rays lowered the thermal stability of AP and enhanced the effects of irradiation [648]. The thermograms of samples containing one mol-% of Cu^{2+} ion, irradiated and unirradiated, exhibited sharp exotherms immediately following a crystalline transition at 543 K (270 °C). The same peak was also enhanced as a result of exposure to X-rays and γ -radiation. Irradiated samples containing Cu^{2+} ion had an exotherm at 509 K (236 °C). These results may be explained in terms of an electron transfer. The DTA thermogram for the irradiated sample containing iodide was similar to that of AP not containing this impurity. Some of the iodide became oxidized and escaped from the sample in the form of elemental iodine.

A TGA study of the thermal decomposition of AP at 487 to 743 K (214 to 470 °C) in air produced the following values of the energies of activation for AP by itself [649]:

Orthorhombic form:	$E_{\text{act}} = 167.4 \text{ kJ/mol (40 kcal/mol)}$
Cubic form:	$E_{\text{act}} = 100.4 \text{ to } 117 \text{ kJ/mol (24 to 28 kcal/mol)}$
Residue from low-temperature reactions	$E_{\text{act}} = 150 \text{ to } 163 \text{ kJ/mol (36 to 39 kcal/mol)}$

The study of the effect of oxides, chlorides, carbonates, and oxalates of a number of metals on the thermal decomposition of AP showed that the compounds of manganese and cobalt lead to complete decomposition of AP at temperatures below 513 K (240 °C). The compounds of iron, nickel, and chromium lead to the complete decomposition of AP at slightly higher temperatures, namely 543 to 553 K (270 to 280 °C). At the same temperature, the maximum rate of decomposition of AP with additives of the compounds of Cu, Mn, Co, as well as ZnO, was greater than the maximum decomposition rate of the pure AP. However, on the other hand, the maximum decomposition rate of mixtures of AP with compounds of iron(?), nickel(II), chromium(III), as well as V_2O_5 was less than for pure AP. The activity of additives of the same element decreased in the following order: carbonate (oxalate), oxide, chloride. The inhibiting effects of iron is more than surprising since all other investigators found iron compounds to be good catalysts for AP decomposition. AP containing 5% Cr_2O_3 did not burn at atmospheric pressure, even if it was pre-heated to 373 K.

AN or AP crystals modified by co-crystallization with isomorphously substituted catalytic salts are more sensitive to impact and have a lower decomposition temperature than pure AN or AP. While increased impact sensitivity may be undesirable for propellant applications, it makes the materials more applicable as explosives. Suitable catalytic salts are sodium chromate, lithium iodate, potassium iodate, calcium permanganate, ammonium chromate, ammonium periodate, or ammonium permanganate [650]. The catalytic effect can be measured by a decrease in the drop height (for 50% positive initiation) and weight loss in TGA. For instance, normal AP would lose 22% of weight after 15 minutes at 573 K (300 °C), whereas AP with 2% $Kmno_4$ would lose 99% after 20 minutes at 449 K (176 °C).

The easiest way to introduce stabilizers or burning rate catalysts into AP is to dissolve the AP in water, mix in the additive(s), and spray dry the solution or even the suspension if the additives are not soluble [651]. AP doped in this manner and the additives tested include ammonium dichromate as the catalyst and ammonium hydrogen phosphate as the stabilizer. The spray-dried AP particles are spherical and 5 to 20 μm in diameter.

The role of silver in promoting the thermal decomposition of AP has repeatedly been studied. It was shown that silver metal and silver chloride reduce the induction period of the LTD of AP and somewhat increased the rate of subsequent reactions [512]. The catalytic effects of silver nitrate and silver oxide were significantly greater than those of $AgCl$. Microscopic observations provided strong evidence that these reactions proceed with local and incomplete melt formation around clusters of additive. It was also shown that the complex salt $[Ag(NH_3)_2]ClO_4$ melts below the onset temperature of reaction and that it promotes AP decomposition, which is usually accompanied by melting. The activity of these silver salts in promoting AP breakdown is a consequence of local reactant fusion. The chemistry of the reactions in these melts is complicated because it involves several participants, including the complex ion $[Ag(NH_3)_2]^+$. Silver catalysis is most effective during the first phase of decomposition. Deactivated silver-

containing compounds accumulate on the outer eroded surface of the AP crystal. The nuclei continue to advance into the remaining undecomposed AP.

The mechanism of thermal decomposition of orthorhombic AP, though studied extensively in the past, still remains controversial. Proton transfer has been proposed as the rate-determining step by some authors, whereas others have inferred the occurrence of electron transfer. More experimental evidence was sought to help clarify this controversy. The isothermal decomposition of orthorhombic AP was studied as a function of the concentration of anionic dopants, sulfate SO_4^{2-} and phosphate PO_4^{3-} [652]. In either case, the rate of decomposition passed through a maximum as the dopant concentration increased. The activation energy of the decomposition process remained unaltered by doping. The results were interpreted as supporting the theory of an electron transfer mechanism.

The proton transfer mechanism has been supported by Boldyrev et al. based on their observation that AP doped with SO_4^{2-} (concentration: 0.889×10^{-2} mol % in solution) or PO_4^{3-} (concentration: 1.181×10^{-2} mol % in solution) exhibited a decrease in the decomposition rate [425]. However, Maycock, and Verneker found that AP doped with SO_4^{2-} had an increase in the rate up to a dopant concentration of 1.0×10^{-2} mol % (in solution), and that the rate decreased if the dopant concentration was increased beyond a maximum concentration [653].

The thermal decomposition of AP has usually been described in terms of chemical reactions with the point defect structure of the solid ignored. Both the isothermal and adiabatic decompositions have been reinvestigated over the temperature range of 473 to 723 K (200 to 450 °C). There is a good correlation between the isothermal d.c. electrical conductance of single crystals, and of conductance as a function of temperature with the extent of decomposition, indicating that electric charge carriers play a significant role in the thermal decomposition of AP [153]. The study of the electrical conductivity as a function of temperature has resulted in the assignment of a probable defect structure to AP. It is likely to have cationic Frenkel type defects below 523 K (250 °C) and Schottky disorder at higher temperatures. This suggests an explanation for the phenomenon of only 30% decomposition below 523 K (250 °C) and 100% above this temperature. The decomposition is very dependent on lattice defects in the crystals. Bivalent foreign anions in the crystal lattice will produce additional anion vacancies. Freshly ground and aged pulverized AP may produce different decomposition behaviors because some of the defects will heal with time. Therefore, when carrying out AP decomposition studies with pulverized samples, it is necessary to use samples of the same age.

These contradictions required a systematic study of the decomposition of AP as a function of SO_4^{2-} content. Similar behavior is to be expected for AP doped with PO_4^{3-} . The thermal decomposition of phosphate-doped AP has not been studied as yet as a function of dopant concentration. The Kannan [652] paper dealt with the isothermal decomposition of sulfate-doped and phosphate-doped AP in the temperature range of 200–230 °C, where AP exists in its orthorhombic modification.

The substitution of NH_4^+ or ClO_4^- by aliovalent ions increases the defects in the crystal lattice and will cause AP to decompose at a lower temperature, possibly increasing the burning rates of solid propellants prepared with doped AP. Thus, the reaction rate of AP measured using a vacuum stability test or TGA was reduced by the partial substitution of NH_4^+ ions by Ca^{++} ions in a 10^{-2} mol ratio by heating a mixture of 10 g AP, 100 mg $\text{Ca}(\text{NO}_3)_2$, and 25 mL H_2O to 363 K (90 °C). Cooling to room temperature then followed, with subsequent drying of the recovered co-crystallized precipitate [642]. In the vacuum stability test at 498 K (225 °C), oxygen evolution from AP increased the pressure from 50 to 100 μm Hg in ten minutes but the doped sample took longer, taking 24 minutes to reach the same pressure. At 523 K (250 °C), the same pressure increase occurred in 2 and 4 minutes, respectively.

The rate of the bulk decomposition reaction of AP was enhanced in both Ba^{2+} and SO_4^{2-} doped crystals [159]. Whereas Ba^{2+} shortened the time to completion of the surface reaction, doping with SO_4^{2-} prolonged it. This was interpreted as supporting the theory of a step-wise proton transfer mechanism with the participation of crystal lattice defects.

The low-temperature thermal decomposition of AP was found to be initiated by a single-stage nucleation process at a lattice defect site on the surface of the crystal [621]. Crystals that are aged at room temperature revealed a decrease in the decomposition rate with storage time. It appears that aging allows the slow repair of crystal defects. Sample impurities and as little as 0.04% copper(II) chloride significantly accelerated the decomposition but did not alter the nucleation process or the rate-determining step. Decomposition was measured using a gasometric method. The addition of 0.2% CuCl_2 increased the rate of gas evolution from 2.05 mL/min. for pure AP with 0% CuCl_2 to 5.92 mL/min. with 0.2% CuCl_2 . The reaction stoichiometry was altered by CuCl_2 addition but not by recrystallization. Some samples were recrystallized as often as four times but there was no change in the decomposition behavior. It was suggested that catalysis occurs through the formation of ammino complexes, which tie up the ammonia on the crystal surface and thereby prevent the reversal of the proton transfer reaction.

4.6.8.9 The Effect of Organic Cations on AP Thermal Decomposition

Guanidinium perchlorate forms a eutectic with AP at 9 mol-% AP, which melts at 490 K (217 °C) [654]. The thermal stability of an 80 mass-% AP/20% guanidinium perchlorate mixture was studied using TGA in the temperature range of 523–553 K (250–280 °C) [654]. After a lengthy induction period, the process begins to accelerate rapidly. It would have been of interest to measure strand burning rates of eutectic crystals and other AP/guanidinium perchlorate mixtures.

DTA and TGA of AP doped with mixed or co-crystallized tetramethylammonium perchlorate (TeMAP) showed that the thermal decomposition of AP is considerably modified when it is mixed or co-crystallized with TeMAP [655]. The DTA of AP usually revealed an endotherm at 513 K (240 °C) due to phase transformation which remained

unchanged when AP was co-crystallized or mixed with TeMAP. The DTA of AP co-crystallized or mixed with 1 mol-% TeMAP revealed only one exotherm corresponding to the complete decomposition. Whereas in the case of the physically mixed sample the exotherm occurred at 623 K (350 °C), the co-crystallized sample with the same TeMAP concentration decomposed completely at 558 K (285 °C). The decomposition of an AP-based propellant revealed considerable desensitization when AP + 1 mol-% TeMAP was used as the oxidizer.

In comparison to similar effects with AP, the addition of trimethylammonium perchlorate to potassium perchlorate catalyzed its thermal decomposition [656]. However, although the additive sensitized the potassium perchlorate/polyurethane (PU) propellant thermal decomposition, its combustion was desensitized. The observed effects have been explained in terms of the role played by the early formation of finely divided potassium chloride.

Because the four MEAP have such a dissimilar effect on the burning rate and thermal stability of AP, the heat of combustion of mono-, di-, tri-, and TeMAP were determined by bomb calorimetry [657]. The data was used to explain why the thermal behavior of AP is considerably modified in the presence of these compounds as shown by DTA or DSC. Above a particular concentration of MAP, AP ignites in a single step around 563 K (290 °C). The minimum concentration of any of the four MEAP (mono-, di-, tri- or tetra-methylammonium perchlorate) needed to cause AP ignition in a single step depends on the intramolecular elemental stoichiometric coefficient of the mixtures. These have the same values regardless of which MEAP is used. It was found that the calorimetric values of these mixtures are the same. The heat evolved upon combustion of such a composition seems to determine the lower concentration limit of combustion at ambient pressure.

The effect of tetrabutylammonium perchlorate (TBAP) on the thermal decomposition of AP has been studied using DSC experiments with a heating rate of 5°/min. with oxidizer-rich, stoichiometric, and fuel-rich compositions [658]. The onset of the decomposition temperature of pure TBAP was very similar to that of the first-stage decomposition of AP, 538 K (265 °C) compared to 542 K (269 °C) for AP. Even though TBAP's decomposition began close to that of AP, its peak decomposition rate was achieved around the temperature at which AP's first-stage decomposition ended. When changing the AP/TBAP composition from an oxidizer-rich system to a fuel-rich system, the temperature of inception of the first-stage decomposition began decreasing, while the temperature of peak decomposition rate and the temperature of completion of decomposition shifted towards a higher temperature regime.

4.6.8.10 The Effect of Metalorganic Compounds on AP Thermal Decomposition

The advantage of metalorganic compounds as burning rate additives is that they are miscible with the binders and can be placed at the surface of AP grains where they are needed the most. The disadvantage of metalorganic burning rate catalysts like ferrocene or metal acetylacetonates is that they are volatile and tend to migrate during

the aging of the propellant. It is thus of interest to study not only the effect of metalorganic additives on the burning rate of formulated propellants but also their effect on the thermal decomposition of AP itself.

Effects of Metallocenes on AP Thermal Decomposition

The effect of metallocenes on the thermal stability of AP and the burning rate of AP-based propellants can be examined at several stages: (1) with AP by itself without the addition of a fuel, (2) with AP in combination with a fuel, or (3) in a completely formulated propellant containing AP, binder, and often a metal powder also.

Solid Fe_2O_3 is the conventional combustion catalyst for AP/HTPB (NH_4ClO_4 /hydroxyl-terminated polybutadiene) type propellants. The catalytic effects of three different liquid ferrocenes (butylferrocene, dimethylferrocene, and dibutylferrocene) were compared to that of Fe_2O_3 as reference material [659]. The comparison for catalytic activity was based on DTA and TGA measurements.

Not all ferrocenes are compatible with AP and some may cause unwanted premature reactions. The effect of the presence of iron-containing compounds on the thermal decomposition of AP was studied using DTA and TGA. The maximum decomposition reaction temperature I of AP was lowered in the presence of iron-containing ("ferruginous") compounds. It is then shifted to lower temperatures as the additive concentration is increased [660]. The temperature lowering ability of catocene [2,2-bis(ethylidicyclopentadienyl-iron) propane] on the thermal decomposition of AP is more efficient than that of two other iron-containing compounds previously investigated. The decomposition mechanism of small particle size AP powder differs from that of coarse particle size AP.

The thermal decomposition of AP with and without ferrocene derivatives was studied using DTA and DSC-TGA [661]. The results indicated that reducing AP particle size or increasing the content of ferrocene derivatives can shorten the gap between high-temperature thermal decomposition peaks of AP and low-temperature thermal decomposition peak of AP. It can also enhance the low-temperature thermal decomposition rate of AP. In the presence of AP, the side-chain of ferrocene derivatives is easily ruptured and the residual main skeleton, ferrocene or ferrocene ion, is the real catalyst in the thermal decomposition of AP. Ferrocene derivatives inhibit proton transfer processes of AP but they are strong catalysts for the decomposition of HClO_4 , one of the initial decomposition products of AP.

The effect of catocene on the thermal decomposition of AP as an oxidizer in composite solid propellants was studied using XPS [662]. Results revealed that the bond energy of iron increased after thermal oxidation. Catocene was oxidized during the thermal decomposition of AP. Fe—C conjugate bonds were broken gradually, according to the spectral intensity change of the $\text{Fe}^{2p^{3/2}}$ peak. The binding energy of chlorine decreased and low binding energy peaks appeared at about 200 eV. The intensity of those peaks increased gradually. The possible explanation for forming a binding state of chlorine at about 200 eV was that catocene decomposed to cyclopentadiene ion,

which then reacted with HClO_4 resulting in the formation of HCl and the accelerated decomposition rate of HClO_4 . The ferrocene-based sandwich structure of catocene was destroyed and Fe was oxidized to form Fe_2O_3 , which is an active catalyst that could also accelerate the decomposition rate of HClO_4 , a dissociation product of AP.

The thermal decomposition of AP and AP/Catocene mixtures was studied using DSC and TGA. The activation energy and the pre-exponential factor was calculated [663]. In the DSC thermogram, there was an additional exothermic peak at 180°C with Catocene, which belongs to the decomposition of Catocene. The activation energy for low- and HTD reactions of AP decreased by 13.2 kJ/mol and 7.1 kJ/mol , respectively, as a result of the addition of catocene.

Simultaneous TGA/DSC-FTIR was employed to study the effect of catocene at high concentrations (5, 15, and 25%) on the thermal decomposition of AP with different particle sizes [664]. The results showed that catocene has an effect on the thermal decomposition of AP. However, the role that catocene played changed with the concentration of catocene and the particle size of AP. High concentrations of catocene (more than 15%) accelerated the decomposition of fine AP at low temperatures but had little effect on the decomposition of the median and coarse AP.

Effects of Metal Acetylacetonates on AP Thermal Decomposition

It is of interest to study not only the effect of metal acetylacetonates (β -diketonates) on the burning rate of formulated propellants but also their effect on the thermal decomposition of AP itself [665].

Effects of Metal Carboxylates on AP Thermal Decomposition

Metal soaps (metal alkylcarboxylates) have been used for a long time as burning rate catalysts and emulsifiers for solid propellants. Many of these metal carboxylates will decompose to finely distributed metal oxides under conditions of the rocket motor.

DSC and TGA-MS catalytic activity measurements were carried out on the catalytic thermal decomposition of AP over CoC_2O_4 [643]. The results showed that nano-cobalt oxides formed during decomposition are active catalysts in the thermal decomposition of AP. Adding 2% of CoC_2O_4 to AP decreased the onset of decomposition temperature by 104°C and increased the heat of decomposition from 655 J/g to 1469 J/g . The oxidation of adsorbed ammonia by cobalt oxides via the superoxide active centers takes place on the surface of cobalt oxide. The presence of oxygen can accelerate the oxidation thermal decomposition process of AP, with a clear increase in DSC heat release.

Effects of Other Metalorganic Compounds on AP Thermal Decomposition

While there is a widespread trend to avoid lead compounds as burning rate modifiers in any propellant, some of the less common lead organic compounds are still being tested as AP decomposition catalysts but this seems to be an academic exercise in futility [666].

The effect of various metal complex catalysts of 1,4,8,11-tetraaza[14]annulenes on the thermal decomposition of AN, AP, and a solid propellant containing AP as the oxidizer was studied using DTA and burning rate measurements [667]. Iron and vanadium catalysts had high activity during the thermal decomposition of AP and an AP-based solid propellant. For the solid propellants, which contained iron or vanadium complexes as catalysts, the burning rate increased by 1.6 times and their pressure index decreased to 80% compared to the burning experiments without a catalyst at a pressure of 5.0 MPa (see [668]).

4.6.8.11 The Effect of Nano-Metals on AP Thermal Decomposition

Nano-metals are added to AP-based propellants for several reasons: The main objective would be to increase the specific impulse by choosing metals with high heats of combustion and to achieve more complete combustion of the metal (see Section 5.18). Another reason would be to add metals that catalyze the thermal decomposition of AP and thus increase the burning rate. There were big expectations for propellant improvements when using nano-metals instead of micron-size metals, however, only time will tell if the hype about nanomaterials in the late 1990s was justified.

Cu and NiCu nano-powders decreased both the higher and lower decomposition temperature of AP while Ni and Al nano-powders just decreased the higher decomposition temperature and increased the lower decomposition temperature [669]. Coarser, micron-sized metal powders had some catalytic effects on the thermal decomposition of AP but their effects were less than that of nanometer metal powders. Increasing the nano-metal content enhanced their catalytic effect on the HTD of AP, however, their effect on the LTD was less pronounced (see [670]).

A study of the decomposition behavior of AP in the presence of Cu nano-powder using DTA revealed that nanometer Cu powder decreased the first and second thermal onset of decomposition temperatures of AP by 35° and 130°, respectively. Additionally, the DTA heat release of AP in the presence of Cu nano-powders increased to 1.20 kJ/g [671]. The catalytic effect of Cu micron-size powder on the thermal decomposition of AP was less than that of Cu nano-powder. Increased Cu nano-powder concentrations enhanced its catalytic effect on the HTD of AP but weakened its catalytic effect on the LTD of AP. It was suggested that metal oxides act as intermediates in the process of electron transfer. Cu nano-powder reacts with the decomposition products of AP and has a special surface effect.

Three types of nanometer transition metals (Ni, Cu, and Co) were prepared from an aqueous solution by reducing their corresponding metal salts. Their catalytic activity on the thermal decomposition of AP was measured using DTA [672]. Results indicated that the catalysis of nanometer Ni and Cu increased with the content of nano-metals. Moreover, the high- and low-temperature AP decomposition peaks have a tendency of overlapping with each other. A suitable content of nano-metal Co powder in the composite is about 5%. The catalysis of nano-metal Co results in the lowest thermal

decomposition temperature of AP. The catalytic capability of nanometer transition metals can be correlated with the stabilization energy of their formed ammino complexes. Such complexes have been postulated as intermediates in the decomposition of AP.

A DTA study of the catalytic effect of Zn nano-powders and micro-powders on the thermal decomposition of AP revealed that both sizes of Zn powders have a similar catalytic effect on the decomposition of AP. The total heat releases of AP catalyzed by Zn nano-powders were generally higher than those of AP mixed with Zn micro-powders [673].

A magnesium-copper alloy can not only be used for hydrogen storage but can also be used to catalyze AP decomposition [674]. Co, Ni, and Ni-P nanoparticles can be pyrophoric in air and are also catalysts for AP decomposition [675, 676].

Ni particles in Ni/TiO₂ nanoparticles exhibit better dispersion. Additionally, the size of most Ni particles is of the order of 10 nm. The catalytic activity of Ni/TiO₂ nanoparticles on the thermal decomposition of AP was investigated using simultaneous TGA and DTA [677]. The improvement of catalytic activity can mainly be attributed to the improvement of Ni dispersion in Ni/TiO₂ nanoparticles. The catalytic activity of Ni/TiO₂ nanoparticles increased by increasing the weight ratio of Ni to AP.

The catalytic activity of 10-nm Pd-B/TiO₂ on the thermal decomposition of AP was investigated using simultaneous TGA-DTA. The results showed that Pd/TiO₂ exhibits very high catalytic activity in the thermal decomposition of AP [678]. The enriched electron state of Pd active sites and high dispersion of the Pd active sites on TiO₂ support are mainly responsible for the improvement of catalytic activity of Pd/TiO₂ amorphous alloy catalysts. Palladium would be a very expensive catalyst to use and is only of academic interest.

Bimetallic nanocrystals made of Cu-Co, Cu-Fe, and Cu-Zn alloys with particle sizes of 10–38 nm can have a significant catalytic effect on the thermal decomposition of AP. They also impact on the burning rate of AP-based composite solid propellants [679]. This catalytic activity has been attributed to the large surface area and the crystal defect nature of the bimetallic nanocrystals.

Nano-metal/carbon (Metal = Fe, Co) composite materials, in which nano-iron and -cobalt particles were uniformly distributed in a carbon matrix, were prepared using pyrolysis of metal-exchanged cation exchange resins (M-PAA) [680]. XRD and TEM results revealed that the particle size and morphology of nano-iron and cobalt could be controlled using the pyrolysis temperature. The particle size of Co and Fe in M/C obtained at 773 K (500 °C) was 15–40 nm and 10–35 nm, respectively. DTA of the thermal decomposition of AP indicated that the decomposition temperature of AP lowered with the addition of M/C-500, and the HTD peaks of AP were lowered by as much as 145 °C and 68 °C by adding 5% of Co/C and Fe/C obtained at 773 K (500 °C). The high- and LTD peaks of AP overlapped with the addition of Co/C.

Transition metal nanoparticles of four of the 3d transition metal series (Cu, Co, Ni, and Fe) were prepared using hydrazine reduction of metal chlorides in ethylene glycol at 333 K (60 °C). These were then characterized using XRD [681]. The XRD pattern showed average particle sizes for Cu, Ni, Co, and Fe of the order of 17, 41, 27, and 35 nm, respectively. The activity of these transition metal nanoparticle accelerants on the thermal decomposition AP was investigated using TGA, DSC, and ignition delay measurements. Isothermal TGA data were used to evaluate the kinetic parameters by model fitting as well as isoconversional methods. The activation energy for the thermal decomposition of AP was found to be 66.8, 68.7, 78.5, and 85.4 kJ/mol, respectively, for Co, Cu, Ni, and Fe, when they were mixed with AP. Hence, the order of catalytic activity was found to be $\text{Co} > \text{Cu} > \text{Ni} > \text{Fe}$. The accelerant effect of nanoparticles of the metals themselves was found to be better than that of their respective nano-oxides.

Nano β -Cu particles were prepared via a wet mechanical grinding method and were characterized using XRD, field emission SEM, and TEM [682]. Nano β -Cu was semi-spherical and homogeneous with a fairly uniform size of 100 nm. A DSC study of the catalytic properties of nano β -Cu revealed that the nano β -Cu had significant catalytic effects on the decomposition of UFAP with different particle sizes. The peak temperature of decomposition for 6 μm and 1 μm AP decreased to 646 and 624 K (373 and 351 °C), respectively, and the apparent decomposition heat increased to 1529 and 1513 J/g, respectively. The reaction rate constant increased approximately ten times. Compared with 6 μm AP, nano β -Cu lowered the peak temperature of the HTD of 1 μm AP, and the reaction rate constant increased, indicating that nano β -Cu exhibits much better catalytic efficiency for accelerating the thermal decomposition of 1 μm AP.

Platinum is not exactly the cheapest catalyst metal to use, however, one of the reasons for investigating the effect of platinum on AP decomposition is that sometimes platinum thermocouples are used for temperature measurements and their presence may disturb the results of the experiment.

The catalytic activity of platinum nano-powders on the thermal decomposition of AP was characterized using DSC/TGA [683]. Results revealed that the addition of flower-like and dendritic Pt nanostructures decreased the high decomposition temperature of AP by 96 °C and 114 °C and increased the total DSC heat release by 1.28 and 1.36 kJ/g, respectively.

Pt- Al_2O_3 aerogels were synthesized via solution-freeze-drying-calcination technology and used catalysts to catalyze the thermal decomposition of AP [684]. The onset of the thermal decomposition temperature of AP was reduced from 691 to 620 K (418 to 347 °C) and the heat release was increased from 165 to 1784 J/g. Pt/ Al_2O_3 aerogel was a good catalyst for the thermal decomposition of AP, but who can afford it?

4.6.8.12 The Effect of Carbon on AP Thermal Decomposition

Activated charcoal and soot have a pronounced effect on the thermal decomposition of AP and are often added as a burning rate catalyst. The carbon additive in propellants acts as a fuel as well as an absorber of IR radiation. The role of carbon in composite

propellants is sometimes described as that of an “opacifier”. Other forms of carbon that have been tested as potential burning rate catalysts are C_{60} (“Buckyballs”, buckminsterfullerene) and carbon nanotubes (CNT).

Graphite is added (at least to the surface) to make the propellant more conductive to prevent the build-up of electrostatic charges leading to accidental ESD ignition.

TGA-DTG, DTA, and oxygen bomb combustion calorimetry experiments were used to evaluate the effects of carbon black, fullerene soot, extracted fullerene soot, and pure C_{60} on the thermal decomposition characteristics of AP [685]. The investigations found that fullerene soot can evidently improve the LTD of AP and increase the exothermic output and the heat of detonation of AP.

AP/CNT mixtures were prepared using three different mixing methods, namely **(1)** dry-mixing, **(2)** water-mixing, and **(3)** acetone-mixing [686]. Combustion and thermal decomposition studies of AP with CNTs showed that the burning rate of AP/CNTs mixtures increased, and pressure exponents decreased with increasing CNT content of the mix. The catalysis of CNTs on AP depends on different mixing methods. For AP/CNT mixtures prepared using methods (1) through (3), the catalytic effect, burning rate increase, and the pressure exponent decreased in the order $3 > 2 > 1$.

The effects of fullerenes, including fullerene soot, extracted fullerene soot, and pure C_{60} on the thermal decomposition of AP compared with traditional carbon black were investigated using TGA, DTA, IR, and ignition temperature experiments [687]. The results showed that the addition of fullerene soot to AP reduced the activation energy as well as the temperature at the maximum decomposition rate. However, it was found that extracted fullerene soot and pure C_{60} had little effect on the thermal decomposition of AP. Among all carbon catalysts, fullerene soot was the most active one.

Graphene has been used as a carrier for manganese sesquioxide as a catalyst for AP decomposition [547].

Three-dimensional hierarchically ordered porous carbon (3D HOPC) was used as a catalyst to improve AP thermal decomposition through synthesizing a series of AP/HOPC nanocomposites with different AP loading fractions [688]. In these nanocomposites, AP nanocrystals (26–69 nm) were space-confined into the 3D HOPC scaffold and demonstrated high catalytic activity for AP thermal decomposition in decreasing the HTD temperature from 714 to 588 K (441 to 315 °C), lowering the activation energy from 176 ± 19 kJ/mol to 131 ± 5 kJ/mol, and increasing the heat release from 371 ± 11 J/g to 3765 ± 10 J/g. Carbon-based materials are proposed as catalysts for AP-based solid propellants.

The catalytic effect of functionalized GO cross-linked with triaminoguanidine ligand and transition metal complexes on the thermal decomposition of AP or RDX was studied using DSC and SEM [689]. These compounds have a strong catalytic effect on the decomposition of AP and may even stabilize RDX crystals before they decompose due to thermolysis.

4.6.8.13 The Effect of Carbon Nitride on AP Thermal Decomposition

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), metal-free or intercalated with transition metal oxide, has intrinsic catalytic activity for the thermal decomposition of AP. Adding 10 mass-% $g\text{-C}_3\text{N}_4$ to AP decreased the onset of decomposition temperature by 70 °C and the activation energy by 119.8 kJ/mol [690]. The apparent decomposition heat of AP in the presence of 10 mass-% $g\text{-C}_3\text{N}_4$ was 1362.6 J/g, which is much higher than that of pure AP (574.2 J/g). The unique surface structure of $g\text{-C}_3\text{N}_4$, consisting of triazine units connected by planar amino groups, favors the adsorption and diffusion of perchloric acid via Lewis acid-base interactions, which decreases the reaction activation energy of AP and facilitates the formation of superoxide radical anions (OO^-) and holes (h^+), thus enhancing the oxidation reaction of ammonia.

The catalytic activity of graphitic carbon nitride can be improved using intercalation of cerium(IV) oxide [691]. $g\text{-C}_3\text{N}_4/\text{CeO}_2$ nanocomposites were synthesized through a simple mixing-calcination method and characterized using XRD, FTIR, EDAX, TEM, and XPS, revealing that CeO_2 nanoparticles with a diameter of 50–100 nm were uniformly loaded on the surface of $g\text{-C}_3\text{N}_4$. The $g\text{-C}_3\text{N}_4/\text{CeO}_2$ nanocomposites catalyzed the thermal decomposition of AP more effectively than pure $g\text{-C}_3\text{N}_4$ or CeO_2 . The weight loss decomposition temperature of AP was decreased by up to 74.6 °C by adding $g\text{-C}_3\text{N}_4/\text{CeO}_2$ nanocomposites. There may be a synergistic effect between $g\text{-C}_3\text{N}_4$ and CeO_2 .

Similar results were obtained with mesoporous graphitic carbon nitride (mpg- C_3N_4) that was modified by the insertion of CuO nanorods [692]. Examination with TEM, SEM, XRD, FTIR, and XPS revealed that CuO nanorods (length of 200–300 nm, diameter of 10–15 nm) were uniformly dispersed throughout mpg- C_3N_4 . The weight-loss decomposition temperature of AP was decreased by up to 118 °C in the presence of 2 mass-% mpg- $\text{C}_3\text{N}_4/\text{CuO}$ nanocomposites. There may be a synergistic catalysis effect between mpg- C_3N_4 and CuO that is similar to the one observed with CeO_2 .

$g\text{-C}_3\text{N}_4/\text{CuO}$ can be prepared using a microwave-assisted method [693]. It was found that, upon adding m- $g\text{-C}_3\text{N}_4/\text{CuO}$ nanoparticles, the weight-loss decomposition temperature of AP was reduced by 136 °C, which was much more pronounced than that from adding other nanocomposites. The amount of released heat from the decomposition of AP mixed with m- $g\text{-C}_3\text{N}_4/\text{CuO}$ was seven times higher than that from pure AP.

The effect of transition-metal-doped graphitic carbon nitride (M- $g\text{-C}_3\text{N}_4$, M = Fe, Nd, Ce, Zr, U) as a catalyst for the thermal decomposition of AP and AP adducts was examined using DSC [694]. Among the tested catalysts, Fe- $g\text{-C}_3\text{N}_4$ had the best catalytic activity for the thermal decomposition of AP adducts. Fe- $g\text{-C}_3\text{N}_4$ shifted the exotherm peak temperature of AP by 75 °C, increased the heat release by 464 J/g, and decreased the activation energy by 55 kJ/mol.

4.7 Autoignition Temperature and the Ignition Delay of Ammonium Perchlorate in the Presence of Catalysts

The autoignition temperature of AP is lowered significantly and the ignition delay is shortened substantially in the presence of catalysts. Often the autoignition temperature and ignition delay of pure AP is compared to that of doped AP. Autoignition temperatures and ignition delay times of unadulterated AP have already been summarized in Table 11 in Section 4.4. Table 17 provides a summary of the autoignition temperatures and activation energies (derived from ignition delay) for catalyzed AP. Table 18 is a summary of similar data. Omitted from the latter table are data with metal oxides that were doped with traces of other metals to determine the effect of catalyst crystal structures and semiconductor electrical conductivity on catalytic activity. This was intended to support an electron transfer (as opposed to proton transfer) mechanism of AP decomposition. These delay time measurements complement other measurements relating to the onset of exotherms examined using DTA or DSC. The autoignition temperatures and delay times depend on the type of surrounding atmosphere and its pressure. It also depends on the purity of the AP before adding the catalysts and on the sample size.

Table 17: Autoignition temperature and activation energy of doped AP.

Author	Year	Additive	Minimum autoignition temperature		Activation energy		Atmosphere	Pressure
			K	°C	kJ/mol	kcal/mol		
Galwey and Jacobs [695]	1960	20% Carbon	533	260	167	40.0	Vacuum	
Hermoni and Salmon	1962	16% MnO ₂	576	303	141	33.8	Air	
Hermoni and Salmon	1962	33% (Co ₂ O ₃ + Co ₃ O ₄)	514	241	192	46	Air	
Jacobs and Kureishy [696]	1961	4.56 mol-% Cu ₂ O	517	244	118	28.1	Nitrogen	250
Jacobs and Kureishy [529]	1962	4.6 mol-% Cu ₂ O	536	263	130	31	Nitrogen	250
Russell-Jones [470]	1964	0.5% copper chromite	573	300	51	12.214	Argon	730
		2.5% copper chromite	560	287	58	13.8		
		5% copper chromite	563	290	59	14		

Table 18: Thermal explosion of catalyzed AP.

Catalyst	Mol ratio AP: Catalyst	Minimum ignition temperature		Activation energy		Comments	References
		K	°C	kJ/mol	kcal/mol		
ZnO	16:1	513	240	125	29.8	Sample size 0.1 g, $E_{\text{act}} = 28.3$; 0.05 g $E_{\text{act}} = 30.9$	[697, 698]
CuO	16:1	528	255	125	29.8	0.11 g, $E_{\text{act}} = 31.2$; 0.55 g, $E_{\text{act}} = 29.9$	[461]
AgClO ₄	1.0 mol-%	550.7	277.6	80.3	19.2		[699]
Cu(ClO ₄) ₂	1.0 mol-%	542.6	269.5	94.6	22.6		[699]
Fe(ClO ₄) ₃	1.0 mol-%	549	276	123.8	29.6		[699]
NH ₄ Br	0.01 mol-%	570.6	297.5	91.2	21.8		[699]
Cr ₂ O ₃	10:1	530	257	116.7	27.9		[462]
Cr ₂ O ₃	1:1	525	252				[462]
TiO ₂	2:1	693–698	420–425				[462]
CdO	16:1	534	261	94.1	22.5		[513]
Cd(ClO ₄) ₂	100:1	560	287	131	31.2		[513]
Cd(ClO ₄) ₂	10:1	537	264	109.6	26.2		[513]
LiClO ₄	1:1	563	290			Very violent	[104]

The delay times for the autoignition of AP with the addition of 0.5 to 5% copper chromite at 563 to 573 K (290 to 300 °C) were 130 to 127 s [470].

The catalyst effectiveness of a group of metal oxides in lowering the autoignition temperature of AP decreased in the following order: CuCO₃, Cu₂O, CuO, Cu₂Cl₂, CuCl₂•2H₂O, with the ignition temperatures being 538, 548, 553, 558, and 560 K (265, 275, 280, 285, and 287 °C), respectively [511].

The critical ignition temperature T_{cr} depends on the AP sample weight and, in some cases, on the catalyst concentration. It does not, however, depend on the composition of the ambient atmosphere [700]. The measurement of the autoignition temperature of pure and catalyzed AP in the absence of any combustibles is done mostly for academic interests. Nonetheless, it can begin to gain practical value if the tests are repeated with added fuels (polymers, binders).

4.8 Effects of Diluents and Coatings on the Decomposition of Ammonium Perchlorate

DTA and DSC of undiluted AP show the phase change as an endotherm and exothermic decomposition before and, in particular, above the phase change. If there is an endothermic sublimation of AP it is overshadowed by the exotherms in pure AP. Attempts have been made to isolate the endothermic dissociation of AP into NH₃ and

HClO_4 by diluting it with 13% of polymethylmethacrylate (PMMA) [701]. A pulse calorimetric method was used for this reason and the samples were contained in a vacuum (initial pressure 0.05 mm Hg). At 573 K (300 °C) the mixture underwent an endothermic transformation, which has been related to the dissociation of AP. The magnitude of the endotherm (500 cal/g AP) was very similar to the theoretical heat of the dissociation of AP. PMMA does not react with AP at 573 K.

AP was coated with PS, cellulose acetate, Novolak (phenol/formaldehyde) resin, and poly(methylmethacrylate) using a solvent/non-solvent method. The effect of polymer coatings on AP decomposition was studied using TGA and DTA [702]. Polymer coatings resulted in retarding the decomposition of AP.

The LTD process of AP may play a critical role in the reaction violence during the cook-off of AP-based propellants. During AP LTD, the formation of linear voids has been observed to start at the AP particle surface and extend completely through the particle along a particular AP crystal plane. Voids are formed from the disassociation and formation of highly reactive species. These species degrade the propellant, resulting in a high level of grain porosity. This can result from slow/fast cookoff environments and those environments encountered after severe mechanical insults. It was hoped that coating and doping commercially available AP (200 microns) with inorganic salts or heterocyclic amines would extend the range of thermal stability.

4.9 Radiation Effects on Ammonium Perchlorate Decomposition

This chapter deals with the effects of radiation (UV, X-ray, γ -rays, or electron beams) on AP thermal stability and strand burning rates. The radiation may cause immediate decomposition or it may implant latent defects which will affect subsequent thermal decomposition and burning in rocket propellant. The current section deals only with AP itself. Similar experiments were conducted with formulated AP-based propellants under the influence of γ -radiation.

4.9.1 Decomposition of AP During Radiolysis

In the past, almost all radiation damage studies on explosives, propellants, or pyrotechnics were conducted by first irradiating samples and then, at a later time, performing some physical or chemical measurements to quantify the extent of radiation damage. There are a number of well-known reasons for performing radiation damage measurements **during** irradiation. One or more radiation-induced effects may decay rapidly and entirely disappear by the time measurements are made. Radiation may trigger or catalyze a reaction, which appears undesirable at a later time but might not be serious during the irradiation. Most importantly, radiation together with some functioning processes, such as propellant burning, may produce large synergistic effects.

The electrical conductivity of AP changed considerably after irradiation with γ -radiation from a ^{60}Co source, 4.5 MeV protons or X-rays. Applied doses ranged from 6.5×10^{-18} to 9.8×10^{-20} eV/g [158].

Decomposition measurements were completed in a constant volume chamber equipped with a capacitance manometer to determine total gas pressure [703]. This chamber was enclosed in a furnace that could be maintained at carefully controlled temperatures up to 973 K (700 °C). In addition, the sample chamber and furnace had optical-quality fused silica windows to facilitate optical absorption, luminescence, and taking other measurements during irradiation. Gas evolution studies were completed on AP single crystals and powder, both at room temperature and at 500 K (227 °C). Gas pressure versus time curve for commercial AP powder being exposed at approximately 100 R/s at room temperature increased in a smooth monotonic fashion. In marked contrast, the single crystal pressure curve showed abrupt burst-like spikes superimposed on a continuous background. The spikes appeared to occur at random times. They are most likely caused by the abrupt release of trapped gas and the subsequent partial readsorption taking place on the surface. Irradiating and heating at the same time caused a marked decrease in the induction period. Simultaneous heat and irradiation produced a large synergistic effect.

4.9.2 Effects of Pre-Radiation on AP Thermal Decomposition

AP-based propellants that are flying in outer space for long-duration missions may be subjected to cosmic radiation that alters their burning rate. Similar changes might occur in upper stage propellants during storage if in the proximity of missiles with nuclear warheads. In another scenario, upper stages during nuclear warfare (heaven forbid) might be subjected to intense radiation from nearby nuclear blasts before they arrive at their destination. Cast propellant grains are routinely inspected for voids using non-destructive examination methods such as X-rays or ultrasound. In all these cases, the potential changes in the burning rates of AP and AP-based propellants must be known. Even irradiation with less energetic UV light can bring about changes in AP crystals.

Irradiation via x-rays or γ -rays lowered the thermal stability of AP [648, 704]. The crystals exposed to radiation appeared to have specks of opaqueness throughout the solid. During decomposition, the opaque areas in the irradiated solid grew in size or were observed to form and grow throughout the entire crystal. When the dose of radiation was increased there was a sharp rise in the exotherm at 543 K (270 °C), which reached a maximum and then decreased. For samples receiving doses greater than 3.4×10^{-4} eV absorbed/molecule an early exotherm at 509 K (236 °C) occurred which increased with increasing dose. The four principal changes in the sequence of the decomposition of AP due to pre-irradiation were: **(1)** more vigorous reaction prior to and during crystalline phase transition, **(2)** strongly exothermic decomposition immediately following the phase transition, **(3)** more extensive reactions over the tempera-

ture range of 583 to 658 K (310 to 385 °C) and (4) a decrease in the extent of the final stage of decomposition at temperatures greater than 658 K (385 °C). The DTA decomposition pattern of irradiated AP was strikingly similar in detail to that of AP sublimate and of AP containing ClO_3^- ion impurities. The presence of ClO_3^- ions in irradiated AP was confirmed using wet analysis, however, they were not found to be present in the sublimate. $\text{ClO}_3^\bullet$ may also be present as free radicals [114].

The visual appearance of decomposing irradiated crystals as observed under a hot stage microscope under reflected light was significantly different from decomposing unirradiated samples [705]. The crystals were irradiated with a dose rate of 1.3×10^6 roentgen/h. On heating, there was a striking contrast between the behavior of the unirradiated and irradiated samples. Whereas in the former, the initial reaction occurred primarily at the surface while the latter irradiated sample underwent a reaction throughout the entire crystal. The apparent homogeneous clouding of the entire crystal indicates that nuclei for reactions were produced via radiation throughout the entire crystal. The irradiated crystals contained chlorate ions. Burning rates similar to irradiated AP could be obtained by doping clean AP with KClO_3 (which of course is a hazardous operation).

Free radicals and radiation damage in AP crystals can be detected using EPR spectroscopy [706]. The EPR spectrum corresponded to an unpaired electron spin strongly localized on an NH_3 molecule. Comparison of the EPR spectra at various temperatures indicated that the NH_3^+ ions were rotating freely at 373 K (100 °C) and the anisotropy observed at 298 K (25 °C) had disappeared. If there was any doubt after this experiment, it could be removed by repeating the test with isotope-labeled ND_4ClO_4 [707]. An additional transient peak was observed and attributed to $\text{ClO}_3^\bullet$. Analysis of the electron magnetic resonance of X-ray damaged AP crystals showed that the long-lived defects are NH_3^+ ions. Isotopic hyperfine splittings were found to be 54.6 MHz for nitrogen and 72.5 MHz for hydrogen. These radicals appeared to be planar and execute restricted rotation at room temperature.

The attribution of the extra peak to $\text{ClO}_3^\bullet$ has been confirmed by repeating the tests with isotope-labeled $^{15}\text{NH}_4\text{ClO}_4$ [708]. The electron spin resonance spectrum of NH_3^+ trapped in AP crystals (95% ^{15}N) was examined at 300, 77, and 4 K. The spectra were interpreted in terms of π -radical theory and demonstrated different stages in the freezing-out of the rotational motion of the ions.

The EPR spectrum indicated the presence of two paramagnetic species in irradiated AP: NH_3^+ and $\text{ClO}_3^\bullet$. The rates of formation and decay of NH_3^+ in both pure AP and AP doped with KMnO_4 , CaO , or MnO_2 were measured at 300–370 K [709]. The rate of NH_3^+ removal was

$$r = 10^{8.5} e^{-8300/RT} \text{ cm}^3 \text{ s}^{-1} \text{ mol}^{-1}$$

while the rate of $\text{ClO}_3^\bullet$ removal was

$$r = 10^{18} e^{-20000/RT} \text{ cm}^3 \text{ s}^{-1} \text{ mol}^{-1}.$$

The rate of $\text{ClO}_3^\bullet$ decay was thus much faster than the rate of NH_3^+ removal. The total concentration of paramagnetic species increased linearly with the dose D up to $D \approx 12$ megarad, after which it decreased rapidly, attaining a limiting value at $D = 18$. The energy of activation for the recombination of the NH_3^+ radicals in pure NH_4ClO_4 was $34.7 \pm 1.2 \text{ kJ/mol}$ ($8.3 \pm 0.3 \text{ kcal/mol}$). The recombination in the presence of CaO and KMnO_4 also is of the second order but with MnO_2 it is of the first order. The activation energy is $36.4 \pm 0.8 \text{ kJ/mol}$ ($8.7 \pm 0.2 \text{ kcal/mol}$).

The NH_3^+ ions take part in vibrational (translational) movement as well as rotation with a potential barrier of $2.3 \pm 0.21 \text{ kJ/mol}$ ($0.55 \pm 0.05 \text{ kcal/mol}$) [214]. The NH_3^+ ions vibrate preferentially anisotropically in the direction of the (100) face of the crystal, the same direction in which the decomposition progresses from the nuclei. This was established using a study of the temperature dependence of the hyperfine splitting in the EPR spectrum of the ion-radical NH_3^+ in single crystals of AP at $T = 77$ to 293 K (-196 to $+20^\circ \text{C}$).

Reagent grade AP was recrystallized twice from deionized water, dried, and then irradiated in stoppered test tubes with ^{60}Co at a dose rate of 0.36 Mrad/h [710]. No precautions were taken to exclude air from the specimens prior to radiolysis. The irradiated AP was dissolved in water and analyzed for chlorate, OClO , chlorite, hypochlorite, chlorine, chloride, and the total of nitrite plus nitrate. NO_3^- and NO_2^- were absent and ClO_2 and ClO_2^- concentrations were very small. The solution of irradiated AP oxidized ferrous ion in acidic media. All yields except that of ClO_3^- were essentially independent of the radiation dose over the range studied. The ClO_3^- yield, however, was observed to fall off and decrease at the higher doses. This probably indicates that ClO_3^- is undergoing radiolytic decomposition. AP radiolysis is quite different from that of metal perchlorates. The rate of AP decomposition is two to five times faster than that of alkali metal perchlorates (see [711, 712]).

The effects of $9.8 \times 10^6 \text{ rad}$ of radiation are a shortening of the induction period and an increase in the rate of three-dimensional growth during the acceleratory period of AP single-crystal decomposition [713]. At 500 K (227°C) the rate constant increased from $0.39 \times 10^{-2} \text{ min}^{-1}$ to $1.05 \times 10^{-2} \text{ min}^{-1}$ for the irradiated crystals. The induction period was shortened from 62 minutes to 5 minutes. The increase of the rate constant has been attributed to an increase in the number of decomposition nuclei. The crystals had turned opaque as the result of the radiation treatment.

The nature and kinetics of formation and recombination of paramagnetic species formed in ionic crystals of KClO_4 and NH_4ClO_4 under the effect of ionizing radiation (electrons, 1.6 MeV). These were investigated by measuring EPR spectra at 77 – 450 K [714]. Different mechanisms may be responsible for the accumulation and recombination of NH_3^+ and O_3^- free radicals in various temperature ranges.

For the decomposition of AP carried out under isothermal conditions, pre-irradiation caused a decrease in the induction period [715, 716]. The dependence of

an induction period on the absorbed dose could be described by the equation

$$I = C_1 - C_2 \log D$$

where I is the induction period, C_1 and C_2 are constants, and D is the absorbed dose.

Pre-irradiated AP was studied by itself and in a mixture with two different binders to determine the separate effects of radiation on oxidizer and binder (rather than compositely in a mixed propellant) [717]. AP crystals were subjected to 25, 60, and 129 megarad of γ -radiation from a ^{60}Co source and then incorporated into polybutadiene and polysulfide formulations. In all cases, severe mixing problems were encountered and cure times were increased. DTA of the irradiated samples revealed a displacement of the first exotherm from 713 K (440 °C) to 544–547 K (271–274 °C). Burning rate data indicated an increase in burning rate and pressure exponent for the 25 megarad irradiated samples. However, the samples with higher irradiation resulted in malfunctions. Heats of explosion for the 25 megarad formulation were lower than the non-irradiated formulations.

The DTA of irradiated AP was very similar to that of AP which had been doped with ammonium chlorate. Irradiation of AP using 200 keV X-rays resulted in a form of AP which decomposed considerably faster than an AP sample that had been adulterated by amending it with chlorate ions in amounts similar to that found in irradiated AP [180, 718]. The DTA of irradiated AP was very similar to that of AP doped with ammonium chlorate but not the same. Thermal decomposition of irradiated AP started before the polymorphic transition. It was suggested that the accelerated decomposition of AP is a result of cationic and anionic crystal lattice defects caused by irradiation. If irradiated AP is annealed for 200 hours at 373 K (100 °C), the effect of activation decreases but does not disappear entirely.

AP was modified using irradiation with 9.8 Mrad of ^{60}Co radiation and also via the use of thermal shock in liquid nitrogen [719]. Both treatments resulted in considerably enhanced rates of thermal decomposition. If sub-surface reactions determine the burning rate, one would expect that propellants containing AP modified in this way would burn faster. Surprisingly, this was not the case at 3.44 to 103 MPa (500 to 15000 psi) chamber pressure. It was concluded that sub-surface reactions do not control the burning rate at high pressures, however, they may well do so below 3.44 MPa (500 psi) (see [720] also).

Samples of AP were irradiated with γ -rays from a ^{60}Co source emitting approximately 1.1 Mrads/h for 30 to 1000 s [721]. After irradiation, the weight loss of AP samples was determined by weighing and then placing them in a constant temperature air oven maintained at 408 K (135 °C). Control samples that had not been irradiated were also placed in the constant-temperature bath. The samples were removed at various times and weighed. Essentially no gaseous products could be detected in the sample tubes during the first 280 hours while they were in the 408 K (135 °C) temperature bath. At the end of the 280 hours, a small peak on the mass spectrometer output was observed, corresponding to a trace of NO. The rate of weight loss increased with the

duration of radiation exposure. The rate change was most pronounced for the samples with 0 and 30 s, and did not change much beyond 1000 s. The induction time was found to be directly proportional to the log of the irradiation time for samples that had been irradiated for less than 1000 s.

Gamma radiolysis causes the formation of dislocations in crystals, which becomes visibly evident once the adsorbed dose goes beyond 10^5 rad and higher [722].

AP crystals were subjected to fast neutron irradiation or to fast neutron irradiation followed by gamma-ray irradiation [723]. Qualitatively, the radiation-induced changes were similar to those obtained in previous studies, with samples exposed to gamma rays only. The induction period was shortened and the rate constants, obtained from an Avrami-Erofeyev kinetic analysis, were different. The acceleratory period constant increased and the decay period constant decreased. When compared on an equal deposited energy basis, the fast neutron-induced changes were appreciably larger than the γ -ray induced changes. Some, or all, of the fast neutron-induced effects might be attributable to the introduction of localized regions of concentrated radiation damage caused by lattice atom recoils, which become nuclei for thermal decomposition sites when the crystals are later heated (see [724] also).

The thermoluminescence of single crystals of AP irradiated with X rays, UV light, or high energy electrons has been measured and found to be between 80 and 420 K [725]. With a heating rate of 5 K/min. prominent peaks occurred at 95, 113, 134, 246, and 320 K; an additional peak was found at 347 K after longer irradiation times. The absorption spectrum of UV-irradiated AP has also been measured and showed bands at 300, 360, and 610 nm. These peaks are most likely due to ClO_3^- , ClO^- , ClO_2 , and F centers as radiation products.

A dislocation model of the effect of pre-irradiation on subsequent thermal decomposition of AP was tested for the cases of the influence of X-ray radiation (copper cathode at 18 kV) and UV light (mercury quartz lamp) [726, 727]. An impervious mask shaded part of the crystal and a latent image was imprinted on the crystal. The effect of the development of the latent image by heating the irradiated crystal of AP was used as a test for the influence of pre-irradiation. It was found that the effect of pre-irradiation was exhibited rather clearly, even for small doses of irradiation with X-rays (10^2 – 10^3 rad), for which the corresponding density of dislocations is not changed. The same was true for irradiation with UV light.

The fact that the effect of pre-irradiation is exhibited for the small doses, which are three orders of magnitude below the threshold at which a noticeable increase in the number of dislocations is observed, was interpreted as an indication that the main factor responsible for the influence of pre-irradiation on the rate of thermal decomposition of AP is the formation of ClO_3^- ions (proton traps) in the lattice under the action of radiation.

When AP was mixed with 2 mass-% of either KMnO_4 , $\text{Ba}(\text{MnO}_4)_2$, or NH_4MnO_4 , an enhanced thermal decomposition of cubic AP was observed over the temperature range 528–573 K (255–300 °C) [728]. An even more pronounced effect was observed when AP was subjected to a radiation dose of 10 Mrad. The activation energy involved

over the acceleratory stage was found to be 46 kJ/mol for the irradiated AP, compared to the normal value of 85 kJ/mol. The value remained unaltered in the case of the first two additives, while in the presence of NH_4MnO_4 it decreased to 55 kJ/mol. Neutron bombardment did not change the decomposition characteristics of AP but some of the ^{38}Cl became radioactive due to neutron absorption and had highly damaged centers (see [729] also).

While normal AP decomposes in two stages (at 315 and 375 °C), 20% of weight loss occurred while at 160 °C when it had absorbed a γ -radiation dose of 1.0 MGy. Increased crystal size caused further changes in the TG/DTA curves. The weight loss approached 85% for particles that were 20 times larger. AP mixed with KCl/KBr in 1:1 ratio led to a formation of potassium perchlorate upon heating and the quantity increased progressively when the AP was pre-treated using irradiation. IR spectral investigations of decomposing irradiated AP provided information about intermediates formed during the decomposition of AP [382, 730].

The moisture sensitivity of the thermal decomposition of irradiated AP changed with the accumulated radiation dose [446]. Thermal decomposition and the evolution of decomposition products of γ -irradiated (dose: 0–3.6 MGy) AP at 373–593 K (100–220 °C) was followed by IR spectroscopy [731]. Increasing temperature and dose resulted in decreased peak intensities of NH_4^+ and ClO_4^- spectra. Loss of peak intensity was rapid up to 0.42 MGy dose, after which it slowed until it reached a 1.4 MGy dose. Radiolytic products $\cdot\text{ClO}_3$ and NH_3 were proposed to initiate the decomposition process using an electron transfer mechanism at an interstitial site in which ClO_4^- and NH_4^+ react to form $\cdot\text{ClO}_4$ and $\cdot\text{NH}_4$ radicals, which then decompose to form NH_3 and $\cdot\text{H}$ radicals (from $\cdot\text{NH}_4$ radical) and water and $\cdot\text{ClO}_3$ (from $\cdot\text{ClO}_4$ radical and $2\text{H}\cdot$ radicals).

A comparison of pre-irradiation AP, a pure sample, and a sample with added aluminum powder with protons, fast neutrons, and γ radiation showed that the most effective radiation is that accompanied by the formation of thermal peaks, as happens during irradiation with fast neutrons and with protons [732]. Irradiation with γ rays, which does not cause the formation of hot spots in perchlorate, was less efficient.

In continuation of these experiments, γ -radiation-induced decomposition of AP pelletized in a KCl/KBr matrix was followed by IR spectrophotometrically [733]. AP absorption peaks decreased in intensity as the γ -dose increased progressively. Irradiation of powdered AP produced ClO_3 ; its yield increased, attained a maximum, and decreased beyond a dose of 0.5 MGy. The result was similar but much slower in the case of γ -irradiated pellets of pure AP.

X-ray irradiation of AP leaves behind disturbed crystal lattice sites that hold $\cdot\text{ClO}_3$ free radicals. An ESR study of free radicals in X-irradiated AP single crystals was aimed at resolving the controversy that had arisen over the possible occurrence of low-temperature phase transitions in AP, which at room temperature has an orthorhombic structure (space group *Pnma*). ESR spectra were recorded as a function of the orientation of the magnetic field *H* in the three orthogonal crystallographic planes at 300, 77, and 4.2 K [114]. No changes in the spectra attributable to any phase

transition were observed. It was concluded that AP does not undergo any phase transitions below room temperature.

Radiolyzed AP oxidized aqueous iodide ions were placed in a solution when it was irradiated in combination with either aluminum, HTPB, copper chromite, or iron oxide. The influence was larger in the case of AP + HTPB and AP + copper chromite [734].

4.10 The Effects of Particle Size, Mechanical Agitation, and Nucleation Sites on Ammonium Perchlorate Thermal Decomposition

4.10.1 Effects of Particle Size on Slow AP Thermal Decomposition

Because particle size has such a pronounced effect on the burning rate of AP and AP-based propellants, it is important to know if particle size affects the thermal decomposition of AP as well. The effect may differ, depending on if the AP particles are surrounded by a polymeric binder or not. AP has varying combustion/decomposition modes depending on the particle size. Fine and coarse AP react via different mechanisms in solid propellants. Since coarse AP in particles larger than about 150 microns are used in the great majority for AP-oxidized solid propellants, the nature of coarse AP in propellant combustion has been studied extensively. Published investigations about AP thermal decomposition have provided insights into what is happening in coarse AP during the combustion of AP oxidized solid propellants. Spontaneous hole productions (porosity) in coarse AP particles during propellant combustion influenced by high thermal flux and in elevated pressure environments are greatly accelerated. However, this is similar to those observed in low-temperature AP thermal decomposition studies

The activation energy for the slow thermal decomposition of AP in the range from 413 to 598 K (240–325 °C) decreases with decreasing particle size (Table 19).

Table 19: Activation energy of AP decomposition as a function of particle size.

Particle size, μm	Activation energy ^a	
	kJ/mol	kcal/mol
<43	83.7	20.0
43–61	89.5	21.4
61–88	97.9	23.4
8–124	98.7	23.6

^abased on the simplified Avrami equation ($n = 4$)
Data source: [471].

The thermal decomposition of AP samples in the shape of 2-mm monocrystals, 265- μm granules, and 3- μm powders and pellets pressed at four and seven tons was studied

using DSC, TGA, and high-pressure DSC [735]. DSC of AP of different crystal sizes revealed that the occurrence and location of exotherms and endotherms in the thermograms depended on particle size. DSC data for a ball-milled 3- μm powder sample exhibited a sharp exothermic peak at 552 K (279 °C) followed by an endothermic event. A coarse granular sample (265 μm) showed a similar pattern of decomposition. However, the exothermic peak was less intense and occurred at a higher temperature (578 K = 305 °C). The subsequent endothermic event was similar to that observed for 3 μm powder. In contrast to the previous two samples, single crystals did not show obvious signs of an exothermic reaction but only an endothermic peak. Later stages of decomposition become endothermic under ambient pressure but can be turned exothermic at elevated pressures or in closed pans. TGA data also showed noticeable differences in the decomposition of samples with different particle sizes. Both the ball-milled 3- μm powder and the coarse granular samples revealed a two-step mass loss process. However, in 3 μm powder, the first step occurred at ~20% mass loss whereas in coarse AP it was at ~30%. For the large single crystal, the mass loss occurred in a single step and started at a higher temperature than in granular samples. DTA data on pressed AP pellets demonstrated a two-step process for two different pellet densities, just as for granular and ball-milled AP. However, these steps began and ended at higher temperatures. The pellet thermal behavior approached that of single crystals as the density of the pellets increased. A unique feature of the pellet experiments was the broadening of the phase transition peak at 513 K (240 °C), which is most likely associated with the large stress inside the pellets that slows down the transition to the larger volume cubic phase. The activation energy for the early stages of sublimation/decomposition for all samples started at ~120 kJ/mol, which was followed by a dramatic drop to ~60 kJ/mol at 20% mass loss. The activation energy for the later stages of sublimation/decomposition varied with sample type ranging from ~95 to 145 kJ/mol.

The decomposition of granular AP was studied under isothermal conditions in argon at atmospheric pressure by measuring the weight loss as a function of time [736]. For orthorhombic AP, the weight loss data were obtained for three size fractions at six different temperatures and analyzed using the Avrami-Erofeyev method, which provided the best fit for $n = 2$. The kinetic parameters for the induction period and decomposition were obtained and found to depend on particle size. For cubic AP, the weight loss of four size fractions was measured as a function of time at 519 K (246 °C). Comparable fits of weight loss data were obtained via the use of the monomolecular law and the contracting volume method. The results obtained for cubic AP indicate considerable changes in the decomposition behavior upon phase transition from orthorhombic to cubic AP.

Contrary to this, Jacobs and Russel-Jones found that AP particle size does not influence the decomposition rate at temperatures above the phase transition point (513 K = 240 °C) [131]. This was confirmed in later DTA tests using AP samples with 50 and 200 μm particle diameters [347]. An excellent book by Shteinberg [347] (p. 124–135) contains a detailed section on thermal decomposition and linear pyrolysis of AP under a variety of conditions. The activation energy under these conditions was 127–

133 kJ/mol for the entire range of the degree of conversion. A reaction scheme and equation for the HTD of AP were derived from these data, assuming that the HTD of AP occurs via two independent parallel reactions. In a first approximation, the fraction of AP decomposing due to the first (fast) step is constant. For the total reaction rate, the equation is

$$-\frac{dC}{dt} = k_1(T)C_1 + k_2(T)\sqrt{C_2}$$

which leads to

$$d\chi/dt = 2.2 \times 10^9 \exp(-32000/RT)(1 - \chi - Z + 0.02\sqrt{Z}),$$

where χ is the degree of conversion and Z is the root of the transcendental equation

$$\sqrt{Z} = 0.01 \ln(1 - \chi - Z) + 0.93.$$

In another study, it was found that 200 μm -sized AP particles could decompose to a 33% extent during AP LTD and 23% with 50 μm sized AP particles [389].

The thermal decomposition of two types of AP with different particle sizes was investigated using DTA and TGA-FTIR coupling [737]. It was proposed that the decomposition of AP crystals obeys the process of “topochemistry” and it was found that there are two steps in the decomposition of the coarse grain size. Based on the gaseous products identified in real-time using rapid scan FTIR, as reported results in existing literature, the different mechanisms of the two steps during AP decomposition process were interpreted and their dependence on particle size explained.

Kinetic measurements for the fine, medium, and coarse size fractions of AP revealed that the kinetic parameters changed with particle size [395]. The correlation between particle size and kinetics may be one of the reasons for the scatter in the kinetic data as reported in the existing literature. The proportion of AP converted to gaseous products became smaller as particle size diminished.

The activation energy of the thermal decomposition of UFAP is lower than that of regular particle size AP [738, 739].

In Figure 28, mass loss is plotted against time for isothermal experiments, which requires the heating of AP for two hours at 499 K (226 °C) with seven different sample sizes. An initial look at these results demonstrated that the decomposition rate of AP increased with a decrease in particle size. This set of experiments was duplicated to demonstrate reproducibility.

The following explanations were offered for the effect of particle size on the rate of AP decomposition: **(1)** The removal of reactants occurs through the surface and a decrease in crystal size improves decomposition reaction conditions by venting the products. **(2)** Grinding induces severe latent damage in the crystal structure and is assumed to be responsible for an abnormal reactivity of ground AP crystals. **(3)** In the absence of a binder, surface energy of small particles and/or humidity promotes the agglomeration of some particles to minimize entropy, so that the initial sizes of particles are not maintained.

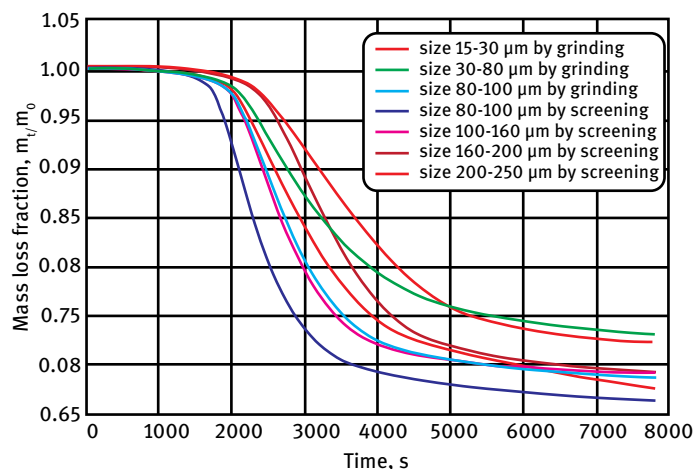


Figure 28: The influence of crystal size (in μm) and grinding on the mass loss of commercial AP by heating to 599 K (226 °C) as a function of time. (Republished and modified from [401], with the permission of © 2009 John Wiley & Sons – Books; permission conveyed through Copyright Clearance Center).

A model of AP deflagration was developed, which takes into account the mechanism of its deflagration which is a balance of volume exothermic decomposition and surface processes (endothermic sublimation and redox reactions with heat release) [740]. Analytical expressions for the burning rate and combustion limits based on the heat balance on the burning surface were derived and compared to experimental results for AP with different particle sizes. It was shown that combustion failure occurs if the total thermal effect of the surface process is negative.

The morphology of AP thermal decomposition under purge gas and in a closed cell was studied experimentally using TGA measurements and SEM observations for four different particle sizes [449]. The AP was first dried at 388 K (115 °C) for four hours, then ground and sieved. AP samples with four different particle sizes were aged, i.e., subjected to a thermal stress test in a closed sample holder. The temperature program consisted of an isothermal hold for ten minutes at 298 K (25 °C), a ramp-up at 10 °C/min. to 498 K (225 °C), and isotherm hold at 498 K (225 °C) for three hours while the pressure in the closed bomb was recorded. To determine the fraction of unreacted product remaining after experiments in **closed** cells, the residues of pre-decomposed (“aged”) AP were collected and subjected to thermal decomposition via TGA **open** cell for 2 hours at 498 K (225 °C). The weight loss rate was recorded on a microbalance. Their micro-structure was studied by taking SEM images, illustrating the evolution of porosity in the granules. The influence of different parameters (particle size, temperature, and atmosphere) was then quantified using TGA. The type of containment is a key variable in the thermal decomposition of AP, along with the particle size, the surrounding atmosphere, and the temperature of the isothermal TGA. The mass loss

as a function of time for four different particle sizes demonstrate how the smaller particles decompose faster than the coarse particles (Figure 29 for closed cell conditions and Figure 30 for open cell conditions).

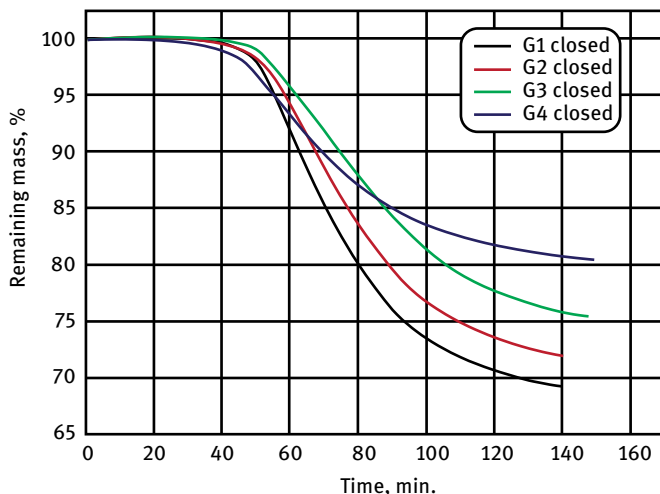


Figure 29: TGA mass loss of aged AP for four different particle sizes; Closed cell under air. (Reproduced and modified with permission from [449].)

$125\ \mu\text{m} \leq G1 \leq 160\ \mu\text{m}$, $160\ \mu\text{m} \leq G2 \leq 180\ \mu\text{m}$, $180\ \mu\text{m} \leq G3 \leq 250\ \mu\text{m}$, and $G4 \geq 250\ \mu\text{m}$.

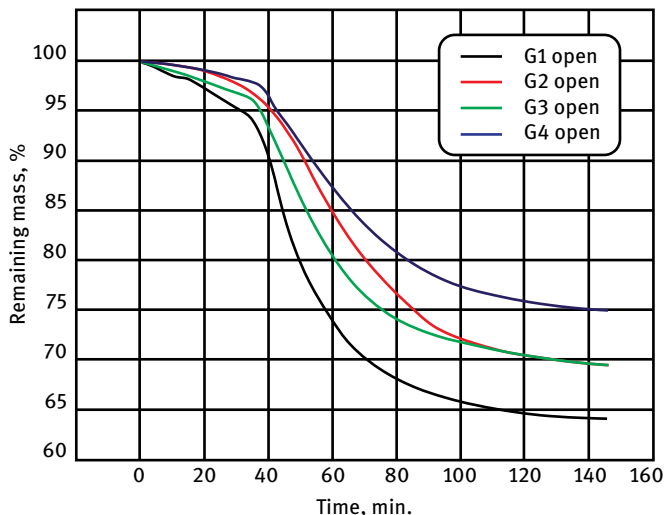


Figure 30: TGA mass loss of aged AP for four different particle sizes; open cell with air purge. (Reproduced and modified with permission from [449].)

$125\ \mu\text{m} \leq G1 \leq 160\ \mu\text{m}$, $160\ \mu\text{m} \leq G2 \leq 180\ \mu\text{m}$, $180\ \mu\text{m} \leq G3 \leq 250\ \mu\text{m}$, and $G4 \geq 250\ \mu\text{m}$.

The results were similar if the aging tests were conducted in an open cell with an air purge instead of a closed cell. However, containment caused a decreased rate of thermal decomposition and the particles were less porous. For closed cell decomposition tests, the pressure rise rate was faster and the maximum pressure was higher for finely ground AP than for the coarse granules. Pores became visible sooner on the small particles than on the coarse particles.

The effects of various grain sizes (10–390 μm) on the rate of decomposition of AP at a heating rate of 40 $^{\circ}\text{C}/\text{min}$ and the decomposition thermal behavior and kinetic parameters (activation energy and pre-exponential factor) were investigated using simultaneous DSC/TGA in a dynamic nitrogen atmosphere [741]. In addition, the specific surface areas were measured using the BET method. The kinetic parameters were determined using a simplified approach based on the isoconversional method. The results revealed that the coarser the AP particle size was, the lower the determined decomposition kinetic parameters. The results were in acceptable agreement with findings in the existing literature.

Coarse AP displays some peculiarities that are not observed with smaller particle sizes. A good survey of the literature about the decomposition and safety properties of coarse AP by itself and incorporated in a binder system was published in 2014 [346]. When coarse AP crystals decompose, they produce porosity within the crystals which cannot be observed in small crystals. Porosity formation in coarse AP in both isolated crystals and during solid propellant combustion seems similar although it may appear at different rates due to pressure and temperature influences. Natural and acquired trace impurities are nuclei for porosity formation. In combustion environments, kinetic rates for coarse AP reactions can be altered by materials on crystal surfaces and occluded within the crystal bodies. Since reaction rates of orthorhombic AP crystals are much faster in combustion environments than those of cubic AP crystals, orthorhombic phase AP is a primary actor during combustions. Coarse AP oxidizer has observable chemical interactions that have not been observed for fine AP oxidizer during thermal decomposition and in combustion environments. Coarse AP oxidizer has widely different chemical kinetic reaction rates between low and high heat fluxes. Widely different reaction rates are also observed between low- and high-pressure confinements. In formulated solid propellants, coarse AP promotes dark zone combustion, a low burn rate pressure exponent, ease of burn rate adjustment, burn rate pressure exponent slope break, and slow cookoff violence.

4.10.2 Effects of Mechanical Agitation on Slow AP Thermal Decomposition

Changes in the density of dislocations and crystal defects in AP crystals as a result of mechanical treatment will affect the thermal stability of AP. It was shown that the mechanical treatment of AP under the action of shock waves causes substantial acceleration of low-temperature thermal decomposition [742]. This may be seen from the comparison of thermograms of mechanically treated AP and untreated AP. AP powder

that was exposed to a shock wave (of insufficient strength to detonate it) was subsequently tested using DTA and TGA. Although no chemical changes occurred in the AP, there was a considerable change in the number of lattice dislocations, resulting in an increasing number of pores. While for the mechanically treated AP the exotherm-peak corresponding to thermal decomposition on the DTA curve occurred before the phase transition at 240 °C, for untreated AP this peak did not occur until above the temperature region of the phase transition. The onset temperature of the LTD was lowered but the rate of the HTD was unchanged.

Prior compression or thermal treatment of orthorhombic AP resulted in a lengthening of the induction period and a decrease in the decomposition rate of the isothermal decomposition in the temperature range of 488–508 K (215–235 °C) [743]. The final extent of the decomposition also decreased from the usual 30% to ~20% for the materials subjected to prior treatment. Prior treatment caused a broadening in the XRD patterns and in the infrared spectra of AP subjected to prior compression and heating.

Two distinct regions of temperature dependence were observed for the rate constants of the decomposition of AP in its cubic modification in the temperature range 573–663 K (300–390 °C) [744]. The activation energies in the two regions were found to be 83.7 ± 8 kJ/mol (20 ± 2 kcal/mol) and 251 ± 8 kJ/mol (60 ± 2 kcal/mol). Prior mechanical and thermal treatment of the materials caused a marked increase in the thermal reactivity of AP in the range of 573–643 K (300–370 °C). DTA of pre-compressed AP showed pronounced changes in the exothermic decomposition of the material. Prior compression of AP also enhanced the sublimation of the material. The activation energies were not altered by the pre-treatment. It was assumed that the differences are due to crystal imperfections and the role of dislocations in the thermal decomposition of AP.

Intense vibration can cause sufficient cracks in AP crystals, which decreases their thermal stability. In one series of tests, two different size AP powders (2–5 µm and 160–300 µm) and single crystals (5 × 5 × 1.5 mm) were subjected to intense mechanical vibration for 30 s [745]. DTA of vibrated and non-vibrated samples showed that the phase transition and the two exothermic peak temperatures were shifted to lower temperatures.

Single crystals of AP that were strained by impressing the diamond tip of a hardness tester would subsequently react differently to shock damage than unstrained crystals. The type of defects this produced were analyzed using XPS (see Section 3.11.1).

It appears that high shear in the orifice of composite propellants extruders can alter the embedded oxidizer crystals. Microscopic analysis of AP crystals from an extruded HTPB composite propellant grain containing a star-shaped internal perforation configuration was conducted after an uncommon ignition phenomenon was discovered within 0.02 inches from the surface of the perforation. The morphological properties of the AP crystals mechanically removed from various areas of the extruded

propellant were compared with AP crystals not subjected to extrusion processes. The unusual morphology, due to a strained condition, was discovered using optical crystallographic techniques in AP crystals removed from the area suffering from unusual ignition phenomena [746].

Investigations of the origin of hot spots in deformed and shocked AP crystals also indicated that stressed and shocked AP decomposed at a different rate from the untreated material [192–194].

Deformation of RDX and AP crystals at low strain rates was studied via diamond pyramid (Vickers and Knoop) micro-indentation hardness testing [747, 748]. RDX is two to three times harder than AP and has relatively limited-slip system activity. While both crystals readily crack, cracking did not reduce hardness in RDX but did so in AP. Strain fields surrounding the hardness impressions in RDX were extremely localized, while in AP they extended well beyond the impressions. Shock experiments were conducted on large (5–9 mm) single crystals in a fluid-filled tank designed to permit high-speed photography and sample recovery. The reaction threshold was determined by varying the shock pressure entering the crystals. Shock-entry orientation and large hardness impressions were used to vary micro-structural responses. When a crystal with a large indentation was shocked near its reaction threshold, significant light appeared in the vicinity of the indentation following shock passage. High-speed photography showed **luminous crack propagation** and reaction in both materials and the same slip deformation in AP as from hardness testing. Orientation affected the micro-structural response and reaction threshold for AP, and hardness impressions sensitized chemical decomposition far from the impressions. Recovered AP crystals were much more plastically deformed than RDX crystals and were often still transparent in the region opposite shock entry. RDX reaction threshold was ~62 kbar versus 17 to 24 kbar for AP, depending on crystal orientation to the shock wave.

When studying the effect of ultrasound on the thermal decomposition of AP, it was found that significant changes in the thermal behavior of AP, as indicated by DTA and TGA, could be observed when AP crystals were subjected to powerful ultrasound while suspended in water [749]. The decomposition temperature of AP was lowered by nearly 25 °C. A similar thermal sensitization was observed when AP was subjected to sonication in the presence of transition metal oxides. Kinetic parameters were calculated for AP, modified AP, and catalyzed AP decomposition using non-isothermal kinetics. The activation energy for the decomposition of the sonicated AP samples was found to be lower than that of normal AP.

The thermal decomposition of AP catalyzed with different transition metal oxides. It was then subjected to ultrasound and studied using DTA and TGA. The onset temperature of AP decomposition was lowered by nearly 30–35 °C when AP was sonicated in an ultrasound bath in the presence of CuO [526]. The lowering of Ti was observed in other AP-metal oxide samples also, however, the sensitization was not so drastic.

Time-resolved Raman scattering measurements were performed on AP single crystals under stepwise shock loading [750]. For a particular set of temperature and

pressure conditions, the intensity of the Raman spectra in shocked AP decayed exponentially with time. This decay was attributed to a shock-induced chemical decomposition in AP crystals. A series of shock experiments, reaching peak stresses from 10 to 18 GPa demonstrated that higher stresses inhibit decomposition while higher temperatures promote it. No anisotropic orientation dependence was found when AP single crystals were shocked normal to the (210) and (001) crystallographic planes. The kinetic and spectroscopic results were consistent with a proton-transfer-reaction as the first decomposition step in shocked AP.

4.10.3 Effects of Nucleation on the Start of AP Thermal Decomposition

There are many AP decomposition studies that use single crystals. In these, the progression of decomposition sometimes documents itself by the initially clear crystal turning opaque as the crystal lattice changes and with the evolution of embedded bubbles. The decomposition zone often spreads and is clearly visible from crystal defects, which act as nuclei for the start of the reaction.

There are several publications reporting the study of nucleation in AP single crystals as the starting point for AP decomposition. Beyond the point of phase transition and lattice transformation from orthorhombic to cubic at 513 K (240 °C), the porosity of AP significantly increases. Sublimation products trapped in the voids and microcracks are in equilibrium with the solid phase.

Bircumshaw and Newman [348, 349] observed slow decomposition at 503 K (230 °C), proceeded by the formation of opaque spots (nuclei) on the crystal surface. These spots then grew in size and eventually coalesced to form a continuous opaque region. The boundary with the transparent region could be seen to progress inward toward the center of the crystal. Once the boundary reached the center of the crystal, decomposition ceased, leaving a porous pseudomorph, which was still pure AP but which had a density of only 70% of that of the starting product.

This porous material was further characterized using DSC, TGA, and DTG measurements [751, 752]. The onset of thermal decomposition temperature of porous residual AP is up to 50 °C lower than that of normal AP and the decomposition time span of porous residual AP is about 20% shorter than that of normal AP. Their thermograms are different in appearance but the same amount of heat is released. The first weight-loss stage of the decomposition of residual AP on the DTG curve occurs about 40 °C below that of normal AP. A catalytic effect was observed in the decomposition of pure normal AP when mixed with residual “infected” AP. The addition of a residue formed during LTD of AP can catalyze the subsequent thermal decomposition of clean AP. DSC results of normal AP in various particle sizes revealed that the surface area has no effect on the decomposition of normal AP. Therefore, this must be attributed to the internal crystal structure.

Nucleation sites are related to imperfections in the AP crystal, such as contaminants, inclusions, dislocations [753, 754], lattice defects, or stack faults. The movement and the multiplication of the nuclei in the zone of reaction and the number of

dislocations determine the AP decomposition rate [453]. At very high pressures, AP self-combustion exhibits anisotropic recession rates depending on whether surface regression is normal or transverse to the principal axis of its orthorhombic crystal structure. This behavior might be described as biaxial burning. The decomposition centers on AP single crystals which are anisotropic, cigar-shaped, and stretched along the principal diagonal of the rhombohedral face. The diameter of the reacting zones rarely exceeded $2\mu\text{m}$. The rate of expansion in the direction of rapid growth was about ten times faster than in the direction at right angles to the rapid growth. At 493 K (220 °C), the reacting zones can expand at a rate of $13\mu\text{m}/\text{min}$. Etching of fresh and partially decomposed, quenched crystals showed that fresh crystals contained a three-dimensional dislocation network, while etching of partially reacted crystals revealed the formation of new dislocations under the influence of stresses and strains near the reacting centers. The onset of AP LTD with coarse AP particles (~ 200 micron-size range) on a hot plate was observed with microscopes [755]. After variable induction period delays, dents appeared on the AP particle surfaces followed by the formation of elongated ellipsoidal holes extending from the dents. Gas evolution was noted as soon as holes in the AP particles appeared. Holes had a length-to-diameter ratio estimated to be about ten. Holes stopped growing after they had reached a certain size. The holes formed in parallel, only along a certain rhombohedral face or plane described as the [010] face. AP LTD started from crystal surfaces extending into AP crystals, with solid material being removed through conversion into volatile product gases. An estimate was made that the number of holes formed on $200\mu\text{m}$ AP particles were in the order of 10^6 per square centimeter. Below the phase transition point, the nuclei at the rhombic face of the crystal were cigar-shaped, while at the prismatic face they were round. The nuclei were near-spherical above the phase transition point.

The rate of growth of the nuclei is dependent on the amount of water present in the crystal to start with and the amount of water in the surrounding atmosphere [440] (see Section 4.5.1).

The effect of co-crystallized cation additives (incorporated into the lattice of AP) on the rate of formation of reaction nuclei were studied by [756], as was their maximum number per unit surface area and the rate of nucleus growth along the principal axis of the ellipse and what was perpendicular to it. It was found that the heterovalent ion additives (divalent cations) caused a decrease in the induction period, an increase in nuclei formation, and a maximal number of nuclei per unit surface area. At the same time, the additives did not affect the rate of nucleus growth in any directions.

If AP crystals are heated, the nucleation sites appear to be randomly distributed on the *c* face; on the *m* face some are randomly distributed but others lie along lines in specific crystallographic directions [757]. When crystals are strained before thermal decomposition, the nuclei are strongly aligned on both faces and oriented (with few exceptions) in the same crystallographic directions as similarly aligned pits formed by chemical etching. It can be concluded that the decomposition nuclei preferentially form where dislocations intersect the crystal surface. During heating at 443 to 483 K

(170 to 210 °C), the first-formed nuclei are widely distributed and appear to be predominantly located on the surface. These and subsequently formed nuclei cease growing once they reach a critical size. Additional nuclei continually appear between previously formed ones until a completely reacted layer is formed. Further decomposition occurs in two ways: The reaction progresses inward and becomes roughly parallel to the surface as successively deeper layers of nuclei are formed, or the reaction produces bands along (001) planes in the [010] and [510] directions. SEM examination revealed that these bands, as well as other parts of the reacted surface, consist of the porous residue of AP.

The shapes of nuclei are different at different faces of the crystal and depend on the temperature at which thermal decomposition is taking place. Below the phase transition point, the nuclei at the rhombic face of the crystal are cigar-shaped, while at the prismatic face they are round. Above the phase transition point, the nuclei are spherical. The growth of nuclei proceeds due to the formation of new seeds near the boundary of a nucleus. The cinematography of single crystals during decomposition helped to establish that the nuclei are moving along the diagonal of the rhomb at a velocity of 7–10 m/min. (for $T = 503 \text{ K} = 230^\circ\text{C}$). With even larger magnification achieved by using the SEM, it was discovered that the nuclei were initially not round as it was suggested earlier but that they have a clearly defined shape corresponding to the crystal chemical features of a given crystal face [403]. For example, on the rhombic face, the nuclei have the shape of a rhomb, while on the prismatic face they are rectangular. During decomposition, the nuclei reached the size of several microns and eventually stopped growing; their shape changes and they gradually become round.

One of the first steps of decomposition in an AP crystal may be the formation of nucleation sites around which the decomposition progresses and spreads like a cancer [758, 445]. The thermal decomposition of crystals of AP at low temperatures starts with the formation and growth of nuclei. To gain an understanding of the mechanism of the decomposition of AP, it is necessary to know which stages of the process are connected with nucleation and which lead to subsequent growth. It was proposed that nucleation occurs because of the course of the primary stage of the dissociation of salt and subsequent secondary reactions. It was also suggested that the growth of the nuclei is caused by the reaction of acidic decomposition products (HClO_4) with unreacted AP and due to the oxidation-reduction reactions of the active oxidizers being regenerated in the course of the process. The addition of strontium perchlorate or ammonium dichromate affected the nuclei growth rates.

AP doped with copper ions contains active sites around which decomposition is enhanced. Doping AP with copper ions does not change the density of dislocations as indicated by the number of etch pits. However, the number of dislocation sliding systems changes substantially [759].

Proton-acceptor additives are effective inhibitors of the nucleation process during the LTD of AP [760]. In contrast to this, the addition of ClO_3^- ion is a catalyst for the decomposition of AP. It increases the rate of nucleation and the maximum concen-

tration of nuclei and decreases the induction period of nucleation. It was found that impurities of ClO_3^- ions are typically present in even the purest commercial samples of AP. ClO_3^- ions may also form as the result of UV irradiation of AP.

The edge components of dislocations in ionic crystals carry an unbalanced electrical charge. Any ion chemistry at these locations may be affected by applying an external electrical field. A study of the effect of a constant electric field on AP single crystals found that a constant electric field with a field strength of 10 kV/cm affects the thermal decomposition in the crystal [761]. The anisotropy of reaction emanating from nuclei increases due to the prevailing growth of nuclei along the main diagonal of the rhombic face of the crystal. When the field was imposed along the direction [100], a decrease in the induction period and increase in the surface density of the initial reaction centers was observed. The number of dislocations may change as a result of mechanical strain arising in the crystal under the action of an electric field. It is unlikely that the burning rate of AP-based propellants can be modulated by applying an external electrostatic field, but on a microscopic scale this is possible.

Phenomenological surface texture changes occurring on the surface of decomposing AP crystals have been visualized using a replication micrographical technique [762]. Soon after attaining reaction temperature, (001) crystal faces develop residual saucer-like hemispherical depressions ascribed to bubble formation during water loss from superficial layers. Subsequently, small holes develop (which penetrate the crystal), as do regions containing parallel-oriented surface ridges.

Nucleation has also been discussed already in several other sections of the AP chapter in connection with the decomposition of AP (see [469] and [621] also).

Solid-state decomposition reactions generally start at specific sites. The first-formed product at these sites are referred to as “the nuclei”. Further reaction takes place at the interface between nuclei and unaltered reactant so that the first-formed nuclei grow in size. Visual observations of large nuclei revealed that these grow at a constant rate. However, in many solid-state decompositions, experimental evidence suggests a slower rate of growth for small nuclei, because the general kinetic equation based on nucleus formation and a constant rate of growth fails to adequately describe the early stages of the reaction before the rate accelerates [402]. In some reactions, structural changes induced by the reaction result in the multiplication (“branching”) of nuclei and a general equation (of which the Prout-Tompkins equation is a special case) can be derived. This general equation is shown to fit experimental data over a wider range than the original Prout-Tompkins equation.

4.11 Effects of Phase Changes on Ammonium Perchlorate Thermal Decomposition

AP undergoes a reversible polymorphic transition at 513 K (240 °C). This temperature is close to its melting point and its point of incipient thermal decomposition. Below 513 K, AP exists in the form of orthorhombic crystals. Above 513 K AP exists in the form

of cubic crystals. The phase transition orthorhombic $\rightarrow$ cubic is endothermic but it is often accompanied by incipient thermal decomposition. Thermal decomposition of AP proceeds differently, depending on if one starts with the orthorhombic or cubic modification. Also, the effect of additives on the dissociation of AP is different, depending on which modification exists at the moment when the additive steps into action [110].

A gravimetric method was used to study the kinetics of crystallographic phase transitions in AP with a particle size of 0.2–0.7 mm upon heating (443–573 K = 170–300 °C) in a vacuum. The anomalous temperature dependence of the reaction rate is caused by a phase transition from orthorhombic to cubic NH_4ClO_4 and by the self-crushing of part of the sample in the later stages of the reaction. The rate of thermal decomposition sharply decreased at the moment of phase transition because the rearrangement of the lattice from a rhombic into a cubic structure leaves no space for decomposition products to accumulate in the crystals [763] (see [764] also).

4.12 Computational Chemistry in Support of the Study of Ammonium Perchlorate Thermal Decomposition

With the advances of computational chemistry, several theoretical studies have looked at the decomposition of AP either as a purely theoretical study or as a way to complement and support experimental studies. Similar computational efforts have been made with other self-decomposing oxidizers like ANI ADN.

Catalyzed and uncatalyzed thermal decomposition of AP was investigated at different temperatures in the range 493–588 K (220–315 °C) using different size particles and the data fitted to a math model [765]. The data were fitted using an integrated form of the relation

$$\frac{dy}{dt} = \frac{ay - by^2}{1 + cy}$$

where y denotes the fraction decomposed at time t and a , b , and c are constants. At lower temperatures $dy \ll 1$, while at higher temperatures $dy > 1$. The constants a , b , and d depend strongly on temperature. The energy of activation of the processes associated with a and b was 188 ± 4 kJ/mol (45 ± 1 kcal/mol), while that for d was 176 ± 4 kJ/mol (42 ± 1 kcal/mol).

There have been numerous investigations into the mechanisms of AP thermal decomposition. Products that have been observed under various conditions, in what are evidently rather complex processes, include HCl, H_2O , N_2 , O_2 , NO, NO_2 , N_2O , Cl_2 , ClO, and HClO_3 . Attempts have been made to theoretically predict thermodynamic data relevant to the various steps that may be involved in AP thermal decomposition. The structures, energy minima, and enthalpies at both 298 and 800 K for 37 atoms, molecules, and ions that are possible intermediates or products were calculated [766].

These data permit the calculation of ΔH_{298} and ΔH_{800} for hundreds of reactions that may be involved. Thirty-nine of these are listed in [766] and several possible decomposition pathways are outlined. ΔH_{298} and ΔH_{800} were found to differ by less than 1.0 kcal/mol. The activation energy of sublimation is considerably less than its overall enthalpy change. Figure 31 depicts some possible pathways for the thermal decomposition of AP. It is likely that several of these (as well as others) proceed simultaneously and include other steps in addition to those shown.

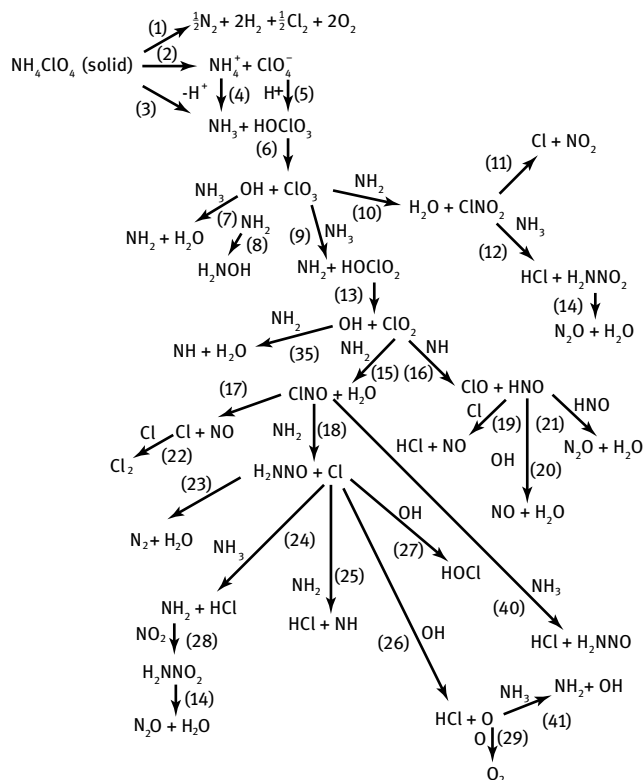


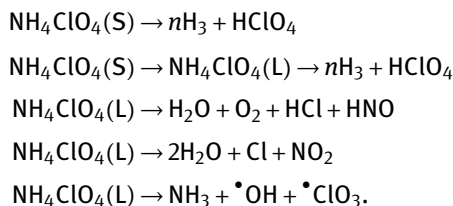
Figure 31: Some of the possible steps in the decomposition of AP. (Republished from [766], with permission of © 1998 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center, Inc.)

Note: This scheme shows reaction paths for which the heat at reaction points 298 K have been computed. The numbers in parentheses are the numbers of the reactions in a table (not shown) that gives kinetic parameters.

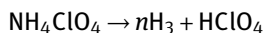
A theoretical study of a series of ClO_x reactions relevant to the combustion initiation of AP included the decomposition of ClO_x ($x=2-4$) and HOClO_y ($y=2-3$), the bimolecular reactions of $\text{HO} + \text{X}$ ($\text{X} = \text{ClO}, \text{OCIO}, \text{HOClO}_3$), $\text{ClO} + \text{Y}$ ($\text{Y} = \text{O}, \text{ClO}, \text{OCIO}$),

H + HOClO₃, and some of their reverse processes [767]. The geometries of the reactants, intermediates, transition states, and products involved in these reactions were optimized by a computational method and final energies were refined. This allowed rate constants for major product channels to be predicted and compared with the available experimental data. Detailed mechanisms for these reactions were then discussed on the basis of predicted potential energy surfaces. The rate constant calculations were carried out using conventional transition state theory (TST), or Rice-Ramsperger-Kassel-Marcus (RRKM) theory. This was used for reactions with well-defined transition states and variational TST. RRKM theory was used for those channels which occur without barriers. The results showed that predicted energies and rate constants were quite satisfactory and in good agreement with available experimental data.

A computational study of AP decomposition and a comparison of the gas-phase and condensed-phase reactions led to the conclusion that strong solvent effects may exist in the AP decomposition reaction [400]. The mechanism considered included the following initiation processes in the solid, liquid, and gas phases:



The results showed that, in the gas phase, the main decomposition channel of AP is the proton transfer from the ammonium cation to the perchlorate anion. This forms ammonia (NH₃) and perchloric acid (HClO₄):



with 59.4 kJ/mol (14.2 kcal/mol) enthalpy change. In solution, the enthalpy change for this channel is 123.4 kJ/mol (29.5 kcal/mol), which is close to the sublimation activation energy (~125.5 kJ/mol = ~30 kcal/mol) in crystalline AP. The other possible channel



has higher enthalpy changes, of 235 kJ/mol (56.3 kcal/mol) and 322 kJ/mol (77.1 kcal/mol) in the gas phase and in solution, respectively, and is less probable. This data indicates that strong solvent effects may exist in the AP decomposition reaction. As shown in Figure 32, the activation energy for the transfer of a proton from the ammonium cation to the perchlorate anion in the gas phase at transient state TS1 is only 2.1 kJ/mol (0.5 kcal/mol). This is considerably lower than the expected value (~125.5 kJ/mol = ~30 kcal/mol) for the proton transfer process in the crystal. This is expected since the surrounding ionic coulombic attractions and hydrogen bonding in crystals are not present in the gas phase. The existence of ion pairs in the gas

phase is not favored energetically (with $467 \text{ kJ/mol} = 111.7 \text{ kcal/mol}$ endothermicity). The production of perchloric acid and ammonia is preferred with only 59.4 kJ/mol (14.2 kcal/mol) endothermicity from the metastable LM1 complex. The second channel, based on a PCM, proceeds by way of the production of ClO_3 and an $\text{H}_3\text{N-HO}$ complex. This has a heat of reaction of 235 kJ/mol (56.3 kcal/mol).

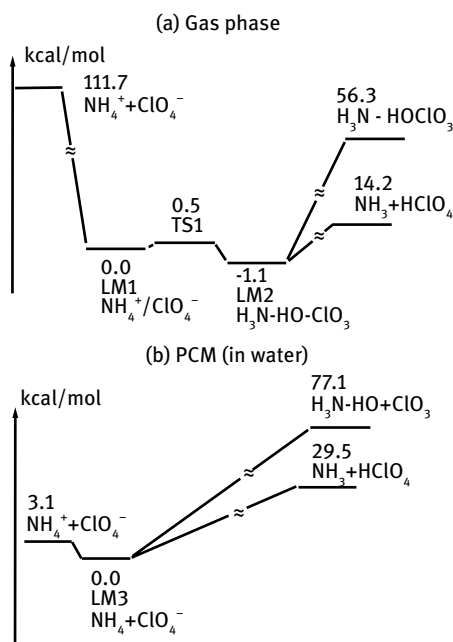


Figure 32: Schematic diagrams for NH_4ClO_4 dissociation computations. (Reprinted and modified from [400], © 2006, with permission from Elsevier; permission conveyed through RightsLink.) (a) relative gas-phase energies and (b) relative PCM energies in kcal/mol.

In an effort to explain how water affects proton transfer on the surface and on solid AP, gas-phase reactions were simulated by computational chemistry methods at various levels of complexity. This involved the use of a generalized gradient approximation with a plane-wave DFT [443, 444, 768] (see Section 4.5.1). Dissociation mechanism and the role water molecule(s) play(s) in the surface decomposition process were compared to those in the gas phase and in solution.

With the increasing capabilities of kinetic modeling software, solid/vapor reactions can be modeled, as can homogeneous gas-phase reactions. A simulation of the combustion of AP with and without contact with a combustible HTPB binder was carried out using Chemkin software. This took place in two stages: during the burning behavior of pure AP and one of AP in contact with HTPB binder [769]. In both cases, the chamber pressure was varied in order to verify its influence on the burning rate. The results were plotted using two different methods: at first as a time-resolved graph and later as a spatially resolved graph. The composition was measured as a function of the distance from the burning surface. The flame structure, composition profile, and

temperature profile could be described by the mol fractions of the burning products and the temperature evolution from the surface of the material to the peak temperature in the flame front.

5 Combustion (= Deflagration) of Ammonium Perchlorate

The word *combustion* is commonly used for reactions of fuels with oxidizers as well as the flame-producing decomposition of energetic materials, typically monopropellants. A more accurate term would be *deflagration* because it describes the decomposition without the aid of an external oxidizer or fuel. We use the two terms here interchangeably. The deflagration of AP by itself and the combustion of AP-based propellants have been extensively investigated for the past sixty years. Once, an entire session of the 11th Symposium (International) on Combustion in 1967 was devoted to AP. The objective of most of the studies was to develop propellants with higher burning rates (in particular for air- and missile-defense applications) and to maintain a reproducible, zero-defect production of the standard AP-based propellants used in Minuteman and M-X/Peacekeeper intercontinental ballistic missiles (ICBM's) and in large strap-on boosters.

5.1 Ignition of Ammonium Perchlorate (No Binders)

This chapter deals with the combustion of AP itself in the absence of fuels or binders. Before AP can burn, it must be ignited. Many studies concentrate just on the initial phase of AP ignition and combustion. This is closely related to measuring the induction periods for the autoignition of AP, when it is heated to a preset temperature and held at that temperature until ignition occurs (see Section 4.4). Numerous studies deal with the ignition of formulated propellants containing AP as the oxidizer.

The ignition of AP, with and without catalysts and a simulated binder (polyethylene), was studied in an arc furnace [601, 602]. A thermal runaway in the condensed phase can account for the ignition phenomena observed. Ignition cannot be interpreted solely as the time required to establish steady-state conditions but is a complex sequence of events. The outcome is different if the exothermic reaction occurs in the condensed phase or in the gas phase. In the case of AP, it was concluded that a condensed-phase reaction is a necessary prerequisite for ignition.

In trying to clarify if AP ignition occurs in the condensed phase or in the gas phase, the AP sublimation-dissociation-ignition multi-step process was separated by simulating only the vapor phase ignition. This was done by impinging jets of perchloric acid and ammonia (and other combustible solids and vapors) with and without the presence of catalysts [770, 771]. Perchloric acid/ammonia/catalyst mixtures ignited faster than perchloric acid/solid fuel mixtures. It was suggested that, for AP subli-

mation products, ignition occurs as a result of heterogeneous reactions between ammonia and perchloric acid vapor on the surface of catalyst particles. Perchloric acid/ammonia ignition was catalyzed using copper(II) chromate or iron(III) oxide, the same substances that also catalyze AP decomposition and ignition.

The ignition and combustion behavior of both pure AP and laminated AP/fuel/AP sandwiches of millimeter slab thickness were studied using a technique that utilized a CO₂ laser beam to supply radiant energy to the surface of an igniting and burning propellant [772, 773]. The burning rate of pure AP as a function of incident laser power density, the ignition delay duration of pure AP as a function of pressure and laser power density, the gas composition and flame temperature for the laser-induced AP flame, the flame structure and flow field from linearized propellant sandwiches of pure AP and PMMA fuel-binder, and the compositional and thermal structure of the AP-PMMA laser-induced flame were measured. The sandwich burning data revealed the gas-phase structure of the fuel-oxidizer interdiffusion flame.

A simplified theory for the ignition of AP was proposed, which was derived from a unified theory that also explained the low-pressure deflagration limit (LPDL) as well as the steady-state deflagration [774, 775]. The theory provides an approximate method for calculating ignition delay and the minimum external heat flux required for a successful ignition (as functions of pressure and initial solid temperature). The ignition calculations revealed that there exists a pressure limit due to the weakness of the igniter strength, in addition to the LPDL, which is an inherent property of the solid independent of the igniter strength. The theory can be extended to other solid monopropellants for which exothermic reactions occur only in the gas phase. The ignition temperature of AP is lowered by the presence of fuel-rich compounds [776]. Chapter 11 of a two-volume set of books on *Energetic Materials* contains a section on the reliable prediction of kinetics and mechanisms for elementary processes in the chapter “Key Combustion Initiation Reactions of AP” [777].

5.2 Strand Burning of Ammonium Perchlorate (No Binders)

There is some overlap between this section and the previous sections which looked at the thermal decomposition of AP with traditional chemical methods without measuring the linear regression rates. The following sections extend those studies with measurements of actual burning rates of AP by itself (without the addition of combustible binders). The rates of thermal decomposition and the burning rates are both affected by various additives (contaminants, catalysts, inhibitors) and operating conditions (initial temperature, pressure, venting, or confined) in a similar way. With adequate precautions, cylinders of compacted AP without a binder can be burned in a Crawford bomb similar to AP-containing solid propellants. In trying to increase the burning rates of propellants, the effect of burning rate additives on the burning rate

of AP-based propellants was quite often first studied with AP alone, thus avoiding any interference from the type of binder used. The next step then would be to try the same burning rate additive in an actual propellant formulation with a fuel present.

The ability of AP to maintain a solid monopropellant-like decomposition reaction (= deflagration) is unique among the solid propellant oxidizers and is shared with only a few other oxidizers, all ammonium, hydrazinium, or hydroxylammonium salts, although stable combustion can only be maintained at very high pressures. For this reason, a very large number of experiments have been performed to examine the strand burning of AP without the addition of fuels. The burning of individual crystals of AP (surrounded by a binder) plays a vital role in establishing the burning characteristics of composite AP-based propellants. Sometimes during such experiments, combustion may cease after initial successful ignition. This indicates that the failure is a propagation problem and not an ignition problem. Combustion of AP in the absence of combustibles is easily quenched by external interference.

Combustion and decomposition processes for AP can take place at temperatures above 513 K (240 °C) directly from the orthorhombic phase. This is because the speed of phase transition to the cubic phase is so slow that advancing burn fronts may move faster than the phase change process. AP is less thermally stable in the orthorhombic phase than in the cubic phase, as shown by differences in mass decomposition rates in the orthorhombic phase compared to the cubic phase until temperatures reach 573 K (~300 °C) or more.

5.2.1 Experimental Methods for the Study of Strand Burning Rates of AP

The rate of burning of AP pellets can be studied by embedding micro-thermocouples or break wires in the pellet or by relying on visual observations (high-speed camera recording) in a windowed bomb. The pressure measurement alone in a constant-volume bomb is not a very accurate indication of the linear burning rate. The surface of quenched AP samples can be examined under the microscope and will reveal details about the structure of the melt layer and crack formation in the underlying solid [778]. High-speed movies of the burning surface have also been recorded [779].

The electrical conductivity of the condensed phase of burning AP was measured at pressures between 26 kPa (200 mm Hg) and 10.1 MPa (100 atm) [780]. Electrical conductivity at 293–573 K (20–300 °C) is caused by the more mobile NH_4^+ ions, and to a lesser extent, by ClO_4^- ions. The gas in close proximity to the burning surface is in a plasma state.

Attempts have been made to measure the A.C. electrical conductivity of the combustion zone of a deflagrating AP pellet in a direction perpendicular to the travel of the flame front [781]. The ohmic resistance was measured as a function of frequency at 1–20 MHz. It was attempted to Differentiations between the conductivity of the melt layer and the ionized flame front were sought.

5.2.1.1 The Linear Strand Burning Rates of AP

The linear strand burning rates depend on the homogeneity of the sample. The most homogeneous sample structure could be achieved with slabs sliced from selected faces of large single crystals. However, these are more difficult to obtain than pressed pellets. Even pressed pellets are not identical; it depends on the particle sizes of the powders from which they were made and on the amount of compaction and residual porosity. The following sections discuss linear strand burning rates of pressed pellets and single crystals of AP under a variety of conditions that affect the burning rate.

In addition to measuring linear strand burning rates and plotting them against pressure, other studies have measured the weight (mass) loss rate and the electrical conductivity and used this as an indication of the progression of the flame front.

Literature on more general (with no emphasis on a specific variable like pressure or catalysts) studies of AP deflagration and linear burning rates are summarized here in chronological order. Some of the investigators may have added burning rate catalysts, while others may not have done so.

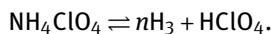
Crystalline AP sublimates to ammonia and perchloric acid vapors via an endothermic process. Heat is generated in a gas-phase oxidation-reduction process, which is perhaps 10^{-5} cm (30 mean free paths) above the surface at 10.1 MPa (100 atm). The final temperature is 1203 K (about 930 °C) but the surface temperature is 100–200 K cooler. Heat is conducted back through this thin layer to supply the energy for preheating and vaporizing the crystal. The propagation rate is governed primarily by the rate of heat generation in the gas phase and the thermal conductivity of the gaseous layer just above the surface. Catalysts accelerate the burning rate by projecting from the surface into the thin gaseous reaction zone then producing local acceleration of the reaction rate. The low-pressure flammability limit is caused by radiative heat loss to the surroundings.

The rates of pyrolysis of AP were measured by pressing a pellet of AP against a heated porous plate [782]. The pyrolysis products could escape through the porous plate where they would no longer interfere with the pyrolysis process. Ammonium chloride, which was non-reactive, was tested in the same apparatus along with AP for comparison. Data compared well with similar data obtained earlier with a compact hot plate instead of a porous plate.

An experimental study of the process of linear pyrolysis of AP at temperatures below 773–823 K (500–550 °C) observed that a stationary flameless decomposition took place [365]. The kinetic constants determined from these experiments corresponded with the data obtained under isothermal conditions. At temperatures above 773–823 K (500–550 °C), NH_4ClO_4 gasifies rapidly and was accompanied by combustion of the products of pyrolysis (see [783] also).

The exothermic decomposition reaction in the condensed phase, followed by sublimation, has been considered as the basic mechanism of AP burning. The kinetic retardation or acceleration of the burning process has been connected with a change of equilibrium concentration of HClO_4 . This was limiting the decomposition under the

influence of sublimated components of different solubility (NH_3 and HClO_4) as well as decomposition products (H_2O and HCl), which shifted the equilibrium state of the reaction



The formulas obtained explain the main characteristic features of the dependence of the burning rate of NH_4ClO_4 on pressure; namely, the initial growth of burning rate with pressure, the plateau or the rate drop, and the subsequent growth at high pressures [784] (see [785] also).

Sample preparation variability influences the rate of AP deflagration and may overshadow the effects of pressure, sample temperature, and acceleration environments on the burning rate [786]. The sample preparation parameters investigated included pellet compaction time and pressure, the particle sizes of the AP powder from which samples were pressed, and the type of AP (ultra-pure, propellant grade, and propellant grade with conditioners) from which the pellets were made.

The strand burning rate of AP by itself may vary from batch to batch depending on its source [787].

5.2.2 Effects of Pressure on the Strand Burning Rates of AP

The dependence of the linear strand burning rate of AP on pressure is the same as that of AP-based solid propellants. This has been thoroughly investigated, sometimes with side-by-side AP-based propellants which are then compared to the oxidizer. The burning rate obeys the Roberts-de Saint Law. Therefore, one needs to determine the pre-exponential factor and the burning rate coefficient to derive combustion theories of AP-based composite propellants. The main question is how the burning rate of AP-based propellants is affected by the condition of the oxidizer in the absence of binders. Since up to 80% of most propellants consist of AP, it has a major impact on the burning rates of formulated propellants.

When conducting burning rate studies, one must differentiate between self-sustained (adiabatic, free pyrolysis) and aided (non-adiabatic, forced pyrolysis) combustion [788]. The combustion of AP in a composite propellant will be a forced pyrolysis since an appreciable fraction of the heat released during the fuel/oxidizer combustion process is fed back to the surface. During experiments in the temperature range of 590 to 1540 K and at pressures between 2.6 kPa to 2.62 MPa (0.026 to 26 atm), it was noted that above 910 K the results were well-represented by an empirical relation which expresses the pressure dependency of the regression rate. Below 2.12 MPa (21 atm) and at a given pressure, the regression rate increased with increasing temperature, whereas it decreased above 2.12 MPa (21 atm). The burning rate or free pyrolysis rate is proportional to the 0.5th power of the pressure at low pressures (1 to 5 atm) and to the 0.9th power at higher pressures. The pressure exponent of the AP regression rate under free pyrolysis conditions (0.505 to 10.1 MPa = 5 to 100 atm) can be compared to the max-

imum values found for the pressure exponents of solid propellants. At low temperatures, the regression rate was not sensitive to pressure.

The rate of deflagration of pressed pellets of AP was measured at different ambient pressures and temperatures, with initial particle sizes ranging from a few microns to several hundred μm in diameter [789]. The density of the pressed pellets was 1.908 g/cm^3 for the as-received material; 1.894 g/cm^3 for the 74-to-105 μm fraction; and 1.896 g/cm^3 for the minus 53 μm fraction. The single-crystal value should be 1.95 g/cm^3 . These results indicated that the material was not perfectly compacted although the molding pressure of the pellets was 100000 psi. No luminosity of the products of deflagration could be seen except for the occasional flashes believed to be due to impurities. Condensation of the combustion products was evident as the high-pressure, moisture-laden gases mixed with the cold ambient nitrogen to form an acid fog. At an ambient temperature of 294 K (21°C), lower and upper deflagration limits were about 4.54 MPa (45 atm) and about 30.3 MPa (300 atm), respectively, for AP pellets pressed from as-received powder. When such pellets were preheated to 343 K (70°C) instead of to 294 K (21°C) before ignition, deflagration rates increased at all pressures. Further, deflagration could be maintained down to nearly 2.02 MPa (20 atm). The pressure above which the deflagration rate began to decrease was raised from 15.15 to 20.2 MPa (150 atm to 200 atm). At higher pressures, however, a novel phenomenon was encountered. The existence of an upper-pressure limit, which is only slightly dependent on particle size but may be raised by preheating, occurred. When the pellets were precooled to 255 K (−18°C), ignition could not be obtained at any pressure.

The deflagration behavior of pure and doped AP was studied over the pressure range 2.064–41.28 MPa (300–6000 psia) using cinephotomicrography of burning samples and SEM of quenched samples [779, 790]. Materials tested were pure AP in single-crystal and pressed-pellet forms and single crystals with controlled isomorphous substitutions of K^+ , MnO_4^- , and $\text{Cr}_2\text{O}_7^{2-}$ ions. The results showed that previous speculations regarding the combustion of AP were based on erroneous assumptions. As such, more realistic views based on these observations were proposed. Some questions regarding the relevance of low temperature, low heating rate, and low-pressure decomposition data to actual combustion in propellants continue to be discussed nowadays.

5.2.3 The Effect of Temperature on Strand Burning Rates of AP

The dependence of the linear strand burning rate of AP on temperature is the same as that of AP-based solid propellants and has been thoroughly investigated [791]. Besides temperature and pressure, there are many other variables that can affect the burning rate of AP and those will be discussed in subsequent sections, including pellet density, particle size, and effect of additives. These variables need to be kept constant if one wants to obtain accurate data on the pressure or temperature dependency of the AP burning rate. Similar temperature dependencies were measured with AP that was doped with various additives. It was later recognized that the temperature sensitivity of the deflagration rate of pure AP is less than previously reported [792].

In extending conventional burning rate and pressure exponent measurements, additional data was used to determine the temperature sensitivity coefficient σ_p of the burning rate of AP and four other oxidizers [793]. The simplest means of determining a value of σ_p is to measure the burning rate of a particular material as a function of initial temperature, take the natural logarithm of the burning rate values, and determine the burning rate temperature sensitivity as the slope of the line through a plot of the natural logarithm of the burning rate versus the initial temperature. The main requirement is to obtain a consistent and reliable set of burning rate data at various initial temperatures and pressures. In the case of AP, the temperature sensitivity goes through a minimum over a wide pressure range (Figure 33).

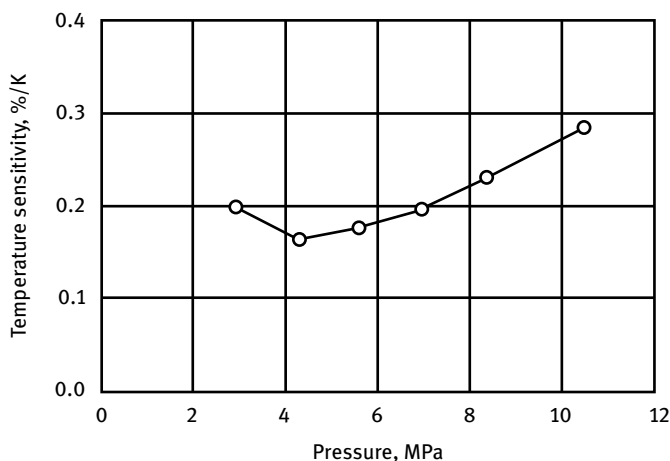


Figure 33: Temperature sensitivity coefficient of the burning rate of AP. (Republished and modified from [792], with permission of © 1999 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center).

5.3 Linear Strand Burning Rates of Ammonium Perchlorate Pressed Pellets

Most AP deflagration and burning studies were done with pressed pellets. These have inhomogeneities and varying degrees of porosity which may affect the burn rate. It is very difficult to press AP pellets with reproducible porosity and burning behavior.

It is surprising how much scatter there is if the burning rate data from eight different investigators are plotted together on the same graph, as has been done in Figure 34. While the data agree quite well with each other in the low-pressure regime up to 13.76 MPa (136 atm = 2000 psia), there is a lot of scatter at pressures above 13.76 MPa (136 atm = 2000 psia). In particular, the U-shaped burning rate minimum at 20.6 MPa (204 atm = 3000 psia) has not been observed by all experimenters, the reason for which is hard to explain.

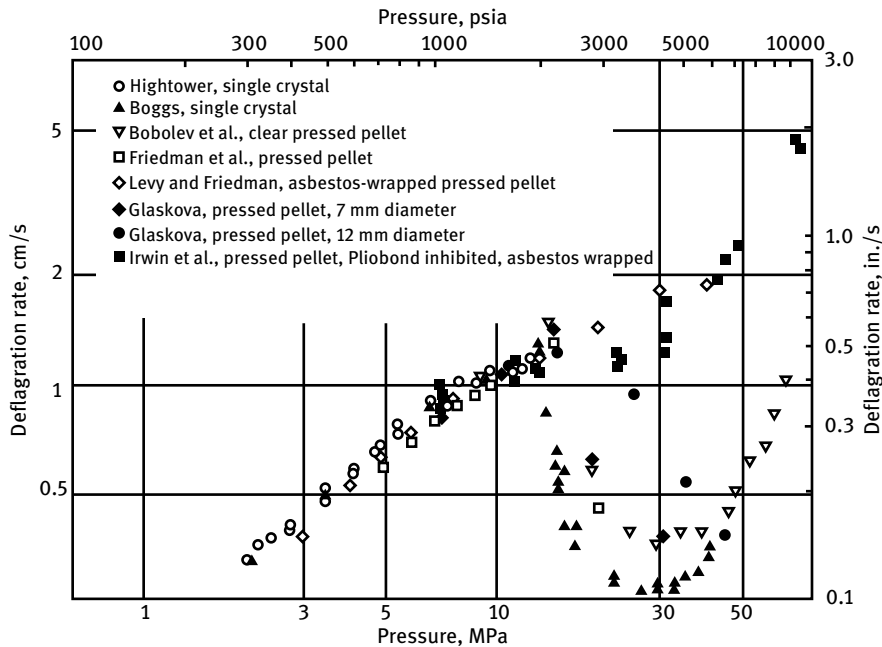


Figure 34: Deflagration rate of AP in a nitrogen atmosphere; Comparison of literature data. (Republished and modified from [794], with permission granted by © 1970 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center, Inc.)

5.3.1 The Effect of Bulk Density on Linear Strand Burning Rates of AP Pressed Pellets

The burning rate of pressed AP pellets is highly dependent on the bulk density of the pellets. It is difficult to press AP powder reproducibly into pellets with uniform burning characteristics. AP was pressed into 10 mm diameter pellets and burned in a strand burner under nitrogen at varying pellet bulk densities (0.65 to 1 g/cm^3), particle sizes (15 to $140\text{ }\mu\text{m}$), different pellet confinements, and two different chamber pressures (60 and 100 atm) [266]. The main objective of the study was to measure the effect of bulk density on the burning rate of pure AP pellets. Urotropine or bitumen was added only for comparison.

The burning rate of AP was measured as a function of the pressure (up to $14.1\text{ MPa} = 140\text{ atm}$), the initial pellet temperature ($293\text{--}393\text{ K} = 20\text{--}120\text{ }^\circ\text{C}$), the size of the particles ($50\text{--}400\text{ }\mu\text{m}$), and the density of the pellet ($1.5\text{--}1.9\text{ g/cm}^3$) [795, 796]. The burning rate increased with an increase in pressure and tends to reach a point of saturation when it reaches a range of $9.09\text{--}11.11\text{ MPa}$ ($90\text{--}110\text{ atm}$). This dependence cannot be described by the known empirical formula $r_b = Ap^n$ since A and n depend strongly on the pressure. The data obtained was not in agreement with the theory of the combustion of volatile substances developed by Zeldovich, and even contradicted it in some cases. The addition of NH_4Cl lowered the temperature of the reaction layer

of the condensed phase and increased the minimum temperature of combustion. If the process takes place in the condensed phase, the addition of NH_4Cl should decrease the rate of combustion. However, it increased it in the gas phase instead.

It is interesting to compare the effect of packing density on the linear strand burning rates of AP and, at the same time, compare it to the burning rates of other nitrogen based (hydrazinium and hydroxylammonium) perchlorates, as shown in Figure 35.

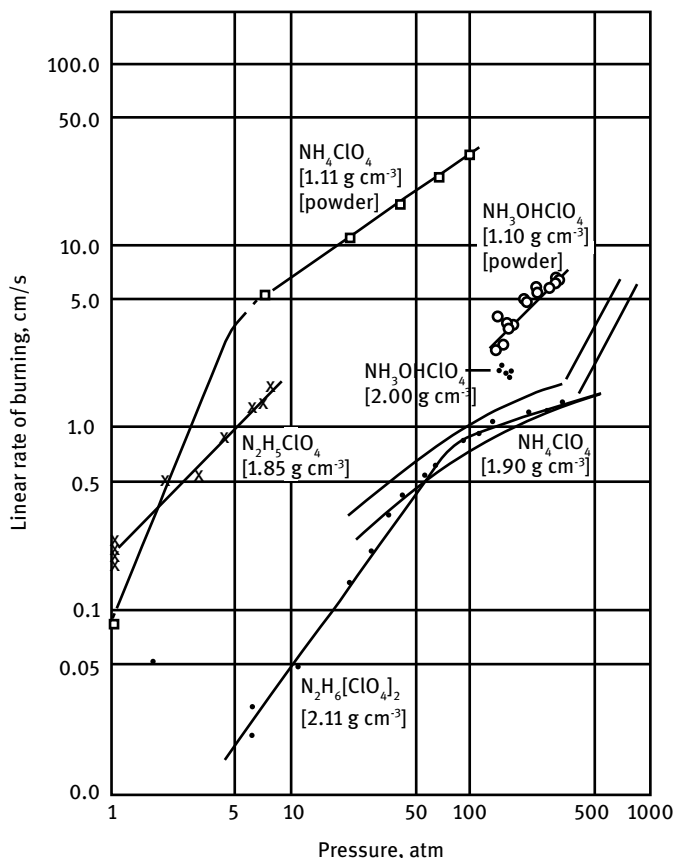


Figure 35: Linear strand burning rates of AP and other perchlorates. (Reproduced and modified from [7].)

In powder form at 1.11 g/cm^3 (top trace, solid line), AP burns much faster and erratically extends to lower pressures (dashed line). However, compressed AP pellets at 1.90 g/cm^3 (the range bracketed by two parallel dashed lines) burns much slower and does not burn at lower pressures. Hydrazinium perchlorates are in between the two AP extremes and burn at lower pressures. The data set for hydroxylammonium perchlorate powder was only for a narrow pressure range but seems to be linear.

5.3.2 Effects of Particle Size on Linear Strand Burning Rates of AP Pressed Pellets

Improved reproducibility of burning rate data was achieved by conducting all tests at 333 K (60 °C) [795]. Up to 7.57 MPa (75 atm), the burning rate agreed well with a linear $r=f(p)$ relationship but the pressure exponents ranged from 0.2 to 1.2. The burning rate increased with an increase in the size of the particles (in the range from 250 to 315 μm), leveling off in the range of around 315–400 μm and converging at high pressures for all sizes. The pressure characterizing the lower pressure limit of stable combustion decreased with increasing particles size. The linear burning rate increased with an increase in density. The temperature coefficient of the burning rate

$$\sigma_p = \left(\frac{\partial \ln r}{\partial T} \right)_p = \frac{1}{r} \left(\frac{\partial r}{\partial T} \right)_p$$

decreased with an increase in pressure and size of the particles and showed a tendency to level off. The limiting pressure of combustion decreased with an increase in temperature. The smaller the size of the particles in the pellet the more strongly it decreased. It was suggested that all these results could be explained on the basis of an exothermic reaction in the condensed phase. However, the fact that the burning rate increases with pressure is a strong argument for exothermic reactions taking place in the gas phase.

Strand burning samples prepared by pressing AP with different particle sizes are significantly different. Samples prepared from large crystals (>200 μm) display stable combustion in a fairly wide range of pressures (≈ 20 atm), whereas the burning rate in samples prepared from fine AP particles (≈ 100 μm) drastically decreases with decreasing pressure. Flame stability becomes unstable at pressure ≈ 70 atm or higher (Figure 36).

These specific features are substantially different from the effect of the particle size of this oxidizer on the combustion laws for usual high-temperature composite propellants with a fuel. They can be caused by problems associated with topochemical features of thermal conversion of AP. It was found that combustion failure occurs if the total thermal effect of the surface process is negative [740]. A set of equations was derived, the results of which agreed quite well with experimental data on the burning rate and combustion limits of AP with different particle sizes.

Pure AP does not maintain burning at pressures below 2.03 MPa (20 atm). The combustion of AP and AN was studied at atmospheric and sub-atmospheric pressures by increasing initial sample temperature and by adding small amounts of fuels [797]. Measurements were conducted in which the gaseous reaction zone and the burning surface of a propellant sample was photographed as the strand was raised to keep the flame front at the same level. The effects of the oxidizer particle diameter on decomposition and burning rates were investigated by using propellants containing fine oxidizer particles and propellants containing coarse particles. It was found that the diameter of AP particles influenced the decomposition rate more than that of AN particles. Both the decomposition and burning rates were increased when the AP particle diameter was decreased (see [66, 798] also).

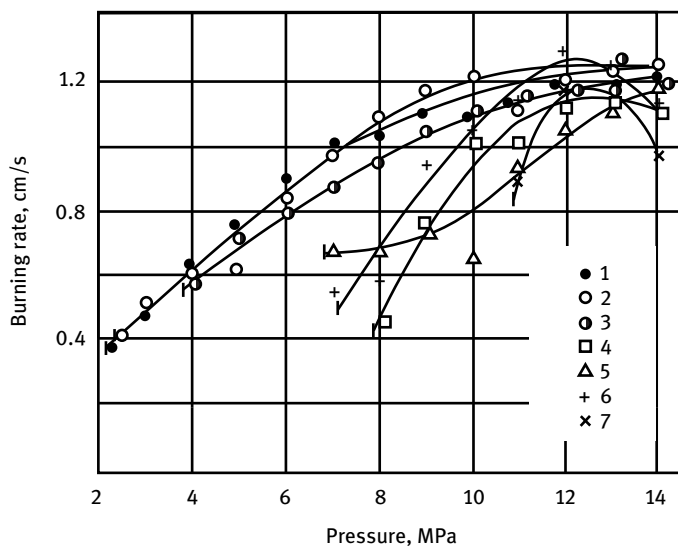


Figure 36: Experimental dependence of AP burning rate on pressure and particle diameter d . (Republished and modified from [740], with the permission of © 2010 Springer Nature BV; permission conveyed through Copyright Clearance Center, Inc.)

Legend: Particle diameter d = 315–400 (1), 250–315 (2), 260–250 (3), 100–160 (4), 63–100 (5), 50–63 (6), and <50 μm (7)

5.4 Single Crystal Linear Burning Rates

Burning rates can be measured more reproducibly with single crystals than with pressed grains. Growing large high-quality single crystals of AP from solution is difficult because it requires pure solutions and precise control of supersaturation [799]. Two methods were evaluated for growing large single crystals of AP, the main difference being in the technique of producing a supersaturated solution. One method induced excess nutrients into a system by slowly cooling a saturated solution in a linear manner by 0.05 °C per day, while the other used a thermal gradient to create a flow of solution from a zone in which it was saturated to a cooler zone in which it became supersaturated.

So far, very few AP burning studies have been done using cultured single crystals. The burning rate may depend on the crystallographic direction of the faces of a crystal. This effect depends on the presence or absence of a melt layer on the surface. One would not expect such a dependency for AN, which melts below the flame front. However, with AP, such a dependency may be measurable. Needle-shaped single crystals were grown from an aqueous solution at 310 K (37 °C) to a length of 8 cm and 0.5 to 0.8 cm wide perpendicular to the c -axis [800]. The crystals contained visible inclusions of saturated solution which could not be removed by week-long drying

under vacuum. While it was easy to prepare specimens for burning along the long c -axis, samples perpendicular to c could only be prepared by sawing a needle into short sections and stacking them up and cementing them by surrounding glue. Since the a and b -axis dimensions are similar, one would not expect much difference in the burning rate between a and b . The burning rate at 4.13 MPa (40.9 atm = 600 psia) in the direction perpendicular to the 110 plane was 0.49 ± 0.06 cm/s (avg. of 7 runs) and the burning rate along the c -axis was 0.43 ± 0.04 cm/s (avg. of two runs). Within the accuracy of this test, there was no measurable difference in the burning rate in the different directions. Single crystal burning rates were below those of compressed powder AP pellets.

The deflagration of AP was studied using cleaved sections of large single crystals grown from a water solution [361]. In addition to the preliminary study of the decomposition of single-crystal sections at the relatively low temperature of 483 K (210 °C), detailed photographic observations were made of burning rate and combustion zone characteristics of samples deflagrating in nitrogen atmospheres at pressures from 1.92 to 14.1 Mpa (19 to 140 atm). Burning rates were higher than those obtained by other investigators using pressed granular AP. The LPDL was slightly lower than that reported for pressed material. Burning rates normal to the m face (210) and c face (001) were the same. The burning surface, when looking at quenched specimens, exhibited a pressure-dependent texture quality consisting of ridges, troughs, and craters with heights in the order of 20 μ m. The surface pattern remained relatively constant for burning distances of 103 μ m. Between 1.92 and 4.04 Mpa (19 and 40 atm) the quenched samples had an array of craters that were ~ 150 μ m in diameter with hollow bubbles around the rim. The discovery of trapped bubbles provided convincing evidence of the presence of a **melt layer** on the surface, at least for operating pressures up to 6.06 Mpa (60 atm). At higher pressures, the surface became flatter and the bubbles were smaller. A slightly altered subsurface layer, roughly 15 μ m thick (which was apparently due to crystallographic phase change) was observed in quenched samples. Crystals heated isothermally for several hours at 483 K (210 °C) (without igniting) turned optically opaque, as reported previously. The results imply that even with the high temperatures and high heating rates present in deflagration waves, the decomposition reactions remain slow enough so that a molten state is reached on the surface, with no conspicuous subsurface decomposition of the solid phase at temperatures up to roughly 773 K (500 °C). The presence of contaminants would cause low-melting eutectics on the surface. Similar experiments were made with crystals doped with KMnO_4 or KClO_4 . However, direct observation of the burning surface of AP-based propellants (not just plain AP crystals) with a telescopic microscope seemed to indicate that it was “dry” [801].

It is difficult to measure the temperature on the surface of deflagrating AP crystals, but one can calculate the temperature from measurements of the orthorhombic to cubic polymorphic phase changes taking place as the crystal heats up. The phase change

occurs at exactly 516 K (243 °C). The crystal becomes opaque where the phase change has taken place. Quenching a burning crystal and examining it under the microscope reveals the depth to which the phase change has taken place. Large single crystals of AP have been systematically burned and quenched by rapid depressurization at various pressures from 2.06 to 6.88 MPa (20.4 to 68.12 atm = 300 to 1000 psia). Microscopic measurements of the quenched crystals have been made utilizing polarized light to accentuate the layer of material which undergoes the crystallographic phase transition. It was found that the thickness of this layer is inversely proportional to the linear burning rate of the crystals. Calculations based on heat conduction and energy release indicate that the surface temperature remains constant over a wide range of pressures and the melt layer is at about 833 K (560 °C) [802, 803]. Other thermocouple measurements produced very low surface temperatures of 683 K (410 °C) at 5.05 MPa (50 atm) and 593 K (320 °C) at 10.1 MPa (100 atm). Allowances were made for the variation of thermal properties (heat capacity, thermal conductivity, thermal diffusivity) with temperature. The solid surface temperature in the absence of fuels was virtually independent of the burning rate.

Burning rates and ignition delays of single crystals of AP were measured over a range of pressures between 4.04 and 14.14 MPa (40–140 atm) at 298 K [804]. The single crystal AP burning rates were compared to those of polycrystalline pellets made from “as received” and recrystallized AP. Single crystals burned at a rate that was 25% faster than that of pressed pellets.

The burning rates of AP in various densities, ranging from single crystals to low bulk powders, were measured using high-speed cinematography in a windowed high-pressure bomb under nitrogen [805, 806]. Single crystals were grown from saturated water solutions by gradually lowering the temperature using a programmed thermostat that was accurate to within $\pm 0.001^\circ\text{C}$. The dried single crystals were examined using electrical conductivity and UV absorption measurements and were found to be of high purity. Single crystals were cleaved along natural face boundaries to prepare wafer-like samples for combustion. The crystal dimensions for combustion samples were $5 \times 5 \times 2$ mm ($0.2 \times 0.2 \times 0.08$ in.) At pressures of 6.19 and 10.3 MPa (61.3 and 102 atm = 900 and 1500 psi), burning rates were 0.8 and 1.05 cm/s (0.314 and 0.415 in./s). These data were in excellent agreement with previously published results obtained by Hightower and Price [361]. The crystals were mostly perfect with a few internal voids and cracks. There were enough clear portions in each crystal, however, to get the perfect crystal burning rate. The interpolated burning rate for combustion at 6.88 MPa (68.1 atm = 1000 psia) is 0.84 cm/s (0.33 in./s). Visual examination of the burning surface showed that the product gases are transparent near the surface but, within less than a millimeter, they become a dense white cloud due to product condensation.

In later studies [794], the crystals were cleaved into 1-mm thick slabs. The self-deflagration behavior of single crystals of pure AP can be divided into four

phenomenological regimes that are apparent when the data is entered into a graph and examined. Regime I is the portion of the curve between 2.06 MPa (300 psia) and approximately 5.50 MPa (800 psia), at which the curve has an equation of the form $r_b = Cp^n$ with a burning rate exponent of approximately 0.77. The portion of the curve between 5.50 and 13.76 MPa (800 and 2000 psia), at which the slope is positive but decreasing, defines Regime II. Regime III is the portion that has a negative slope in the pressure range between 13.76 and 27.52 MPa (2000 and 4000 psia). Above 27.5 MPa (4000 psia) is the domain of Regime IV. Burning rate measurements were taken at pressures between 2.06 and 42.66 MPa (300 and 6200 psia) and represented data included: (1) deflagration rates as a function of pressure for the AP crystals, (2) combustion characteristics as seen using high-speed cinephotography, and (3) surface and subsurface characteristics of quenched samples as observed under the SEM.

It was proposed that exothermic condensed-phase reactions occurring in a liquid melt layer at the surface of AP, coupled with exothermic gas-phase reactions, are responsible for the steady-state deflagration of AP in the pressure regime between 2.02 and 10.1 MPa (20 to 100 atm) [807–809].

The deflagration behavior of pure single crystals of AP can be divided into four phenomenological regimes. This is based on experimental data which includes the deflagration rate as a function of pressure for the AP crystals, the combustion characteristics as seen using high-speed cinemicrophotography, and the surface and subsurface characteristics of quenched samples as observed under the SEM. From these data, the energy transfer mechanism for each regime can be inferred. Pure AP doped with 0.05% K^+ produce burning rates very similar to those reported by others who were using AP of dubious purity [810].

The strand burning rates of AP were compared to those of ADN, RDX, HMX, CL20 (=HNIW), and HNF [811]. AP samples used for this study included large high-purity single crystals as well as pressed pellets. The AP single crystals were cleaved to approximately $1\text{ cm} \times 0.5\text{ cm} \times 0.2\text{ mm}$ size samples. Pellets from various powders of AP were pressed at internal die pressures of 335 MPa with a dwell time of about 30 minutes. The densities of the resulting pellets were 99.2–99.4% of the theoretical maximum density. There was no difference in burning rates between the pressed pellets and single crystals as long as high-purity AP was used in the pellets. Only data for ultrapure AP are presented here.

The AP self-deflagration rate data at three initial temperatures (298, 373, and 423 K) over the pressure range of 2.16–10.3 MPa are shown in Figure 37. One should note that the spacing between the burning rate curves at different temperatures is not uniform. The increase in burning rate, and thus temperature sensitivity, becomes greater with increasing temperature.

In these experiments, the LPDL for pure AP at ambient initial temperature was approximately 2 MPa.

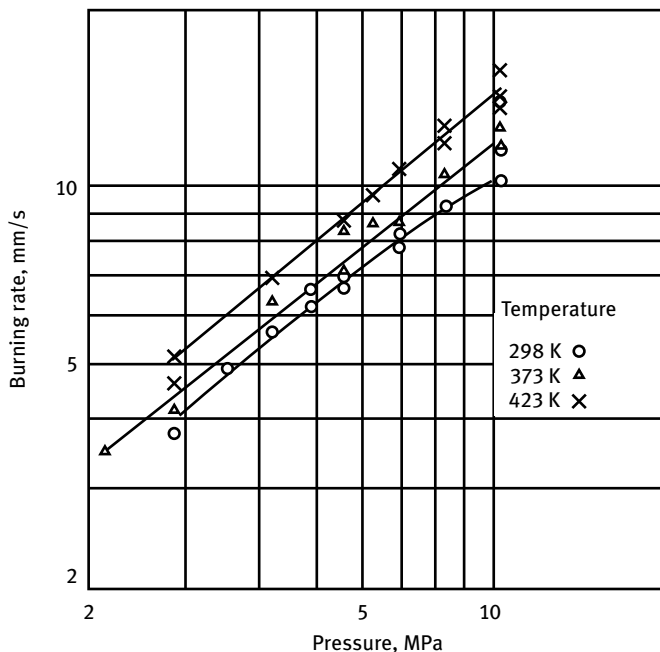


Figure 37: Strand burning rates of AP pellets at three different temperatures. (Republished and modified from [811], with the permission of the American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center, Inc.)

5.5 Lower Pressure Limits for the Deflagration of Ammonium Perchlorate

Solid propellants, or oxidizers by themselves, have a lower pressure limit below which stable burning is not sustained. These limits have been determined for AP by itself (no fuel or binder added), and also with or without doping the AP with various catalytic or inhibiting additives. The lower pressure limit is also dependent on the temperature of the sample prior to ignition but is not very dependent on the strand geometry. The lower limit is encountered due to self-cooling. This is mainly due to a loss of radiant heat from the burning surface of the solid, per unit mass burned, which increased as the pressure was lowered. A critical value of the activation energy exists. Below this value the rate of heat generation is less sensitive to surface temperature than is the rate of heat loss. A solid monopropellant with a sufficiently large heat release rate should theoretically be able to burn down to zero pressure.

Table 20 is a summary of experimental studies of the lower pressure limits for AP deflagration in strand burners.

The decomposition flame of AP has been studied by measuring burning rates, flame temperatures, and perchlorate surface temperatures [814]. At pressures below

Table 20: Results of experimental studies of the lower pressure limits for AP deflagration in strand burners.

Pressed strand cross section mm	AP condition	Density g/cm ³	Particle size μm	Lower pressure limit		References
				MPa	atm	
5 × 5	Recrystallized			7.09	70	[812]
4 × 4	Reagent grade 0.25% Pt black powder		As received	2.23 12.1	22 120	[813]
5 × 5	Recrystallized Preheated to produce a final flame temperature of 1203 K (930°C)		76–104	10.1 ~0.1	100 ~1	[814]
8		1.51	200–350	5.37	53	[798]
8		1.67	3–7	4.86	48	
8		1.92	55–95	3.85	38	
12.7		1.92	200	3.34	33	
8			300	11.65	115	
8			1000	6.69	66	
8				3.85	38	
8				3.85	38	
8				2.43	24	
5	Analytical grade	1.93	As received	5.07	50	[815]
7		1.93		3.04	30	
15 × 5 × 2, 15 × 5 × 3, 15 × 5 × 5 mm and also in the form of cylinders diameter = 13 and 25 mm	Not specified	1.50 1.92	<19 <80 200–315 >1000	3.24 2.23	32 22	[816]

that at which deflagration of pure AP is self-sustaining, combustion was maintained via minor additions of fuels or by preheating the salt. Most people developing models for AP combustion assumed a smooth phase boundary between the condensed phase and the gas phase. However, it was observed that particles get ejected into the reaction zone, a process which would substantially increase the burning surface area. The reaction that drives the particle ejection may be the LTD of AP, which usually stops after 30% weight loss has taken place. Particles impacted and were collected on cold witness plates inserted 0.5 to 1 cm above the burning surface. This observation may explain the dependence of burning rate on particle size.

Tests with pellets pressed to different densities between 1.51 and 1.92 g/cm³ revealed that the lower pressure limit decreases with increasing density. On the other hand, slightly compacted samples of different particle sizes revealed that the lower pressure limit drops with increasing particle size. It is thought that the flame front can better penetrate between the coarser particles. Water content up to 0.7% had little effect on the lower limit of burning but pressed pellets with 2% H₂O could not be ignited even at pressures up to 15.15 MPa (150 atm) [798].

The lower pressure limit for AP strand burning is quite sensitive on the initial temperature of the pellets. The lower pressure limit of AP single crystals has been determined by establishing a known temperature gradient in the crystal and then igniting it from its warmer end. Deflagration then would only propagate to a certain depth into the pellet and extinguish at a known temperature [817–819]. The pressure was adjusted so that the flame would not propagate through the entire solid and the length of the sample remaining unburned determined the limiting solid temperature corresponding to the set pressure. The AP single crystal deflagration rates were measured using high-speed motion photography and were essentially the same in helium and nitrogen ambient atmospheres. In direct contrast to the catalytic effect of KMnO₄ on AP thermal decomposition, a preliminary study revealed that 0.4–2.0 mol-% KMnO₄ isomorphously substituted into the AP crystal lattice prevented deflagration from occurring [820].

Quenching of AP combustion is not just an academic exercise. The lower pressure limit of AP burning has practical significance for thrust termination of missiles that need to impart less than the full motor total impulse. Applying laminar flame theory to an adiabatic, steady-state one-dimensional AP single crystal surface with Arrhenius temperature dependence for the condensed phase gasification and the gas phase reactions allows one to predict a LPDL only when the activation energy of the overall surface reaction is less than half the activation energy of the gas phase reaction [821]. Applying this model to AP, the extinguishment limit can be predicted if one assumes that the activation energy of the condensed phase gasification is 41.8 kJ/mol (10 kcal/mol) and the activation energy of the gas phase reaction is 125 kJ/mol (30 kcal/mol).

The lower pressure limit of pressed AP pellets may be quite dependent on the method used for mounting the pellets. Two different mounting techniques were used in an investigation on the deflagration of pressed AP [822]: In the first, tubular sam-

ples were cemented into the burner with epoxy resin which inhibited all of the grain surface except the inner perforation. In the second, the grains (either tubular or disk shape) were press-fitted into metal sleeves that were subsequently fitted into the motors. It was noted that whatever little combustion occurred at the interface between the AP and the epoxy mount was sufficient to sustain combustion down to 303 kPa (3 atm) while the metal-mounted ones extinguished at 2.32 MPa (23 atm).

The lower pressure limit of pressed AP pellets increased with the bulk density of the pellets, burning surface area, and the initial sample temperature [816]. It decreased when coarser AP powder was used to make the pellets. The lower pressure limit was typically reached when the burning rate dropped to 0.17–0.19 cm/s, regardless of the other variables involved. The addition of 5–30% CuO lowered the lower pressure limit from 2.02 to 0.02 MPa (20 to 0.2 atm). Nir also studied the combustion of AP/Al and AP/B mixtures [816]. In summary, it was concluded that:

1. The burning rate of AP does not approach zero as the pressure limit is approached. For samples with different physical parameters, the pressure deflagration limit is obtained approximately for the same mass burning rate (0.17–0.19 cm/s).
2. The LPDL decreases with increasing the strand density, the burning surface area, and the sample initial temperature (see Figure 38 for two different burning surface areas: 10 and 133 mm²).
3. The internal structure of an AP pellet compressed for several hours is different from that of a pellet compressed briefly. In the first case the structure is more uniform and homogeneous and the volume of the voids is reduced. Heat losses due to voids are then less important and AP deflagration can be maintained down to near 2.02 MPa (20 atm).
4. AP particle size determines the LPDL. It decreases as the particle size increases. When the mean initial size of AP particles exceeds 1 mm, the pressure limit of the strand is slightly higher than that of a large single crystal.

The pressure limit is reduced with increasing strand density. The solid lines in Figure 38 is the result of applying the equation

$$P_L = \frac{K}{e^{\alpha(T_0 - T^*)}}$$

where P_L is the lower pressure limit, K is a constant, $\alpha = 0.003^\circ\text{C}^{-1}$ is the temperature coefficient, $\alpha = 2\beta$, T_0 is the initial sample temperature, T^* is a reference temperature, and the particle size ϕ is 1000 μm . It can be seen that the LPDL, P_L , changes linearly with the strand density, ρ . At 20 °C, for $\rho = 1.50 \text{ g/cm}^3$, one finds $P_L = 32 \text{ atm}$ whereas with a higher density of 1.92 g/cm^3 , the pressure limit is only 22 atm. This value is in excellent agreement with that obtained by other authors.

The addition of 2–5% of copper, cobalt, or manganese compounds as catalysts lowered the lower pressure limit all the way down to atmospheric pressure [823]. The following efficiency series for 5% additives of metal oxides for AP combustion at atmo-

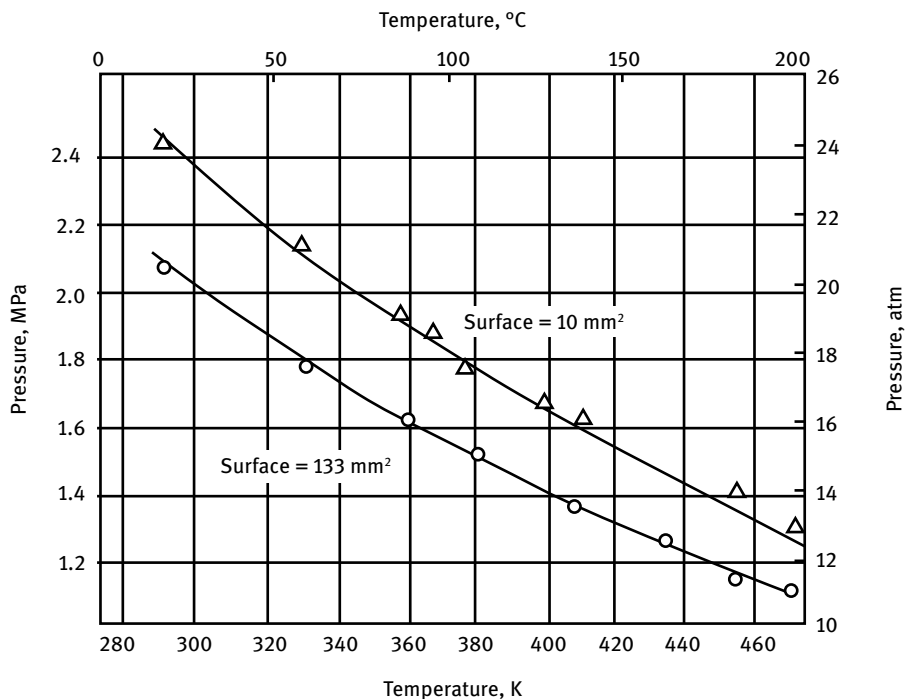


Figure 38: The lower deflagration limit of AP as a function of initial temperature. (Reprinted and modified from [816], © 1973, with permission from Elsevier; permission conveyed through RightsLink.)

spheric pressure was reported as: $\text{Cu}_2\text{O} > \text{CuO} > \text{MnO}_2$ at $T_0 = 20^\circ\text{C}$ and $\text{Cu}_2\text{O} > \text{CuO} > \text{MnO}_2 > \text{Co}_2\text{O}_3 > \text{ZnO}$ at $T_0 = 100^\circ\text{C}$. At the same time, Fe_2O_3 , NiO , Ni_2O_3 , Cr_2O_3 , CdO or MgO did not ensure stable combustion under these conditions [824].

Pure AP single crystals could not sustain a flame at pressures lower than about 2.06 MPa (300 psia) [794, 825]. The AP burning behavior could be readily divided into four pressure range regions. In pressure region I between about 2.4 and 5.5 MPa (350 and 800 psi), a steady and positive burn rate pressure exponent was exhibited. Pressure region II in the 5.5 to 13.8 MPa (800 to 2000 psi) range had a positive burn rate pressure exponent that gradually declined. Near 13.8 MPa (2000 psi) an abrupt change to a strongly negative burn rate pressure exponent set in that had a lessening negative exponent until bottoming out near 27.6 MPa (4000 psi) (Region III). At about 27.6 MPa (4000 psi) in pressure region IV the burn rate pressure exponent reversed this trend at increasing pressure and reached positive values, which increased to exceed exponent values well above 1.0. The high exponent trend continued up the test limit of about 42.7 MPa (6200 psi). Cleaved AP crystals burned fairly evenly at pressures near

65.9 MPa (1000 psi). However, AP crystals burned quite unevenly in the 13.8 to 27.6 MPa (2000 to 4000 psi) Region III.

The lower pressure limits of AP and KClO_4 /AP mixtures with organic fuels with and without catalysts were determined in a closed bomb [826]. Predicting the lower pressure limit for AP strand burning using theoretical models has been attempted, however, only with limited success (see Section 5.17).

A unified theory was proposed to explain the various aspects of the combustion of AP, which has been separately treated up to now via burning rate, LPDL, and ignition using a single framework model [827]. The model, on the basis of which the theory was formulated, incorporated the experimentally observed micro-structure of the burning surface of AP, which provides an intermediate heat sink in an overall adiabatic system. The theory explained the existence of the LPDL of AP, which has eluded previous attempts at theoretical explanation. The model accurately predicted the variation of the limiting pressure with an initial solid temperature and also the nearly constant burning rate at the LPDL, regardless of the initial solid temperature. A comparison of the theory and experiments for the LPDL and burning rate of AP indicated that the same reaction mechanisms prevail during deflagration and near the pressure limit and that the extinction is due to heat loss rather than due to a change in reaction mechanism. The rates of the gas-phase reactions were found to be well-represented by second-order overall kinetics.

The type of insulation applied to inhibit burning along the sides of the strands and the modes of heat loss play a critical role in AP combustion. They also determine the LPDL of AP itself and the steady-state burn rate of AP at higher pressures. The common use of silica-filled poly(dimethylsiloxane) grease to prevent heat loss from the sides of the pellet and the ignition methodology influence the strand burning results. Using a slow depressurization method, wherein the LPDL was independent of ignition transients, the LPDL of pure AP was found to be 1.4 MPa (14 bar) [828]. The burn rate of well-insulated pure AP at 7 MPa (70 bar) under near adiabatic conditions was found to be 10.66 mm/s, which was much faster than burn rate data reported in the literature. The pressure exponent for this case was 0.71. This result completely changed the current understanding of AP combustion and called for a new set of parameters to be developed to predict the results obtained with insulating silica-filled grease on the sides of the strands. Using the same set of parameters, along with a heat loss model for the case when there was no silica grease applied, the predictions were in reasonable agreement with the experimental data reported in the literature without any silica-filled poly(dimethylsiloxane) grease on the sides of the AP pellet.

5.6 Upper Pressure Limits for the Deflagration of Ammonium Perchlorate

Some investigators (Levy and Friedman [813]) have observed an upper pressure limit for the deflagration of AP near 25.2 MPa (250 atm). In an attempt to explain this, re-

searchers have pointed to changes in the heat transfer mechanisms between the flame front and the subliming surface but others have not confirmed this observation. The existence of an upper pressure limit has been questioned by other investigators. Differences in upper limit measurement results have been blamed on different methods of containment used by several investigators. For instance, some experimenters pressed the AP powder into PMMA tubes.

It has been suggested that the upper pressure limit is due to small sample diameters. In experiments by Glazkova [815], the 5-mm diameter strand had an upper pressure limit of 27.3 MPa (270 atm). However, with 7-mm diameter strands, no upper limit was observed within the pressure capability of the apparatus (34.3 MPa = 340 atm).

The deflagration characteristics of pure AP strands have been investigated by means of a closed-bomb strand burning technique at pressures between 6.88 to 158 MPa (68.1 to 1566 atm = 1000 to 23000 psi) [829]. The data was in general agreement with vented-chamber AP burning-rate data obtained by other investigators at pressures between 6.88 to 34.4 MPa (68.1 to 340 atm = 1000 to 5000 psi). There are two regimes with a transition around 30.3 MPa (300 atm) with pressure exponents of 0.25 and 1.75. At pressures above 34.4 MPa (5000 psi) (the pressure limit of previously reported studies), a marked increase in pressure dependence of the linear burning rate occurred. It is postulated that the observed increase in burning rate results from an increased burning surface area, i.e., surface break-up, under the action of the very high pressures existing in the closed bomb, forming new cracks and pores or by enlarging existing cracks and pores. A geometrical model was proposed which considered the accelerated burning process as a development of micro-cracks that form into conically-shaped burning surfaces, the area of which depends upon the pressure. The model is in good agreement with the experimental burning-rate data and with the pressure versus time data for individual burning-rate experiments at pressures above 34.4 MPa (5000 psi). The steepening of the temperature gradient with increasing pressure causes thermal stresses in the crystals.

5.7 Isotope Effects on the Burning Rate of Ammonium Perchlorate

In a study of deflagration of NH_4ClO_4 and ND_4ClO_4 , it was noted that visual changes always began in the bulk of the crystals and not on the surface [483]. In both cases decomposition stopped when the degree of conversion was about 30%, at which point porous products formed which underwent the same phase transition as the parent single crystals. Thermal decomposition of the deuterated sample was slower, the volume fraction of pores appeared to be lower, and the sample had a small quantity of "snow" on the surface. These isotope effects were blamed on proton transfers at the intersections of dislocations in the bulk of the crystals. The rate would be different for the movement of H^+ as opposed to D^+ ions.

5.8 Temperature Profiles in Burning Ammonium Perchlorate

The current section on temperature profiles in burning AP deals with phenomena very similar to those discussed in a later section based on the surface temperature of burning AP. There is some overlap between these two sections and we may very well have combined the two to create one section, however that would have created an unwieldy large section.

The temperature distribution in burning AP was studied with the aid of thin thermocouples [830–832]. AP was compressed into 7 mm pellets with a bulk density of 1.93–1.94 g/cm³ and ignited in a constant pressure bomb at 3.04–35.4 MPa (30–350 atm) in a nitrogen atmosphere. Above 15.2 MPa (150 atm), a regular temperature oscillation in the gaseous phase with a period of about 50 μ s and an amplitude of up to 773 K (500 °C) was noted. The pressure range of 16.2–35.4 MPa (160–350 atm) was called the region of unstable burning. In the region of stable burning (4.05–15.2 MPa = 40–150 atm), an increase in the total heat emission in the gaseous phase was observed, whereas the heat emission in the condensed phase decreased with an increase in pressure. At 15.2 MPa (150 atm), the heat emission was 80 cal/g, which is a critical lower limit. This was the threshold separating the regions of stable and unstable burning. Below 80 cal/g, burning was quenched. It was assumed that during burning catalysis of the decomposition of AP took place on the surface. This was caused by reaction products and active centers passing from the flame zone to the surface of the condensed phase. This assumption probably explains the mechanism by which the gaseous phase controls the decomposition of the condensed phase. The maximum burning temperature first increased with pressure, passed through a maximum value at 1333 K (1060 °C) and 10.1–15.2 MPa (100–150 atm), and then decreased, although the pressure continued to rise. The decrease of burning rate with increasing pressure is unusual and has been explained as a catalytic effect exerted by the decomposition products diffusing from the flame front to the burning surface. The reaction takes place in the gas phase and not in the condensed phase (see [833, 834] also).

The emission spectroscopy of burning AP can provide information about the reacting species in the flame front [835, 836].

Measurements of temperatures and the concentration profiles of reacting components in an AP flame provide at least some of the data needed to verify or dispute previously unproven combustion models established by various other investigators [837].

Based on numerous thermocouple-aided experimental studies on the combustion of different energetic oxidizers like AP, IN, or ADN, it has been shown that a salt in the condensed phase can be heated up to its dissociation temperature. In contrast to the gas-phase model, the condensed-phase burning rate model has an energy limitation. In condensed-phase reactions the burning rate increases at the expense of surface temperature increase with pressure. A situation can arise where the heat effect of en-

ergetic material decomposition is no longer sufficient for warming-up the decomposing substance to the surface temperature. This induces an instability of combustion and burning rate oscillations [838, 839].

The surface temperature in the combustion wave of AP, as well as in ADN, HNF, and AN, is controlled by a dissociation process, similar to that postulated for other onium salts [840].

5.9 Effects of Initial Temperature on Ammonium Perchlorate Burning Rates

The dependence of burning rate of solid propellants σ_p is typically expressed by the equation:

$$\sigma_p = \left(\frac{\partial \ln r}{\partial T} \right)_p = \frac{1}{r} \left(\frac{\partial r}{\partial T} \right)_p$$

This same equation applies to the burning of AP by itself in the absence of combustibles, and with or without the addition of catalysts.

The effect of initial temperatures on the rate AP combustion at initial temperatures in the range of 297–423 K (20–150 °C) was investigated at pressures up to 35.35 MPa (350 atm) [841, 842]. The purpose of this work was to explain the earlier observed anomalies of combustion characteristics and to explore the possibility of eliminating the upper explosion limit and of increasing combustion stability by increasing initial temperature. The burning rate of compacted 7 mm diameter samples increased, the lower explosion limit decreased, and the region of stable combustion was extended when the initial temperature was increased. Unstable combustion of a different kind appeared at an initial temperature of 448 K (175 °C). The minimum temperature coefficient of the burning rate coincided with the maximum burning rate at 15.15 MPa (150 atm) in the region of stable combustion. Heat evolution in the reaction zone of the solid phase and conductive heat transfer from the gas phase into the solid phase do not depend on the initial temperature and actually decrease with increasing pressure. The observed anomalies were believed to be the result of combustion inhibition caused by water which was accumulated in the reaction zone.

Uncoated AP in the shape of 7 mm pellets compressed to crystal density was burned at a constant pressure. The initial temperatures ranged between 293–423 K (20–150 °C) and pressures were up to 35.5 MPa (350 atm) [843]. As expected, an increased initial temperature increased the combustion velocity, lowered the lower pressure limit, and raised the upper limit. The critical pressure, below which the burning rate decreases and deflagration become pulsating, rose from 15.2 MPa (150 atm) at an initial temperature of 293 K = 20 °C to 20.27 MPa (200 atm) at an initial temperature of 323 K = 50 °C and to 25.33 MPa (250 atm) at an initial temperature of 373 K = 100 °C.

The temperature coefficient β of strand burning rates of easily gasified propellants is expressed by

$$\beta = \partial \frac{\ln r}{\partial T_0} = \frac{E_a}{2RT_c}$$

where r is the burning rate, E_a is the activation energy of the gas phase reaction and T_c is the combustion temperature. The effect of pressure, p , on the temperature coefficient β of the combustion rate of the condensed energetic materials were analyzed and compared to experimental data obtained for AP [844]. The theory demonstrated that a low p , β is markedly dependent on the initial temperature, T_0 , and only slightly dependent on the activation energy E_a of the decomposition reaction and the activation energy of evaporation E_{vk} . At high pressures, the increase in β is determined mainly by E_a and E_{vk} . While at low pressures, β increases with T_0 , at high pressures, β decreases with increasing T_0 . The theory was confirmed by published experimental data on strand burning of AP.

5.10 Counterflow Diffusion Flames Supported by Ammonium Perchlorate Decomposition

This technique for studying the decomposition processes on the surface of AP crystals or AP slabs is similar to a sandwich burner, except that the fuel is not in solid form but enters the reactor as gas and impinges on the solid oxidizer in a direction opposite to the flow of oxidant. One can thus vary the oxidizer : fuel ratio during the experiment by throttling the fuel flow as in an inverse hybrid rocket engine. A two-dimensional set of governing equations for modeling the structure of AP counterflow diffusion flames (in which the products of AP combustion are flowing against a methane fuel stream) was used to formulate a detailed transport, finite-rate chemistry system for the temperature, velocity, and species mass fractions of the combined flame system [845–847]. The two-dimensional problem can be reduced to a one-dimensional boundary value problem along the stagnation point streamline through the introduction of a similarity transformation. The results of this model were compared with a series of experimental measurements in which the temperature was measured with radiation-corrected thermocouples and the OH rotational population distribution. Several important chemical species, including OH, CN, NH, NO, CH₄, and O₂ were measured with planar laser-induced fluorescence (PLIF), emission spectroscopy, and Raman spectroscopy. Both the model and the measurements revealed a multi-stage structure within the counterflow system, comprised of an AP decomposition flame (above and close to the AP surface), followed by an AP-products/methane diffusion flame. Both flame zones lie to the AP side of the stagnation plane.

This concept is similar to sandwiching a slab of AP between two layers of combustible solid fuels or sandwiching a layer of solid fuel between two blocks of oxi-

dizer. In either case, the burning rate is influenced by mass transfer and its diffusion limitations.

Other pyrolysis techniques involve convective heating using an impinging jet from a gas rocket and also surface-temperature measurement using IR radiometry [133]. An apparent activation energy of 92 kJ/mol (22 kcal/mol) was reported for AP with surface temperatures between 698 and 848 K (425 and 575 °C) and with regression rates between 0.002 and 0.04 cm/s. The overall pyrolysis mechanism was proposed to be a rate-controlled dissociative sublimation. The technique used allows for consideration of partial pressures and heat fluxes at the pyrolyzing surface in addition to measurements of regression rates and surface temperatures during pyrolysis.

The burning of AP in composite solid propellants was simulated in a counterflow burner in which the heat feedback from the hot, inert, opposing, and stagnating flow stabilized the AP monopropellant flame above a pressed AP pellet [848]. The heat feedback mechanism was investigated using thermocouples and a heat-flux meter. The regression rate data were analyzed using activation-energy asymptotics and the overall activation energy of the AP flame was found to be 59.8 kJ/mol (14.3 kcal/mol). The typical burning structure of AP at 101 kPa (1 atm) consisted of a 5000- μ m thick thermal gradient layer in the solid phase and a 500- μ m thick AP flame in the gas phase. Temperature measurements using fine wire thermocouples showed the surface and flame temperatures to be 810 and 1220 K, respectively.

Although AP does not normally self-deflagrate at pressures below 1.376 to 5.504 MPa (200 to 800 psia), it was possible to stabilize a counterflow diffusion flame above a deflagrating AP pellet even at 1 atm. A nearly perfect planar flame structure could be imaged, measured, and compared to computational model predictions [849–851] (Figure 39). Methane or ethylene was used as fuels. Fuel mixtures can be selected to simulate the decomposition products of various binders, or a single fuel can be used if one wants to simplify the kinetics and compare experimental and theoretical results. The fuel exit orifice was 7.7 mm and the AP pellet diameter was 10 mm. Both the fuel orifice and the AP pellet were surrounded by annular nitrogen shrouds (25 mm).

The fuel flow rate can be controlled using a flow meter and a needle valve, however, the oxidizer flow rate is determined by using the rate of ablation of the AP. The AP regression rate was 0.11 mm/s. The burning AP surface was kept at a constant distance from the fuel orifice by pushing the grain from below into the reactor with a threaded rod drive rotating at variable rpm. Flame temperatures were measured using thermocouples and also spectroscopically via OH rotational planar PLIF. The computational model assumed a laminar counterflow flame stabilized in the vicinity of the stagnation plane. The AP surface temperature was assumed to be 825 K. The model predicted an AP decomposition flame above the AP surface followed by a fuel/AP-products diffusion flame, in agreement with experimental observations.

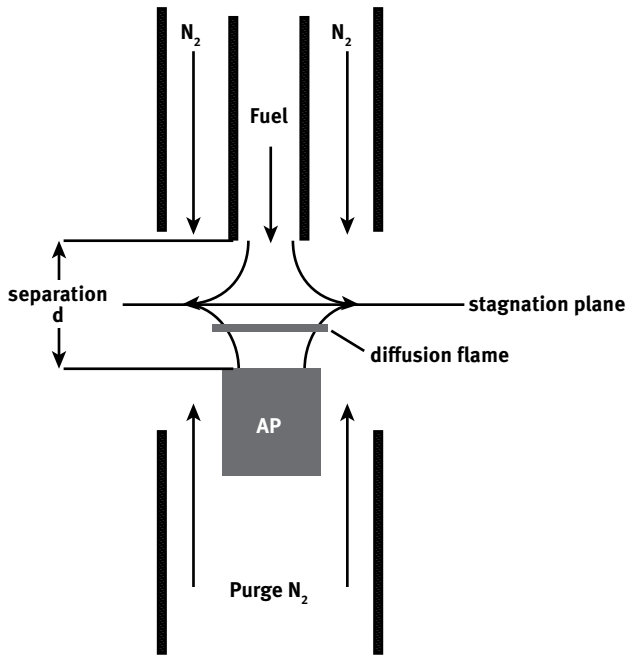


Figure 39: Counterflow burner for AP regression rate studies. (From [850].)

5.11 Concurrent Flow Diffusion Flames Supported by Ammonium Perchlorate Decomposition

Instead of impinging the fuel gas on an AP surface in a direction opposing the flow of reaction products, a flow of combustible gas can be passed through a PAP grain and lit at the surface. In this arrangement, the direction of the incoming gas and the outflowing reaction product is the same. The porous plugs were made from slightly compressed powder which was moistened by moist air and then dried to bond into a coherent cylinder.

If methane is flowing through a PAP grain and ignited, the regression rate of the oxidizer is of the same order of magnitude as that in composite propellant grains [852, 853]. The particle sizes used were 74–105 μm , 149–210 μm , and 297–420 μm . Smaller particles resulted in higher burning rates. The burning rate was linearly dependent on pressure at 25.2 kPa (0.25 atm) and this dependence increased to a fractional power with increasing pressure. It was concluded that the vaporized products were not in thermodynamic equilibrium with the solid, the rate of AP surface regression was not related by an Arrhenius function to the surface temperature, and the final flame zone did not supply the major fraction of the heat conducted back to vaporize the AP. This

heat came mostly from the AP decomposition flame augmented by the back diffusion of a small amount of fuel. The logarithm of the total mass consumption plotted against the reciprocal of the final flame temperature produced a straight line with a slope corresponding to an activation energy of 92 kJ/mol (22 kcal/mol). The porous burner technique might even find an application in hybrid motors where the regression rate can be increased by almost two orders of magnitude.

Instead of bonding the AP particles together by moistening them, others have created PAP grains by using glue made of PMMA in acetone. Burning rates of PAP grains prepared in this manner and perfused by fuel gases were measured at atmospheric pressure [854, 855]. The AP regression rates increased in the order $\text{H}_2 > \text{C}_2\text{H}_2 > \text{C}_2\text{H}_4 > \text{CH}_4$ and occurred near stoichiometric O:F ratios. Except with NH_3 , the maximum rate was achieved only with fuel-lean mixtures.

A variant of the fuel flow through a PAP pellet is the combustion of spherical AP particles suspended on a wire mesh in a flow of combustible gas [856, 857]. Small (6–15 mm diameter) spheres of AP were placed on a wire mesh through which the gas entered the chamber and was then ignited using a hot wire. The sphere burned evenly on all sides. Depending on the fuel, a decomposition flame near the surface and a diffusion flame surrounding the decomposition flame was observed. When ammonia was used as the fuel gas, the sphere was enclosed by concentric flame zones. Results showed that the diffusion flame alone controls the sphere combustion rate. The parameters investigated in that study were the gaseous fuel flow velocity, type of fuel gas, chamber pressure, and the initial AP spherule diameter (with and without the addition of catalysts to the AP prior to its forming into microspheres) (see [858] also).

Most AP combustion studies have been conducted using stagnant or slow flow over the AP solid surface. However, this is now what is happening in an actual rocket motor, where combustion products flow over the burning surface and cause erosive burning. The erosive burning of AP by itself has not been thoroughly examined. The effects of turbulence on the mean reaction rate and on reaction rate correlations (combustion-turbulence interaction) were analytically investigated with applications to the erosive burning of AP [859]. The analysis indicated that regions of both decreased and increased reaction rate and turbulent diffusivity can exist in the flame zone. Further to this, it was found that the decreased reaction rate may account for the decrease burning rate (“negative erosion”) observed for some propellants. The results showed that: (a) although significant changes in reaction rate and turbulent diffusivity profiles are obtained, no appreciably decreased burning rate was predicted for AP using either combustion model; (b) for both normal and erosive burning, the flame height produced by some models is substantially greater than that produced by other models; and (c) as a consequence of the disparate flame heights, a much greater susceptibility of AP to erosive burning can be predicted. The erosive burning response of propellant can be used in determining its relative flame height.

5.12 Sandwich Burning Supported by Ammonium Perchlorate Decomposition

The burning of alternating layers of oxidizer and fuel in a sandwich burner can give valuable information on the mechanism of heterogeneous propellant burning and on the effects of various additives (mostly burning rate catalysts) that could not be obtained by processing the oxidizer and the fuel into a thoroughly mixed propellant grain. The general method of sandwich burning will be discussed in future volumes dealing with solid propellants. That section describes the experimental technique and its analytical interpretation in general, regardless of which oxidizer is used in slab form. The current section describes sandwich-burning experiments specifically with AP.

Catalysts were incorporated into AP oxidizer sandwiches with oxidizer sections laminated between thin layers of CTPB as a binder [860]. Catalysts investigated were copper chromite and Fe_2O_3 . Burning of the sandwiches at 4.23 MPa (600 psig) and 13.86 MPa (2000 psig) was recorded using cinematography at 1600 frames/s and 2:1 magnification. Copper chromite was a more active catalyst than Fe_2O_3 and appeared to more effectively promote AP deflagration, catalyze gas-phase reactions, and promote gas-phase reactions in cracks between the solid fuel and the binder without modifying the pyrolysis mechanism of the binder. Fe_2O_3 produced similar effects but inhibited AP deflagration at 4.23 MPa (600 psig). Eventually, these tests were extended to higher pressures of up to 22.11 MPa (3200 psig) [861].

Combustion experiments of sandwiches made of alternating layers of AP and a matrix of AP particles in a polymeric binder performed over an expanded pressure range from 0.34 to 13.8 MPa (50–2000 psig) resulted in sandwich burning rates with plateaus in the 6.9–13.8 MPa (1000–2000 psig) pressure range (but only for specific lamina thickness) [862]. Lamina thicknesses were varied over a wide range. These plateaus were correlated with similar plateau (mesa) trends in the burning rates of composite propellant formulations with bimodal oxidizer particle size distribution. The dependence of the sandwich burning rates on the matrix lamina thickness and the quenched surface features were examined to explain the plateau burning rate trends. The results indicated that the two-dimensional coupling of heat feedback from the hot near-surface parts of the oxidizer/fuel diffusion flamelets is diminished at higher pressures due to their greater proximity to the burning surface and the corresponding shrinking of their lateral extent. The 2003 publication [862] is an extension of past works in the pressure range of 2.07–6.9 MPa (300–1000 psig), wherein sandwiches with the middle lamina made of (1) pure binder lamina, (2) an uncatalyzed matrix of fine AP and binder, and (3) a fine AP/binder matrix with the addition of a nanoparticle-size iron(III) oxide burning rate catalyst, were tested.

Some AP formulations not only went into a mesa-burning mode but extinguished altogether in the mid-pressure range. The mid-pressure extinction of AP matrices with monomodal particle size distribution and HTPB binder was observed in the pressure range around 2–5 MPa [863]. Quenched surfaces (self-extinguished or intentionally interrupted during burning) of all the three types of samples were analyzed using an

SEM. The burning history of the samples was captured with a high-speed digital camera. The results indicated the prevalence of intermittent burning of the matrixes as the pressure was varied across the boundary between continuous burning and self-extinction (burn/no-burn boundary) of the matrixes.

5.13 Oscillatory Combustion During Ammonium Perchlorate Deflagration

Combustion instability has plagued solid rocket motors since they first came into use. It has been attempted to suppress combustion instability by either adding additives to the propellant or by using proper grain and motor geometry.

AP-based propellants are susceptible to combustion instabilities. Even AP by itself is not an exception to this. In an investigation exploring the contribution of AP deflagration to the amplification of pressure waves during combustion instability, 17 firings were made at pressures ranging from 1 to 60 atm. [822]. Oscillatory combustion was observed only in two of the tests. The occurrence of oscillatory behavior at low frequency may be related to the high-pressure exponent.

There are two regimes of AP burning: a stable regime at 4.04–15.15 MPa (40 to 150 atm) and an unstable regime at 16.16–35.35 MPa (160 to 350 atm). Between 16.16 and 35.35 MPa (160 and 350 atm) temperature oscillations were observed in the gas phase. The oscillations had a period of $\sim 50 \mu\text{s}$ and an amplitude of 500°C while measuring temperature profiles of burning AP pellets and the reaction space above it [831].

The mass burning rate versus pressure curve for unconfined pure AP has a region where the combustion starts pulsating and becomes unstable. Strangely, in the range 16.15 to 25.25 MPa (160–250 atm), the burning rate falls with pressure. However, in the range of 25.25 to 50.5 MPa (250–500 atm), it remains constant. Only above 50.5 MPa (500 atm) does it increase with pressure [864].

5.14 Ammonium Perchlorate Combustion at Very High Pressures

The deflagration rate of pure AP demonstrates an unusual “mesa burning” trend in the 13.8–27.56 MPa (2000–4000 psi) pressure range. This observation has been reported not only for pure single crystals of AP but also for pellets pressed from granular high-purity AP. The mesa burning trend is extremely sensitive to the presence of impurities, as can be shown by burning AP single crystals that were isomorphously doped with known amounts of impurities. The onset of the mesa burning trend shifts to higher pressures at higher initial temperatures of the sample (pressed pellets of AP). The mesa burning rate trend is associated with a transition from steady regression to a rather complex mode of deflagration. This is characterized by the following features: **(1)** macroscopically irregular surface regression, **(2)** locally intermittent flamelets on the same spatial- and timescales as the irregularities in surface regression, and **(3)** an

extraordinarily complex topochemistry on the surface of quenched samples in which locally recessed areas of the overall burning surface consisted of arrays of parallel needles 100–200 μm long and 5 μm across. The exact physicochemical mechanisms involved in this mode of deflagration, the explanation for the mesa burning rate trend, and interpretation of the corresponding surface features were difficult to explain. For this reason, the behavior has been called “anomalous” [865].

The rate of self-deflagration of AP decreases sharply with an increase in pressure between 13.8 and 27.56 MPa (2000–4000 psi), depending on the initial temperature and purity of the sample. This is associated with sporadic burning and the formation of “needles” in regions of accelerated regression on the surface of self-deflagrating AP in that pressure regime. SEM observations of the surface of quenched and partially burned samples of both single crystals and pressed pellets of AP deflagrating at different pressures in the 2.75–15.82 MPa (400–2300 psi) range were made in order to obtain a better understanding of high-pressure phenomena [866]. It was noted that needle formation could potentially be an artifact of the method used to quench the burning of samples at pressures below 13.8 MPa (2000 psi), which is contrary to previous results. There are multi-dimensional heat transfer processes taking place at the burning surface that may cause the formation of needles.

The multi-dimensional combustion front of AP was investigated at a pressure range of 2.52–10.1 MPa (25–100 atm) where the combustion of AP is usually considered to be stable [867]. The surface of the samples extinguished by three different methods was examined under the microscope in order to determine the combustion mechanism.

An analysis was conducted of the surface of burned AP samples quenched by a sudden pressure drop or by an injection of coolant spray onto the burning surface, as well as an analysis of samples extinguished due to their diameter being close to the quenching diameter. This revealed that at pressures that lead to steady burning rates (2.5–7.0 MPa), the burning surface is non-planar and non-uniform but features a cellular hotspot-type pattern [868]. Hotspots emerged and disappeared at the burning surface. Their diameter and depth were pressure-dependent and the maximum diameter of hotspots depended on the pressure. It exceeded the characteristic thickness of the heat conduction zone by about two orders of magnitude but was smaller than the critical quenching diameter by a factor of 1/2. Measurements of the electric conductivity of the surface layer and of the local luminosity of the flame revealed the existence of pulsations of approximately the same frequency. The period of these pulsations was close to the lifetime of hotspots.

5.15 The Effect of Additives on the Strand Burning Rates of Ammonium Perchlorate

The addition of additives to AP may increase or decrease its burning rate. Additives that increase the burning rate are called catalysts. Additives that decrease the burning rate

or inhibit burning altogether are called inhibitors. A chemical that acts as a catalyst in the thermal decomposition of AP does not necessarily have to be a catalyst that actively increases the burning rate of AP by itself or propellants formulated with AP. A catalyst that accelerates the deflagration of pure AP, may fail to do so when AP is incorporated in a binder to make a propellant. The effect of catalysts on both the burning rate and the lower pressure limit is a subject that continues to lack an explanation yet has considerable data regarding it. Burning rate increasing additives tested with AP are mostly transition metal oxides or transition metal metallocene complexes. Because it is easier to study thermal decomposition in a DTA or DSC with very small samples than to carry out burning rate measurements, all of these catalysts had been previously studied for their effect on the rate of thermal decomposition of AP. Many will be discussed in subsequent volumes for their effectiveness in changing the burning rates of AP-based propellants. Table 21 gives a summary of burning rate catalysts for AP. One of the most thoroughly studied burning rate catalysts is copper chromite. Several of these studies were conducted where the investigators measured both the effect of additives on the thermal stability (see Section 4.6.8) and the linear burning rate of pressed strands of AP. In some cases, they also determined the lower pressure limit for stable burning. Section 4.6.8 and the current chapters need to be read in context with each other.

It is very difficult to systematically arrange the information on the catalytic or inhibiting action of the various metal oxides. There is not a single study where all oxides were tested side-by-side under identical conditions. Most investigators have studied just a handful of additives and moved on to something else. This makes it difficult to compare results from different investigators. There is a lot of contradictory information in the literature. It seems that other factors (pressure, temperature, particle size of catalyst, amount of catalysts, particle size of AP, other contaminants, moisture, porosity of pressed grains) have dominated over the effects of catalysts and have not always had carefully enough controlled and maintained constants. Singh [869] has attempted to collect information from 68 sources in an effort to summarize the situation as it existed in 1978.

It was surprising to discover that the burning rate of pressed AP pellets varied substantially with the source of the material and depended on how many times it had been recrystallized to purify it. This indicates that the burning rate of AP is very sensitive to contaminants and moisture [870]. The burning rates of polycrystalline pellets of AP from three different sources and with different degrees of recrystallization were measured and compared. The burning rate changed considerably in the first three successive recrystallizations. The data showed that the impurities affected the burning rate, especially at high pressures. Impurities could be removed via recrystallization. It was found that occluded water in AP pellets changed the deflagration rate considerably. These results indicate that one of the causes for the disagreement among different investigators on the burning rate of AP might well be the effect of traces of residual impurities. These were present in the crystals and pellets used in the studies even after purification using recrystallization. The study results also indicated that the nature of

impurities in the “as-received” or recrystallized AP depends on the source of supply. It was also noticed that pressing uniform pellets of reproducible quality is very difficult. Considerable experimental evidence exists which indicates that the distribution of catalysts has relatively little effect on its performance. A mathematical model was developed to calculate the effectiveness factor for surface reactions. This was coupled with surface diffusion on a solid-catalyst surface or bulk diffusion near the burning surface, with discrete adsorption centers. The mathematical model assisted with explaining the experimental data assuming integral-order global reactions.

It is interesting to note that burning rate modifiers used in AP propellants are not effective in potassium perchlorate-based propellants. This supports the idea that the catalysts in AP propellants are active because they catalyze HClO_4 decomposition or NH_3 oxidation.

5.15.1 Effects of Metal Oxide Catalysts on the Burning Rate of AP

There exists a flood of publications on the effect of catalysts on the burning rate of AP either by itself or in a mixture with combustible fuels or binders. In addition to measuring the burning rate as a function of pressure, some investigators extended the experiments to the lower pressure limit, beyond which burning ceases and the flames extinguish. Catalysts accelerate the burning rate by projecting from the surface into the thin gaseous reaction zone and producing local acceleration of reaction rate. Very low concentrations of a catalyst, however, acts primarily to reduce flammability by raising the lower pressure limit, because the catalyst increases the emissivity of the burning surface and, hence, the rate of radiant heat loss

The effect of various additives on the burning rate of AP and AP/carbon mixtures in PMMA tubes was measured at a constant pressure [871]. Potassium dichromate increased the burning rate better than chromium(III) oxide. A stoichiometric mixture of AP and iron powder had a very high burning rate. Another fuel tested was calcium stearate, which can also be used as a pelletizing aid.

The effects of additives on the rate of deflagration of AN and AP have been summarized in a book on the catalysis of explosive combustion by Glazkova [872].

A summary of the publications on the effects of catalysts on the burning rate of the self-deflagration of AP (in the absence of combustible fuels) is provided in Table 21.

Because there are so many publications on this subject, it was difficult to get the references fully organized. Due to a lack of other sorting criteria, we have arranged the literature here chronologically by the decade in which it was published.

The burning rate of copper-chromite doped AP can be enhanced by mixing in small amounts of charcoal, both as a fuel and as an opacifier. In trying to derive a correlation between theory and experimental results, a relationship between energy flux density I and exposure time τ was derived, which defines the boundary conditions necessary to cause initiation [204, 205]. A theory based on partial differential equations describes the space-time temperature distribution in the pellet in terms

Table 21: Burning rate increasing catalysts for AP.

Compound Name	Formula	References
Potassium permanganate	KMnO ₄	[873]
Iron(III) oxide	Fe ₂ O ₃	[873]
Copper(II) oxide	CuO	[873]
Calcium oxide	CaO	[567]
Potassium dichromate	K ₂ Cr ₂ O ₄	[874]
Copper chromite	CuCrO ₄	[875]
Copper(I) oxide	Cu ₂ O	[876]
Copper(II) oxide	CuO	[876]
Iron(III) oxide	Fe ₂ O ₃	[876]
Chromium(III) oxide	Cr ₂ O ₃	[876]
Copper chromite	CuCrO ₄	[876]
Ammonium chromate	(NH ₄) ₂ CrO ₄	[876]
Ammonium dichromate	(NH ₄) ₂ Cr ₂ O ₇	[876]

of chemical reaction rates, heat of reaction, thermal conductivity, heat capacity, optical absorptivity, and surface reflectivity. Integration of the equation using the experimentally determined chemical and physical parameters and boundary conditions provided the temperature of the pellet and the temperature of the pellet surface as a function of time with flux as a parameter. From this solution, one was able to obtain the following two parameters for a given flux density (I). **(1)** The temperature $T(0, \tau)$ of the initiating surface at the moment τ_i of cut-off of the energy pulse. **(2)** A lower boundary for the minimum thermal ignition time.

Potassium dichromate is a very effective burning rate catalyst for AP [871]. Chromium(III) oxide is less effective and accelerates burning rates only up to 50.5 MPa (500 atm). Mixtures of AP and iron powder burn very fast.

The burning rate of AP-based composite propellants was unaffected by the addition of potassium chlorate to the AP [262], but metal chelates and metal acetylacetonates increased the burning rate at chamber pressures below 6.88 MPa (68.1 atm = 1000 psi). The activity of metals decreased in the order $\text{Cu} > \text{Fe} > \text{Co} > \sim \text{Mn}$. The most effective catalysts were those based on transition metals having two stable oxidation states which can readily flip-flop by exchanging a single electron. The addition of 1% of tributylamine reduced the burning rate.

Vanadium(V) pentoxide accelerates the burning of AP and its mixtures with fuels and metals [877, 878].

A correlation of experimental results for the burning rates of AP was derived from three areas of propellant research: **(1)** low-temperature isothermal sublimation studies; **(2)** the measurement of linear regression rates using the hot-plate pyrolysis technique; and **(3)** the combustion of AP at low ambient pressures through either preheating the AP, the use of solid volatile fuel, the passing of gaseous fuels through a porous bed of AP, or the formation of a diffusion flame above the AP using a counterflow of

fuel gases [879]. Each of these experiments should yield information about the rate of sublimation of AP. At first glance, even if one allows for experimental errors in the various types of measurements, the agreement between the results from the different techniques was not very good. In particular, the activation energy for the rate-controlling step was in doubt, with values ranging all the way from 20 to 60 kcal/mol being suggested by various authors ("all over the ballpark"). It was shown that, when allowances were made for the pressure-dependence of the sublimation rate, an acceptable degree of correlation between all the sublimation data could be obtained and sublimation rates could be calculated from a simple kinetic theory formula with reasonable values of the evaporation coefficient.

Using 38-mm diameter pressed end burning grains, it was shown that the burning rate pressure exponent for pure AP was positive and constant between 8.26 and 20.64 MPa (1200 and 3000 psi) [264]. There is no evidence of a negative pressure exponent in this pressure region if the AP surface area to perimeter ratio is large enough. Isothermal kinetic studies had shown that diammonium hydrogen phosphate negatively catalyzes the low-temperature AP decomposition while chlorate is a positive catalyst for this decomposition. Despite causing significant changes in the rate of the LTDs, these materials have only a limited effect on the AP combustion rate. The phosphate may affect the rate of surface diffusion of HClO_4 , and thereby the bimolecular reaction of HClO_4 with gaseous products. The decomposition of AP containing 0.025% chlorate was approximately an order of magnitude faster than pure AP. The decomposition proceeds via six different reaction mechanisms. The phosphate and chlorate or their decomposition products do not appear to affect the dissociative evaporative rate of the AP residue which is left after the LTD. Additives such as diammonium hydrogen phosphate and potassium chlorate, which change the AP LTD by as much as an order of magnitude, have only a limited effect on the burning rate of pressed AP strands. Pressed AP strands containing a relatively high concentration of phosphate (0.64%) have a smaller change in their burning rate pressure exponent near 6.88 MPa (1000 psi) than strands of pure AP. It is very dangerous to mix ammonium salts with chlorates because ammonium chlorate is very unstable and may render the mixture more sensitive to accidental ignition.

The decomposition, pyrolysis, and deflagration of pure and isomorphously doped AP containing K^+ , $\text{Cr}_2\text{O}_7^{2-}$, and MnO_4^- ions were followed by visual observations of quenched surfaces, which involved taking high-speed movies of the burning surface [779].

Copper chromite, iron(III) oxide, copper(II) oxide, and potassium permanganate were used to study the effect of catalysts on the deflagration pressure limit and the burning rate of AP [873, 880–882]. Copper chromite, Fe_2O_3 , and CuO increased the lower pressure limit of deflagration when present at small concentrations but decreased it at large concentrations. Potassium permanganate, both mechanically mixed and co-crystallized with AP, had a similar effect on the lower pressure limit. However, at large concentrations of KMnO_4 , an upper-pressure limit was observed,

above which deflagration could not be maintained. The effect of these catalysts on the burning rate varied over a wide pressure range. It was further observed that the effect of catalysts depended strongly on the way they are dispersed as well as their overall concentration. Catalysts were much more effective at smaller particle sizes.

Quenching the deflagration of catalyzed AP grains and examining the surface in the vicinity of the catalyst particles with SEM was done in the hope of explaining the mechanism of catalysts and to invent more active ones [883]. The catalysts used were ultra-fine copper(II) oxide and iron(III) oxide. Catalysis of burning of AP and its mixtures with combustible substances was investigated using optical and SEM and the effects of catalyst dispersion on burning rates were studied [884]. Fe_2O_3 , CuO , and CuCr_2O_4 were used as catalysts in amounts of 1–2.5 mass-% [885].

CuO or Cu_2O added to AP at 2 or 8% and pressed into pellets failed to sustain deflagration at room temperature and 373 K (100 °C) [876]. It was suggested that CuO is a better catalyst for thermal decomposition and Cu_2O is a better catalyst for the deflagration burning of AP.

In some cases, literature abstracts do not identify the types of compounds that were added to AP in an effort to change its burning rate. One must assume that most of these elements were added in the form of their oxides or perchlorates. The effects of various catalyzing additives such as Cu, K, Bi, Li, Co, Ba, Zn, Cr, V, and Fe compounds on AP combustion were measured and compared to 0.05–10% of $\text{K}_2\text{Cr}_2\text{O}_7$ [886]. The coefficient of catalysis (K) is defined as the ratio of the catalyzed burning rate to the uncatalyzed burning rate. Various regimes of the AP combustion rate were considered as well as changes in the coefficient of catalysis and combustion rate dependence on the amount and type of catalyst. Two pressure zones could be identified: 5.05–15.15 MPa (50–150 atm) where a slight increase of catalytic efficiency (K) occurs along with an increase in the linear burning rate (U_0), and 30.3–101 MPa (300–1000 atm) within which range K decreases with an increase in U_0 .

The combustion of AP in mixtures containing 2 or 8% of additives (metal oxides, other perchlorates, other ammonium salts, opacifiers) was measured at pressures ranging from 0.688 to 10.32 MPa (100–1500 psi) and initial temperatures of 298 or 373 K (25 or 100 °C) [876]. Additives tested included Cu_2O , CuO , Fe_2O_3 , Cr_2O_3 , CuCrO_4 , $(\text{NH}_4)_2\text{CrO}_4$, and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. The addition of TiO_2 , ZnO , NH_4Cl , NH_4F , $(\text{NH}_4)_2\text{SO}_4$, NH_4HF_2 , $(\text{NH}_4)_2\text{HPO}_4$, $\text{Cd}(\text{ClO}_4)_2$, $\text{Cu}(\text{ClO}_4)_2$, or CaC_2O_4 inhibited the burning. Two per-cent of Fe_2O_3 increased the deflagration rate and temperature sensitivity significantly over that of pure AP. Samples with 8% of Fe_2O_3 at room temperature led to lower burning rates, a raised lower pressure limit and a higher slope than for pure AP. Raising the initial temperature to 373 K (100 °C) brought the burning rate back up to that of pure AP.

The effects of additives on the rate of deflagration of AP have been summarized in a book by Glazkova [872]. A well-written summary comparing the occasionally contradictory observations and conclusions about the effectiveness of copper oxides

and other catalysts on the decomposition and burning rate of AP was provided by Singh [869].

The combustion of mixtures of AP with various inorganic compounds of the following types were studied: oxides of copper and chromium, oxides of other metals, other perchlorates, other ammonium salts, and darkening agents [887]. The additives were generally added at the 2 and 8 mass-% levels. The rate of regression was measured from high-speed photography in a windowed bomb. Deflagration rates of AP with a total of 32 different additives were tested at two different additive concentrations, two initial sample temperatures (room temperature and 373 K = 100 °C), and several pressures from 0.69 to 10.32 MPa (100 to 1500 psi). Additives tested included various metal oxides and chromates, other perchlorates [LiClO_4 , KClO_4 , $\text{Zn}(\text{ClO}_4)_2$, $\text{Cd}(\text{ClO}_4)_2$, $\text{Cu}(\text{ClO}_4)_2$], and other ammonium salts [$(\text{COONH}_4)_2$, $(\text{NH}_4)_3\text{PO}_4$, $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , NH_4Cl , NH_4F]. Much of the work that has been reported in existing literature relates to AP-catalyst reactions. Unfortunately, much of it is of questionable relevance to the deflagration situation.

The apparatus used in this investigation consisted of a stainless-steel window bomb that was capable of being pressurized at 13.76 MPa (2000 psi) and heated to 423 K (150 °C). A high-speed motion-picture camera was also utilized. Burning rates were calculated from surface regression distances per 0.10-second time intervals from high-speed motion-picture films. When this procedure was used to determine the burn rates of pure AP (both single crystals and pellets), the data scatter was of the order of ± 0.02 in./s. A SEM was used to view the surfaces of samples quenched while burning at various pressures. The quenching was accomplished using rapid depressurization ($dp/dt > 10^5$ psi/s).

The burning rates of AP catalyzed using calcined Cr_2O_3 , CuO , or Fe_2O_3 and the dependence of the burning rate of AP on pressure were measured in one set of experiments [888]. The surface properties of Cr_2O_3 , CuO , and Fe_2O_3 catalysts were examined using XPS. Attempts to establish correlations between the catalytic activity and surface properties were made. An electron-transfer catalytic mechanism was postulated in the catalytic combustion of AP with Cr_2O_3 and CuO as catalysts.

The effects of metal oxides applied to the surface of AP crystals and introduced into the propellant in the form of colloidal suspensions on the burning rate and thermal decomposition of AP were investigated [889]. It was found that the possibility of changing the burning rate by means of applying small additive concentrations (up to 0.5%) of the catalyst on the oxidizer crystal surface is determined by the chemical nature, the content of the compounds deposited on the oxidizer surface, and the structure of the coating formed on the AP surface.

5.15.2 Effects of Inhibitors on the Burning Rate of AP

The inhibiting effect of ammonium salts, such as ammonium carbonate, oxalate, citrate, tartrate or fluoride, and a reducing agent, such as diphenylamine, on the burning

rate of AP or AP/AN mixtures was investigated [890]. It was theorized that the effect of easily dissociating ammonium salts would consist of shifting the equilibrium of the reaction to the left, while the effect of diphenylamine would be either a reduction or a binding of the acid formed in the dissociation, thus inhibiting the further oxidation of ammonia. This assumption was verified experimentally through the combustion of “ammamol 80/20” (instead of pure AN which does not burn in the bomb) or AP (with or without the additives mentioned above) added in the amount of 5%. The rate of combustion was measured at varying pressures up to 101 MPa (1000 atm) in a constant-pressure bomb.

The deceleration of chemical reactions in the deflagration of AN or AP and some of their mixtures was studied in a constant pressure bomb over the pressure range from 1 to 1000 atm [891]. The deflagration of AP and ammonite 80/20 was decelerated also by adding readily-decomposed salts of ammonia. Assumptions regarding the mechanism of deceleration of the combustion process were suggested, based on the assumption of the possible role of nitric oxides and of a dissociation reaction of AN and AP.

The effects of the addition of up to 5% of organic additives on AP combustion characteristics (lower pressure limit of stable combustion, combustion rate, coefficients of inhibition in the exponential equation of combustion, and its dependence on pressure) at pressures up to 68 MPa (100 atm) were investigated [261]. There are three possible ways to inhibit the AP combustion process [892].

The burning rate of AP composite propellants is decreased significantly by the addition of SrCO_3 without increasing the pressure exponent of the burning rate. Results of micro-thermocouple measurements indicated that the burning surface temperature increased from 700 to 970 K due to the addition of SrCO_3 , although the heat-release rate in the gas phase remained unchanged [893]. DTA and TGA revealed that the AP decomposition temperature increased from 590 K to 620 K by adding SrCO_3 . The results of the analysis revealed that the reduction of the burning rate is caused by the increased AP decomposition temperature.

5.15.3 Effects of Contaminants on the Burning Rate of AP

Small traces of contaminants can have a noticeable effect on the rate of deflagration of pressed polycrystalline AP or AP single crystals. Pure AP doped with 0.05% K^+ produces burning rates very similar to those reported by others who have used AP of dubious purity [810].

Excess perchloric acid accelerates decomposition and the linear burning rate of AP while excess free ammonia retards it. Bircumshaw and Newman [348, 349] have suggested that the formation of centers of decomposition on the AP crystal surface may be associated with the formation of adsorbed perchloric acid. The induction period can be shortened by crystallizing an AP sample with 2% excess perchloric acid. Conversely, the induction period can be lengthened by passing some ammonia over the salt.

5.15.4 Effect of Chlorates on the Strand Burning Rate of AP

Chlorate ions are a potential contaminant in AP and are either carried over during the production or may form due to an interaction with a reducing agent in contact with AP with which AP is not compatible. Chlorates may form during radiolysis of AP. Investigations have been made on the effect of chlorate on the burning rate of AP. The burning of pure ammonium chlorate has been studied as well, although nobody would want to use it as a rocket propellant; its inadvertent formation must be avoided for sure. All pyrotechnic formulators have been warned against mixing ammonium salts with chlorates because ammonium chlorate may form during storage, which is very unstable and may render the mixture more sensitive to accidental ignition.

The thermal decomposition of AP containing 0.025% chlorate was approximately an order of magnitude faster than that of pure AP [264].

ClO_3^- ion is a catalyst for the decomposition of AP. It was found that impurities of ClO_3^- ions are typically present in even the purest commercial samples of AP [760].

Ammonium chlorate in the form of samples pressed into acrylic tubes of 4 mm diameter is capable of sustained combustion at atmospheric pressure [627]. Sample diameter influences the burning rate due to heat losses. Strand burning rates of ammonium chlorate are presented in Figure 40 in comparison to those of AP.

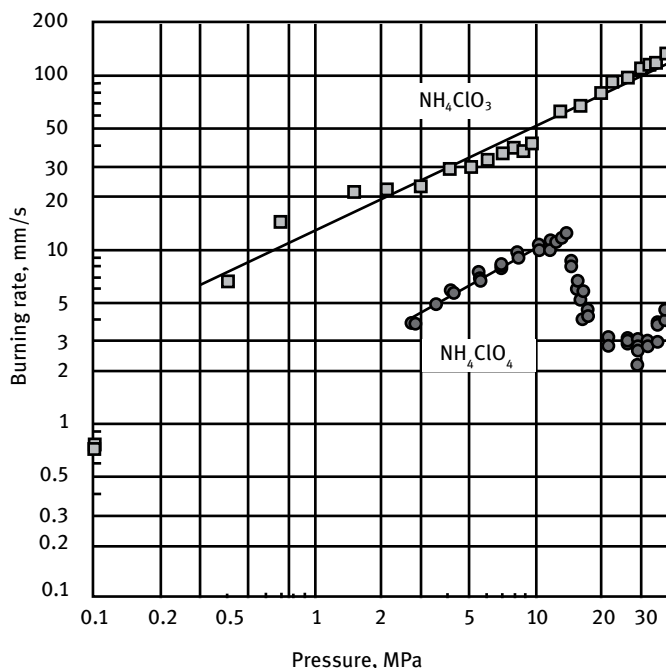


Figure 40: Comparison of combustion behaviors of ammonium chlorate and perchlorate. (Reproduced and modified from [627]; Cent. Eur. J. Energ. Mater.; licensed under Creative Commons <https://creativecommons.org/licenses/by-nc-nd/4.0/>).

In the pressure interval 0.4–40 MPa, the burning rate of NH_4ClO_3 can be described as

$$r_b = 12.96p^{0.6}$$

where r_b is the burning rate in mm/s and p is the pressure in MPa. For comparison, the burning rates of AP are also shown in Figure 41. As can be seen from the figure, ammonium chlorate burns much faster than AP in spite of having a lower burning surface temperature. The autoignition temperature of NH_4ClO_3 is much less than that of AP; it was reported as 393 K (130 °C) or even as low as 343–373 K (70–100 °C) compared to 623 K (350 °C) for AP. For the decomposition of some ammonium salts, a gas-phase model had been proposed. However, a calculation of the heat balance in the decompo-

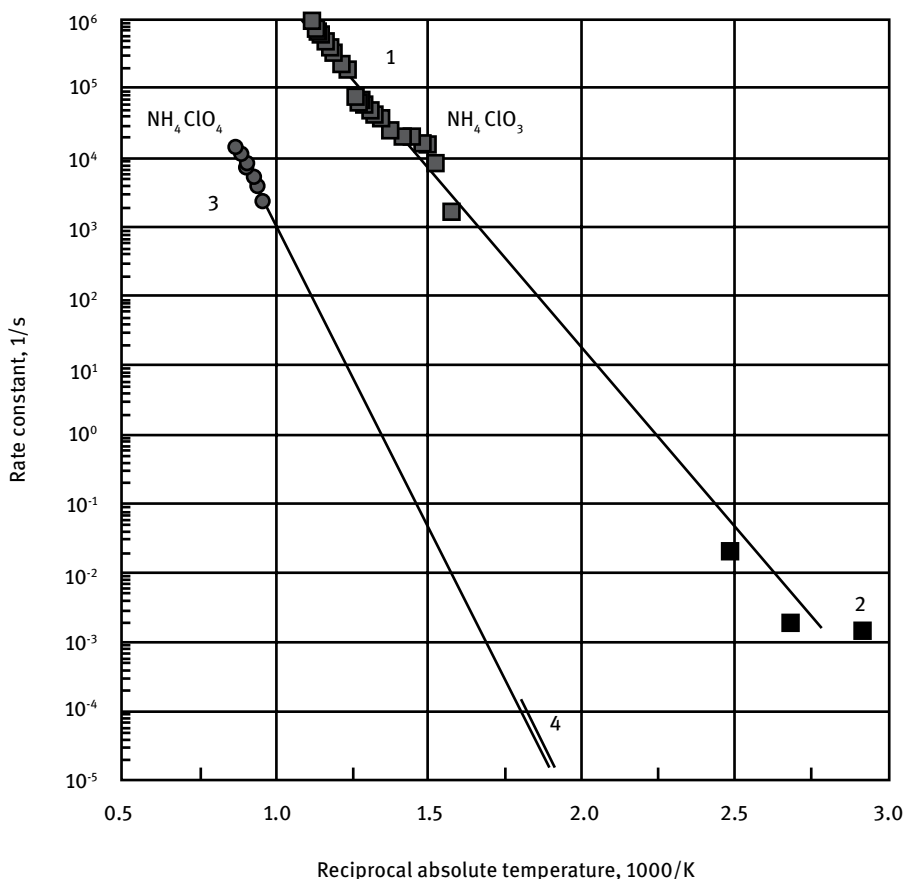


Figure 41: Comparison of kinetic parameters of the combustion leading reaction (1 and 3) with decomposition kinetics in liquid states (2 and 4) for ammonium chlorate and perchlorate. (Reproduced and modified from [627]; Cent. Eur. J. Energ. Mater.; licensed under Creative Commons <https://creativecommons.org/licenses/by-nc-nd/4.0/>).

sition zone revealed that the heat available is insufficient to transform all salt into the vapor phase. Therefore, a significant part (at least 30%) of the decomposition reaction must take place in the condensed phase. The temperature sensitivity of the burning rate is much better represented by a condensed phase model rather than by a gas-phase model. Kinetic data of the rate-determining reaction of AP combustion and the kinetic data of AP decomposition in a liquid state are presented in Figure 41 in comparison to such data for NH_4ClO_3 .

A comparison of the constants reveals that the decomposition rate of NH_4ClO_3 is almost three orders of magnitude higher than that of AP combustion. This is the reason that ammonium chlorate burns much faster than AP.

5.15.5 Effects of Metal Perchlorates on the Strand Burning Rate of AP

At low concentrations, $\leq 30\%$ KClO_4 , the burning rate of the compressed AP/potassium perchlorate pellets increases with KClO_4 content. However, above 40% KClO_4 , it is difficult to maintain combustion [894]. The results can be explained in terms of the melt layer thickness, flame temperature, the resultant surface temperature, and the heat-wave penetration into the solid. A melt layer on the burning surface influences the deflagration behavior of the AP/potassium perchlorate pellets.

5.15.6 Effects of Non-Metal Perchlorates on the Strand Burning Rate of AP

Other perchlorates that have been added to AP in an effort to alter its burning rate and thermal stability include hydrazinium(1+) perchlorate, hydrazinium(2+) perchlorate, hydroxylammonium(1+) perchlorate, and nitronium (nitryl) perchlorate.

AP with an increased burning rate can be produced via “doping”, i.e., incorporating accelerators into the crystal structure. Unfortunately, the process also increases shock sensitivity. Thus, 100 g of AP and 0.0125 g of nitronium perchlorate were dissolved in 100% fuming HNO_3 at $<353\text{ K}$ ($<80^\circ\text{C}$). The solution was then cooled and the precipitate vacuum dried and pulverized [895]. Burning rate straws (5 cm long by 4 mm diam.) were packed with the material and burned. The average burning rates at 3.44, 6.88, and 10.32 MPa (500, 1000, and 1500 psia) were 27, 41, and 56 cm/s (10.74, 16.18, and 22.16 in./s), respectively. The burning rate of undoped AP at 6.88 MPa (1000 psia) was 34.8 cm/s (13.70 in./s) and calculated rates at 3.44 and 10.32 MPa (500 and 1500 psia) were 22 and 45 cm/s (8.74 and 17.85 in./s), respectively. A ~12% burning rate increase was achieved over that of undoped AP.

Compressed pellets made of mixtures of AP and trimethylammonium perchlorate burning at ambient pressure revealed an increase in the linear burning rate with increasing trimethylammonium perchlorate content, topping out at a maximum for a mixture containing 80 mass-% trimethylammonium perchlorate [896]. Isothermal thermogravimetry and DTA measurements indicated the possibility of eutectic melt formation.

5.15.7 Effects of Other Ammonium Salts on the Strand Burning Rate of AP

The addition of ammonium picrate in different concentrations to AP caused a slight increase in the burning rate of propellants prepared with this doped AP [897]. The thermal stability of doped AP was adversely affected but there was no systematic variation of the loss of stability with the dopant concentration.

5.15.8 Effects of Organic Compounds on the Strand Burning Rate of AP

The reactions of AP with organic compounds and the thermal stabilities of such mixes have already been discussed in Section 4.1.2.3. Strand burning rates of actual propellant formulations containing AP will be summarized in future volumes on solid propellants. Quite often, non-polymeric organic compounds have been mixed with AP as simulants for polymeric binders, which are easier to process than the sticky and messy prepolymers of real binders. In particular, investigators used fusible and volatile solid fuels that sublimed readily and allowed burning in the gas phase instead of pyrolyzing like polymeric binders. Such mixtures are not really useful as rocket propellants. They were mixed and burned just to satisfy academic curiosity. Because these organic compounds have no binder qualities, the ingredients are usually dry-mixed and then pressed into pellets for combustion studies. Some of the organic compounds were evaluated as stabilizers and as coolants for AP-based propellants.

Fuels tested for that purpose include paraformaldehyde [812, 814, 854, 855, 898, 899], hexamethylenetetramine [854, 855], and naphthalene [815].

The strand burning rates of mixtures of AP and organic fuels of the various chemical structures were measured by pressing $8 \times 4 \times 3.5$ mm pellets at $1000 \text{ kg}_f/\text{cm}^2$ and burning them in a constant pressure combustion bomb at pressures of 3, 20, and 40 atm [900]. High burning rates were observed with paraffin, stearic acid, palmitic acid, *o*-toluidine, and diaminodimethylmethane. It has been suggested that the burning rate of the mixtures depends on the calorific value of fuels of similar structures. Or, if the calorific value is the same, the burning rate of the mixtures depends on the strength of the chemical bonds and the structure of the molecules.

At low pressures, potassium perchlorate-based mixtures burn at higher rates than AP-based mixtures. Combustible substances were selected which do not contain carbon in their molecule and which yield ammonia (ammonium chloride) as the primary decomposition product. Other compounds with small carbon content (e.g., ammonium oxalate) were selected because they form ammonia upon decomposition. Urea was selected because it does not form ammonia during decomposition [826]. Also, hydrocarbons (naphthalene, paraffin) and other organic compounds were mixed with AP (with and without a catalyst), *o*-phenylenediamine and, finally, pure carbon-carbon black. Stoichiometric mixtures with particle dimensions of $\sim 250 \mu\text{m}$ were prepared and burned, then compared to mixtures with catalytic agents added in amounts of 5%. The lower combustion limits with respect to pressure and the dependence of

combustion rate on the pressure in the range up to 101 MPa (1000 atm) were determined.

The deflagration of AP and its mixtures with dicarboxylic acids (oxalic acid, malonic acid, phthalic acid) was evaluated experimentally. Attempts were made to develop a computer model based on partial differentiation of a basic thermodynamic equation that predicts the LPDL of AP and its mixtures [901]. For AP without the addition of dicarboxylic acid, the limit was at 2.02 MPa (20 atm). In the presence of dicarboxylic acid additives, a new subcritical regime below the conventional lower pressure limit was discovered in which AP does not burn. One of the parameters in the model is the melt layer thickness (see [902]).

5.15.9 Effect of Metal-Organic Compounds on the Strand Burning Rate of AP

The advantage of metalorganic compounds as burning rate additives is that they are miscible with the binders and can be placed at the surface of AP grains where they are needed the most. The disadvantage of metalorganic burning rate catalysts like ferrocene or metal acetylacetonates is that they are volatile and tend to migrate during aging of the propellant. It is thus of interest to study not only the effect of acetylacetonates (β -diketonates) on the burning rate of formulated propellants but also their effect on the strand burning of AP by itself.

The effect of various metal complex catalysts of 1,4,8,11-tetraaza[14]annulenes on the thermal decomposition of AN, AP, and a solid propellant containing AP as the oxidizer was studied using DTA and burning rate measurements [667]. For the solid propellants, which contained iron or vanadium complexes as catalysts, the burning rate increased by 1.6 times and their pressure index decreased to 80% compared to the burning experiments without a catalyst at a pressure of 5.0 MPa.

5.15.10 Effects of Other Additives on the Strand Burning Rate of AP

The mass burning rate versus pressure curve for unconfined pure AP has a region where the combustion starts pulsating and becomes unstable. Strangely, in the range 16.15 to 25.25 MPa (160–250 atm), the burning rate falls with pressure, while in the range of 25.25 to 50.5 MPa (250–500 atm) it remains constant. Only above 50.5 MPa (500 atm) does it increase with pressure [864]. Trying to explain this unusual behavior of AP by measuring the temperature distribution in the flame front with fine thermocouples revealed another anomaly: The heat release and the surface temperature were diminished even in the range between 4.04 to 15.15 MPa (40–150 atm) where the burning rate increased with pressure. It was suspected that water condensation may be the culprit. The addition of 1 mass-% of silica, silicone oil, or calcium stearate increased the burning rate and widened the range of stable combustion but calcium oxide prevented ignition in the range of 14.1 to 50.5 MPa (140 to 500 atm). The addition of 5% of SiO_2 stabilized the combustion of AP in PMMA tubes over the entire pressure range

up to 101 MPa (1000 atm). But the addition of 5% of ammonium oxalate reduced the burning rate of AP.

The burning rates of AP single crystals doped with K^+ and three concentrations of MnO_4^- exhibited one consistent feature in that the burning rates for the doped crystals were always below the pure AP rate over the pressure range tested [364]. In addition to this, the K^+ -doped AP had a pressure exponent of approximately 1.0 as compared to approximately 0.77 for pure AP. The highest (0.04% MnO_4^-) concentration doped AP, which would undergo self-deflagration, displayed a much lower burning rate. Therefore, it is presumed that increasing the MnO_4^- concentration results in lowering the single-crystal deflagration rate.

The deflagration behavior of pure AP in single-crystal and pressed-pellet form, and single crystals with controlled isomorphous substitution of K^+ , MnO_4^- , and $Cr_2O_7^{2-}$ ions were studied over the pressure range 2.06 to 41.3 MPa (300 to 6000 psia) using cinephotomicrography of burning samples and SEM of quenched samples [903]. The same additives can also be incorporated in micron-size whisker-shaped crystals of AP which are doped with co-crystallized burning rate catalysts [29].

5.15.11 Effects of Crystal Defects on the Strand Burning Rate of AP

A systematic study was undertaken on the combustion and thermal decomposition of AP pellets to investigate the effects of pelletizing pressure and the dwell time on the combustion and thermal decomposition of pelletized AP [904]. At constant pressure, increasing the dwell time resulted in an increase in the burning rate up to a maximum and thereafter decreased it. The dwell time required for the pellets to have a maximum burning rate was a function of pressure. The maximum burning rate was the same for all the pressures used. It was also unaffected by increasing the initial particle size of AP used to the range of 90 to 250 μm . In order to explain the occurrence of a maximum burning rate, pellets were examined for their thermal sensitivities, physical appearance, and the changes that occurred during pelletization with dwell time and pressure.

5.16 The Surface Temperature of Ammonium Perchlorate Combustion

Several experimenters have measured the surface temperature of deflagrating AP single crystals or pressed pellets, with or without additives, as part of other ongoing studies (mostly burning rate studies). Deriving the dependence of the surface temperature on pressure for AP is difficult. Finding the surface temperature is complicated due to not only a very steep temperature rise in profiles to a maximum value but also due to high-temperature oscillations in the zone near the surface. It is also rather difficult to establish whether AP melts at the burning surface. The presence of the liquid phase has been observed in several studies using microphotography of quenched samples

but it was not well-defined whether the liquid layer was produced during melting of AP or if it was a solution of decomposition products in AP. The AP surface temperature depends on the operating pressure. It increases from 880 to 1070 K as pressure increases from the lower pressure limit (~ 2 MPa) to 6 MPa [203].

The burning surface temperature of AP and AP/fuel mixtures has been measured using an IR optical method [814]. At atmospheric pressure, the temperature remained constant at 723 ± 30 K (450 ± 30 °C), irrespective of the rate of burning of the perchlorate-fuel mixture or the nature of the fuel. The disintegration process at the surface is most likely sublimation rather than kinetic decomposition controlled by a surface temperature. The rate of sublimation is thought to be controlled by the temperature gradient at the surface, which in turn is maintained by the gaseous ammonia-perchloric acid flame surrounding each particle. The temperature of this decomposition flame will increase if fuels are added.

The relation between the burning rate and the surface temperature of AP must be investigated to elucidate the combustion mechanism of composite propellants. The burning rate parameters that typically vary are the chamber pressure and the AP particle size. Optical or IR emission techniques can be used to measure surface temperatures but problems are posed by gas-phase emission, transparency of the AP, and the subsurface temperature gradient. A two-wavelength type of analysis of the surface-emission was proposed to overcome the subsurface-temperature-gradient problem [905].

In addition to thermocouple readings, measurements of the surface temperature of pressed strands of AP (done by recording the radiation from the surface at specific IR wavelengths) provided additional clues about the burning mechanism [898, 906]. Since they wanted to get AP to burn at lower (subatmospheric) pressures, the AP contained just enough of a volatile fuel (paraformaldehyde) to keep it going. IR measurements of the burning surface temperatures of oxidizer-rich AP/paraformaldehyde mixtures were made from sub-atmospheric pressures up to pressures of 2064 kPa (300 psia). Temperature determinations up to 413 kPa (60 psia) were reasonably reproducible, the values being compatible with the existence at the surface of an equilibrium between solid AP and the gaseous decomposition products, NH_3 and HClO_4 . Results above 413 kPa (60 psia) were rather erratic. The temperature gradients within the solid became too steep even for this method, which can penetrate as little as $2 \mu\text{m}$ of surface depth (see [899, 907]).

Calculations based on heat conduction and energy release indicate that the surface temperature remains constant over a wide range of pressures and the melt layer is at about 833 K (560 °C) [802, 803]. Other thermocouple measurements produced very low surface temperatures of 683 K (410 °C) at 5.05 MPa (50 atm) and 593 K (320 °C) at 10.1 MPa (100 atm). Thermocouple measurements may be inaccurate due to the catalytic action of the thermocouple metals if the wires are not shielded by an inert material.

The surface temperature of burning AP can be enhanced using laser illumination. The burning rate can thus be modulated by turning the laser on and off. The radiant flux-induced deflagration of AP at 1 atm has been investigated [908]. A 6-kW CO₂ laser was used as the radiant energy source and a force transducer was used to measure both steady and unsteady burning rates. The steady data were analyzed using the equivalence principle to obtain the burning rate-initial temperature sensitivity parameters k^* and σ_p^* . The dependence of σ_p^* on mean flux was also obtained from the equivalence principle and showed a decreasing trend with increasing flux (Figure 42).

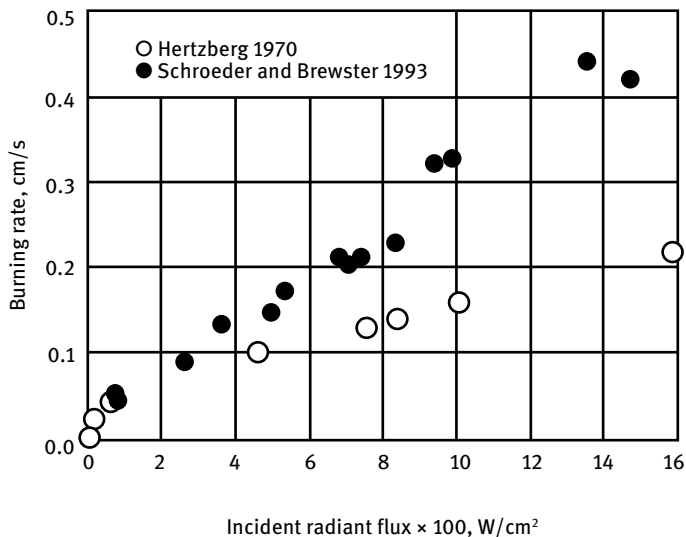


Figure 42: Burning rate of AP as a function of laser radiant flux. (Reproduced and modified from [908].)

These findings have implications for steady-state burning rate predictions in motors with appreciable thermal radiant flux levels. These results are also useful for comparison with predictions of detailed models of the chemical kinetics and micro-structural combustion behavior of AP, both as a monopropellant and as an ingredient in composite propellants. In addition, the applicability of the one-dimensional momentum balance for obtaining the burning rate from recoil force was demonstrated.

Table 22 provides a summary of reported or calculated surface temperatures of burning AP. Most investigators reported that the surface temperature is not very dependent on operating pressure or burning rate.

As illustrated in Figure 41, experimental results obtained using thermocouple-aided measurements or burning surface pyrometry are scattered over a wide range. They can be grouped together along two lines that correspondingly describe the equilibrium gas pressure over the solid and melted AP surface [203].

Table 22: Summary of reported or calculated surface temperatures of burning AP.

Temperature		Pressure	References
K	°C	MPa	
1003–1103	730–830	0.1–30	[909]
723 ± 30	450 ± 30	0.1	[814]
833	560		[802]
683	410	5.05	[803]
593	320	10.1	[803]
698–848	425–575		[133]
810			[848]
700–970			[893]
825			[850, 851]
880		2	[203]
1070		6	[203]

5.17 Theoretical Treatment and Mathematical Models of Ammonium Perchlorate Combustion

AP by itself is not a useful rocket propellant. Nevertheless, mathematical models have been developed to interpret the burning mechanism of solid AP and to expand it to AP-based propellants with fuels. The establishment of a theoretical model requires the consideration of reactions in both the condensed (solid and molten) phase and in the gas phase and their interaction. Unfortunately, there is not sufficient information on the reactants in the AP condensed-phase reaction and the flame front to build an *a priori* model of its combustion. Various investigators have had to make different simplifying assumptions and that is where the inconsistency starts. Attempts have repeatedly been made to express the processes that take place during AP or other solid auto-decomposing compounds' combustion using a sequence of mathematical equations that will allow us to predict the burning rate as a function of input variables. So far, these efforts have only had limited success.

A small-perturbation investigation of AP deflagrations was made to determine the intrinsic stability of a one-dimensional burning configuration [910]. It was found that, above a certain pressure and dependent upon the numerical values used, a stable one-dimensional flame cannot exist. If the calculations are correct, for a preferred set of parameters, the pressure above which stability is impossible is between 4.26 MPa and 14.72 MPa (42.2 and 145.7 atm = 620 and 2140 psia), depending on whether the AP-gas interface is in equilibrium or is pyrolysis controlled. There are two reasons for the stability investigation in addition to the one given concerning its relevance to solid propellant combustion. First, there has never been a satisfactory theoretical explanation for the observed lower deflagration limit at roughly 2.064 MPa (20.43 atm = 300 psi). Secondly, it is known that deflagration ceases to be macroscopically steady and one-dimensional above about 13.76 MPa (2000 psi).

An attempt to derive a quantitative theory of the burning of AP used a rate law for the surface gasification. It examined the adjustable parameters and compared its predictions to earlier lower pressure limit measurements detailed by other investigators [911]. According to this model, the heat loss from the gaseous products was too small to account for the lower pressure limit (also called “lower deflagration limit”, which is abbreviated as P_{DL}). In order to compensate for this, it was assumed that the gas phase heat release per unit mass burned decreased with pressure. This accounted for the observed lower pressure limit but revealed other discrepancies. The disagreement in slope between the theoretical and experimental curves of burning rate versus pressure for pure AP may be in part due to an unknown experimental scaling factor on the radiant energy absorbed by the pellet. Experimentally, it was observed that:

- (1) P_{DL} was insensitive to sample size and to the substitution of helium for nitrogen as the ambient atmosphere;
- (2) P_{DL} increased as the particle size (sieve dimension) decreased; the particles are those of AP from which the pressed pellet is formed; and
- (3) Preheating the pellets lowered P_{DL} , and precooling the pellets raised P_{DL} .

Theories of the effect of catalysts on the burning rate of AP-based composite propellants differ in the interpretation of whether the effect of catalysts is stronger in the condensed phase or in the aerosolized gas phase. It was difficult to match the predictions of such theories with the experimentally determined burning rate data at varying catalyst levels and with different catalyst types. A model for the burning of AP was developed based on the following assumptions [563]:

1. An equilibrium pressure of $\text{HClO}_4 \cdot \text{NH}_3$ is established on the burning surface at the surface temperature for which the rates of Inami, Rosser, and Wise [128, 600] were used.
2. A surface exothermic reaction occurs in the condensed phase. The assumption that the decomposition reaction is a surface reaction is confirmed by experimental data, according to which the velocity of decomposition of AP is proportional to its specific surface.
3. The reaction in the gas phase is taken as a first-order reaction with respect to HClO_4 and zero-order with respect to NH_3 . Equality of the coefficients of diffusion and thermal diffusivity occurs.
4. Heat losses are disregarded.

One of the models that deals with competing evaporation processes and decomposition reactions in general terms (not just for AP) predicted a burning rate for AP at 6.88 MPa (1000 psia) of 1.2 mm/s. This is almost an order of magnitude below the actual measured data [912]. The divergence was explained by the formation of a liquid phase on the surface of the burning material.

An analytical model has been developed to describe the burning behavior of catalyzed AP for pressures below 10 MPa and used to explain the increase in both the

burning rate and the lower deflagration pressure limit (LDPL) of AP with catalyst content [913]. The peculiar increase of LDPL of AP by catalysts can be understood on the basis of inherent instability of the condensed phase deflagration wave decoupled from the gas phase deflagration wave. The effects of the addition of external heat, preheating, and the fuel added to AP on the LDPL were also explained using the model.

The deflagration of AP in the subcritical regime, below the LPDL (<2.03 MPa) designated as regime I', was modeled using a thermodynamic approach [902]. In this regime, deflagration was affected by augmenting the initial temperature (T_0) of the AP strand and by adding fuels like aliphatic dicarboxylic acids or polymers like CTPB. From this thermodynamic model, considering the dependence of burning rate (r) on pressure (P) and T_0 , the true condensed ($E_{a,c}$) and gas phase ($E_{a,g}$) activation energies, just below and above the surface respectively, were obtained. The data clearly distinguished the deflagration mechanisms in regime I' and regime I (2.03–6.08 MPa). A substantial reduction in the $E_{a,c}$ of regime I', compared to that of regime I, is attributed to the HClO_4 -catalyzed decomposition of AP. The excess heat transferred onto the surface from the gas phase is used to melt AP and hence $E_{a,c}$ in regime I, which corresponds to the melt AP decomposition. This was consistent with the similar variation observed for both the melt layer thickness and r as a function of P . Thermochemical calculations of the surface heat release supported the thermodynamic model and revealed that the AP sublimation reduced the required critical exothermicity of 1108.8 kJ/kg at the surface. It accounted for the AP not sustaining combustion in the subcritical regime I'. Further support for the model came from the temperature-time profiles of the combustion train of AP. The gas and condensed phase enthalpies, derived from the profile, was in excellent agreement with those computed thermochemically. The proposed thermodynamic model also satisfactorily explained certain unique features like intermittent, plateau, and flameless combustion in AP/polymeric fuel systems (see [901] also).

An AP deflagration model was proposed, which included combustion processes in the solid phase, liquid/gas mixed phase, and the gas phase, including detailed kinetic mechanisms [914]. It was assumed that AP decomposition proceeds via two parallel decomposition paths to form bubbles in which gas reactions can occur. The calculated results showed good agreement with experimental data in burning rate characteristics between 2.02 and 12.12 MPa (20–120 atm) and final equilibrium properties. The two mechanisms produced very different flame stand-off distances. The predicted temperature and species profiles were quite different also. To expand this model, a three-phase combustion model of the deflagration of AP was developed [915, 916].

A modified model was applied to compute the linear and non-linear combustion response properties of monopropellant AP burning [917, 918]. The kinetics constants were changed to achieve good agreement with response function data as well as with steady-state data. Supplemental mathematical analyses connected the AP model to the basic two parameters of the classical theory. It demonstrated the key factors which determine the nature of the combustion response.

In another model [919], a one-dimensional aero-thermo-chemical flow field was described through the solution of mass, energy, and species conservation equations. The unsteady one-dimensional phase heat transfer accounting for regression was solved in the condensed phase. The uncertain parameters for AP pyrolysis, gas-phase reaction, and extent of surface exothermicity were selected to ensure that the most certain of the measured parameters of AP combustion were correctly predicted. Parameters of interest are pressure index of stable combustion (an index of 0.77 between 2 and 7 MPa), the initial temperature sensitivity of the burn rate, σ_p (about 0.0021 to 0.0015 K⁻¹), range of surface temperatures (~850 to 875 K), and LPDL at 300 K (~2 MPa). The results obtained showed that the pressure index of AP combustion was 0.77 and σ_p was 0.0024–0.0023 K⁻¹. It was suggested that the LPDL is caused by a combination of loss of the liquid layer and transient conduction into the condensed phase and not by heat loss.

An interface model for AP deflagration flames included complex chemistry and detailed transport in the gas phase and heat conduction in the solid phase [920]. The interface condition considered sublimation of AP as well as reaction products obtained through a molten liquid phase. The resulting parameterized two-point boundary value problem was solved using a phase-space, pseudo-arclength, continuation method that employed Euler predictors, Newton-like iterations, and global adaptive gridding techniques. The use of boundary conditions for the temperature at the solid phase cold boundary led to a better understanding of reasons for extinguished flames such that it was possible to predict qualitative pressure extinction limits of AP flames subjected to heat losses. Preheated low-pressure flames, as well as high-pressure flames, were simulated in good agreement with experimental results.

To obtain rate constants of the dominant reaction on the combustion of AP, Sinditskii et al. used the Zeldovich condensed-phase model, data on AP burning rates in the pressure interval of stable combustion 2–6 MPa, surface temperatures derived from the generalized expression for gas pressure over the solid or melted AP surface, and took into account heats of phase change and melting, which are 88 and 251 J/g (21 and 60 cal/g), respectively [838]. The results are shown in Figure 43 in comparison with decomposition kinetics of gaseous perchloric acid, initial rates of decomposition of a liquid eutectic of AP with guanidine perchlorate, and low- and high-temperature AP decomposition in the condensed phase.

An excellent agreement was demonstrated between rate constants of the rate-determining reaction in combustion

$$k = 10^{11.8} \cdot \exp(-20210/T),$$

perchloric acid decomposition reaction, and AP initial decomposition in the liquid state. This was claimed to be convincing evidence for the previously stated assumption of the leading role of chemical processes in the thin liquid surface layer on the surface of burning AP (see [921] also).

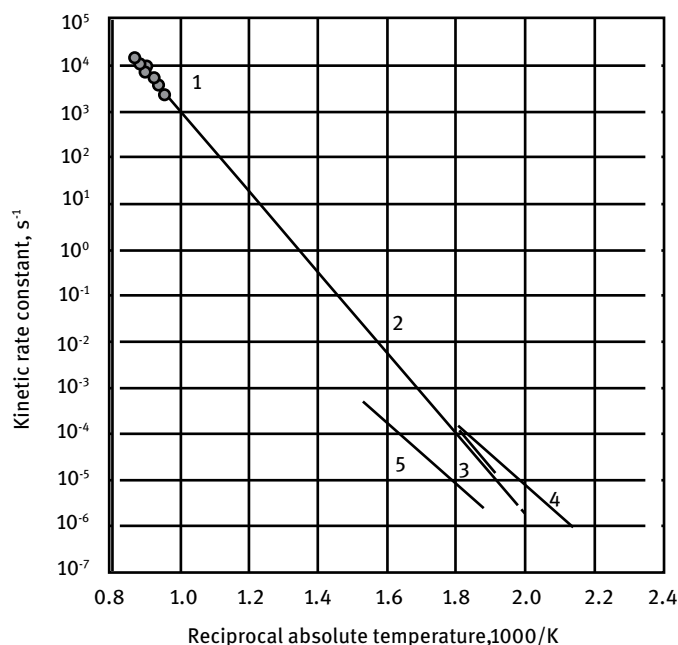


Figure 43: Rate constants versus reciprocal temperature for the rate-determining reactions during AP combustion. (Republished and modified from [203], with the permission of © 2009 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center).

Legend: Points (1) and dashed lines (2): perchloric acid decomposition in the gas phase; initial decomposition of liquid eutectic of AP and guanidine perchlorate (3); AP decomposition in the solid-state at low (4) and high temperatures (5).

More recently, and due to the improvement of computers and kinetic data, models based on global kinetics are being replaced by modeling of gaseous flames above burning propellants based on gas-phase detailed kinetics. Most of the models are essentially a modern development of the Beliaev-Zeldovich gas-phase model. Due to different activation energies, the decomposition reaction is the rate-limiting stage at low temperatures, and secondary redox reactions are the limiting ones in the high-temperature regime. In most cases, the heat release in the condensed phase is controlled by decomposition kinetics. Knowledge of detailed chemistry is needed only for the modeling gas phase. Thermocouple-aided experimental studies on the combustion of different energetic materials have found that the surface temperature is equal to boiling point or, in the case of salts, dissociation temperature [838, 839]. One can suppose, therefore, that there exists a microscopic (not a macroscopic) equilibrium at the surface between boiling substances. Energetic materials can be heated in the condensed phase to their maximum temperature, which is the boiling point, or in the case of onium salts, their dissociation temperature. It is very interesting to compare

the surface temperature of decomposing ammonium salts to the acid strength of the parent acid, which relates to the dissociation equilibrium constant for the dissociating salt (Figure 44).

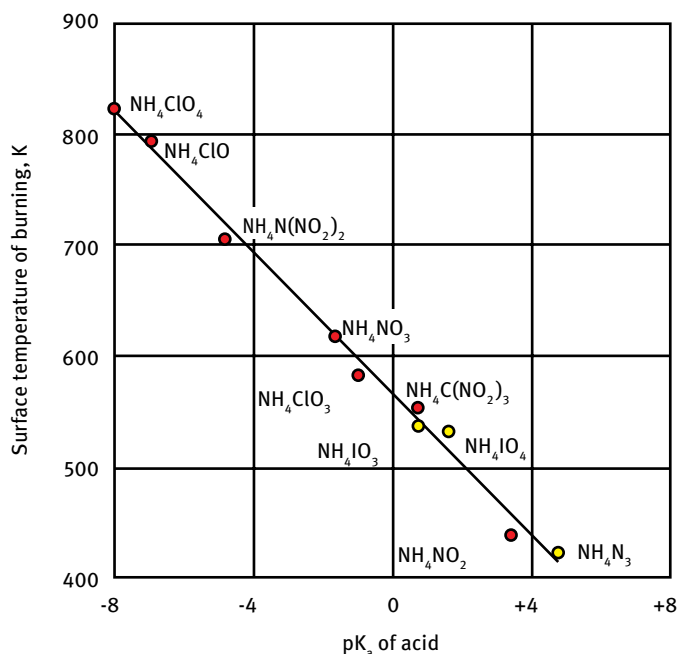


Figure 44: Comparison of surface temperatures of burning onium salts and strength of acids. (Reproduced and modified from [203].)

5.18 Combustion of Ammonium Perchlorate in Solid Propellants

There are too many publications on the combustion of AP in rocket propellants and we cannot reference them all in this book. The main application aspects of such papers will be discussed in future volumes on solid propellants, mostly concerned with formulating and processing composite propellants. Here we have assembled some related papers where the emphasis is on the kinetics of AP decomposition as an oxygen source and the effects of AP particle size and additives on the burning rates of such propellants. In many cases, the studies were conducted side-by-side using AP, with and without combustible fuels (binders or simulated binders). Therefore, there is some overlap and some unavoidable repetition between this chapter and some of the preceding chapters.

Because there are so many publications on this subject, it was difficult to get the references organized in a systematic way. Due to a lack of other sorting criteria, we

have arranged the literature here chronologically by the decade in which it was published.

The results of surface temperature measurements on AP burning under a variety of conditions from 5.5 to 2064 kPa (0.05 to 20.43 atm = 0.8 to 300 psia) point to the possibility that some heat release is likely to occur within the solid surface although the combustion in all pressure regions appears to be dominated by gas-phase reactions [922]. Results with catalysts that are supposed to increase the extent of the condensed phase reaction do not alter this conclusion.

Experimental evidence of the gasification process of AP burning under a very wide variety of conditions showed that AP dissociation is generally better represented by a kinetic decomposition law than by an equilibrium law [858]. A kinetic decomposition law would predict an activation energy of 125 kJ/mol (30 kcal/mol). During combustion, some exothermic redox reactions in the condensed phase accompany the dissociation of the salt. At low pressures, the burning rates of composite mixtures of AP with organic fuels were little affected by fuel-binder properties (other than by the heat of combustion), however, at high pressures the opposite was true. Possible explanations for this have been proposed. At constant final-flame temperature, the volumetric oxidizer loading of a binder appears to be more important than its thermal stability, and the idea of a fuel “barrier” hindering propagation of the AP monopropellant flame at high pressures is supported. Rates of flame travel along AP/binder interfaces in sandwiches are not very different from the burning rates of the corresponding composite propellant. This does not seem to be a rate-controlling process.

If propellants are prepared from AP, which has been preheated until the low-temperature reaction was complete, the burning rate was not different from that of controls that had not been preheated [879]. It was theorized that any thermal decomposition occurring in the solid phase ahead of the combustion zone has no significant effect on the burning rate (see [15, 923, 924] also).

The burning rates of fine, coarse, and bimodal particle size mixtures of AP with PS and poly(methylmethacrylate) were investigated [925]. Fe_2O_3 with a specific surface of $5.3 \text{ m}^2/\text{g}$ was used in an amount of 1% as a catalyst. In the finely dispersed systems, the efficiency of the catalyst was lowest in mixtures with the maximum burning rate. In coarsely dispersed mixtures the efficiency decreased with increasing content of combustible material. In mixtures containing a bimodal oxidizer particle size distribution, the efficiency changed with the ratio between the fine and coarse fractions of oxidizer and the change was not linear. An attempt was made to explain the dependence of the efficiency of the catalyst on the degree of dispersion of the ingredients based on the general theory of combustion of mixtures.

An evaluation of the decomposition kinetics of energetic materials (including AP) in the combustion front of solid propellants was based on experimental data and theoretical calculations (see [838, 921] also). This paper is an excellent summary of the relationship between decomposition kinetics and burning rates, supported by a long literature reference list containing 96 references of prior publications.

6 Compatibility With Ammonium Perchlorate

AP comes into contact with many different materials during its manufacture, transport, storage, grinding, sifting, and final processing stages (with binders into propellants and casting into a motor casing). Formulated propellants then are put in contact with ignitors, inhibitors, liners, and moisture barriers while they are stored in the field under a variety of conditions. Although AP is a solid, and solid-solid reactions are much slower than reactions with liquid rocket propellants, the compatibility of AP with various materials must be known in order to avoid problems.

6.1 Compatibility of Ammonium Perchlorate With Metals

The compatibility of AP with metals is very dependent on the moisture content of the material. Moist conditions will accelerate corrosion.

6.2 Compatibility of Ammonium Perchlorate With Polymers

Essentially all AP eventually comes into contact with polymers when it is processed into composite solid propellants with polymeric binders. The volume on solid propellants contains several chapters on solid propellants with AP and diversity of binders. AP is compatible with most, but not all of them. Protective coatings were necessary in some instances.

6.3 Compatibility of Ammonium Perchlorate With Wetting Agents

Sometimes AP is coated with wetting agents to improve the bond between the inorganic and organic phases in a heterogeneous mix. AP must be compatible with binders, curing agents, and wetting agents.

A dendritic bonding agent that can coat AP was characterized using SEM, XPS, and micro-infrared [926]. This coating forms a viscous film on the surface of AP; the coverage can be up to 47% based on XPS analysis. The coverage can be improved by increasing the CN group content. Micro-IR analysis indicated that H-bonds are formed between the wetting agent and N—H groups.

6.4 Compatibility of Ammonium Perchlorate With Plasticizers

Several of the plasticizers used in composite modified double-base (CMDB) propellants are nitrate esters that may react with AP and degrade with time [927].

6.5 Compatibility of Ammonium Perchlorate With Pyrotechnics

Most pyrotechnic formulations contain potassium perchlorate, which is compatible with AP. Pyrotechnics of various compositions may be in contact with AP where igniters are installed in the immediate vicinity of AP-based solid propellant grains. Contact with pyrotechnics that contain chlorates must be avoided.

7 Toxicity of Ammonium Perchlorate

Prior to the development of AP as a rocket propellant, potassium perchlorate had been used as a medicine at various times during the last 60 years to treat hyperthyroidism. Since World War II, AP has been used as a propellant for rockets, resulting in increased production and, unfortunately, dispersion of perchlorates in the environment. In 1997, the assay sensitivity for perchlorate in water was improved by two orders of magnitude from 0.4 mg/L (ppm) to 4 µg/L (ppb). As a result, public water supplies in Southern California were found to contain perchlorate ion concentrations in the range of 5 to 8 ppb, and those in Southern Nevada were found to contain 5 to 24 ppb. Research programs have been developed to assess the safety or risk from these exposures and to assist state and regulatory agencies in setting a reasonable safe level for perchlorates in drinking water.

The extent of perchlorate contamination of water sources nationwide was not discovered until 1997. As of 2005, over 11 million people had perchlorate in their public drinking-water supplies at concentrations of 4 ppb (4 µg/L) or higher. The reasons for the increased interest and awareness of the potential accidental exposure to perchlorates from drinking water are the development of ever more sensitive methods of analysis (sensitive to below ppb levels) and the concern about adverse effects in sensitive populations (fetuses, babies, elderly). However, there has been a great amount of uncertainty and controversy about the suspected and purported effects of perchlorates on human health and the environment [928]. In response to the concern of the public, the DoD in the US and other government agencies initiated a series of programs with the following three objectives: **(1)** development and testing for effective remedial technologies for clean-up in drinking water, soils, and groundwater, **(2)** improved methods to characterize perchlorate-contaminated sites, and **(3)** improved understanding of the human and ecological health effects of perchlorate exposure.

There are several summaries of perchlorate toxicity, environmental effects, and occupational health implications, particularly following the discovery of widespread pollution of aquifers and drinking water which became apparent in the 1990s [929–931]. Even the legal and liability aspects of perchlorate pollution are now dealt with in a book [932].

The *Toxicological Profile for Perchlorates* report was published by the US Department of Health and Human Services, the Public Health Service, and the Agency for

Toxic Substances and Disease Registry [933]. It is a very comprehensive summary that includes chapters on Public Health (Chapter 1), Relevance to Public Health (Chapter 2), Health Effects (Chapter 3, which occupies almost half of the volume of the entire study), Chemical and Physical Properties (Chapter 4, which is very short), Production, Import/Export, Use and Disposal (Chapter 5), Potential for Human Exposure (Chapter 6), and Analytical Methods (Chapter 7). This report also contains data on perchlorates other than AP, including magnesium, potassium, sodium, and lithium perchlorate. It provides a very good introduction to the potential problems with widely dispersed perchlorate contamination in the vicinity of inhabited areas and drinking or irrigation water sources.

The chemical and rocket propellant industry have combined forces to provide up-to-date information on the perchlorate situation in the US. The Perchlorate Information Bureau (<http://www.perchlorateinformationbureau.org>, formerly the Council on Water Quality) is supported by Aerojet, AMPAC, and Lockheed Martin. These companies have worked co-operatively with the EPA to increase scientific and medical understanding of perchlorate risk to human health. The aforementioned website will help get the true facts out about perchlorates, based on more than five decades of peer-reviewed scientific research and study, and will ensure that it has its rightful place in public discussion. According to credible data and research available, perchlorates do not cause cancer in humans or birth defects and it is not stored within the body.

Since the 1950s, potassium perchlorate has been used in the US and abroad to treat thyroid disorders in human patients. As a result, a wealth of information exists about perchlorate toxic effects and how it relates to human health. The doses used for medical treatment are tens of thousands of times greater than the low levels of perchlorate detected in drinking water.

During the past two decades, millions of dollars have been spent studying the possible health risks of perchlorate because of its presence at trace levels in some water supplies. Scientific and medical research shows that the low levels of perchlorate being detected in drinking water are not dangerous to human health. These studies on adults, newborns, and children provide a reason to believe that low levels of perchlorate (even at levels many times higher than the minute amounts being found in some drinking water supplies) have no measurable effect on pregnant women or fetuses. Scientific evidence (e.g., the National Academy of Sciences [NAS] report and other credible and peer-reviewed studies by respected and independent medical researchers) does not link low levels of perchlorate to thyroid problems or thyroid cancer in humans.

In February 2005, the EPA established its official reference dose (RfD) of perchlorate at $0.0007 \text{ mg kg}^{-1} \text{ d}^{-1}$ and translated that number to a Drinking Water Equivalent Level of 24.5 parts per billion. This level is consistent with the recommended RfD included in NAS' January 2005 report on the health implications of perchlorate [934].

Several of the toxicity studies referenced in this section have been conducted with potassium perchlorate or sodium perchlorate instead of AP. The type of cation present does not appear to have much of an influence on perchlorate toxicity.

In 2005, the Government Accountability Office (GAO) in the US issued a report on perchlorate monitoring and detection. They concluded that a system to track sampling and clean up results is needed [935].

In August 2010, the same Government Accountability Office issued a report on perchlorate occurrence and the regulatory actions taken to date [936]. It stated that occurrence is widespread but at varying levels and that federal agencies have taken some actions to respond to and lessen releases. GAO was asked to examine **(1)** what is known about the extent to which perchlorate occurs in the nation's water and food supply and its likely sources; **(2)** what actions DoD, NASA, and Department of Energy (DoE) have taken to respond to or lessen perchlorate releases; and **(3)** what actions states such as California and Massachusetts have taken to regulate perchlorate. To address these questions, GAO analyzed data from the EPA, DOD, NASA, and DOE, then reviewed agency documents, and interviewed federal and state officials, researchers, and others (see [937, 938]).

7.1 Acute Toxicity of Ammonium Perchlorate – Animal Studies

It is surprising that considering the huge quantities of AP consumed around the world, there are only a few very antiquated sources for the lethal dose 50% (LD_{50}) of AP in animal studies. Published toxicological studies on perchlorates have focused primarily on laboratory mammals such as rats and mice. This is partly due to the medical interest in perchlorate use as a drug to block iodine uptake and thus prevent hyperthyroidism (Graves' disease). Most toxicity evaluations of perchlorates focus on the levels of thyroid hormones triiodothyronine (T3) and thyroxine (T4) because it is generally assumed that deficiencies of these hormones affect growth and development as well as metabolism in animals.

7.1.1 Oral Toxicity of AP – Animal Studies

The oral LD_{50} of AP in white rats was reported to be 3556 mg/kg [939]. Looking at the title of this paper, one must ask, "How come the Russians already had concerns about perchlorates in drinking water reservoirs in 1963?" It is quite possible that they recognized the hazards of perchlorate releases into surface waters before the US did. In general, it appears that rabbits are more sensitive to the acute effects of perchlorate than other rodents.

The AMPAC Material Safety Data Sheets (MSDS) lists the following LD_{50} data, but the source of these data was not stated:

- Oral LD_{50} : rat; 4200 mg/kg
- Rat-par-LDLo = 3500 mg/kg
- Oral LD_{50} : rabbit; 1900 mg/kg
- Rabbit-par-LDLo = 750 mg/kg

Other sources state:

Toxicity:

- ORL-RAT LD₅₀ 4200 mg/kg
- SCU-RAT LD₅₀ 1600 mg/kg

Toxicity data

- ORL-RAT LD₅₀ 4200 mg/kg
- SCU-RAT LD₅₀ 1600 mg/kg
- ORL-RBT LD₅₀ 1900 mg/kg
- IPR-MUS LDLO 2000 mg/kg

Because perchlorate salts are completely dissociated in water and the associated cations (Na⁺, K⁺, NH₄⁺) are widely distributed in nature, many toxicological reviews assume that the contribution from the cations to overall toxicity is negligible and report the perchlorate ion concentration only, such as in Table 23.

Table 23: Summary of median lethal dose (LD₅₀) data for perchlorate salts.

Species	Route of administration	Chemical form	Perchlorate ion concentration ^a (mg/kg)
Rabbit	Oral	NH ₄ ClO ₄	635–1610
Mouse	i.p.	NaClO ₄	934
Mouse	Oral	NH ₄ ClO ₄	1610–1690
Guinea Pig	Oral	NH ₄ ClO ₄	2800
Rat	Oral	NH ₄ ClO ₄	2960–3560

i.p. = intraperitoneal

^aPerchlorate ion concentration is determined by multiplying the concentration of perchlorate salts by weight fraction perchlorate ion (NH₄ClO₄ = 0.847, NaClO₄ = 0.812, KClO₄ = 0.718).

Data source: [938], also reported in [940].

7.1.2 Pulmonary Toxicity of Perchlorates – Animal Studies

In addition to the thyroid gland, other potential target organs of perchlorate toxicity are the lungs and kidneys. Perchlorate toxicity can also impact blood.

In order to explore whether AP could cause pulmonary fibroblast proliferation, pulmonary fibroblasts of mice were cultured *in-vitro* [941, 942]. After three generations, cell cultures were treated with 50, 200, and 500 mg/L AP for 48 hours. The fibroblasts exposed to quartz (300 mg/L) were taken as the positive control and normal cultured fibroblasts as the negative control. Comparing morphological changes in the AP-treated groups with the negative control group, there was no significant difference in the shape of the cell slice, dimension, proportion between karyon and cytoplasm, the density of collagen, or cell thickness. However, in the positive control

group treated with quartz, there were a series of changes, such as cell enlargement, increase in cell quantity, enrichment in cytoplasm, and density of collagen. It was concluded that proliferation and collagen hyperplasia of fibroblast were not affected by AP *in-vitro*.

Similar results were obtained in rats. The levels of cell counts, tumor necrosis factor TNF α , MDA, hydroxyproline (HYP), and the synthesis of collagen in rat lungs after rats were injected with AP by intratracheal instillation were measured. It was found that AP could bring about acute lung damage and inflammatory reaction [943]. The levels of TNF α of different groups at different times were obviously higher than the normal control group ($P \sim 0.05$). AP adversely affected the levels of MDA, HYP, and the synthesis of collagen. But AP caused no obviously pathological change of pulmonary fibrosis.

In a similar experiment, rats were injected with AP by intratracheal instillation for seven to 29 days to allow a pathological examination of lung tissue [944]. This revealed that AP could bring about an acute inflammatory reaction but no obvious pulmonary fibrosis. There was no obvious change in the level of HYP in embryo pulmonary fibroblasts after administering AP. The level of TNF- α in the low dose group was higher than that of a negative control group ($P \sim 0.01$). The highest level was found after 29 days.

AP appears to be cytotoxic to alveolar macrophages [945]. In another experiment, alveolar macrophages were treated with AP for 24 hours [946]. Pulmonary fibroblasts were cultured with the supernatant of an alveolar macrophage medium. Rats were treated with AP by intratracheal instillation and euthanized after three days following which the TGF- $\beta 1$ mRNA content in the lung was examined. The positive staining macrophages in low and high AP groups and the quantity of TGF- $\beta 1$ in the high AP group were obviously higher than those in the control group ($P \sim 0.01$). However, there was no significant difference in the proliferative activity and the HYP content of pulmonary fibroblasts in all groups. The mRNA contents of TGF- $\beta 1$ in three AP groups were all significantly higher than that in the control group.

7.1.3 Hematotoxicity of Perchlorates – Animal Studies

In order to study the effect of AP on routine blood tests and serum biochemical indices in animals, 80 rats were randomly divided into four groups: one control group (physiological saline) and three AP treatment groups [947]. For the treatment groups, AP was administered once into the trachea of the rats at doses of 48, 96, and 192 mg/kg body weight, respectively. There was no significant difference among routine blood indices of various dosed groups following this AP treatment ($P \sim 0.05$). On the third day of treatment, the serum activities of alanine aminotransferase (ALT) for both middle and high dose AP groups (86.7, 85.5 U/L) were higher than that of the control group (56.6 U/L, $P \sim 0.05$). On the seventh day of the treatment, the contents of HYP of the AP low, middle, and high dose groups (17.4, 17.1, 18.2 $\mu\text{g/mL}$) were higher than that of

the control group (13.3 µg/mL, $P \sim 0.01$). On the 28th day of treatment, the content of urea nitrogen (19.4 mmol/L) was higher than that of the control group (14.7 mmol/L, $P \sim 0.05$). There were no toxic effects of AP found upon routine blood tests of rats. The ALT and HYP in the serum of rats increased significantly in the short term.

7.2 Metabolic Pathways of Ammonium Perchlorate

The bloodstream carries perchlorate to all parts of the body. Perchlorate is not changed or metabolized inside the body. A few internal organs (for example, the thyroid, breast tissue, and salivary glands) can take up relatively large amounts of perchlorate from the bloodstream. Perchlorate generally leaves these organs within a few hours. In the blood, perchlorate passes into the kidneys, which then release it into the urine. The body begins to clear itself of perchlorate through the kidneys within ten minutes of exposure. Perchlorate is excreted unchanged by the kidneys with a half-life of approximately six hours.

Perchlorate reached a maximum concentration (>3% of the administered dose/g tissue) in the thyroid gland of rats four hours after an intraperitoneal injection of radio-labeled potassium perchlorate ($K^{36}ClO_4$; 18 or 24 mg ClO_4 /kg) [948]. The elimination half-time for the thyroid was estimated to be approximately ten to 20 hours in rats.

A model for the metabolic pathways, consumption, and excretion of perchlorate in rats can eventually be extended to other mammals [949].

7.3 Thyroid Gland Interference by Ammonium Perchlorate

The majority of perchlorate salts are extremely soluble and mobile in natural water. As a result, they have become ubiquitous in surface, ground, and drinking water in several states of the US. The ingestion of perchlorate from contaminated water can interfere with the production of thyroid hormones because perchlorate competes with iodide uptake via the thyroid gland. It is especially dangerous for fetuses and neonates because thyroid hormones play a significant role in neurodevelopment. New analytical methods have been developed to detect perchlorates in water [950].

The main target organ for perchlorate toxicity in humans is the thyroid gland. Perchlorate anion affects the functioning of the thyroid and pituitary glands. Perchlorate has been shown to partially inhibit the thyroid's uptake of iodine (iodide) and is called a thyroid endocrine disruptor [951, 952]. Perchlorate and iodide compete for the same receptors. The competitive absorption of perchlorate and iodide is due to the similar energy of hydration and ion radii of the two ions [953]. Although not demonstrated in humans, it is anticipated that people exposed to excessive amounts of perchlorate for a long time may develop a decreased production of thyroid hormones. The medical name for this condition is *hypothyroidism*. Iodine is required as a building block for

the synthesis of thyroid hormone. Nowadays most table salts contain added iodide to assure an adequate supply of iodide in the diet even in the absence of a challenge by perchlorate. Populations living near seashores are less likely to develop iodine deficiency diseases because the ocean spray carries seawater (and iodide) aerosols inland. The thyroid gland produces two hormones, thyroxine (T4) and triiodothyronine (T3) from their precursor thyroglobulin, which circulate in the bloodstream and are primarily bound to protein. Thyroid hormone synthesis and secretion are normally maintained within narrow limits by an efficient regulatory mechanism. Specifically, decreases in serum thyroid hormone concentrations lead to increases in the secretion of thyrotropin (thyroid-stimulating hormone, TSH) by the pituitary gland, and increases in serum thyroid hormone concentrations lead to decreases in TSH secretion. TSH stimulates virtually every step of thyroid hormone production and secretion, and such tight control of TSH secretion maintains thyroid hormone production and secretion within normal or nearly normal limits. This thereby protects against both hypothyroidism (deficiency of thyroid hormone production) and hyperthyroidism (excess of thyroid hormone production). The pituitary gland produces and releases TSH, which is released when circulating levels of thyroxine and triiodothyronine decrease.

T4 is largely a precursor hormone with little or no intrinsic biologic activity. It is converted to T3, the biologically active thyroid hormone, in most tissues of the body. T3 is required for the normal development of the central nervous system in fetuses and infants. Its actions include stimulation of the development and growth of neurons (nerve cells) and glial (supporting) cells, the formation of synapses (connections) between neurons, the formation of the myelin sheaths that surround neuronal processes, and the development of neurotransmitters that transmit signals from one neuron to another.

Iodine is a component of T4 and T3, and the transfer of iodide from the circulation into the thyroid gland is an essential step in the synthesis of the two hormones. Iodide transport into the thyroid is mediated by a protein molecule known as the sodium (Na⁺)/iodide (I⁻) symporter (NIS). NIS molecules bind iodide with very high affinity but they also bind other ions that have a similar shape and electric charge such as perchlorates. Perchlorates can affect thyroid function because it is an ion that competitively inhibits the transport of iodide into the thyroid by the NIS.

Perchlorates have been used as a medicine to reduce hormone outputs in patients with hyperthyroidism, hyper-functional thyroid glands associated with Graves' disease, but its use has now been discontinued. These patients unwittingly served as "guinea pigs" and their medical history data were mined retroactively in an effort to establish the safe no-effect level of perchlorate in drinking water. Doses of perchlorate range from <1 mg kg⁻¹ d⁻¹ to >20 mg kg⁻¹ d⁻¹ with typical doses in the range of 6–14 mg kg⁻¹ d⁻¹. The effects observed include the blockage of iodine uptake and iodine discharge by the thyroid gland. Because of side effects and the development of better anti-thyroid drugs, the use of perchlorate to treat hyperthyroid patients largely ceased in the US by the late 1960s.

Children and developing fetuses and people with pre-existing thyroid disorders may be more susceptible to perchlorate than normal adults because thyroid hormones are essential for normal growth and development [954–957]. Two studies were conducted of newborn babies and school-age children from an area in Chile where levels of perchlorate in the drinking water were much higher than those detected in some US water supplies due to natural sources of perchlorate. No evidence of abnormal thyroid function was found among the babies or the children. The effects of perchlorate are neglectable as long as normal diets contain sufficient iodine (iodide). Perchlorate is accumulated in thyroid follicle cells and lumen where it competes with iodide [958].

7.3.1 Thyroid Gland – Animal Studies

The pituitary-thyroid system of rats is similar to that of humans. For example, decreases in thyroid hormone production result in increased secretion of TSH, which then increases thyroid production and releases T4 and T3. However, differences in binding proteins, binding affinities of the proteins for the hormones, turnover rates of the hormones, and thyroid stimulation by placental hormones lead to important quantitative differences between the two species. Therefore, although studies in rats provide useful qualitative information on the potential adverse effects of perchlorate exposure, they are limited in their utility for quantitatively assessing human health risks associated with perchlorate exposure.

Several animal studies have demonstrated the effect of perchlorates on the thyroid and its hormones.

Orally administered perchlorate failed to affect deciduoma formation or pregnancy but thyroid gland weights were significantly increased in Wistar rats exposed to 1% KClO_4 in the drinking water on days two through eight of gestation [959].

Thyroid weights of Wistar rat dams and their litters were significantly increased as the result of 2440 mg/kg KClO_4 in the drinking water during gestation [960]. The controls with potassium chloride suffered no such effects.

There is a lack of dose-response studies on the effect of perchlorate on the thyroid-pituitary gland system. Only a few studies have quantified the effect. Mannisto et al. [961] detected perturbations in the thyroxine and triiodothyronine and TSH levels in male Sprague-Dawley rats fed with 0 to 500 mg/L ClO_4^- in their drinking water for four days.

Suckling Wistar rats became acutely iodine deficient by dam exposure to 1.23 g/L NaClO_4 in the drinking water from birth through day ten after birth [962]. Pharmacokinetic modeling of the plasma, thyroid, and skin equilibrium demonstrated decreased iodide concentrations compared to controls, increased iodide uptake by the thyroid, and decreased skin iodide uptake. In a similar test using Sprague-Dawley rats that were fed with 0 to 250 mg ClO_4^- in drinking water for 14 days, the thyroglobulin and TSH levels increased but the triiodothyronine level decreased.

The thyroid follicle lumen sizes of thyroid glands of five-day and 90-day-old rat pups whose dams were exposed to AP were measured and morphometrically assessed to establish a RfD for AP. The dams were exposed to a daily oral intake of 0, 0.1, 1, 3, or 10 mg AP/kg body weight [963]. The post-natal evaluation spanned 81 days. The pups received further exposure to perchlorate through day ten of lactation. Tissue samples were stained and measured with a charge-coupled device (CCD) camera on a microscope and a digital image analysis system for follicle count and follicle lumen area. Female samples taken from five-day-old animals formed a smooth dose-response curve with decreasing follicular lumen sizes at each increasing dose level with a significant difference at the highest dose (10 mg/kg). Observations in five-day-old female rats gave a smooth dose-response curve but the data for five-day-old males at 1 mg/kg were not much different from the controls. The dose-response of the males was valid if the 1 mg/kg data points were omitted. Animals that were kept for 81 days post-exposure showed no significant differences between dosage groups and controls for either sex. Based on these data, the **no observable adverse effect level** (NOAEL) of $1 \text{ mg kg}^{-1} \text{ d}^{-1}$ was recommended. The **lowest observable adverse effect level** (LOAEL) was at $3 \text{ mg kg}^{-1} \text{ d}^{-1}$.

Significant gender differences in sensitivity to AP were observed when eight groups of 12 Sprague-Dawley rats, six male and six female, were exposed to incremental doses of AP in their drinking water [964]. The results indicated that triiodothyronine (T3) levels in male and female rats fell. However, thyroxine (T4) levels in male rats remained relatively unchanged. Reverse triiodothyronine (rT3), thyrotropin (TSH), and thyroglobulin (Tg) all increased in both males and females. These results confirmed that the AP anion blocked the uptake of iodine in the thyroid. Although an estimated threshold could not be determined, the NOAEL for AP on the TSH levels was 0.44 mg/kg/d for male rats and 0.124 mg/kg/d for female rats. These NOAELs were consistent with the assumptions made by the EPA, which estimated a NOAEL of 0.14 mg/kg/day for perchlorates.

In a 14-day drinking water pilot study in rats, the animals were exposed to one of seven doses of perchlorates ranging from 0.1 to $39.9 \text{ mg ClO}_4^- \text{ kg}^{-1} \text{ d}^{-1}$. Perchlorate administration induced dose-related increases in TSH and decreases in T4 and T3 in both males and females, but females appeared to be more sensitive than males. The lowest administered dose, $0.1 \text{ mg kg}^{-1} \text{ d}^{-1}$, increased TSH and decreased T4 and T3 in females roughly by 15, 12, and 34%, respectively, relative to controls [965].

Fourteen and 90-day exposures of mice to 0, 0.1, 1.0, 3.0, and $30 \text{ mg kg}^{-1} \text{ d}^{-1}$ in drinking water produced no significant changes in thymus weight, thymus cellularity, and thymus to body weight ratio for any of the 14- or 90-day treatments [966]. AP is known to cause hypothyroidism with subsequent increases in TSH and decreases in both circulating T3 and T4. However, the profile obtained in mice exposed to AP was one of no change in TSH and T3, with significant decreases in T4. Histology indicated some pathological effects in the thyroid. AP affected thyroid hormone levels in the serum. The primary effect observed in mice treated with AP was decreased phagocyto-

sis function of peritoneal macrophages. White blood cell count, red blood cell count, hematocrit, hemoglobin were not affected. Body, spleen, liver, thymus, and kidney weights were normal. AP did not alter the susceptibility to infections.

No gross or microscopical alterations were observed in the lungs or heart of rats and there was no sign of hematotoxicity in rats administered AP via drinking water at doses of up to $8.5 \text{ mg perchlorate kg}^{-1} \text{ d}^{-1}$ for up to 90 days [967].

A two-generation reproductive study examined the effects of AP on male and female reproductive systems in rats and on the growth and development of offspring [968]. Adult Sprague-Dawley rats (30/sex/group) were given continuous access to AP in their drinking water at doses of 0, 0.3, 3, and $30 \text{ mg kg}^{-1} \text{ d}^{-1}$. F1 generation rats were given the same AP doses as their respective P1 generation sires and dams beginning at weaning and continuing through the day of sacrifice. Standard reproductive parameters were evaluated; blood was collected for determination of serum TSH, triiodothyronine (T3), and thyroxine (T4) levels. Histopathological examination was conducted on major tissue including the thyroid. No significant changes in developmental parameters were observed. In the F1 generation adult rats, relative thyroid weights were significantly increased in all dose groups for female rats and in the 3.0 and $30 \text{ mg kg}^{-1} \text{ d}^{-1}$ dose groups for male rats. Histopathologic changes in the thyroid consisted of hypertrophy and hyperplasia that increased in incidence and severity in a dose-related manner. Dose-related, statistically significant changes in TSH and T4 or T3 occurred at doses higher than those that resulted in changes in thyroid weight and thyroid histopathology, $30 \text{ mg kg}^{-1} \text{ d}^{-1}$. Thus, perchlorate is not a reproductive toxicant in rats when administered in the drinking water at doses up to 30 mg/kg-day , but it can affect the thyroid at doses $\geq 3 \text{ mg kg}^{-1} \text{ d}^{-1}$. Based on these findings, $0.3 \text{ mg kg}^{-1} \text{ d}^{-1}$ is identified to be the NOAEL for this animal.

Beginning at three to four days post-hatch, bobwhite quail chicks were used to investigate AP effects on thyroid function and growth. The bobwhite quail chicks were administered a wide range of AP concentrations ($50 \mu\text{g/L}$ – 4000 mg/L) in their drinking water for relatively short (two weeks) and longer (eight weeks) exposures [969]. Thyroidal thyroxine (T4) content, the most sensitive index of decreased thyroid function, decreased markedly in response to increasing perchlorate exposure. Thyroid weight and plasma T4 were less sensitive indicators.

Despite many physiological similarities, humans and rats exhibit notably different susceptibilities to thyroid perturbation. While the data indicate that humans and rats exhibit similar dose-response relationships in terms of acute inhibition of thyroidal iodide uptake, the two species appear to exhibit notable differences in terms of thyroid hormone response, the toxicologically significant consequence of iodide uptake inhibition [970]. Comparing dose-response data for changes in serum T3, T4, and TSH levels from studies in humans, rats, mice, and rabbits, it was found that thyroid homeostasis in rats appeared to be strikingly more sensitive to perchlorate than any

of the other species. If rat data is used to develop toxicity criteria for perchlorates in humans, one must remember that the interspecies uncertainty factor is less than one.

In another test, 24 pregnant Long-Evans rats were exposed to either 0, 5, or 50 mg/L AP from GD 7-21 and to **post-natal day** (PND) 24-25 through maternal exposure and lactation [971]. On PND 24-25, female pups were euthanized and ovaries were examined histologically. The number of ovarian (preantral and antral) follicles were reduced in the $4 \text{ mg kg}^{-1} \text{ d}^{-1}$ groups but not in the $0.4 \text{ mg kg}^{-1} \text{ d}^{-1}$ groups. Co-administered T4 ameliorated the effects of perchlorates. No changes in mean ovarian area were observed between treatments.

Triggering of the HPT feedback response in profound iodide deficiency can affect the response of the thyroid to perchlorates. Rats maintained on an iodine-deficient diet for sufficient periods to lower serum T4 levels exhibited higher 24-hour thyroid radioiodide uptake when exposed to perchlorates in their drinking water ($1.1\text{--}28 \text{ mg/L}$) for five weeks than iodine-replete rats [972]. The increased resistance to perchlorate-induced inhibition of thyroid iodide uptake in iodine deficiency has been attributed, at least in part, to an induction of NIS in the thyroid. This partially overcomes the competitive inhibition of NIS resulting from a given dosage of perchlorates (see [973] also).

7.3.2 Thyroid Gland: Controlled Studies With Human Volunteers

Burgi et al. [974] studied perchlorates at a dosage of $9.7 \text{ mg kg}^{-1} \text{ d}^{-1}$ on five subjects for eight days, while Brabant et al. [975] studied perchlorates at a dosage of $12 \text{ mg kg}^{-1} \text{ d}^{-1}$ on five subjects for four weeks. Both studies observed perchlorate effects on the thyroid at these doses and found that it reduced thyroid iodide uptake, increased serum iodide levels, and increased urinary iodide excretion. Inhibition of thyroid iodide uptake is the only effect that has been consistently documented in humans exposed to perchlorate.

As of 1998, only a few studies had examined the effects of perchlorate in healthy volunteers, but within ten years many more study results were published. Studies were carried out in nine healthy male volunteers who had normal thyroid function and negative thyroid antibodies to determine whether the ingestion of 10 mg of ClO_4^- daily (approximately 300 times the estimated maximum amount of ClO_4^- consumed from the affected water supplies) would affect any aspect of thyroid function [976]. The volunteers ingested 10 mg of ClO_4^- dissolved in a liter of spring water during waking hours for 14 days in a row. Baseline serum thyrotropin (TSH), free thyroxine index (FTI), total triiodothyronine (TT3), four-, eight-, and 24-hour thyroid ^{123}I uptakes (RAIU), serum and 24-hour urine ClO_4^- , 24-h urine iodine, complete blood count (CBC), and chemistry profiles were determined. All blood and urine tests were repeated on days seven and 14 of ClO_4^- administration and thyroid radioactive iodine uptake (RAIU) on day 14 of ClO_4^- administration. All tests were repeated 14 days after ClO_4^- was discontinued. No effect of ClO_4^- on serum thyroid hormone or TSH concentrations, urinary

iodine excretion, CBC, or blood chemistry was observed. Urine and serum ClO_4^- levels were appropriately elevated during the course of ClO_4^- ingestion in all subjects, demonstrating compliance. By day 14 of ClO_4^- administration, the four-, eight-, and 24-hour thyroid RAIU values decreased in all nine subjects by a mean value of 38% from baseline and rebounded above baseline values by 25% at 14 days after ClO_4^- withdrawal. It is well-known that the major effect of ClO_4^- on the thyroid is a decrease in the thyroid iodide trap due to competitive inhibition of the sodium/iodide symporter (NIS). The study demonstrated the sensitivity of the thyroid iodide trap to ClO_4^- because a low dose of 10 mg daily significantly decreased the thyroid RAIU without affecting circulating thyroid hormone or TSH concentrations. It is possible, however, that the daily consumption of low levels of ClO_4^- in drinking water over a prolonged period of time could adversely affect thyroid function but no evidence of hypothyroidism was observed at 10 mg of ClO_4^- daily in this two-week study. It was suggested that, to determine a no-effect-level for ClO_4^- on the inhibition of the thyroid RAIU a long-term ClO_4^- exposure study would be required to be carried out.

Application of a sensitive new detection method has revealed widespread perchlorate contamination of groundwater in the southwestern areas of the US, typically at 0.005–0.020 mg/L (5–20 ppb). Perchlorate is a competitive inhibitor of the process by which iodide is actively transported from the bloodstream into the thyroid. This inhibitory action of perchlorate is the basis of its pharmaceutical use (in the treatment of hyperthyroidism) as well as its potential toxicity. In order to establish the dose-response in humans for perchlorate inhibition of thyroidal iodide uptake and any short-term effects on thyroid hormones, perchlorate in drinking water at 0.007, 0.02, 0.1, or 0.5 mg kg⁻¹ d⁻¹ was administered to 37 volunteers for 14 days [977]. In 24 subjects, eight- and 24-hour measurements of thyroidal ¹²³I uptake (RAIU) were taken before exposure. The same was performed on days two (E2) and 14 (E14) and upon day 15 post-exposure (P15). In another 13 subjects, both E2 studies and the eight-hour P15 study were omitted. There was a strong correlation between the eight- and 24-hour RAIU over all dose groups and measurement days. There was no difference between E2 and E14 in the inhibition of RAIU produced by a given perchlorate dose. On both E2 and E14, the dose-response was a negative linear function of the logarithm of dose. Based on the dose-response for the inhibition of the eight- and 24-hour RAIU on E14 in all subjects, estimates of the true no-effect level were derived: 5.2 and 6.4 µg kg⁻¹ d⁻¹, respectively. Given default body weight and exposure assumptions, these doses would be ingested by an adult if the drinking-water supply contained perchlorate at concentrations of approximately 180 and 220 µg/L (ppb), respectively. On P15, RAIU was not significantly different from the baseline. In 24 subjects, serum levels of thyroxine (total and free), triiodothyronine, and thyrotropin were measured in blood sampled 16 times throughout the study. Only the 0.5 mg kg⁻¹ d⁻¹ dose group showed any effect on serum hormones: a slight downward trend in thyrotropin levels in morning blood draws during perchlorate exposure, with recovery by P15. The study identified a no-observed-effect level (NOEL) for inhibition of iodide uptake by the thyroid at 0.007 mg kg⁻¹ d⁻¹.

A study was conducted to determine whether prolonged exposure (six months) to low levels of perchlorate would perturb human thyroid function [978]. This was a prospective, double-blinded, randomized trial. The study population consisted of 13 healthy volunteers. The dosage was 0.5 mg or 3.0 mg potassium perchlorate daily. Serum thyroid function tests, 24-hour radioactive iodine uptake, serum thyroglobulin (Tg), urinary iodine and perchlorate, and serum perchlorate were measured. Mean urinary perchlorate value during the ingestion of 0.5 mg perchlorate daily was $332.7 \pm 66.1 \mu\text{g}$ per 24 hours or $248.5 \pm 64.5 \mu\text{g/g}$ creatinine. Mean values for the four subjects who received 3 mg perchlorate daily were $2079.5 \pm 430.0 \mu\text{g}$ per 24 hours or $1941.7 \pm 138.5 \mu\text{g/g}$ creatinine. There was no significant change in the thyroid ^{123}I uptakes during perchlorate administration. There were no significant changes in serum T3, free T4 index, TSH, or Tg concentrations during the exposure period (compared to baseline or post-exposure values). Urine iodine values for the 3-mg perchlorate group were higher, but not significantly so, at baseline than during perchlorate exposure. It was concluded that a six-month exposure to perchlorate at doses up to 3 mg/d had no effect on thyroid function, including inhibition of thyroid iodide uptake as well as serum levels of thyroid hormones, TSH, and Tg. In summary, the duration of the studies of potassium perchlorate administration in healthy subjects varied from two weeks to six months. In all these studies, there were no changes in serum T4, T3, and TSH concentrations to suggest that there had been any decrease in thyroid hormone secretion. Some doses of perchlorate administered for two weeks did inhibit thyroid uptake of radioiodide. A high dose administered for four weeks lowered thyroid iodide content by 25%, indicating some decrease in iodide uptake [975], and resulted in a very small fall in serum-free T4 concentrations. However, serum TSH concentrations were also lower rather than higher, as would occur if serum-free T4 concentrations decreased to a critical extent.

There has been concern that naturally occurring perchlorate and industrial contamination of water supplies with perchlorate might pose a health hazard by inducing or aggravating underlying thyroid dysfunction. A series of studies have been conducted with normal volunteers. Volunteers included perchlorate production workers exposed intermittently to high levels of perchlorate for years and human volunteers administered perchlorate for between two weeks to six months. No abnormalities of circulating thyroid hormones, TSH, thyroglobulin, or ultrasound evaluation of thyroid structure were observed even though the thyroid ^{123}I uptake was decreased in some studies [979]. Further studies of the effects of perchlorates on thyroid function in normal volunteers have become more difficult to carry out due to the adverse publicity that perchlorate and the studies on its effect have received.

7.3.3 Thyroid Gland Function in Workers Occupationally Exposed to Perchlorates

Employees at an AP production facility in Nevada and a larger control population from the same chemical complex without direct AP exposure were monitored exten-

sively for airborne perchlorate exposure [980]. Single-shift and working-lifetime cumulative dose estimates were made using standard breathing-rate estimates and assuming rapid absorption, based upon solubility. Calculated single-shift doses ranged from 0.2 to 436 $\mu\text{g}/\text{kg}$, with an average of 36 $\mu\text{g}/\text{kg}$. Working-lifetime cumulative doses in the higher exposure group ranged from 8000 to 88000 $\mu\text{g}/\text{kg}$, with an average of 38000 $\mu\text{g}/\text{kg}$. Thyroid profiles, including free thyroxine index and TSH level, were obtained both before and after shifts to assess thyroid-axis perturbation due to single working-shift perchlorate exposure. Thyroid-function data were also analyzed with respect to estimates of cumulative exposure to assess any measurable chronic effects on thyroid gland function. Additionally, standard clinical blood test parameters of liver, kidney, and bone marrow function were evaluated to assess any measurable chronic effects of perchlorate exposure on those organs. Multiple regression was used to assess the effects of exposure variables and demographic variables on organ function parameters. No perchlorate-attributable effects on the thyroid, bone marrow, kidney, or liver function were detected.

Since pharmaceutical exposures to perchlorate are known to suppress thyroid function in patients with hyperthyroidism, a study of employees at a perchlorate manufacturing plant was conducted to assess whether occupational exposure to perchlorate suppresses thyroid function [981]. Exposure to perchlorate was assessed using measurements of ambient air concentrations of total and respirable perchlorate particles. Systemic absorption was assessed by measuring urinary perchlorate excretion. Airborne exposures ranged from 0.004 to 167 mg total particulate perchlorate per day. Urinary perchlorate measurements demonstrated that exposure to the airborne particulate perchlorate resulted in systemic absorption. Workers were grouped into four exposure categories with mean absorbed perchlorate dosages of 1, 4, 11, and 34 mg perchlorate per day. Thyroid function was assessed by measuring serum TSH, free thyroxine index, thyroxine, triiodothyronine, thyroid hormone binding ratio, thyroid peroxidase antibodies, and via clinical examination. No differences in thyroid function parameters were found between the four groups of workers across approximately three orders of magnitude of exposure and of dose. Thus, human thyroid function was not affected by these levels of absorbed perchlorate. In addition, no clinical evidence of thyroid abnormalities was found in any exposure group. The blood-cell counts were normal in all groups, indicating no evidence of hematotoxicity in this exposure range. The absence of evidence of an effect on thyroid function or blood cells from occupational airborne perchlorate exposure at a mean absorption of 34 mg/d demonstrates a NOAEL that can assist in the evaluation of human health risks from environmental perchlorate contamination.

Perchlorate and thiocyanate (SCN^-) are potent and nitrate a weak competitive inhibitor of the thyroid sodium/iodide symporter. Thiocyanate is not likely to occur in the air of perchlorate factories and can be ignored here. To determine the effects of long-term, high ClO_4^- exposure on thyroid function, a study of 29 workers employed for at least 1.7 years (50% over 5.9 years) in an AP production plant in Utah was con-

ducted [982]. The cohort was divided into three groups: Pre, During and C. Serum ClO_4^- , SCN^- , and NO_3^- ; serum T4, free T4 index, total T3, thyroglobulin (Tg), and TSH; 14-hour thyroid RAIU; and urine iodine (I) and ClO_4^- were assessed after three days off (Pre) and during the last of three 12-hour night shifts in the plant (During) and in 12 volunteers (C) not working in the plant. Serum and urine ClO_4^- were not detected in C; urine ClO_4^- was not detected in 12 of 29 and was 272 $\mu\text{g/L}$ in 17 Pre workers; serum ClO_4^- was not detected in 27 of 29 Pre workers; and serum and urine ClO_4^- were markedly elevated during ClO_4^- exposure to 868 $\mu\text{g/L}$. Thyroid RAIUs were markedly decreased in During compared to Pre workers (13.5 versus 21.5%; $P < 0.01$, paired t) and were associated with an increase in urine I excretion (230 versus 148 $\mu\text{g I/g Cr}$; $P = 0.02$, paired t) but were similar to those in the C group (14.4%). Serum TSH and Tg concentrations were normal and similar in the three groups. Serum T4 (8.3 versus 7.7 $\mu\text{g/dL}$), free T4 index (2.4 versus 2.2), and total T3 (147 versus 134 ng/dL) were slightly but significantly increased in the During versus Pre workers ($P < 0.01$, paired t). Thyroid volumes and patterns observed using ultrasound were similar in the 29 workers and 12 community volunteers. In conclusion, high ClO_4^- absorption during three nights work exposure decreased the 14-hour thyroid RAIU by 38% in ClO_4^- production workers compared with the RAIU after three days off. However, serum TSH and Tg concentrations and thyroid volume observed using ultrasound were not affected by ClO_4^- , suggesting that long-term, intermittent, high exposure to ClO_4^- does not induce hypothyroidism or goiter in adults.

The National Research Council AP report [983] contains a very detailed summary of the epidemiological and occupational studies and an interpretation of the results. Particular focus is given to vulnerable populations, including pregnant women and children.

7.4 Epidemiological Studies of Unintended Exposure to Perchlorates

Epidemiological studies have been performed on populations living near natural sources of perchlorate (and nitrate) in the groundwater or populations who live downstream of industrial sites where the amount of perchlorate contamination was being monitored for several years while corrective or mitigative action was being taken.

7.4.1 Epidemiological Studies in the US

Model-based exposure assessment is one of the least reliable methods in establishing a link between environmental exposure and health effects. The accuracy and precision of exposure assessments can be improved by simultaneous environmental monitoring and human biological monitoring, or biomonitoring [984]. Biomonitoring quantifies exposure by directly measuring the contaminant (perchlorate) in human

matrices such as blood, urine, saliva, or other tissue. The direct measurement of a biomarker proves irreputably that an exposure has occurred. Such calculations are reliable for perchlorate because most of the perchlorate is excreted unmetabolized in the urine [333].

The results of perchlorate exposure in a representative sample of the US population were compared to the NAS-recommended RfD [985]. The study comprised of 2820 participants who had completed the National Health and Nutrition Survey (2001–2002) and were above six years of age. The investigators assessed perchlorate exposure based on urinary perchlorate, urinary creatinine concentration, and physiological parameters predictive of creatinine excretion rate. By measuring perchlorate in urine, the investigators assessed combined exposure to perchlorate from all sources. In adults, the estimated median dose of perchlorate was $0.066 \mu\text{g kg}^{-1} \text{d}^{-1}$ and the 95th percentile of the distribution of estimated daily dose was $0.234 \mu\text{g kg}^{-1} \text{d}^{-1}$ (CI, $0.202\text{--}0.268 \mu\text{g kg}^{-1} \text{d}^{-1}$). Both values are lower than the MRL of $0.0007 \text{mg kg}^{-1} \text{d}^{-1}$ ($0.7 \mu\text{g kg}^{-1} \text{d}^{-1}$) that ATSDR adopted from the NAS. Only 11 out of 1532 adults aged twenty and older had estimated perchlorate exposure that exceeded the NAS-recommended RfD. Since the study included participants above six years of age, the investigators did not have exposure information for infants. In women of reproductive age, the median estimated perchlorate dose was $0.057 \mu\text{g kg}^{-1} \text{d}^{-1}$ and the 95th percentile $0.214 \mu\text{g kg}^{-1} \text{d}^{-1}$. For a subset of 110 pregnant women, the estimated median perchlorate dose was $0.066 \mu\text{g kg}^{-1} \text{d}^{-1}$. The median dose of $0.066 \mu\text{g kg}^{-1} \text{d}^{-1}$ for adults is in the same range of the lower-bound range of average perchlorate food intakes for men and women over 20 years of age of $0.08\text{--}0.11 \mu\text{g kg}^{-1} \text{d}^{-1}$. This dose was estimated by the Food and Drug Administration (FDA) in the Total Diet Study (TDS) [986]. These data provided the first thorough population-based assessment of the magnitude and prevalence of perchlorate exposure in the US.

The levels of three physiologically relevant NIS-inhibitors (perchlorate, nitrate, and thiocyanate) and iodide in maternal and fetal fluids collected during cesarean-section surgeries on 150 women from the US were measured [987]. The geometric means of perchlorate levels in maternal urine ($2.90 \mu\text{g/L}$) were similar to previously published results. Perchlorate was detected in most samples: urine (100%), maternal serum (94%), cord serum (67%), and amniotic fluid (97%). Maternal urinary perchlorate levels were positively correlated with perchlorate levels in amniotic fluid ($r=0.57$), indicating that maternal urine perchlorate is an effective biomarker of fetal perchlorate exposure. There was no evidence of either disproportionate perchlorate accumulation or lack of iodide in the fetal compartment. In this panel of healthy infants, there was no association between cord blood levels of these anions and newborn weight, length, and head circumference.

Any condition, such as genetic abnormality or inherited susceptibility affecting processes by which circulating iodide ultimately becomes part of a functional thyroid hormone, will increase the susceptibility to substances that affect thyroid function such as perchlorate. Among these conditions are genetic factors [988,

989]. Increased susceptibility to perchlorate can also result from defects in iodide organification, a process by which iodide is oxidized and bound to thyrosine residue in thyroglobulin.

All studies investigating possible adverse effects of environmental perchlorate exposure on thyroid function in adults or in pregnant women and their newborns were critically evaluated. It was concluded that there is no credible or consistent evidence from any of the numerous studies (that used a variety of designs) that environmental exposure to perchlorate has any adverse effect on thyroid function whether measured as changes in thyroid hormone levels or, among newborns, as the diagnosis of primary congenital hypothyroidism [990]. The absence of adverse effects of environmental perchlorate on the thyroid reflects the very low perchlorate exposure levels worldwide, compared with much higher levels of exposure to nitrate and thiocyanate, goitrogens that inhibit thyroid function via an identical mechanism of action proposed for perchlorate. Adjusted for potency, perchlorate accounts for <1% of the inhibition of iodide uptake in the thyroid resulting from environmental exposure to nitrate and thiocyanate. Occupational studies of workers with substantially higher perchlorate exposure than the general population indicate that even extended exposure to high perchlorate levels did not adversely affect thyroid function. There is no epidemiologic evidence that environmental or occupational exposure to perchlorate adversely affects thyroid function in the US. Even if all perchlorate could be removed from the environment, more than 99% of the inhibition of iodide uptake in the thyroid resulting from exposure to environmental goitrogens would remain.

7.4.2 Other Epidemiological Studies in North America

One-hundred-and-fifty food samples of imported and domestic fruits and vegetables available from retail outlets in Ottawa, Canada, were analyzed using ion chromatography tandem mass spectrometry (IC-MS/MS) to determine the concentrations of perchlorate [991]. Perchlorate was found in most of the tested food types with concentrations appearing to vary by commodity and country of origin. Levels ranged from non-detectable to 536 µg/kg, with Guatemalan cantaloupes (156 ± 232 µg/kg), spinach from the US (133 ± 24.9 µg/kg), Chilean green grapes (45.5 ± 13.3 µg/kg), and Romaine lettuce from the US (29.1 ± 10.5 µg/kg) having the highest concentrations. Dietary exposure to perchlorate from analyzed fruits and vegetables was estimated to be approximately 36.6 and 41.1 ng/kg body weight/day for toddlers (1–4-years-old) and children (5–11-years-old), respectively.

7.4.3 Epidemiological Studies in South America

Perchlorates are a natural contaminant in nitrate deposits that have been mined in South America for several centuries. Most of the nitrates mined were used as fertilizer. Particular emphasis has been placed on studying potential perchlorate effects in contaminated areas on pregnant women and their babies.

A group of 184 pregnant women and their newborns in northern Chile were evaluated for neonatal weight, length, head circumference, gestational length, and FT4, T3, thyroglobulin, and ClO_4^- in cord serum. The evaluation showed no significant differences between the three cities regarding indicators of fetal development or in FT4 or TSH. T3 and thyroglobulin were significantly lower among neonates from Chañaral (low perchlorate, 5.8 $\mu\text{g/L}$) than in the other two cities [992]. This epidemiologic study on public drinking water, which examined pregnant women from three cities in northern Chile (Taltal with 114 $\mu\text{g/L}$, Chañaral with 6 $\mu\text{g/L}$, and Antofagasta with 0.5 $\mu\text{g/L}$ ClO_4^-) was done to test the hypothesis that long-term exposure to perchlorate at these levels may cause a situation analogous to iodine deficiency. This could cause increases in thyrotropin (TSH) and thyroglobulin (Tg) levels and decreased levels of free thyroxine (FT4) in either the mother during the early stages of gestation, in the neonate at birth, or in the fetus where it may cause growth retardation. There were no increases in Tg or TSH and no decreases in FT4 that could be related to perchlorate concentration in the drinking water among either the women during early pregnancy (16.1 ± 4.1 weeks), late pregnancy (32.4 ± 3.0 weeks), or the neonates at birth. Neonatal birth weight, length, and head circumference were not different among the three cities and were consistent with current US norms. Therefore, it was concluded that perchlorate in drinking water at 114 $\mu\text{g/L}$ does not cause changes in neonatal thyroid function or fetal growth retardation.

In an often-quoted study that is considered as reliable, Crump et al. [993] conducted a study of school-age children from three cities in northern Chile with different concentrations of perchlorate in drinking water [993]. The city with the highest perchlorate concentration was Taltal, 100–120 $\mu\text{g ClO}_4^-/\text{L}$ (ppb). The study comprised of 162 children between the ages of 6 and 8-years-old, of which 127 had resided continuously in their respective cities since conception. The children underwent examination of the thyroid gland and a blood sample was taken for analysis of TSH, T4, FTI, T3, and anti-peroxidase antibody. After adjusting for sex, age, and urinary iodide excretion, the children from Taltal and Chañaral had slightly lower TSH levels than children from Antofagasta (which was opposite to what would be expected), but the differences were not statistically significant. Serum T4 levels in the city with the highest perchlorate levels were significantly higher than in the city with no perchlorate (which was also opposite to what would be expected). Analysis of all of the children included in the study revealed a small non-significant increased risk of goiter in the cities with perchlorate compared with the city without perchlorate, however, there was virtually no difference in risk when only lifelong residents were analyzed. The study also found that lifelong residents of Taltal (high perchlorate) were >5 times more likely to report a family history of thyroid disease compared with lifelong residents of Antofagasta (no perchlorate). Assuming a reference daily consumption of water of 1–2 L and using body weight for the children of approximately 25 kg (measured in the study), a concentration of ClO_4^- in the drinking water of 100 $\mu\text{g/L}$ would provide doses of

approximately $0.004\text{--}0.008\text{ mg ClO}_4^- \text{ kg}^{-1} \text{ d}^{-1}$ via drinking water alone. Notably, the Chilean population also has additional large dietary sources of perchlorate.

The same study [993] also evaluated TSH levels in neonates from the three aforementioned cities in northern Chile. A total of 9784 neonatal records were analyzed for TSH levels, sex, and date of screening for infants born between February 1996 and January 1999. The study did not control for iodine intake, ethnicity, or birth weight. The rate of congenital hypothyroidism detected in Chile from 1992 to 1999 was 1 per 3484 cases (based on 773440 newborns screened). In their study, Crump et al. [993] detected seven cases of presumptive congenital hypothyroidism corresponding to a rate of 1 per 1270 newborns. All of these cases originated in the city with no detectable levels of perchlorate. Linear regression comparisons of TSH by city demonstrated a statistically significant decline in TSH with increasing perchlorate concentration in the drinking water, which is opposite to the known effect of perchlorate. The magnitude of the differences in TSH concentrations did not seem to be clinically significant.

7.4.4 Epidemiological Studies in Asia

Perchlorate concentrations in Japanese dairy milk samples ranged from 5.47 to $16.40\text{ }\mu\text{g/L}$ with a mean value of $9.39\text{ }\mu\text{g/L}$ and a median value of $9.34\text{ }\mu\text{g/L}$ [994].

The concentration of perchlorate in rice, bottled drinking water, and milk collected in China was in the range of $0.6\text{--}380\text{ }\mu\text{g/kg}$, $0.16\text{--}4.9\text{ }\mu\text{g/kg}$, $0.04\text{--}2\text{ }\mu\text{g/L}$, and $0.3\text{--}9\text{ }\mu\text{g/L}$, respectively [995]. The results showed that perchlorate pollution has been widespread in China but the sources are uncertain.

7.5 Correlations Between Perchlorate in Drinking Water and Thyroid Gland Function

There has been a lot of concern about the effect of perchlorate in drinking water on the thyroid function of the population at large and, in particular, in newborns and children [993]. Although there has been no nationwide sampling for perchlorate recently, nationwide sampling under the EPA's Unregulated Contaminant Monitoring Rule 1 (UCMR 1), which was in force between 2001 and 2005, detected perchlorate at or above 4 ppb in at least one sample in approximately 4.1% of all the public drinking water systems tested. According to EPA data, perchlorate was reported in 160 of 3865 public drinking water systems, with detections ranging from 4 to 420 ppb. Thirty-one of the 160 systems, or about a fifth, had detections above 15 ppb, which is the EPA's current interim drinking water health advisory level. Based on EPA monitoring conducted from 2001 to 2005, 153 drinking water sources in 26 states were found to contain perchlorate. In Riverside and San Bernardino, CA, some drinking water wells contain up to $216\text{ }\mu\text{g/L}$ and nine wells have been closed in this area.

The DOD reported perchlorate detections at 284 of its installations, or almost 70% of the 407 installations sampled from fiscal years 1997 through 2009, with detections ranging from less than 1 ppb to 2.6 million ppb. Maximum detection in parts per billion included 30 in drinking water, 230 in sediment, 6600 in surface water, 786000 in soil, and 2600000 in groundwater. Fifty-three of the 284 installations, or about 20%, reported perchlorate concentrations above 15 ppb.

The southwestern areas of the US are facing a drought and water shortage due to climate changes, overpopulation, irresponsible real estate speculation without adequate infrastructure, and geological/hydrological limitations. Aquifers do not remain filled forever. In this situation, any loss of potential water sources due to groundwater contamination is a severe blow to the local economy. In 2003, California agreed to reduce its water intake from the Colorado River by 20%. With less Colorado River water available, the dependence on groundwater sources have increased, and any contamination in groundwater sources is a serious problem. In California, 43% of the drinking water comes from groundwater supplies [996].

Data from neonatal screening programs of the state health departments in California and Nevada were analyzed statistically for any increased incidence of congenital hypothyroidism [997]. County-specific, ethnicity-specific data for Nevada and California were obtained for 1996 and 1997. Within seven counties, nearly 700000 newborns had been screened. In total, 249 cases were identified (243 were expected) for an overall risk ratio of 1.0 (95% confidence interval, 0.9 to 1.2). The risk ratios for the individual counties ranged between 0.6 and 1.1. These data do not indicate an increase in the incidence of congenital hypothyroidism with the reported perchlorate levels of 4 to 16 $\mu\text{g/L}$.

A study of newborn TSH levels compared TSH levels between two cities in Arizona, Yuma and Flagstaff. These two areas represented areas of exposure and non-exposure, respectively [998]. The study covered a three-year period between October 1994 and December 1997. The final analysis comprised of 1099 newborns from Yuma and 443 from Flagstaff. The study controlled for age at screening and Hispanic ethnicity, but not for gender, gestational age, or birth weight. The median first TSH level in Yuma was significantly higher than in Flagstaff (19.9 $\mu\text{g/L}$ versus 13.4 $\mu\text{g/L}$). These results were not confirmed in a later critical review [999].

The concentrations of perchlorate measured in six water supply wells that serve the city of Loma Linda, CA, during 1997–1998 ranged from <4 to 29 $\mu\text{g/L}$ [1000].

Perchlorate accumulation above 0.5 $\mu\text{g/L}$ was detected in 179 out of 254 public water systems and private wells in nine counties in the Texas Southern High Plains. Perchlorate concentrations were >4 $\mu\text{g/L}$ in 88 wells [1001]. The maximum concentrations were 58.8 $\mu\text{g/L}$ for private wells and 45.6 $\mu\text{g/L}$ for public water system wells.

Perchlorate and nitrate are both goitrogens, i.e., agents that can prevent the thyroid from absorbing iodide. Data from the California Department of Health Services Division of Drinking Water and Environmental Monitoring database of source water monitoring results were analyzed. These indicated that nitrate occurred in signifi-

cantly higher concentrations than perchlorate (and over a much broader geographic area) and co-occurred with perchlorate [1002]. Drinking water sources that contained detectable levels of perchlorate had, on average, much higher concentrations of nitrates. Before taking corrective action, one must first determine if these contaminants share a common source or infiltration route.

The prevalence of perchlorate in drinking water was analyzed and mapped by compiling data from existing perchlorate occurrence surveys [1003]. The existing surveys included studies conducted by utilities and by the states of Arizona, California, Massachusetts, and Texas. Perchlorate was detected in 26 states, Puerto Rico, and the Mariana Islands and was found in at least one source of approximately 5% of the nation's large (>10000 population) public water systems. When found, perchlorate was typically present at concentrations of <12 µg/L. Some water utilities that detected perchlorate have discontinued the use of perchlorate-contaminated sources. On the basis of the results of a 2007 phone survey, it was estimated that at least 50 million gallons per day of potable water production had been taken offline as a result of perchlorate contamination.

Estimates of perchlorate intake by the population of the US can be derived from either urinary excretion data or through simulation of dietary intake. Estimates from surveys of urinary excretion (National Health and Nutrition Examination Survey, NHANES) are subject to substantial uncertainty owing to the small numbers of subjects for which data is currently available. In addition, current excretion estimates are derived from "spot" urine samples and include an uncertainty component of short-term (intra-day) variability that may give biased estimates of the variability in average daily intakes. Using statistical analysis, it was found that including the drinking water contributions in the dietary simulations yields increases in the population's geometric mean perchlorate intake of 3–8%, with a conservative maximum of about 24%, compared to intakes estimated based on food intake alone [1004]. The analyses indicated that a reasonable upper-bound estimate for the 95th percentile perchlorate intake among women of reproductive age in the US is on the order of $1.5 \times 10^{-4} \text{ mg kg}^{-1} \text{ d}^{-1}$.

The extent of perchlorate contamination of drinking water becomes evident if one places all well locations on a map, as has been done for the State of California (Figure 45) (see [1005] also).

7.5.1 Drinking Water Studies Outside the US

7.5.1.1 Drinking Water Studies in Asia

Perchlorate in the Tone River Basin in Japan was analyzed using IC/MS. Perchlorate was found at high concentrations in the upper Tone River and its tributary, Usui River. The maximum concentrations were 340 and 2300 µg/L, respectively [1007]. The sources of perchlorate in the two areas were attributed to industrial effluents. In the case of the upper Tone River, perchlorate concentration in an effluent was 1100 µg/L



Figure 45: Perchlorate contamination detected in public wells (from [1006]).

and its concentrations in a tributary directly downstream of the outlet of the effluent ranged from 44 to 1500 $\mu\text{g/L}$. In the case of the Usui River, perchlorate concentration in another effluent was 15000 $\mu\text{g/L}$ and its concentrations downstream of the outlet of the industrial effluent were 1100–3900 $\mu\text{g/L}$. Perchlorate concentrations in 27 tap water samples were 0.06–37 $\mu\text{g/L}$. Perchlorate concentrations were more than 1 $\mu\text{g/L}$ in 19 tap water samples and more than 10 $\mu\text{g/L}$ in 13 tap water samples. In summary, it was found that tap water from the Tone River Basin was widely contaminated with perchlorate.

Perchlorate levels in drinking water in India were not known until water samples were collected from 13 locations in six states ($n = 66$) and saliva samples were collected from four locations in three states ($n = 74$). These were analyzed for perchlorate using high-performance liquid chromatography (HPLC) interfaced with tandem mass spectrometry (HPLC-MS/MS) [1008]. Perchlorate was detected in most (76%) of the water samples analyzed at concentrations above the quantitation limit of 0.02 $\mu\text{g/L}$. Con-

concentrations ranged from <0.02 to $6.9\text{ }\mu\text{g/L}$ (mean: $0.42 \pm 1.1\text{ }\mu\text{g/L}$; median: $0.07\text{ }\mu\text{g/L}$). Mean concentrations of perchlorate in drinking water, groundwater, bottled water, surface water, and rainwater were 0.1, 1.0, <0.02 , 0.05, and $<0.02\text{ }\mu\text{g/L}$, respectively. From a total of 66 water samples analyzed, only three samples contained perchlorate levels above $1\text{ }\mu\text{g/L}$; all three were groundwater samples. Perchlorate was found in the saliva samples analyzed at concentrations above $0.2\text{ }\mu\text{g/L}$ and up to $4.7\text{ }\mu\text{g/L}$ (mean: $1.3 \pm 1.3\text{ }\mu\text{g/L}$; median: $0.91\text{ }\mu\text{g/L}$). Perchlorate concentrations in water samples from India are one to two orders of magnitude lower than the concentrations reported for the US.

Three hundred water samples were collected from 15 locations in 13 provinces and municipalities of mainland China. These were analyzed for the presence of perchlorate [1009]. In addition to this, other inorganic anions that commonly occur in water (such as iodide, bromide, and nitrate, and the disinfection byproducts bromate, chlorate and, chlorite) were determined using HPLC interfaced with tandem mass spectrometry. Perchlorate was detected in 86% of the samples analyzed at concentrations ranging from <0.02 to $54.4\text{ }\mu\text{g/L}$ (mean $\pm$ SD $2.20 \pm 6.39\text{ }\mu\text{g/L}$; median $0.62\text{ }\mu\text{g/L}$). Mean concentrations of perchlorate in tap water, groundwater, surface waters, and bottled water were 2.46, 3.04, 2.82, and $0.22\text{ }\mu\text{g/L}$, respectively. Significant positive correlations were found between the concentrations of perchlorate and nitrate as well as perchlorate and chlorate.

7.5.1.2 Drinking Water Studies in Europe

Monitoring of 20 raw and treated drinking water sites in England and Wales, away from known missile production or test operations and covering four seasonal periods, revealed that perchlorate is a low-level background contaminant of raw and treated drinking water [1010]. Low concentrations (treated drinking water: <0.020 – $2.073\text{ }\mu\text{g/L}$, mean $0.747\text{ }\mu\text{g/L}$) were detected at every higher-risk site. The concentrations were comparable in each of the four sampling exercises and no significant trends were apparent relating to the time of year, the type of risk, or the method of chlorination.

7.6 Correlations Between Perchlorate in Food Stuff and Thyroid Gland Function

7.6.1 Total Diet Studies

The Department of Agriculture in the US has been funding several studies on the prevalence of perchlorate in foodstuff. Current research and results can be searched at <http://cris.csrees.usda.gov/search.html>.

The most comprehensive study of perchlorate in food is contained in the FDA's 2006 TDS [1011]. This found perchlorate in 74% of the 285 food items tested across the country. These food items represent the major components of the American diet, such as dairy, meat, fruits, and vegetables. Certain foods, such as tomatoes and spinach, had higher perchlorate levels than others. In each of the four geographic regions of

the US (West, North Central, South, and Northeast), the FDA took samples of each of the 285 food items. Of these items, 211 had perchlorate in at least one of the samples.

Now that the omnipresence of perchlorate (even that predating the rocket propellant environmental pollution) has been recognized, one will want to know how much perchlorate is in a normal diet and if the normal diet contains sufficient iodide to prevent any perchlorate-induced hypothyroidisms.

The FDA has conducted the TDS since 1961. It is designed to monitor the food supply in the US for chemical contaminants, nutritional elements, and toxic elements. After 2007, perchlorate was included in TDS sampling and analysis. Intake estimates of perchlorate and iodine, a precursor to iodide, were provided for population groups using the analytical results from the TDS [986]. Estimated average perchlorate and iodine daily intakes, as well as the contribution of specific food groups to total intakes, were estimated for 14 age/sex subgroups of the population of the US. The estimated smallest lower bound to the largest upper bound average perchlorate intakes by the 14 age/sex groups ranged from 0.08 to $0.39 \mu\text{g kg}^{-1} \text{d}^{-1}$, compared with the EPA RfD of $0.7 \mu\text{g kg}^{-1} \text{d}^{-1}$. Infants and children demonstrated the highest estimated intakes of perchlorate on a bodyweight basis. The estimated average iodine intakes of the 14 age/sex groups revealed a lower bound (ND = 0) and upper bound (ND = LOD) range of average intakes from 138 to $353 \mu\text{g person}^{-1} \text{d}^{-1}$. Estimated iodine intakes of infants that are six to 11 months old exceeded their adequate intake. Intakes by children and adult age/sex groups exceeded their relevant estimated average requirement.

A preliminary estimation of perchlorate dietary exposure was performed based on the FDA's 2004/2005 exploratory data. The FDA's Center for Food Safety and Applied Nutrition (CFSAN) estimated human exposure to perchlorate through the consumption of 27 foods and beverages for which CFSAN has collected data (on perchlorate levels) [1012, 1013]. Data sources for the 27 foods and beverages were from exploratory surveys conducted by the FDA in Fiscal Years (FY) 2004 and 2005. These exploratory surveys were conducted in regions where water sources were known to be contaminated with perchlorate and thus the perchlorate levels are likely biased and on the high side. Although the exploratory and limited nature of the surveys did not allow the FDA to provide a representative exposure assessment, the FDA conducted this preliminary exposure assessment because of significant public interest in the issue of perchlorate exposure from food. The FDA planned to update a comprehensive and nationally representative exposure assessment periodically. In the list of 27 food items, the highest perchlorate concentrations were found in spinach (115 pp), "greens" (lettuce?) (92.4 ppm), cantaloupe (28.6 ppm), and shrimp (19.8 ppm). Averaging the estimated total mean population (all persons aged two and above) for a normal diet showed the perchlorate exposure from the 27 foods and beverages to be $0.053 \mu\text{g/kg bw/day}$, which is below the RfD of $0.7 \mu\text{g/kg bw/day}$ recommended by NAS and adopted by the EPA.

In addition to diet studies covering the entire population, specific diet studies were directed at the diet intake of infants from commercial baby formula products [1014]. Perchlorate exposure may be higher in infants compared with older

persons due to bodyweight to food intake weight ratios. A quantitative assessment of perchlorate concentrations in commercially available powdered infant formulas was done to estimate the exposure in infants under different dosing scenarios, then to compare them with the perchlorate RfD. The perchlorate RfD may be exceeded when certain bovine milk-based infant formulas are ingested and/or when they are reconstituted with perchlorate-contaminated water.

7.6.2 Perchlorate in Vegetables

Perchlorate content in 11 edible cantaloupe and ten whole cantaloupe samples was median (range) 9.6 (<2.0–18.2) and 23.9 (<2.0–39.3) $\mu\text{g}/\text{kg}$, respectively (fresh/dry weight not specified) [334].

Perchlorate concentrations in lettuce irrigated with Colorado River water (5 mg/L perchlorate concentration) ranged from below quantifiable levels to 142 $\mu\text{g}/\text{kg}$ (fresh weight) in the total above ground plant, 195 $\mu\text{g}/\text{kg}$ (fresh weight) in the frame and wrapper leaves, and below detection to 26 $\mu\text{g}/\text{kg}$ (fresh weight) in the edible head [1015].

Perchlorate was detected above 0.2 $\mu\text{g}/\text{L}$ in 144 out of 438 leafy vegetable samples produced and sampled in California (outside the Colorado River region), Colorado, New Jersey, New Mexico, New York, Michigan, Ohio, and Quebec [1016]. Quantifiable perchlorate concentrations ranged from 18 to 104 $\mu\text{g}/\text{kg}$ fresh weight in conventionally grown vegetables and from 21 to 628 $\mu\text{g}/\text{kg}$ fresh weight in organically grown vegetables (see [1017, 1018] also).

Citrus fruit grown on trees in the Southwest that were irrigated with perchlorate contaminated water (mean concentration of approximately 6 $\mu\text{g}/\text{L}$) contained mean, median, and maximum perchlorate concentrations of 2.3, 1.3, and 14.8 $\mu\text{g}/\text{L}$ fresh weight, respectively, in 33 lemon samples. Similar results were 3.3, 1.3, and 16.2 $\mu\text{g}/\text{L}$ fresh weight, respectively, in 15 grapefruit samples, and 7.4, 4.8, and 37.6 $\mu\text{g}/\text{L}$ fresh weight, respectively, in 28 orange samples [1019].

The Colorado River is the primary source of irrigation water for most food crops grown in Southern California and Southwestern Arizona. A comparison of perchlorate levels in broccoli, cauliflower, and cabbage grown in fields irrigated with water from the Colorado River, which contains perchlorate (with levels of thiocyanate and nitrate, which are two other anions that also inhibit iodide uptake) led to the conclusion that brassica irrigated with Colorado River water does indeed accumulate trace levels of perchlorate. However, the levels of perchlorate observed are much lower than the levels of nitrate and thiocyanate, which are naturally present in these vegetables and which may also affect the thyroid gland [1020].

The major food commodities in addition to vegetables produced in the region were sampled and perchlorate levels were determined by using ion chromatography followed by detection using either conductivity or tandem mass spectrometry depending on analyte levels [1021]. Perchlorate exposure estimates derived in this study were

comparable to exploratory estimates found by the FDA. For infants and children, over 50% of the estimated perchlorate exposure was from milk. The relative impact of vegetables and fruit toward perchlorate exposure increased by age through adulthood. Cumulative perchlorate exposure estimates based on this hypothetical analysis could approach or exceed the NAS RfD for some population groups but only where drinking water levels exceeded 6 µg/L. However, few individuals are exposed to perchlorate in drinking water at levels above 4 µg/L in the US and very few would be exposed to perchlorate levels exceeding the RfD, whether consuming food crops from within or outside the lower Colorado River region.

Perchlorate's adverse effects would be less severe if there is sufficient iodine in the diet. Most studies have only evaluated the uptake and distribution of ClO_4^- by plants without considering the potential for concurrent uptake of iodine by the plant and the subsequent impacts on ClO_4^- and iodine uptake and distribution on human health. When studying the relative uptake of ClO_4^- and I supplied as either KI or KIO_3 in butter head lettuce, it was found that if lettuce is grown using fertilizers containing both ClO_4^- and I^- , then the final ratio of $\text{I}^-/\text{ClO}_4^-$ in the leaves will be essentially equal to the ratio in the fertilizer but lower if the I is supplied as IO_3^- [1022]. Therefore, the impact of the consumption of lettuce containing ClO_4^- may be mitigated if the lettuce is grown using fertilizer with an appropriate amount of I to maintain the existing ratio of serum I to total goitrogen load.

7.6.3 Perchlorate in Meat and Milk

Perchlorate exposure and its potential effects were evaluated in beef cattle by monitoring heifer calves placed on a site with the only access to water being from a perchlorate-contaminated groundwater spring (25 ng/mL) [1023]. Blood was collected from two calves on the site (and two control calves from an uncontaminated site) approximately every two weeks for analysis of perchlorate residues and thyroid hormones. During the 14-week study, perchlorate was detected (D.L. = 13.7 ng/mL) in blood plasma twice (15 ng/mL and 22 ng/mL). Constant exposure to 25 ppb perchlorate in drinking water had no effect on circulating thyroid hormones (T3 and T4) in the heifer calves.

It has been attempted to categorize the sources of perchlorate found in our daily food intake, depending on the geographical area where we live [1024].

It was estimated that infants breastfed for six months may have daily doses of perchlorate that exceed the NAS recommended RfD of $0.7 \mu\text{g kg}^{-1} \text{d}^{-1}$ [1025].

Cattle that are fed with grass grown in pastures that are irrigated with contaminated water will pass the perchlorate into the milk. It has been attempted to establish a correlation between the contamination of the feed and the perchlorate content of the milk [1026]. Based on a nine-week long experiment in which 16 dairy cows were administered perchlorate, an equation was derived for the dose-response relationship between perchlorate concentrations in feed/drinking water and its appearance in

milk. Examination of background concentrations of perchlorate in the total mixed ration (TMR) fed in addition to the variable dose supplied to treated cows as a ruminal infusate revealed that cows receive significant and variable exposure to perchlorate from the TMR. Weekly examination of the TMR disclosed that a change in ingredients midway through the experiment caused a significant (78%) change in TMR perchlorate concentration. Analyses of the ingredients comprising the TMR revealed that 41.9% of the perchlorate came from corn silage, 22.9% came from alfalfa hay, and 11.7% was supplied by Sudan grass. It was demonstrated that the transfer of perchlorate from feed to cows was a significant source of perchlorate in subsequent milk samples.

Mean perchlorate concentrations measured in the blood, milk, urine, and feces of cows with calculated perchlorate intakes of 0.46 mg/day from feed and 0.03 mg/day from water were 0.24, 4.37, 3.68, and 5.84 ng/mL, respectively [1027].

There is an even higher concern about perchlorate accumulation in the milk of nursing human mothers. Measurements of perchlorate concentration in mother's milk indicated a mean level of 10.5 µg/L (range 0.6–92 µg/L) and a maximum level of 92 µg/L in 35 human milk samples from 18 states [1028, 1029].

Perchlorate concentrations in dairy milk from Japan are higher than values reported by the FDA in the US. Perchlorate concentrations in the Japanese samples ranged from 5.47 to 16.40 µg/L, with a mean value of 9.39 µg/L and a median value of 9.34 µg/L [994].

The concentration of perchlorate analyzed by using ion chromatography-electrospray tandem mass spectrometry in sewage sludge, rice, bottled drinking water, and milk collected in China was in the range of 0.6–380 µg/kg, 0.16–4.9 µg/kg, 0.04–2 µg/L, and 0.3–9 µg/L, respectively [995]. The results revealed that perchlorate pollution has been widespread in China, however, the sources are uncertain.

A study was conducted to evaluate perchlorate in the feed of cattle in dairy farms in the southwestern areas of the US [1030]. All feed products collected at dairies had detectable levels of perchlorate as analyzed using ion chromatography-tandem mass spectrometry. The calculated total perchlorate intake across dairies ranged from 1.9 to 12.7 mg/cow per day. Alfalfa products were the single most important source of perchlorate. The estimated perchlorate intake from drinking water ranged from 0.01 mg per cow per day and was generally less than 2% of the total perchlorate intake. The perchlorate content of milk ranged from 0.9 to 10.3 µg/L and was similar to levels reported by the FDA's TDS. The perchlorate content of milk was significantly related to the presence of perchlorate in feed but the variation of perchlorate in milk could not be explained by feed intake alone.

7.7 Ammonium Perchlorate Exposure in the Workplace

Worker monitoring in the workplace was mostly concerned with the thyroid gland response. Very little work has been done to monitor the other effects of long-duration

low-level exposure to AP on workers. The most likely path of ingestion would be through inhalation of perchlorate dust during grinding and powder transfer operations. For this reason, animal tests were performed where the lungs of test animals were dosed with AP solutions aerosols via inhalation (see Section 7.1.2).

Sixty-six workers occupationally exposed to AP dust from two factories, A and B, were selected as the exposed and 48 workers were selected as the unexposed control groups to study the effect of AP dust on the health of workers [1031]. Investigations on the working condition and sampling of dust in the workplaces and a special medical examination were conducted for both groups. This included occupational history, clinical manifestations, blood routine tests, hepatic and renal functions, indexes of thyroid hormones, spirometric tests, and chest X-rays. The average concentration of AP dust in the two factories were 2.53 mg/m^3 and 31.36 mg/m^3 , respectively. Dust concentrations in factory B were higher than those in factory A. The mean age and employment duration of the exposure group and the control group were 40.97 and 40.04 years, and 19.8 and 20.8 years respectively. The symptoms of respiratory and digestive systems (31.8% and 18.2%) in the exposure group were significantly higher than those in the control group (10.4% and 4.2%), ($P \sim 0.05$ or 0.01) respectively. The pulmonary function tests showed that Forced Expiratory Volume in One Second/Forced Vital Capacity (FEV1.0/FVC%) in the exposure group was significantly higher than that of the control group. One retired worker exposed to AP for 26 years in the exposure group, who had a diagnosis of pneumoconiosis, was found to have irregular opacities showing interstitial fibrosis under X-ray examination. It was concluded that long-term exposure to AP dust at high levels may cause respiratory system adverse effects and even induce pulmonary fibrosis.

7.8 Liver Metabolism and Hepatic Toxicity Effects of Ammonium Perchlorate

No evidence of liver toxicity, as judged by blood chemistry tests, was observed in a group of nine human volunteers who ingested approximately 0.14 mg of perchlorate/kg/day as potassium perchlorate for 14 consecutive days [976]. Similar results were reported by Greer et al., [977] in a study of 37 volunteers who consumed up to $0.5 \text{ mg ClO}_4^- \text{ kg}^{-1} \text{ d}^{-1}$ also for 14 days.

A study by Crump et al. [993] examining 162 school-aged children from three cities in northern Chile with different perchlorate concentrations in the drinking water (up to $100\text{--}120 \mu\text{g/L}$) found no indications of altered liver function among the children, as measured by serum aspartate aminotransferase (AST), alkaline phosphatase, or lactate dehydrogenase (LDH) activities.

Godley and Stanbury [1032] reported no evidence of liver toxicity in a series of 24 hyperthyroid patients treated with potassium perchlorate (600 mg , prox. 6 mg perchlorate $\text{kg}^{-1} \text{ d}^{-1}$) for up to 52 weeks. However, it is not clear what tests were conducted to monitor effects on the liver or how frequently such tests may have been conducted.

An animal feeding study in rats found that the administration of AP in drinking water at doses up to 8.5 mg perchlorate $\text{kg}^{-1} \text{d}^{-1}$ for up to 90 days caused no significant alterations in liver weight, in the gross or microscopic appearance of the liver, or in serum transaminase activities [967].

No effects on liver weight were reported in 14- and 90-day studies using mice that were administered up to 25.5 mg perchlorate/kg/day in their drinking water in the form of the ammonium salt [966].

7.8.1 Metabolic Effects

No studies were sourced regarding the metabolic effects and enzyme disturbances in humans after oral exposure to perchlorate.

Researchers in India conducted a number of animal studies investigating the metabolic effects of perchlorate in rats who were given 500 mg $\text{kg}^{-1} \text{d}^{-1}$ of potassium perchlorate, sodium perchlorate, or AP via daily gavage for 45 days [1033–1038]. They found that perchlorate increased protein metabolism (increased liver arginase activity and serum urea levels). It also altered carbohydrate metabolism (decreased serum glucose and increased liver and kidney glycogen levels, reflecting increased activity of aldolase, lactate dehydrogenase, and glycogen synthase, and decreased activity of glucose-6-phosphatase and glycogen phosphorylase), modified lipid metabolism (increased cholesterol, triglyceride, and phospholipid, and decreased free fatty acid levels, reflecting decreased activity of lipase and phospholipase). They also found that perchlorate reduced the activities of mitochondrial enzymes involved in cellular respiration, apparently due to changes in lipid composition of mitochondrial membranes (increased cholesterol and decreased phospholipid) reducing membrane fluidity.

Other studies reported no effect on serum glucose in rats exposed to 0.1% potassium perchlorate (approximately 175 mg perchlorate/kg/day) in their drinking water for 25 days [1039]. No effects were observed on serum glucose levels in rats that were exposed to up to 8.5 mg of perchlorate/kg/day as AP in the drinking water for up to 90 days [967].

7.9 Renal Toxicity and Ammonium Perchlorate Excretion in Urine

7.9.1 Renal Effects of AP

Limited information exists regarding renal effects of perchlorate in humans. Two studies in euthyroid volunteers who ingested up to 0.5 mg $\text{ClO}_4^- \text{kg}^{-1} \text{d}^{-1}$ as the potassium salt for 14 days found no evidence of renal effects, as judged by standard clinical chemistry tests [976, 977]. Also, no alterations in blood urea nitrogen (BUN) concentration or in serum creatinine levels were observed in a group of 60 school-aged children from

northern Chile exposed to perchlorate in their drinking water at concentrations up to 100–120 µg/L [993].

In 14- and 90-day drinking water studies in rats, doses of up to 8.5 mg kg⁻¹ d⁻¹ produced no significant alterations in kidney weight or in gross or microscopical appearance of the kidneys [967]. In addition, kidney function, monitored by measurements of BUN and serum creatinine, was not affected by exposure to perchlorate [967]. A similar study in mice also found no effects of AP on kidney weight following 14 or 90 days of exposure to up to 25.5 mg ClO₄⁻ kg⁻¹ d⁻¹, however, kidney function tests were not performed [966].

7.9.2 Perchlorate in the Urine

Almost all perchlorate that enters the body via eating or drinking is excreted in the urine. Urine sampling and analysis of large populations are, therefore, a lot easier to do than blood analysis from a certain population group. Thus, it is of particular interest to find a correlation between perchlorate excreted in the urine and potential thyroid gland interference caused by high perchlorate levels.

The potential relationship between urinary levels of perchlorate and serum levels of TSH and total thyroxine (T₄) was studied in 2299 men and women, ≥12 yr of age, participating in the NHANES during 2001–2002 [1040, 1041]. Perchlorate in the urine was not a significant predictor of T₄ or TSH levels in men. However, for women overall, perchlorate was a significant predictor of changes in both T₄ and TSH. For women with low urinary iodine <100 µg/L, perchlorate was a significant negative predictor of T₄ ($p < 0.0001$) and a positive predictor of TSH ($p = 0.001$). For women with higher urinary iodine ≥100 µg/L, perchlorate was a significant positive predictor of TSH ($p = 0.025$) but not T₄ ($p = 0.550$). These associations of perchlorate with T₄ and TSH were coherent in direction and independent of other variables known to affect thyroid function, however, they were detected at perchlorate trace exposure levels that were unanticipated based on previous studies.

A simple two-compartment first-order pharmacokinetic model that predicts concentrations of perchlorate in blood and urine was constructed and validated [1042]. The model was validated using data from a high-dose experiment in humans where doses and resulting concentrations of perchlorate in blood and urine were well documented. Specifically, data were available for individuals who had been dosed at 0.5, 0.1, and 0.02 mg kg⁻¹ d⁻¹ for 14 consecutive days. This was a significantly higher than the average background dose, which is estimated to be less than 0.0001 mg kg⁻¹ d⁻¹. The average measured urine concentration in the high-dose regime during the experiment was 15.4 mg/L compared with an average prediction of 17.3 mg/L. In the medium-dose regime, the average measured was 3.0 mg/L compared with 4.1 mg/L predicted. In the low-dose regime, the average measured was 0.53 mg/L compared with 0.68 mg/L predicted.

7.10 Ammonium Perchlorate in the Blood

Severe hematological effects have been found in several cases where hyperthyroid patients were treated with potassium perchlorate for a long time. Some patients developed aplastic anemia, which was characterized by drastic reductions in circulating granulocytes, erythrocytes, and thrombocytes, and a lack of erythropoietic and granulopoietic cells in the bone marrow. Aplastic anemia was the cause of death in most of the documented fatalities associated with treatment of thyrotoxicosis using potassium perchlorate. All of the documented cases of aplastic anemia and agranulocytosis were females (Graves' disease, the most common cause of hyperthyroidism, is far more common in women than in men).

For epidemiological studies, it is common practice to analyze for AP concentrations in body fluids. It has been attempted to establish a correlation between AP concentration in the blood and in other body fluids. For instance, for worker health monitoring and workplace surveillance, it would be a lot easier to rely on saliva or urine samples than having to take blood samples before and after work shifts.

Thyroid gland and blood hematology effects of occupational exposure to perchlorates was assessed by measuring ambient air concentrations of total and respirable perchlorate particles in the workplace. Systemic absorption was also assessed by measuring urinary perchlorate excretions. Airborne exposures ranged from 0.004 to 167 mg total particulate perchlorate per day. Urinary perchlorate measurements demonstrated that exposure to the airborne particulate perchlorate resulted in systemic absorption. Workers were grouped into four exposure categories with a mean absorbed perchlorate dosages of 1, 4, 11, and 34 mg perchlorate per day. No clinical evidence of hematological abnormalities was found in any exposure group. The blood-cell counts were normal in all groups, thus indicating no evidence of hematotoxicity in this exposure range [981]. This is also supported by animal studies using higher doses. The absence of evidence of an effect on blood cells from occupational airborne perchlorate exposure at a mean absorption of 34 mg/d demonstrates a NOAEL that can assist in the evaluation of human health risks of the general population from environmental perchlorate contamination.

Hematological parameters were evaluated in an epidemiological study of school-age children from three cities with different concentrations of perchlorate in drinking water in northern Chile [993]. The city with the highest perchlorate concentration was Taltal, 100–120 µg perchlorate/L (ppb), where water is drawn from the city of Chañaral had 5–7 µg/L. Perchlorate was not detected in water from the city of Antofagasta. Analysis of CBC showed no significant differences between the three groups of children.

A liquid chromatography – tandem mass spectrometry (LC-MS/MS) method was optimized to analyze for perchlorate in blood sera and plasma samples from 84 donors [1043]. In addition, 15 volunteers provided saliva and serum samples concurrently, to enable assessment of the ratio of perchlorate in these two matrices. Perchlorate concentrations in serum and plasma ranged from below the limit of

quantitation (0.05 ng/mL) to a maximum of 7.7 ng/mL. The mean and median concentrations of perchlorate in 84 serum and plasma samples were 0.32 and 0.17 ng/mL, respectively. No significant difference existed in perchlorate concentrations between serum and plasma. Analysis of paired saliva and serum samples revealed a significant positive correlation for log-normalized perchlorate concentrations ($r^2 = 0.60$) and perchlorate concentrations themselves ($r^2 = 0.86$). The mean saliva : serum concentration ratio of perchlorate was 14 : 1.

7.11 Establishment of a RfD for Ammonium Perchlorate

Typically a NOAEL or a LOAEL for potentially toxic chemicals is identified using published data or government-commissioned carefully controlled experiments on which the RfD can be based.

The EPA has issued a provisional RfD that would restrict the discharge of AP-containing waters to less than 1 ppm. This may significantly increase the cost of wastewater disposal at rocket propellant installations where the old propellant is demilitarized by high-pressure water washout and attempts are made to recycle some of the materials. It was estimated that the demil of 1200 Minuteman III first and second stage motors will require the processing of 15900 metric tons (35 million pounds) of propellant consisting mostly of AP (68–73% AP). As of 1998, an additional 57 SRMs were awaiting disposal via water washout. In addition to this burden, AP waste streams accumulate at AP production sites, rocket propellant mixing sites, and static firing test sites.

The EPA, which has responsibility for establishing national drinking-water standards, issued a draft risk assessment of perchlorate in 2002 [1044]. In February 2005, the EPA established its official RfD of perchlorate, which was set at $0.0007 \text{ mg ClO}_4^- \text{ kg}^{-1} \text{ d}^{-1}$, and translated that number to a Drinking Water Equivalent Level (DWEL) of 24.5 ppb. This level is consistent with the recommended RfD included in the National Academy of Sciences' January 2005 report. An RfD is a scientific estimate of a daily exposure level that is not expected to cause adverse health effects in humans. See the website [1045] (*Perchlorate and Perchlorate Salts*), which provides a summary of EPA actions. However, as of 2005, the assessments have come under criticism on the grounds that the conclusions presented in them were based on flawed scientific studies and that not all available data had been incorporated appropriately into them. In view of the controversy surrounding the concentration at which perchlorate should be regulated, Government agencies in the US then asked the NRC to independently assess the adverse health effects of perchlorate ingestion from clinical, toxicologic, and public-health perspectives. A committee at the NRC has subsequently evaluated the data and issued recommendations [934]. The NRC Committee suggested that animal test data should **not** be used as the basis of a perchlorate risk assessment.

NAS based its derivation of the RfD on the findings of a study by Greer et al. [977]. The RfD was based on a no-observed-effect level (NOEL) of $0.007 \text{ mg ClO}_4^- \text{ kg}^{-1} \text{ d}^{-1}$ for thyroidal uptake of RAIU in 37 healthy (euthyroid) volunteers (16 males, 21 females) who consumed potassium perchlorate in drinking water in doses of 0.007, 0.02, 0.1, or 0.5 $\text{mg ClO}_4^- \text{ kg}^{-1} \text{ d}^{-1}$ for 14 days. In 24 subjects, thyroidal uptake of RAIU was measured eight and 24 hours after each administration of radioactive iodine on exposure days 2 and 14 and also 15 days after the last exposure. To estimate daily iodine intake, 24-hour urine samples were collected. Free and total T4, T3, and TSH were sampled 16 times throughout the study. The RfD was calculated by dividing the NOEL of $0.007 \text{ mg ClO}_4^- \text{ kg}^{-1} \text{ d}^{-1}$ for inhibition of radioiodide uptake and serum hormone levels by an uncertainty factor of 10.

In January 2009, the EPA issued a health advisory to assist state and local officials in addressing local contamination of perchlorate in drinking water [1046]. The interim health advisory level of $15 \mu\text{g/L}$, or ppb, is based on the RfD recommended by the NRC of the National Academy of Sciences.

In ATSDR's *Toxicological Profile for Perchlorates* [1047], which is a 299-page comprehensive summary of toxicity data for perchlorate and perchlorate salts, Section 1.9 notes that "The EPA is currently undertaking efforts to make a determination as to whether or not a national primary drinking water regulation (NPDWR) is needed for perchlorate. To make this determination, EPA is evaluating information to more fully characterize perchlorate exposure to determine if regulation of perchlorate in drinking water would represent a meaningful opportunity for reducing risks to human health as required under the Safe Drinking Water Act (SDA)." More recently, the EPA has presented a Preliminary Regulatory Determination on Perchlorate in the Federal Register (73FR198:60262-60282) stating that the EPA has determined that an NPDWR for perchlorate would not present "a meaningful opportunity for health risk reduction for persons served by public water systems". However, this position was reversed under pressure from some of the representatives and senators in Congress.

Section 1.9, as well as Chapter 8 of the *Toxicological Profile* notes that the "EPA's Office of Solid Waste and Emergency Response has provided guidance for perchlorate that indicates that the RfD and its corresponding DWEL of 24.5 ppb are respectively the recommended **to be considered** (TBC) value and the preliminary remediation goal (PRG) for clean up under the *Comprehensive Environmental Response, Compensation, and Liability Act* of 1980 (CERCA)." Table 8-1 of the profile also lists the existing PRG. However, the EPA's Preliminary Regulatory Determination on Perchlorate also notes that the EPA will replace its existing PRG of 24.5 ppb with a health reference level (HRL) of 15 ppb for drinking water. The EPA explained that the existing PRG was calculated with the assumption that all exposure comes from groundwater at National Priorities List (NPL) sites, whereas the HRL was calculated using the RfD of $7 \mu\text{g/kg/day}$ and a relative source contribution from water, which was relative to a calculated contribution from food. The EPA states that the final HRL will be the basis for a health advisory in the health advisory document that the agency expects to issue when the

final Regulatory Determination on Perchlorate is released. The EPA notes that it may be appropriate to use the HRL as a TBC value in developing potential clean-up levels for perchlorate NPL sites.

ATSDR summarized its Toxicological Profile for Perchlorates [1048] in a two-page summary of toxicity data for perchlorate and perchlorate salts in September 2008. It was amended by an addendum [1049] in October 2008.

On 10 October 2008, the EPA issued a preliminary determination for perchlorate in the Federal Register (73 FR 60262) stating that there was not a “meaningful opportunity for health risk reduction” through a national drinking water regulation. As of 2009, the EPA has received more than 32000 comments on the notice and is now requesting additional input before making a final regulatory determination on whether to issue a national regulation for perchlorate in drinking water. In response to stakeholder comments that provided additional scientific evaluation of the information the EPA used to make its preliminary determination, in January 2009 the EPA announced that it planned to seek additional input from the NRC on assumptions regarding the possible effects of perchlorate on infants and young children. Around the same time, the EPA’s Office of Water published an interim health advisory for perchlorate that included a health advisory level of 15 parts per billion. This interim health advisory level took into account exposure from food as well as drinking water for pregnant women and their fetuses (the most sensitive life stage identified by NRC). The advisory provided informal technical guidance to assist state and local officials in protecting public health where perchlorate contamination of drinking water has occurred. Meanwhile, the EPA evaluated the opportunity to reduce risks through a national drinking water standard (DWS). Following the establishment of the interim health advisory, the EPA’s Office of Solid Waste and Emergency Response withdrew its PRG for perchlorate of 24.5 ppb. In its place, the EPA recommended the interim health advisory level of 15 ppb be used as the PRG when assessing sites for clean-up under CERCLA.

On 8 January 2009, the EPA issued an interim health advisory of 15 parts per billion (ppb) to assist state and local officials in addressing local contamination in drinking water. This interim health advisory of 15 ppb also replaced the existing PRG goal of 24.5 ppb (established in 2006, EPA Memorandum 26 January 2006) used to establish clean-up levels for perchlorate at Superfund sites. The advisory level was based on earlier recommendations by the NRC, which functions under the National Academy of Sciences. States have the right to establish and enforce DWSs and the EPA encourages state-specific situations to be addressed at local levels. The EPA expects to issue a final health advisory concurrent with the final regulatory determination for perchlorate.

In August 2009, the EPA published a notice that it would not seek additional input from the NRC and instead was seeking public comment on additional approaches for interpreting the available data on the level of health concern, the frequency of occurrence of perchlorate in drinking water, and the opportunity for health risk reduction through a national DWS.

In April 2010, the EPA's Office of Inspector General released a report that reviewed and critiqued the risk assessment process and procedures used by the EPA to develop and derive the perchlorate RfD [1050]. As of July 2010, the EPA had not yet made a final decision as to whether it would establish a regulatory standard for perchlorate in drinking water.

Some of the EPA's actions were critiqued by industry representatives as lacking scientifically correct foundations and as causing unnecessary expenses to the industry. The benefit : risk evaluation of issuing new regulations continued for a very long time.

The extent to which perchlorate, which occurs naturally and as an industrial contaminant, should or should not be regulated has become controversial [1051]. A number of inconsistent conclusions have been drawn based on thyroid hormone serum concentrations, urinary iodine concentrations, and perchlorate exposure among women participating in the 2000–2001 NHANES and based on a body of epidemiologic and clinical evidence reporting no associations between effects on thyroid hormones and similar or much higher levels of perchlorate exposure. For example, studies associating perchlorate with thyroid effects at low exposures did not control for anti-thyroid agents with modes of action that differ from that of perchlorate, such as some organochlorines. Available evidence does not support a causal relationship between changes in thyroid hormone levels and current environmental levels of perchlorate exposure but does support the conclusion that the EPA's RfD for perchlorate is conservatively health-protective. Potential perchlorate risks are unlikely to be distinguishable from the ubiquitous background of naturally occurring substances present at much higher exposure levels that can affect the thyroid via the same biological mode of action as perchlorate such as nitrate and thiocyanate.

7.11.1 Legislative Actions Regarding Perchlorate

In view of the contamination of numerous drinking water sources by perchlorate in California, legislation (S. 24, S. 2298, H.R. 4798 [109th Congress]) was introduced in 2006 (but not enacted) to accelerate the remediation of polluted water sources and to inform the general public about the hazards of perchlorate in drinking water.

Perchlorate contamination received a lot of attention in the 110th Congress [1052]. Responding to the EPA's decision not to require further monitoring for perchlorate as an unregulated contaminant, S. 24 was introduced to require community water systems to test for perchlorate and disclose its presence in annual consumer reports. S. 150 and H. R. 1747 would require the EPA to establish a DWS for perchlorate. In September 2008, the Senate Environment and Public Works Committee reported S. 24 (S. Rept. 110–483) and S. 150 (S. Rept. 110–484). Another bill, H. Con. Res. 347, expresses the intent of Congress to ensure that the CDC and the FDA should take action to educate the public on the importance of adequate iodine intake. (Iodine is protective against perchlorate exposure.) The House Energy and Commerce Committee's En-

vironment and Hazardous Substances Subcommittee marked up and approved H. R. 1747 in late 2007. Other legislative actions relating to perchlorate contamination were: 110th Congress 2007–2008 S. 24 *Perchlorate Monitoring and Right-to-Know Act of 2008* [1053]

111th Congress 2009–2010 H.R. 3481: *Lower Colorado River Protection Act*

111th Congress 2009–2010 H.R. 3206: *Safe Drinking Water for Healthy Communities Act of 2009*

111th Congress 2009–2010 H.R. 2316: *Inland Empire Perchlorate Ground Water Plume Assessment Act of 2009*

111th Congress 2009–2010 H.R. 4252: *Inland Empire Perchlorate Ground Water Plume Assessment Act of 2010*

The toxicological database on ClO_4^- as of March 1997 was determined by an expert peer-review panel to be inadequate for the purpose of deriving an oral RfD. For example, little or no experimental data existed on the sub-chronic, reproductive, or developmental toxicity of perchlorate. To fill gaps in the toxicological database, eight animal studies were designed by a government-industry consortium that included the EPA and the Air Force Research Laboratory (AFRL). These studies were performed in 1997 and 1998. Upon review of complete study reports from four of the studies and incomplete data from the other two, the EPA/National Center for Environmental Assessment (NCEA) issued a document in December 1998. This stated that the critical effects were hormone and histology data from the neurodevelopmental/behavioral toxicity study that had been performed in rats. An RfD was proposed based upon the observation of thyroid-follicular-cell hypertrophy in five-day-old pups of dams given perchlorate in drinking water at 0.1 mg/kg-day (the lowest dose tested) in this study [1054].

Getting tired of waiting for the federal EPA to establish a drinking water safe limit for perchlorate, several states went ahead and established their own limits. California proposed an enforceable limit of 6 ppb for perchlorate in drinking water, four times more stringent than the EPA's standard of 24 ppb. The State of Massachusetts' perchlorate RfD and DWS are considerably lower and more health-protective than related values derived by several other agencies. Before setting this limit, the Massachusetts Department of Environmental Protection scientists, with input from a science advisory committee, assessed a wide range of perchlorate risk and exposure information [1055]. Health outcomes associated with iodine insufficiency were considered, as were data on perchlorate in drinking water disinfectants. A health protective RfD (0.07 $\mu\text{g}/\text{kg}/\text{day}$) was derived using an uncertainty factor approach with perchlorate-induced iodide uptake inhibition as the point of departure. The DWS (2 $\mu\text{g}/\text{L}$) was based on risk management decisions weighing information on perchlorate health risks and its presence in certain disinfectant solutions used to treat drinking water for pathogens.

In February 2011, the Obama administration announced that the EPA will establish the "first federal DWS for a toxic rocket fuel ingredient linked to thyroid problems

in pregnant women and young children.” The EPA issued a *Final Regulatory Determination* for Perchlorate but the standard itself could take up to two years to develop, the EPA stated. This decision reversed a 2008 preliminary determination and considered input from almost 39000 public commenters on multiple public notices (May 2007, October 2008, and August 2009) related to perchlorate. Pentagon officials have spent years questioning the EPA’s assessment of perchloate risk but have denied influencing the agency’s decisions. The military could face liability for contaminating water during rocket and missile testing due to the standard forcing water agencies around the country to clean up the pollution caused by this (see [1056–1062] also).

In 2018, Docket EPA-HQ-OW-2018-0780 proposed an upper limit of 56 ppb for perchlorate in drinking water. It was argued that a less restrictive limit for perchlorate in drinking water would disregard the risks to children’s health, ignore the latest results of scientific research, and fail to follow the requirements of the Safe Drinking Water Act to use the best available peer-reviewed science for setting DWSs.

7.11.2 Economic Impacts of New Perchlorate Regulations

Compliance with the new perchlorate regulations increases the cost of producing, handling, and disposing of AP and other perchlorates. The economic impact of the new regulations on the AP and solid rocket propellant industry has not yet been quantified [1063]. The impact of overly restrictive perchlorate regulations on the drinking water industry could be substantial [1064].

7.12 Carcinogenicity of Ammonium Perchlorate

The thyroid gland is the main target organ for perchlorate toxicity in animals. The thyroid changes caused by perchlorate in animals may lead to tumors in the thyroid after a long period or high-concentration exposure. This has occurred after administering high amounts (928 to $2573 \text{ mg ClO}_4^- \text{ kg}^{-1} \text{ d}^{-1}$) of perchlorate to the animals [1065]. The data from these studies are limited for assessment of carcinogenicity, however, because only a high dose level was used. Still, it was evident that the main target of toxicity was the thyroid gland as thyroid adenomas and/or carcinomas were observed in some of the animals. The NAS concluded that based on the understanding of the biology of human and rodent thyroid tumors, it is unlikely that perchlorate poses a risk of thyroid cancer in humans. Perchlorates have not been classified for carcinogenic effects by the Department of Health and Human Services (DHHS) or the International Agency for Research on Cancer (IARC). The EPA has determined that perchlorate is not likely to pose a risk of thyroid cancer in humans, at least at doses below those necessary to alter thyroid hormone homeostasis. This is based on the hormonally-mediated mode of action in rodent studies and differences seen across species in thyroid function.

A 2001 study found no significant association between perchlorate in drinking water and the prevalence of thyroid diseases or thyroid cancer residents in Nevada counties [1066]. However, no information was available on age, gender, ethnicity, iodine intake, and other risk factors. A study of cancer among residents of San Bernardino County, California, was limited by mixed exposures and lack of correction for potential other contributing factors [1067].

7.13 Teratogenicity of Ammonium Perchlorate

A developmental toxicity study was conducted to evaluate the embryo-fetal toxicity and teratogenic potential of AP in New Zealand white rabbits [1068]. Pregnant rabbits were given continual access to AP in drinking water at target doses of 0, 0.1, 1, 10, 30, and 100 mg kg⁻¹ d⁻¹ on gestation days six through 28. The actual consumed doses in the study were 0, 0.1, 0.9, 10.4, 30, and 102 mg kg⁻¹ d⁻¹. The rabbits were sacrificed on gestation day 29 and fetuses were examined for developmental alterations. In addition, blood was collected from does for determination of serum TSH, triiodothyronine (T3), and thyroxine (T4) levels and the thyroid was subjected to histopathologic examination. No maternal deaths were attributed to perchlorate exposure. The litter averages for corpora lutea, implantations, litter sizes, live and dead fetuses, percent dead or resorbed conceptuses, and fetal body weights were comparable and did not differ significantly in the six-dose groups. The maternal thyroid was the target organ for AP in this study. Increased incidence of thyroid follicular hypertrophy was observed in does treated with ≥ 10 mg kg⁻¹ d⁻¹ perchlorate and significantly decreased T4 was observed in does treated with ≥ 30 mg kg⁻¹ d⁻¹. Based on these data, the maternal NOAEL for AP was 1 mg kg⁻¹ d⁻¹. The developmental NOAEL for AP was found to be 100 mg kg⁻¹ d⁻¹ for rabbits.

In order to study the neurodevelopmental effect of AP-caused hypothyroidism, a neurobehavioral test for spontaneous locomotor activity was used to assess rat pups following pre- and neo-natal exposure to perchlorate [1069]. Pregnant dams were exposed to one of five doses of AP in their drinking water (0, 0.1, 0.3, 1.0, 10 mg mL⁻¹ kg⁻¹) beginning two weeks prior to gestation through to PND 10. The statistically reliable results indicated increased activity at older ages and reduced activity from the start of a given test session to the end of the session. Overall, the results suggest there was not a significant change in general locomotor activity due to pre- and neonatal perchlorate exposure at the doses tested.

Pregnant Sprague-Dawley rats were administered AP via their drinking water at doses of 0 or 1 mg ClO₄⁻ kg⁻¹ d⁻¹ from GD 2 to PND 21 [1070]. Cross-fostering was done on PND 1, such that four groups of pups were formed: never exposed, exposed in utero and via maternal milk, exposed only in utero, and exposed only via maternal milk. The results suggest that: (1) exposure in utero to perchlorate at the dose tested had little or no impact on serum levels of thyroid hormone and TSH measured in pups on PND 10,

(2) the changes in serum thyroid hormone and TSH levels seen in PND 10 pups exposed both in utero and via maternal milk appeared to be completely due to postnatal exposure to perchlorate through lactation, and (3) perchlorate could be acting directly on the pups' thyroid and/or may be limiting the availability of iodide to nursing pups by inhibiting NIS in breast tissue.

Perchlorate seeped into the aquifer extending from the Israel Military Industries plant in Ramat Hasharon. T4 levels in human newborns from mothers living in areas with very high ($\leq 340 \mu\text{g/L}$, $n = 97$), high ($42\text{--}94 \mu\text{g/L}$, $n = 216$) and low ($< 3 \mu\text{g/L}$, $n = 843$) levels of perchlorate did not reveal significant differences in T4 levels among the three groups [1071]. Levels of perchlorate in blood from donors living in the three areas were used as proxy indicators of exposure. Respective blood perchlorate levels in the very high, high, and low exposure proxy groups were 5.99, 1.19, and $0.44 \mu\text{g/L}$. Blood samples from the newborns collected at the age of 36 to 48 hours did not reveal significant differences in T4 levels among the three groups. Mean T4 values in the very high, high, and low exposure groups were 13.9, 13.9, and $14.0 \mu\text{g/L}$, respectively. In addition, neither birth weight nor gestational age was significantly different among the three groups. Although individual iodine measures were not conducted, the investigators stated that the study was conducted in iodine-sufficient areas. The NRC's RfD ($0.7 \mu\text{g kg}^{-1} \text{d}^{-1}$) is likely to be protective of thyroid function in neonates of mothers with adequate iodide intake.

7.14 Developmental Effects of Ammonium Perchlorate

7.14.1 Animal Studies

In a neurobehavioral study of rats, exposure began two weeks before mating and was terminated on PND 10 [1072]. On PND 5, all of the pups were weighed and the litter culled to four males and four females. Tests of motor activity were conducted on one male and one female selected randomly on PND 14, 18, and 22. Nine measures of motor activity were monitored: frequency and time of ambulatory movements, frequency and time of stereotypic movements, frequency of movements in the horizontal plane, distance traveled in the horizontal plane, frequency of rears, total number of horizontal movements made while in rearing position, and time spent resting. Each measure of activity was recorded for 90 consecutive minutes on each test day. Data were divided into nine ten-minute blocks. The results showed that the main effect for perchlorate dose was not significant for any of the nine dependent variables and there were no reliable interactions for treatment. The highest dose tested, $8.5 \text{ mg perchlorate/kg/day}$, is considered a NOAEL for neurodevelopmental effects in this study. A replication of this study [1073–1075] showed that there were no significant alterations in test results due to the consumption of perchlorate relative to controls.

In an evaluation of AP in the endocrine disruptor screening protocol, no changes in delay of puberty in male Wistar rats and no changes in reproductive organ histol-

ogy were observed [1076]. Organ weights were equal to controls at $500 \text{ mg kg}^{-1} \text{ d}^{-1}$ but thyroid and TSH/T4 changes were observed at 62.5 and $125 \text{ mg kg}^{-1} \text{ d}^{-1}$, respectively.

7.14.2 Human Studies

An excellent summary of the developmental effects of perchlorates, both in humans and in animals, is provided in Section 3.2.2.6 (*Developmental Effects*) of the ATSDR study ([1047], pages 69–78).

An evaluation of the potential association between exposure to perchlorate via the drinking water and the incidence of attention-deficit-hyperactivity disorder (ADHD) and autism among children less than 18 years of age who were recipients of Medicaid in Nevada revealed that the rates for ADHD and autism in the area with perchlorate in the drinking water did not exceed the rates in the areas without perchlorate in the drinking water [1077]. Furthermore, there was no difference between the three groups regarding overall fourth-grade school performance. The study included subjects from Clark County, which includes Las Vegas, where the concentration of perchlorate in the public water supply ranged from undetected to $23.8 \mu\text{g/L}$ (mean $10.9 \mu\text{g/L}$), as measured between 1997–2001.

8 Environmental Effects of Ammonium Perchlorate

This book is mainly a book for rocket propellant formulators. However, it is also intended to be a valuable information resource for propellant ingredient production and disposal covering the entire “cradle to grave” life cycle of propellants. For this reason, chapters on toxicity and the environmental effects of perchlorates have been dealt with in substantial detail, amassing several hundred literature references on this topic alone.

When perchlorates were first produced, none of the chemists involved anticipated that it would ever find this widespread distribution and affect drinking water resources in many densely populated areas. The introduction and scaled-up production of new chemicals in the 1950s did not require an environmental review or pre-manufacturing Toxic Substances Control Act (TSCA) notification as it does now. Even now, the environmental impact statements for the continued use of perchlorates leave much to be desired. This was illustrated in a critical review [1078] of the programmatic Environmental Impact Statement prepared by Missile Defense Agency in 2007 for the development, testing, and deployment of a Ballistic Missile Defense System (BMDS). Although the amount of perchlorate anticipated to be used for BMDS is small in comparison to ICBM and Space Shuttle solid rocket booster use, the program has undergone environmental scrutiny [1079–1081].

Perchlorate anion has been found in drinking water supplies throughout the southwestern area of the US where its accidental or negligent releases were primarily

blamed on defense contractors and military operations [1082]. Traces of natural perchlorate are found in Chile saltpeter but the use of such fertilizer has not been associated with large-scale contamination. Many studies involving perchlorate are still underway and many more research papers are being published every month.

In short succession, four significant books on the environmental between the year 2000 and 2009. The four books are:

- [1083] Urbansky (Ed.), *Perchlorate in the environment* (2000)
- [1084] Gu and Coates (Eds.), *Perchlorate: Environmental occurrence, interactions and treatment* (2006)
- [1085] Sellers et al., *Perchlorate: Environmental problems and solutions* (2007)
- [1086] Stroo and Ward (Eds.), *In situ bioremediation of perchlorate in groundwater* (2009)

Combined, these four books constitute a rich and compact source of information on perchlorate pollution. However, in the meantime, the remediation technology continues to make rapid progress. As such, in a few years' time, the books will need to be updated.

The book by Urbansky [1083] is largely based on the proceedings of a symposium held in conjunction with the Fall 1999 American Chemical Society meeting. The book starts with the fundamental chemistry of perchlorate and moves on through other topics. Topics range from toxicology to analytical techniques to treatment and remediation. It contains 25 chapters (derived from papers) organized into three parts. It was the first book published on perchlorate as an environmental contaminant since the discovery of the widespread problem in 1997. Each of these 25 chapters is referenced individually under its appropriate topic at other locations in our book at hand.

A book by Gu and Coates (Eds.) [1084] is a very comprehensive publication with 17 chapters written by individual contributors. It provides a complete review of the environmental effects of perchlorate contamination and offers potential ways to clean up the polluted sites [1087]. The titles of the 17 chapters are:

1. Perchlorate: Challenges and lessons
2. The chemistry of perchlorate in the environment
3. Occurrence and formation of non-anthropogenic perchlorate
4. Alternative causes of widespread, low concentration perchlorate impacts to groundwater
5. Stable isotope composition of chlorine and oxygen in synthetic and natural perchlorate
6. Recent developments in perchlorate detection
7. The ecotoxicology of perchlorate in the environment
8. Perchlorate toxicity and risk assessment
9. Using biomonitoring to assess human exposure to perchlorate
10. Recent advances in ion exchange for perchlorate treatment, recovery, and detection

11. Field demonstration using highly selective regenerable ion exchange and perchlorate destruction technologies for water treatment
12. The microbiology of perchlorate reduction and its bioremediative application
13. The biochemistry and genetics of microbial perchlorate reduction
14. Field demonstration of in situ perchlorate bioremediation in groundwater
15. Perchlorate removal by modified active carbon
16. Titanium catalyzed perchlorate reduction and applications
17. Membrane and other treatment technologies-pros and cons.

Each of these 17 chapters is referenced individually under its appropriate topic at other locations in this publication at hand.

The first two books are just collections (juxtapositions) of chapters (papers) contributed by several authors. A book by a group of authors working with Sellers et al. [1085] is a more homogeneous and coherent exploration of the subject. It is a valuable resource because it contains several case studies and information on the success of several perchlorate pilot-scale and full-scale treatment facilities in the field (as opposed to just laboratory *in-vitro* studies). It also shows photos of several of these installations so the reader can get a feel for the size of the installations (and the expense of building them).

The book by Stroo and Ward (Eds.) [1086] contains 11 chapters, all of which are individually referenced in the current book at hand.

In addition to what was collected in the four books listed above, there is enough information about environmental and public health impacts of perchlorates out there to fill another four books. Besides hard-copy books and essays and reports printed on paper, there are numerous sources on the environmental impact of perchlorates accessible only in electronic form on the internet. Because the URLs of many of these websites are sometimes short-lived, we have abandoned an attempt to list a few representative examples.

In several dozens of many such survey articles, the environmental occurrence, toxicity, analytical chemistry, and remediative approaches are discussed. These publications provide a good introduction into problem areas and some are written in easily understandable terms that even a non-toxicologist can understand [1088–1091].

The EPA has compiled and published a summary of known perchlorate releases in the US. This indicates that perchlorate contamination is a widely spread problem. Maps of the US have been drawn that show the hot spots of perchlorate contamination in the southwestern area of the country. Perchlorate has been detected in fertilizer, milk, lettuce, and many other food products. In an effort to identify the sources of perchlorate and to prevent further spread of the contamination, the EPA has assembled a database of all known perchlorate manufacturers and users in the US. Likewise, the Department of Defense has documented known perchlorate users and has summarized the remedial action taken on behalf of the DoD installations and DoD contractors and has summarized it in a report to Congress [1092]. This is a 31-page table

listing many installations but it lacks an estimate of the quantities of perchlorates that were once manufactured, stored, or disposed at these locations (see [1093] also).

Srinivasan and co-workers [1094] have produced excellent summaries in two publications regarding the health effects of perchlorate and technologies that can be employed for its removal from water sources. The first one contains 107 references, which guide the reader to further in-depth study of this problem. Most of the references are also discussed and are referred to in the book at hand. The first publication was updated and supplemented with a similar review article a few months later [1095]. As of 2011, although some technologies such as microbial reduction and ion-exchange had become more established than others, there was still not a single technology that could be directly applied to a drinking water treatment system for complete removal of perchlorate.

The Department of Defense's Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) have funded numerous perchlorate remediation and clean-up studies and can serve as a resource for publications on this subject [1096]. As of February 2011, a search for final reports in the SERDP database revealed 299 entries for "perchlorate" and 163 entries for "ammonium perchlorate" along with links to where the reports can be quickly downloaded as .pdf documents.

8.1 Ammonium Perchlorate Distribution and Migration in Aquifers

The release of AP into the environment as a result of accidents or carelessness has caused a significant amount of concern for the health of residents living downstream of the releases as they, of course, depend on pure drinking water for subsistence. Fortunately for the hydrologist studying the migration of contaminant plumes in aquifers, perchlorate ion can now be detected in very low concentrations. Its concentration does not change rapidly by adsorption and chemical or biodegradation during the migration. This makes perchlorate ion a good marker but, unfortunately, it is a very persistent marker.

There are many industrial sites where the perchlorate ion migration in aquifers have been studied after the levels of concern increased in the 1990s [1097]. One of the reports provides detailed data for pollution at the Tronox (formerly Kerr McGee) and AMPAC (referred to as PEPCON in previous reports) plants located in Henderson, NV.

One of the most heavily polluted industrial sites outside the US is a chemical facility in the Ramat Hasharon area in Israel. For 25 years, an AP manufacturing plant disposed of untreated wastewater in four unlined ponds. The research site consisted of the four old infiltration ponds located close to the AP manufacturing plant, about 3 km north of the city of Tel Aviv, Israel. The amount of AP leaked was calculated as ~2400 tons based on the contaminated section of the aquifer, the aquifer thickness, and perchlorate concentrations in the groundwater. The transport mechanisms of perchlorate

infiltrated from 1965 to 1990 from one of these active storage ponds into a deep (40 m) layered vadose zone. As such, the underlying coastal aquifer was measured [1098]. Perchlorate migration from 1990 (when the wastewater disposal ceased) until 2008 (with infiltration due only to natural rain [~ 500 mm/y]) was studied by taking water samples from different depths. Several indirect methods were used, including mass balance in the unsaturated zone profile, concentration profiles below the pond, and a comparison of the same sediment profiles taken in 2005 and 2007. The ^{18}O and ^2H isotopic composition of the pore water could be divided into two separate groups: lighter (depleted) and heavier (enriched) samples. All samples in the lighter group were from the shallow vadose zone, above two clay layers, and represented dilution by natural infiltration of rainwater. The enriched samples were from the deeper section of the unsaturated zone (20–40 m) and represented water used for perchlorate manufacturing 14 years prior to drilling. Consequently, the overall maximum infiltration rate was estimated to be 1.4 m/y. Almost identical perchlorate concentrations were found below the clay layer, along the sediment profile in 2005 and 2007 (two boreholes, 3 m apart). Very different perchlorate profiles were observed above the clay layers. This suggests that perchlorate below the clay layers (20–40 m) is practically stagnant under the current natural conditions. The reduction in perchlorate concentration in groundwater below the ponds versus its increased concentration further downgradient supports the contention that the current migration of perchlorate from the vadose zone to the groundwater is very slow. It was estimated that perchlorate concentration in the groundwater under the infiltration pond, which was 187 mg/L in 2004, will drop to 10 $\mu\text{g/L}$ within about 14 years. The existence of a clay layer crossing the thick vadose zone was found to significantly change the infiltration rate when ponded conditions were replaced with natural precipitation.

A drinking water survey conducted between 1997 and 1998 detected no perchlorate (reporting limit = 4.0 $\mu\text{g/L}$) in the surface water samples from 40 sites in 11 states [1099]. Out of 367 groundwater wells in 17 states which were tested during this survey, only nine wells located in California and New Mexico contained perchlorate. Concentrations in samples from these wells ranged between <4–7 $\mu\text{g/L}$.

Adsorption and release of perchlorate in a variety of soils, minerals, and other media were studied by exposing the solid media to low and high concentrations of perchlorate salts in water [1100]. Low-level ClO_4^- exposure was investigated by subjecting triplicate 5-g portions of a solid medium (38 different soils, minerals, or dusts) to 25 mL of an aqueous AP solution containing 670 ng/mL (6.8 mM) perchlorate. This corresponds to a perchlorate-to-soil ratio of 3.4 mg/g (34 nmol/g/L). At this level of exposure, more than 90% of the perchlorate was recovered in the aqueous phase, as determined by ion chromatography. In some cases, more than 99% of the perchlorate remained in the aqueous phase. The forced perchlorate anion exchange capacities (PAECs) were studied by soaking 5-g portions of the solid media in 250 mL of 0.20-M NaClO_4 followed by repeated deionized water rinses until perchlorate concentrations fell below 20 ng/mL in the rinse solutions. The dried residua were leached with 15 mL

of 0.10-M sodium hydroxide. The leachates were analyzed by using ion chromatography. The perchlorate concentrations found were subsequently used to calculate the PAECs. The measurable PAECs of the insoluble and settleable residua ranged from between 4 to 150 nmol/g, with most in the 20–50 nmol/g range. Overall, the findings support the widely accepted idea that perchlorate does not appreciably sorb to soils and that its mobility and fate are largely influenced by hydrologic and biologic factors. Sorption (anion replacement) of perchlorate appears to occur in some soils. Therefore, the measurement of perchlorate in soils requires accounting for ion exchange phenomena; leaching with water alone may give inaccurate results. If perchlorate anion exchange is confirmed to be negligible, then a sample collection using leaching procedures may be simplified accordingly.

Based on modeling of AP distribution in aquifers, it was predicted that the denser AP/saline brine solutions sink to the bottom of the aquifer where they will remain for a long time and will be a long-term source of perchlorate pollution, even after the primary supply of AP has been stopped. Release from the bottom of the aquifer is mass transfer limited and (in the absence of biodegradation) will have time-scales of approximately 100 years [1101].

Three environmental forensic methods were used as part of an integrated evaluation to determine the extent of dissolved perchlorate in groundwater originating from a former rocket propellant testing site in Southern California [1102]. The methods included the evaluation of groundwater modeling, subsurface environmental conditions, and isotopic fingerprinting. While these methods have been used independently in other environmental forensic studies, this work was the first to document the combined use of these methods to evaluate the extent of dissolved perchlorate in groundwater. Taken together, the results indicated that the perchlorate originating from a former rocket propellant testing site is under hydraulic control and that multiple sources of perchlorate exist within the same hydrogeologic basin.

8.2 Environmental Fate and Biodegradation of Ammonium Perchlorate

Perchlorate anion is not subject to biodegradation as rapidly as nitrate or nitrite anion. It is relatively persistent to both chemical reactions and biodegradation under aerobic conditions. The interest in biodegradation of perchlorate is for several reasons: Hydrologic studies assume that the perchlorate ion in deep aquifers remains unchanged due to biological activity. So, if there is any biological activity affecting perchlorate migration and survival, it has to be quantified. Secondly, it would be very valuable to breed a kind of “superbug” of bacteria that can thrive on perchlorate and be used in bioremediation of contaminated sites and wastewater treatment from industrial processes.

The effects of AP concentration in soil and in water on seed germination, plant growth rate, photosynthesis, microbial respiration, microbial growth, and total biomass have long been studied, well before widespread perchlorate contamination

became apparent [1103]. The select use of bacteria for bioremediation of perchlorate was already patented in 1976, describing the biochemical reduction of perchlorates and chlorates under anaerobic conditions by means of a strain of the micro-organism *Vibrio dechloraticans* Cuznesove B-1168. This is grown by way of successive inoculations on a liquid nutrient medium containing sources of carbon, nitrogen, and phosphorus under anaerobic conditions in the presence of a perchlorate as a donor of oxygen [1104]. It was claimed that such bacteria can reduce perchlorates to chlorides at a rate of 5 g of perchlorate for 3 d per 1 g of the biomass solids and may continue to grow at a concentration of AP as high as 300 mg/L.

A bacterial isolate, strain *perclace*, was shown to reduce the groundwater contaminant perchlorate ClO_4^- to levels <0.005 mg/L when grown on acetate under anaerobic conditions [1105]. The ability of *perclace* to simultaneously reduce perchlorate and another groundwater pollutant, nitrate, NO_3^- , was examined in batch studies and in a sand-packed column under saturated flow conditions. Nitrate removal was monitored using ion chromatography, and perchlorate removal was monitored using a perchlorate ion specific electrode or ion chromatography. In batch studies, the reduction of 0.089, 0.92, 12.0, and 122 mg/L perchlorate was examined in the presence and absence of 62 mg/L NO_3^- . Perchlorate was reduced more rapidly in the absence of NO_3^- than in its presence. However, both perchlorate and NO_3^- were reduced by more than 10-fold within 48 hours. A sand-packed column inoculated with *perclace* simulated a flow-through biotreatment system for water contaminated with a low level of perchlorate and a much higher level of NO_3^- . Biotreatment could reduce perchlorate to <0.005 mg/L in a 3-h residence time. *Perclace* may be used as a substitute for anaerobic bacteria which are otherwise used in biological systems for removing perchlorate and/or nitrate from water or soil [1106].

There has been an intense interest in the environmental fate of spilled perchlorates and there have been several conferences and books devoted entirely to this topic [1107].

When released to the environment, perchlorates are expected to be highly mobile in water-percolated soil and to partition to surface water or groundwater [1090]. They are not expected to significantly adsorb to sediment or suspended organic matter. If airborne, they are also expected to readily settle from the atmosphere by wet and dry deposition. No degradation process for perchlorates in the environment has been unambiguously established. Laboratory experiments suggest that they may be reduced by anaerobic microbes in soil and water, although the presence of sulfates and nitrates in the environment attenuates this process. Laboratory experiments also suggest that perchlorates may undergo uptake by some plants and may be subsequently reduced to chloride. Neither the types of plants that take up perchlorate nor the types capable of reducing it have been well categorized.

Perchlorates have been found to be quite persistent. It was stated that the necessary criteria for perchlorate degradation in soil are anaerobic conditions, an adequate carbon source, and an active perchlorate-degrading microbial population [1108]. Per-

chlorate applied to Yolo loam at 180 mg/L during an anaerobic flooded batch experiment was completely biodegraded after 30 d.

During an analysis of perchlorate-contaminated streambed sediment located near a Naval Weapons Industrial Reserve Plant in McGregor, TX, it was concluded that microbial degradation of perchlorate was taking place based on a sequential depletion of electron acceptors and a constant Cl^- concentration in the sediment [1109]. The level of nitrate found to result in inhibition, 100 mg/L, was on the low end of the range typically found in soils, 0–1200 mg/L. In the absence of nitrate, perchlorate was removed to levels below the detection limit ($<4\text{ }\mu\text{g/L}$) in wetland columns with perchlorate influents of 4, 8, 16, and 32 mg/L [1110, 1111].

The reduction of perchlorate using micro-organisms has been found to be inhibited by the electron acceptors most commonly found in anaerobic environments (nitrate and/or sulfate). In a few cases, they were found to be reduced preferentially. The initial product from the respiration of perchlorate is chlorate (ClO_3^-). This in turn is reduced by some of the bacteria to chlorite (ClO_2^-) and, ultimately, to chloride (Cl^-) and either oxygen or bicarbonate [1112, 1113]. The same bacteria can reduce chlorate as well as perchlorate [1114–1116] (see [1117–1119] also).

8.3 Soil Contamination Case Studies

As of April 2004, the EPA's Office of Solid Waste and Emergency Response and the Federal Facilities Restoration and Reuse department had documented 58 federal sites with known perchlorate releases. These sites included a combination of Air Force, Navy, Army, Department of Energy, and NASA sites. Of these sites, 51 were DoD sites. The office also listed 40 private sites, many of which were owned or operated by military contractors with known releases. Groundwater contamination existed at all of these sites, with perchlorate concentrations as high as 3700 mg/L. Perchlorate in vadose-zone soil existed at many of these sites and can serve as an ongoing source of groundwater contamination. Twenty of the 51 DoD sites were listed as having soil contamination.

The vadose zone is below ground but above groundwater level. It may store spilled contaminants for a long time since it is only purged by precipitation trickling down to the groundwater level. Contaminants in the vadose zone in arid climates are bound to stay there for a long time.

While there has been a lot of publicity about the explosion at PEPCON and the subsequent spill at Henderson, NV, the main source of groundwater pollution is actually another perchlorate plant not far away from the explosion site. Perchlorate production was initiated at the Kerr McGee Chemical Company at other plant locations in 1945, and full commercial production of AP began in 1951 under the prior owners/operators. Kerr McGee acquired the property in 1967 and the company name was changed to Tronox in November 2005.

Perchlorate-contaminated groundwater from the Kerr McGee/Tronox plume flows north, about three miles from Tronox to Las Vegas Wash. Tronox is the most significant source of perchlorate entering Las Vegas Wash; prior to controls being put into place, the Tronox plume released about 900 to 1000 pounds per day (average) of perchlorate-contaminated groundwater to Las Vegas Wash. It was estimated that the plume emanating from the Kerr McGee plant contains 9000 metric tons (20 million pounds) of perchlorate dissolved in 3.4 million m³ (9 billion gallons) of water. The EPA has issued a summary report on the findings of soil and groundwater analyses in the Henderson, NV area [1097].

The former PEPCON/AMPAC perchlorate plant also has a plume of perchlorate but it is smaller and much less concentrated than the Tronox plume. It has been estimated that the plume emanating from the PEPCON plant holds 500 metric tons (1.1 million pounds) of perchlorate in 3.4 million m³ (9 billion gallons) of water. AMPAC conducted an *In-Situ* Bioremediation Pilot Study from December 2002 to April 2003. This effort was successful, reducing perchlorate concentrations from about 500 ppm to less than 2 ppb. During 2003 and 2004, AMPAC conducted additional investigations of the nature and extent of their perchlorate plume.

The environmental pollution situation is slowly improving. Groundwater concentrations are declining as a result of Tronox's capture and control efforts at three locations: a slurry wall on Tronox property, on Athens Road (about halfway to Las Vegas Wash), and a seep area near Las Vegas Wash. Groundwater extraction wells in these three locations are removing approximately 1700 to 2000 pounds of perchlorate per day. Surface water concentrations in Las Vegas Wash, Lake Mead and the Lower Colorado River have declined by 85%, 70%, and 60%, respectively, since seep capture and treatment began in November 1999.

In Israel, widespread perchlorate contamination with peak concentrations of 1200 mg ClO₄⁻/kg sediment has been found in the 40-m deep vadose zone near an AP manufacturing plant that is north of Tel Aviv and above the central part of Israel's coastal aquifer. The perchlorate-reduction potential by native microbial communities along a deep contaminated vadose zone profile was examined [1120]. The effect of various concentrations of nitrate on perchlorate reduction had to be considered because it is possible that perchlorate concentrations in the profile are toxic to the native microbial population. All experiments were performed in soil slurries with sediments taken from the contaminated site. Perchlorate was reduced to chloride in three (1, 15, and 35 m) of the four examined sediment samples taken from different depths (1, 15, 20, and 35 m below surface). No activity was observed in the sediment sample from 20 m below land surface, suggesting low viable microbial communities and water content and high surviving perchlorate concentrations. In the presence of nitrate, the lag time for perchlorate degradation was inversely correlated to nitrate concentration. There was no perchlorate degradation as long as nitrate was present in the system, and perchlorate degradation started only after all the nitrate had been consumed. Nitrate-reduction rates were correlated to the initial

concentrations of nitrate and no lag period was observed for nitrate reduction. Viable microbial populations were observed at both high concentrations (10000 mg/L and 20000 mg/L) and with no addition of perchlorate, at levels of 2.3×10^5 , 4.0×10^5 , and 3.4×10^3 colony forming units (CFU)/mL, respectively. These results were well correlated to those found by polymerase chain reaction (PCR) amplification analysis of chlorite dismutase [1121]. It was suspected that the microbial community has adapted to the conditions of high perchlorate concentrations in the unsaturated zone following 30 years of exposure. That would make them suitable bacteria for the treatment of other contaminated sites. When no external carbon source was added to the slurry of soil from land surfaces, all perchlorate was removed after 134 days of incubation. The average perchlorate-reduction rate using natural organic matter as a carbon source was 0.45 mg/d, while the average rate using acetate as an external carbon source was 7.2 mg/d.

The potential for contamination resulting from discharges at facilities that manufacture and use perchlorate was studied following the accidental fire and subsequent explosion at the PEPCON AP production site in Henderson, Nevada in May 1988 [1122]. Perchlorate concentrations as high as 630000 µg/L were observed in nearby surface water samples following the accident. Nearby groundwater samples were also contaminated with perchlorate at concentrations ranging from 51400 to 630000 µg/L. Monitoring data from 50 wells obtained near the Kerr-McGee AP producing facility, also located in Henderson, NV, had perchlorate levels as high as 3.7 g/L [1122].

Surface water samples taken in August 1997 from the Las Vegas Wash, which feeds into Lake Mead, had perchlorate concentrations of 1500–1680 µg/L [1117].

A mean perchlorate concentration of 450 µg/L was reported in 24 water samples from three sites at the Las Vegas Wash collected in March 2002 near Henderson, NV [1123].

The Los Angeles Metropolitan Water District has detected perchlorate at 8 µg/L at an intake located in Lake Mead [1122]. In a separate study, perchlorate was detected in 57% of 147 surface water samples and 50% of ten pore water samples collected in the Lake Mead area, with average (maximum) concentrations of 10.5 (130) and 19.6 (98.0) mg/kg, respectively [1057]. Reported concentrations of perchlorate in the Colorado River are 5–9 µg/L [1015]. In Utah, perchlorate concentrations in groundwater wells at Alliant Techsystems, a rocket manufacturing site, ranged from 4 to 200 µg/L [1122]. According to a report issued by the EPA in December 2005, surface water concentrations in Las Vegas Wash, Lake Mead, and the Lower Colorado River have declined by 85, 70, and 60%, respectively, since the inception of a seep capture and treatment program at the Kerr-McGee site in Henderson, Nevada, began in November 1999 [1097].

Groundwater samples from a shallow aquifer near the Aerojet General Corporation's solid rocket propellant facility near Sacramento, California, had maximum perchlorate levels of 8000 µg/L [1117].

The frequency of detection of perchlorate and its impacts to soil, groundwater, and surface water (causes that are unrelated to military activities) has increased in the past several years as more and more water utilities have begun to analyze for this constituent as part of their monitoring programs. Based on more detailed product and process information, perchlorate was found to be present (intentionally or unintentionally) in many more products and processes than people were initially aware of. Furthermore, evidence surfaced that perchlorate can be formed naturally in evaporate deposits and through atmospheric mechanisms. The most significant domestic users of perchlorate in North America are the DoD in the US, NASA, and related defense contractors, thus making perchlorate impacts attributable to these groups and facilities. However, cases where perchlorate impacts result from non-military and/or natural inputs need to be included in future studies [1124].

Soil samples from an agricultural field were amended with perchlorate solution and set aside in a shelter exposed to air at the farm for periodic sampling and analysis. The perchlorate content decreased significantly within 20 days, but the cause for the perchlorate degradation was not identified [1125].

8.4 Groundwater Contamination Case Studies

At one point, the state of Nevada Division of Environmental Protection's (NDEP's) website provided a chronological timeline of the events at two perchlorate manufacturing sites near Las Vegas, NV [1126]. That report also provided a map outlining the path of two underground plumes as they migrate toward the Colorado River (Figure 46).

The sources of the perchlorate in Lake Mead were traced upstream to the Las Vegas Wash, which discharges into Lake Mead. Perchlorate was entering the Las Vegas Wash through contaminated groundwater and surface water stemming from a manufacturing facility once owned and operated by Kerr-McGee Chemical LLC (which was renamed to Tronox LLC, as mentioned earlier). Perchlorate-contaminated groundwater was also found to originate from PEPCON, which is owned by AMPAC. The US Navy, Western Electrochemical Company and the American Potash and Chemical Company have owned and operated the current Tronox facility. Perchlorate was produced at this facility from between 1945 until 1998. Perchlorate was manufactured at the AMPAC facility from 1958 to 1988 when an explosion destroyed the PEPCON plant. From 2005 through to 2009, Tronox operated a remediation system that extracted perchlorate-contaminated groundwater for *ex-situ* treatment. This uses a fluidized bed reactor (FBR) treatment system using bioremediation to reduce the perchlorate concentration followed by discharge into the Las Vegas Wash. The discharge water from this remediation system has been consistently less than the Nevada Interim Action Level for perchlorate of 18 µg/L or 18 ppb. AMPAC operated an *in-situ* remediation system where perchlorate-contaminated groundwater was

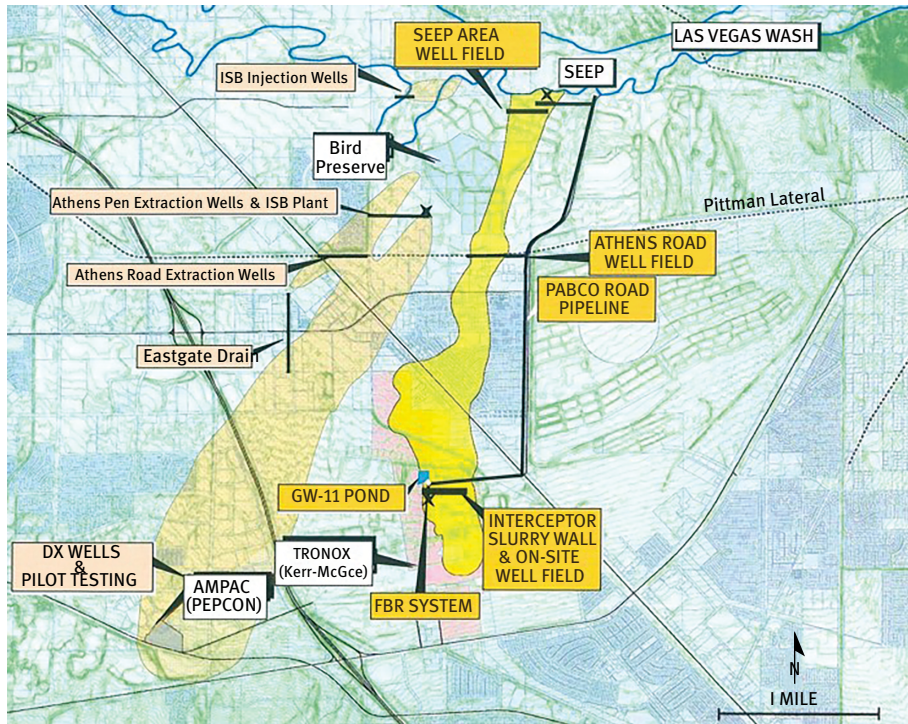


Figure 46: Migration of perchlorate contaminated groundwater plumes toward Las Vegas Wash and Colorado River. (From NDEP <http://ndep.nv.gov/bca/perchlorate05.htm>.)

extracted and amended with nutrients followed by re-injection into the subsurface near the Las Vegas Wash. This system has achieved the reduction of the perchlorate concentration in the re-injected groundwater from $18\text{ }\mu\text{g/L}$ to non-detectable concentrations of less than 6 ppb by the time it reached the first performance monitoring well. Concentrations in the Las Vegas Wash have decreased by more than 90 percent since 1997. Sampling data from the Willow Beach, AZ, sampling point on the Colorado River (approximately 11 miles downstream from Hoover Dam), revealed a reduction from a high of 9.7 ppb in June 1999 to 1.8 ppb in May 2008. Sampling data from the Northshore Road sampling point in the Las Vegas Wash downstream from Lake Las Vegas revealed a reduction from a high of 1200 ppb in October 1998 to 61 ppb in May 2008. NDEP continued to work with the EPA, Southern Nevada Water Authority, Metropolitan Water District, City of Henderson, Tronox, AMPAC and Black Mountain Industrial complex to develop opportunities to further refine groundwater capture and treatment technologies.

One source of perchlorate contamination of drinking water in Massachusetts in the US was traced to the use of perchloric acid to bleach surgical and medical equipment in an upstream town on the Merrimack River.

In order to obtain a consistent and reproducible set of data on the extent of perchlorate pollution and the effectiveness of clean-up efforts, the DoD has issued a *DoD Perchlorate Handbook* [1127]. Chartered under the leadership of the Department of the Navy, this inter-component task force is responsible for promoting “the generation of environmental data of known and documented quality”. The handbook has the following objectives:

- Ensure cost-effective and consistent approaches across the DoD for sampling and testing activities involving perchlorate;
- Ensure that collected data are of the quality necessary to support decision-making;
- Ensure that information disseminated to the public associated with perchlorate sampling and testing complies with Information Quality Guidelines put forward by the DoD.

The handbook includes guidance for the following areas:

- Use conceptual site models to develop project quality objectives associated with sampling and analysis for perchlorate;
- Design sampling strategies and implementing appropriate sampling techniques;
- Select qualified and certified analytical laboratories and analytical methods based on required performance objectives.

8.5 Seawater Contamination Case Studies

Perchlorates may be released into the environment from booster rockets during a catastrophic failure or aborted flight. Following the Delta II flight failure that occurred at Cape Canaveral in January 1997, it was estimated that 200000 pounds of perchlorate-containing HTPB solid propellant was released [1128].

8.6 Effects of Perchlorate Salts on Plant Growth

It is known that chlorates (predominantly sodium chlorate) have been used extensively as herbicides and that this was one of the possible pathways in which perchlorate (present as contamination in industrial grade sodium chlorate) entered the environment, where it remained for a long time.

Perchlorate itself is less active as an herbicide and not likely to be used for that purpose.

It is known that some plants (e.g., seaweed) have the ability to enrich iodine from seawater [1129]. Likewise, some plants have the ability to enrich perchlorate (perchlorate often mimics the properties of iodide). There is concern that some vegetables in-

tended for human consumption can become enriched in perchlorate if the irrigation water is contaminated with it.

Cucumber (*Cucumis sativus* L.), lettuce (*Lactuca sativa* L.), and soybean (*Glycine max*) were used to determine the uptake of the perchlorate anion (100 ppb) from sand [1130]. Perchlorate concentrations in sand and plant tissues were determined weekly. Perchlorate uptake was observed in all three plant species. In most experiments, perchlorate was completely depleted from sand in which plants were growing. Perchlorate concentrations in lettuce were also significantly higher than those in cucumber and soybean. The results of an eight-week uptake study in cucumber and a six-week uptake study in lettuce suggest that a threshold perchlorate concentration is reached: for cucumber it is 150 ppm, and for lettuce it is 750 ppm.

Notably, during the remediation of perchlorate-contaminated sites, some plants not only absorb perchlorate and enrich it in their tissue, they are also able to reduce it to create a harmless chloride [1131]. Thus, if contaminated sites are revegetated with non-food vegetation, one should select plants that have the ability to reduce perchlorate ion.

Chilean saltpeter, a naturally occurring material proven to contain perchlorates, has been marketed mainly as a granular product for fertilizers. Chilean researchers initiated a study in 1967 to establish why soybeans were exhibiting stunted growth, rugose, and crumpled leaves as a result of domestic fertilizer application and to determine what levels of perchlorate these plants could tolerate [1132]. The saltpeter used to produce the fertilizer at that time contained 0.12–0.26 mass-% perchlorate as a contaminant [1133].

Fertilizer derived from Chilean saltpeter has been traditionally applied mainly to tobacco plants but has also been marketed for citrus fruits, cotton, and some vegetable crops [1133]. The amount of perchlorate present in recent samples of these fertilizers was found to range from 0.7 to 2.0 mg/g. Steps have been taken to reformulate these products to remove perchlorate. Other synthetic fertilizers do not contain perchlorate.

8.7 Aquatic Toxicity of Perchlorates

An *in-vitro* developmental toxicity screen was performed to determine the developmental hazard index (A/D ratio) for AP using the hydra assay. *Hydra attenuata* have the capability for whole body regeneration. Both adult hydra and “artificial embryos” composed of disassociated hydra cells were exposed to AP to investigate developmental toxicity [1134]. Results from the hydra assay of AP indicated that the minimal effective concentrations required to elicit a toxic response in the adult hydra and in the regenerating hydra were 600 mg AP/L and 350 mg AP/L, respectively. The A/D ratio of 1.71 indicated that AP should not be considered a primary developmental toxin in the context of this assay.

Shortly after the perchlorate contamination in aquifers and surface waters were discovered, a battery of screening-level ecological tests were selected based on their availability, rapid turnaround, interpretation power, and susceptibility of organisms [1135]. The test species selected were *Daphnia magna* and *Ceriodaphnia dubia* (free swimming freshwater aquatic invertebrates commonly called water fleas), *Pimephales promelas* (fathead minnow), *Eisenia foetida* (the redworm), and *Lactuca sativa* (a leaf lettuce). An ecological risk assessment was then conducted incorporating a toxicity evaluation, exposure analysis, and risk characterization. Effects, measured as growth and mortality, ranged from a no observed effect concentration (NOEC) of 10 mg/L in *Ceriodaphnia dubia* to a NOEC of 155 mg/L in *Pimephales promelas*. The range of LC₅₀s was 66 mg/L in *Ceriodaphnia dubia* to 4450 mg/L in *Eisenia foetida*.

Limited data indicate that perchlorate may accumulate in living organisms as it has been detected in vegetation, fish, amphibian, insect, and rodent samples collected near known contaminated sites [1136]. Microbial (algal and bacterial) and fish tissues bio-accumulated ClO₄⁻ to high levels and to the magnitude of ClO₄⁻ accumulation corresponded well to exposure levels. The concentrations of ClO₄⁻ in three male spine stickleback fish (*Gasterosteus aculeatus*) were 0.63, 0.54, and 4.47 µg/g, corresponding to aquarium water perchlorate concentrations of 0, 1, and 10 ppm, respectively [1137]. The presence of potassium perchlorate at concentrations up to 10 ppm and ClO₄⁻ concentrations nearing 30 ppm in aquaria containing solid propellant had no effect on stickleback mating or the birth and growth of fry. Fry mortality occurred in all treatments but none were statistically different from controls.

Eggs and larvae of *Xenopus laevis* were exposed to varying concentrations of AP or a control medium for 70 days [1138–1140]. Most treatment-related mortality was observed within five days after exposure and was due in large part to reduced hatching success. The five- and 70-days median lethal concentrations (LC₅₀s) were 510 ± 36 mg AP/L and 223 ± 13 mg AP/L, respectively. AP did not cause any concentration-related developmental abnormalities at concentrations below the 70-day LC₅₀. Although AP was not teratogenic, concentrations reported in contaminated surface waters did inhibit metamorphosis. AP inhibited metamorphosis in a concentration-dependent manner, as evident from effects on forelimb emergence, tail resorption, and hind limb growth. It can be concluded that AP pollution may pose a threat to normal development and growth in amphibian populations.

Thirteen reports that examine the ecological risk of AP on aquatic animal life were summarized in [1141]. The reports deal with the uptake and elimination of perchlorate in American bullfrog larvae, the effects of AP-contaminated and reference surface waters on metamorphosis in *Xenopus Laevis*, and the lethal concentration determination of sodium perchlorate on *Xenopus Laevis*, fish, and amphibians as aquatic sentinels for perchlorate exposures. They also report on *in-situ* exposure of fish and amphibians to perchlorate.

Adult zebrafish were reared up to eight weeks in control water or in water containing AP at measured perchlorate concentrations of 18 ppm (environmentally relevant, high) or 677 ppm [1142]. At 677 ppm, spawn volume was reduced within one week and became negligible after four weeks. At 18 ppm, spawn volume was unaffected even after eight weeks. An eight-week exposure of adult zebrafish to 18 ppm perchlorate affected the histological condition of their thyroid follicles but not their reproductive performance. The effect of 677 ppm perchlorate on reproduction may be due to extrathyroidal toxicity.

The kidney is also a potential target of the direct (association with iodide transporters) or indirect (decreased thyroid hormones and increased TSH) actions of perchlorate. To study the histopathological effects of AP on zebrafish kidneys, adult zebrafish were exposed to water-borne perchlorate at concentrations of 18 ppm for eight weeks and 677 ppm for four weeks [1143]. At the end of the exposure period, the fish were processed for histological analyses of the trunk region of the kidney. The results indicated that exposure to AP at 18 ppm for eight weeks caused a significant increase in the incidence of renal macrophage aggregates when compared with the control fish. The other lesions showed no changes in incidence at any AP dose. The study also suggests a link between thyroid disruption and increases in renal macrophage aggregates.

Fillets and heads of fish collected from Lake Waco and Lake Belton in Texas (located near the Naval Weapons Industrial Reserve Plant where solid rocket motors are manufactured) were analyzed for perchlorates [1144]. Perchlorate concentrations in positive samples ranged from 146 to 2740 µg/kg wet weight in fillets and from 626 to 4560 µg/kg wet weight in heads. Possible routes of exposure for these fish include the ingestion of contaminated periphyton (algae film), contaminated detritus, and the ingestion of perchlorate-containing invertebrates.

The long-term effects of perchlorate on developing amphibians (e.g., growth, metamorphosis) and on the general health and reproductive capacity of adult females were studied *in-vitro* [1145]. The studies examined the effects of perchlorate present in the water as well as perchlorate available through the food chain. Because perchlorate competes for iodine binding sites in the thyroid, the addition of iodine to culture water was examined to determine if perchlorate effects can be mitigated. Perchlorate was found to affect the normal pigmentation of amphibian embryos, however, so does UV irradiation.

Mosquitofish (*Gambusia holbrooki*) adults and fry were exposed to aqueous sodium perchlorate at 1, 10, and 100 mg/L, and growth and reproductive performance were determined [1146]. Five-day acute toxicity tests were also performed. The LC₅₀ of sodium perchlorate was 404 mg/L. Growth was enhanced at 1 mg/L but inhibited at 10 mg/L. These results suggest that, at environmentally relevant concentrations, perchlorate does not induce acutely toxic effects but may have mild stimulatory effects on fitness parameters in this species. In another study, the same type of fish were exposed to 0.1–1000 mg/L NaClO₄ for 12 hours and one, two, five, ten, and 30 days, and perchlorate was determined in whole body extracts [1147]. Perchlorate

was not detected in fish exposed to the low concentrations of perchlorate (0, 0.1, and 1 mg/L), regardless of the exposure time, whereas it was detected when fish were exposed to 10, 100, and 1000 mg/L. The tissue concentrations were approximately ten times less than that in the water (see [939, 1148]).

From AMPAC MSDS (no specific sources of these data were listed):

- *Daphnia Magna* Acute 48-hour LC₅₀ 490 mg/L water with sodium perchlorate
- *Pimephales promelas* Acute 96-hour LC₅₀ 1655 mg/L water with sodium perchlorate
- *Ceriodaphnia dubia* Chronic six-day LC₅₀ 77.8 mg/L water with AP
- *Pimephales promelas* Sub-Chronic six-day LC₅₀ 270 mg/L water with AP
- *Eisenia fetida* Acute seven-day LC₅₀ 4450 mg/kg soil

The toxicity of sodium perchlorate to earth worms *Eisenia fetida* was evaluated in sub-chronic tests in artificial soil. The sub-chronic (21-day sand tests) EC₅₀ for sodium perchlorate to *E. fetida* reproduction (cocoon production) was 1.3 µg/g. The sub-chronic (28-day artificial soil tests) EC₅₀ for sodium perchlorate to *E. fetida* reproduction (cocoon production) was 350 µg/g [1149].

8.8 Toxicity of Perchlorates to Wildlife

Animals living on or near perchlorate-contaminated sites may ingest perchlorate with their forage and scatter it with their excrements.

Raccoons were chosen to evaluate perchlorate exposure and AP effects on large mammals inhabiting the contaminated Longhorn Army Ammunition Plant (LHAAP) located in East Texas [1150]. Many locations on the site were directly involved with perchlorate handling, maintenance, and detonation. Soil and water samples collected on the site had perchlorate concentrations up to 1030 ppm [1136]. Potential forage items had varying levels of perchlorate concentrations of up to 5557 ppm (crabgrass). Concentrations of perchlorate in amphibians ranged from below detectable levels to 2.5 ppm in tadpoles. The decision to study raccoons was based on the types of food a raccoon consumes. Blood samples were collected from trapped raccoons. Samples were analyzed for perchlorate residues and thyroid hormone concentrations. Fifty plasma samples were analyzed for perchlorate residue but they were all below the detection limit of perchlorate in plasma (~100 ppb) except for one animal which had a trace of perchlorate in its plasma. Results from this study did not detect any appreciable perchlorate exposure among raccoons at the LHAAP or resulting effects on thyroid function. If perchlorate exposure had resulted in thyroid changes among raccoons, one would expect to see a negative correlation between T3, T4, and TSH. For example, TSH levels would be high while corresponding T3 and T4 levels would be low. One lonely raccoon with trace amounts of perchlorate present in his blood

plasma had lower concentrations of T3 and T4 and higher concentrations of TSH in relation to the rest of the captured population, in line with expected changes.

Preliminary data from experiments in which pairs of deer mice (*Peromyscus maniculatus*) were exposed to 0, 1 nM, 1 μ M, and 1 mM AP (0, 1.59×10^{-5} , 1.60×10^{-2} , and $15.78 \text{ mg kg}^{-1} \text{ d}^{-1}$ perchlorate ion; ten pairs per dose group) in drinking water suggested that AP adversely affected growth (i.e., a decrease in pup body weights at the highest dose), and development (i.e., differences in kidney, liver, and heart weights in pups) [1151, 1152]. However, there was much scatter in the data. Subsequent studies using the same dose groups extended the exposure time to the weaning of the third litter. Reproductive and growth parameters in the second litter pups at PND 21 revealed a dose-related decrease in litter size, however, this decrease was not significant at any dose level. Additionally, there were no significant differences in body or organ weights when the data was analyzed using individual litters as experimental units. The only statistically significant dose-related effect was in the 1 μ M and 1 mM dose groups with a decrease in heart weights in male pups on PND 21.

The most comprehensive summary of the effects of perchlorate releases on wildlife is a 66-page report by the US Army Center for Health Promotion and Preventive Medicine. This provides a thorough literature survey of published data (including items published through 2006) which includes a wide range of wildlife species, including mammals, birds, and amphibians. It also provides data for laboratory animals exposed to perchlorates [940].

8.9 Remediation of Ammonium Perchlorate Pollution

Once perchlorate ion enters the environment, it is very difficult to reverse its spreading to adjacent surface water bodies and aquifers. Conventional water treatment technologies, including aerobic biodegradation are not efficient at removing perchlorate from water. As of 2009, the DoD in the US had spent over 114 M\$ (megadollars = million dollars) on research regarding perchlorate treatment, substitutes, and detection methodologies. This is in addition to substantial funds spent by other government agencies, local administrations, and water districts. The rate of degradation under the effect of natural influences is very slow (see Section 8.2). Methods are sought which will accelerate natural degradation processes, either in retaining ponds or in natural environments. In selecting remediation technologies, one must differentiate between *in-situ* and *ex-situ* remediation methods. If possible, one will attempt to eliminate the problem at the source (*in-situ*). Any of the *ex-situ* methods would require that the contaminated media (soil, water) be moved to a treatment site.

The Interstate Technology and Regulatory Council (ITRC, <http://www.itrcweb.org/home>), a coalition of state environmental regulators working with federal partners, industry, and stakeholders to advance innovative environmental decision making, has formed a working group on perchlorate remediation. The ITRC Perchlorate Team

reviews new and/or innovative perchlorate remediation technologies to determine the availability and effectiveness of these technologies to reduce concentrations of perchlorate in groundwater and/or soils. A pair of two excellent summary reports on remediation technologies was issued in 2005 [1153, 1154]. Appendix A in the latter report contains a detailed narrative of case studies of perchlorate contamination and remediation. The federal US, as well as the California State Environmental Protection Agencies, have published lists of available, tested, and untested treatment technologies [1155, 1156], including lists of planned and operational water treatment installations (see [1157]).

There currently are two major above-ground technologies used to treat large volumes of water that contain perchlorate: ion exchange and biological treatment. Other technologies under evaluation include membrane filtration and electrodialysis.

A very detailed report summarizing various treatment technology options and compiling a list of clean-up projects in progress in the US was compiled by Ground-Water Remediation Technologies Analysis Center (GWRTAC) in Pittsburgh, PA [1158].

The NDEP along with the SNWA, the EPA, the City of Henderson, and Kerr-McGee began to investigate the source of the perchlorate. When the sources of perchlorate had been identified, remediation plans were enacted to remove perchlorate from groundwater and surface water. The perchlorate flow rate entering the Las Vegas Wash has been reduced by approximately 90% since 1997. As of August 2008, approximately 2638 tons of perchlorate had been removed from the environment. NDEP continues to monitor perchlorate levels reported in the Lower Colorado River, which is below the safety limit set by the EPA in February 2005.

The California-based Department of Toxic Substances Control, which forms part of the EPA, and the Office of Pollution Prevention and Technology Development has compiled a list of perchlorate contamination treatment alternatives [1159], including a nine-page detailed table where various technologies are compared and evaluated.

The Hazardous Waste Clean-Up Information (CLU-IN) website (<http://www.clu-in.org/>) provides information about innovative treatment and site characterization technologies to the hazardous waste remediation community for perchlorate and other pollutants. It describes programs, organizations, publications, and other tools for federal and state personnel, consulting engineers, technology developers and vendors, remediation contractors, researchers, community groups, and individual citizens. The site was developed by the EPA but is intended as a forum for all waste remediation organizations.

In the meantime, the problem of perchlorate contamination in groundwater has spread to other spacefaring nations and improved methods are sought for wastewater remediation [1160]. It has also been recognized that there are natural sources of perchlorate in some groundwaters.

Previously, prior to perchlorate pollution problems becoming known, groundwater pollution due to nitrate had been a persistent concern, particularly so in agricultural communities. This was due to runoff from fertilized fields seeping into

the groundwater and drinking water supply wells. It now appears that the new water treatment technologies stimulated by the need of perchlorate removal from drinking water can be beneficially used for the removal of nitrate from drinking water as well.

8.9.1 AP Removal by Using Ion Exchange

Perchlorate removal from groundwater via ion exchange has been commercially accepted by the water treatment industry and is now being used in dozens of installations across the US. Ion exchange technology uses an anion exchange resin loaded with chloride ion to absorb perchlorate and remove it from drinking water. The contaminated water is pumped through columns containing resin beds, which are two to six feet in diameter and one to six feet high, releasing harmless chloride in its place and affording the opportunity for safe and appropriate disposal. The most promising physical removal process for treating perchlorate-contaminated water uses ion exchange technology. Commercially available ion exchange resins such as Purolite® and Amberlite® resins have been tested for perchlorate sorption. Perchlorate can be removed from water using ion exchange columns. The exhausted resin is regenerated using sodium chloride. The perchlorate brine, containing 7–12% perchlorate, is disposed of in accordance with local regulations.

A study was conducted to evaluate the performance of a small-scale ion exchange unit for the removal of nitrate and perchlorate from groundwater at Lawrence Livermore National Laboratory's Site 300 [1161]. The unit contained 2.5 cu. ft. of Sybron SR-7 resin and was able to treat 3600 gallons of groundwater at an average influent concentration of 100 mg/LNO₃⁻ before breakthrough occurred. Seventy gallons of regeneration waste was generated in the process. The effluent concentration was about 20 mg/LNO₃⁻, which is equivalent to a treatment efficiency of at least 80%. There were several options for implementing this technology: A target well had a 3 to 4 gpm flow rate and concentrations of 90 mg/LNO₃⁻ and 40 µg/L perchlorates. The different treatment options included ion exchange treatment of nitrate only, both nitrate and perchlorate, or perchlorate only. If only perchlorate is to be removed with selective ion exchange resins, a 55-gallon canister filled with ion exchange resin should be able to reduce perchlorate concentrations in the groundwater from 40 µg/L to non-detect levels. The contaminant-laden resin would be disposed of as hazardous waste. It is not practical to regenerate this resin because of the difficulty of removing perchlorate from the resin. Due to the selectivity of the ion exchange resin, it is possible to selectively remove perchlorate from nitrate-contaminated water.

In 2003, Kerr McGee (now Tronox, as mentioned previously) constructed a new FBR, biologically based perchlorate treatment plant to replace the existing ion exchange units at Henderson, NV. The Plant Ion Exchange Units (12) began operating in October 2002 while the Wash Ion Exchange Units (3) began operating in November 1999. The new FBR plant was in startup/shakedown mode from December 2003 through September 2004 and became fully operational in November 2004. The per-

chlorate concentration and mass discharged from the new treatment plant have decreased to less than 18 ppb and less than 0.21 pounds per day, respectively, based on a flow of 1000 gallons per minute. The Plant Ion Exchange Units have not operated since March 2004; the Wash Ion Exchange Units have not operated since June 2004. All ion exchange units were decommissioned by Tronox during the fall of 2005 but the units still remain on site. If one looks at the cumulative amount of perchlorate removed by these units, one arrives at astoundingly large numbers. It seems that there is enough perchlorate in the ground under these former production sites to make it worthwhile to mine it as a mineral resource.

There are two types of ion exchange methods for perchlorate removal: (1) a selective but non-regenerable PS anion exchange resin or (2) a polyacrylic non-selective anion exchange resin with NaCl brine regeneration (described by Gu and Brown in Chapter 10 of [1160]). In the first case, the spent resin cannot be regenerated. As such, it has to be discarded, which is not cost-effective. In the second case, the regenerable resins have poor selectivity and absorb all other anions other than chloride. For instance, the doubly negative charged sulfate ion is more strongly adsorbed than the singly charged perchlorate ion. Non-selective ion exchange resins can be regenerated but they require frequent treatment because they are quickly exhausted by adsorbing other ions beyond the one of interest. Newly developed highly selective ion exchange resins include Amberlite PWA-2 and Purolite A530E, which promise to reduce secondary waste generation and reduce both capital and operating costs of perchlorate removal [1162].

Two demonstration projects in California used a highly selective bifunctional resin for ClO_4^- sorption and a FeCl_3 -HCl solution for the regeneration of the resin [1163].

Selective ion exchange using bifunctional synthetic resins is one of the most effective treatment technologies for removing low levels of perchlorate from contaminated water because of its high efficiency without adverse impacts on the water quality caused by adding or removing any chemicals or nutrients. A bifunctional resin, D-3696, was found to be highly selective toward ClO_4^- and performed much better than one of the best commercial nitrate-selective resins (Purolite A-520E) and more than an order of magnitude better than the Purolite A-500 resin (with a relatively low selectivity) [1164]. At an influent concentration of $\sim 450 \mu\text{g/LClO}_4^-$ in groundwater, the bifunctional resin bed treated ~ 40000 empty bed volumes (BVs) of groundwater before a significant breakthrough of ClO_4^- occurred. Regeneration of the resins after groundwater treatment was also evaluated using the FeCl_3 -HCl regeneration technique.

Treatment of perchlorate-contaminated water using highly selective regenerable ion-exchange and perchlorate-destruction technologies was demonstrated at a field site in California [1165]. Four treatment and four regeneration cycles were carried out and no significant deterioration of resin performance was noted during the two-year operating time. The bifunctional resin (Purolite A-530E) treated about 37000 empty BVs of groundwater before a noticeable breakthrough of perchlorate occurred at an

average flow rate of 150 gpm (or 1 BV/min) and a perchlorate concentration in the feed of about 860 $\mu\text{g/L}$. Sorbed perchlorate was quantitatively recovered by eluting with as little as 1 BV of the $\text{FeCl}_3\text{-HCl}$ regenerant solution. The eluted ClO_4^- was highly concentrated in the third quarter of the first BV of the regenerant solution, with a concentration up to 100000 mg/L. This concentrated effluent greatly facilitated subsequent perchlorate destruction or recovery by precipitation as KClO_4 .

Instead of eluting the adsorbed perchlorate and generating another waste stream, the perchlorate that is adsorbed on the ion exchange resin can be reduced while it is immobilized by a recirculating stream of a strong reductant such as a titanium(III) solution. The Ti(IV) is then reduced back to Ti(III) electrochemically and returned to the ion exchange column in a closed loop [1166]. In 2005, Siemens Water Technology installed a dual 12-foot diameter ion exchange system on a treatment well downgradient of a former landfill in the City of Rialto, CA [1167]. The Siemens solution features throw-away, single-use ion exchange technology. These throw-away resins are highly selective for perchlorate. Complete destruction of the perchlorate ion can be accomplished through the incineration of the spent resin.

Ion exchange is not a disposal technique. It is only a separation technology that transfers the perchlorate from contaminated waters to the waste solutions used to regenerate the resins. Therefore, the perchlorate problem is only really moved from one location to another. The question is what should be done with the perchlorate-rich effluent when the ion-exchange resins are regenerated. The waste solutions ("brine") contain high perchlorate concentrations and treatment technologies for these regenerant solutions are needed. It was proposed to combine ion-exchange (for perchlorate removal and concentration) and biological reduction (effective perchlorate destruction) for treating the waste solutions resulting from resin regeneration [1168].

A biological process for perchlorate and nitrate destruction in concentrated brine from ion exchange processes demonstrated that the salt-tolerant anaerobic culture consistently reduced perchlorate and nitrate in spent brine to below detection limits within 24 hours in the presence of varying concentrations of brine constituents such as salt (3 to 10% NaCl), nitrate (400 to 4000 mg/L), sulfate (600 to 6000 mg/L) and pH (5 to 9) [1169].

The removal of perchlorate and nitrate from contaminated drinking water using regenerable ion-exchange processes produces a high salt brine (3–10% NaCl) laden with high concentrations of perchlorate and nitrate. A bench-scale experiment evaluated the operation of acetate-fed granular-activated carbon (GAC) based FBR for perchlorate-only and also for combined nitrate and perchlorate removal from synthetic brine (6% NaCl) [1170]. The GAC was inoculated with a salt-tolerant culture used previously in batch systems. The FBR was an effective design for perchlorate reduction and exhibited first-order degradation kinetics with respect to perchlorate concentrations. Nitrate was also removed by the organisms in the column and had no negative effects on the removal of perchlorate.

Single-use ion-exchange resins can be regenerated in biological batch systems. Experimental studies demonstrated that perchlorate exhausted resin was effectively regenerated by a salt-tolerant perchlorate-reducing culture [1171]. A mathematical model was developed that incorporates physical desorption and biodegradation parameters and was confirmed by experimental data.

Apparently, the ion exchange plant installed by the Calgon Carbon Corporation (now Kuraray) at La Puente, San Gabriel Valley, CA is one of the largest drinking water purification plants in the world. A similar installation is demonstrated in Figure 47.



Figure 47: Perchlorate removal by using ion exchange. (Photo courtesy of Calgon Carbon Corporation – Kuraray; Reproduced with permission.)

Another full-scale installation using non-regenerable ion exchange installed by Calgon Carbon Corporation is demonstrated in Figure 48.

In an effort to identify ion exchange resins with the best selectivity for perchlorate, 17 different commercially available anion exchange resins were tested and characterized by their matrix, functional group, percent crosslinking, and porosity [1172]. The three matrices were PS, polyacrylic amide, and polyvinylpyridine. The most common quaternary amine functional group is trimethyl(polyalkyl)ammonium but four others were also evaluated. More hydrophobic resins had higher separation factors. The highest separation factors were for resins with triethyl and tripropyl ammonium functional groups, but only at the expense of very slow equilibrium attainment.

The affinity between perchlorate ions and resins is extremely high, which makes it difficult to regenerate resins and results in large amounts of brine that need to be disposed of otherwise. Several BVs of 12% NaCl solution can remove only a small frac-



Photo courtesy of Calgon Carbon Corporation

Figure 48: The California Water Company's single-use ion exchange system. (Photo courtesy of Calgon Carbon Corporation – Kuraray; Reproduced with permission.)

tion of the perchlorate loaded onto PS-type resins. Heating during regeneration did not lead to much improvement. Acrylic-type resins are easier to regenerate [1173]. In some cases, it is more economical to discard the resins after they are exhausted instead of trying to regenerate them. In the ion exchange process, not only is the affinity of the single perchlorate ion important but the affinities of all other competing ions in the untreated water is of equal importance because they will compete with perchlorate for resin sites. It was noted that the selectivity coefficient of some quaternary ammonium resins increased and almost tripled as the perchlorate loading increased. This behavior prompted speculation that the ions may form ion pairs in concentrated aqueous solutions. The formation of dimerized perchlorate ions $(\text{ClO}_4)_2^{2-}$ has not been experimentally proven; it is just a theory at this point [1174]. The best resin for treating perchlorate-contaminated water is a hydrophobic resin. A hydrophobic resin was able to adsorb the most perchlorate per cycle and was easier to regenerate.

Bifunctional anion exchange resins carry two types of quaternary ammonium groups: the first has long alkyl chains for higher selectivity and the second has shorter alkyl chains for improved reaction kinetics [1175]. They were selected based on systematic experiments where the length of the alkyl chains on the quaternary ammonium groups was varied and its effect on the selectivity was measured. Results indicate that the bifunctional resins performed ~5 times better than the best monofunctional resin (e.g., Purolite® A520E) tested up to that time.

The Calgon Carbon Corporation has designed an ion exchange system that generates substantially less waste brine because the perchlorate-loaded brine from the resin regeneration effluent is passed through a catalytic reactor where nitrate and perchlorate are reduced to nitrogen and chloride using ethanol as a reductant [1176]. The system involves sequential segmentation of the mass transfer zone where the loaded segment of the resin is continuously removed from the top of the mass transfer zone and the regenerated resin is returned to the bottom of the mass transfer zone. This leads to better utilization of the ion exchange resin during the adsorption cycle. Pilot testing of several units was conducted at two different field sites for a total period exceeding six months, generating treated water that met all DWSs.

As it turns out, ion exchange resins that were developed specifically for the removal of radioactive pertechnetate ion from contaminated groundwater in nuclear reprocessing plants are equally effective in the removal of perchlorate [1177]. It was found that selectivity for large and poorly hydrated ions (like perchlorate) can be improved by increasing the size of the organic resin-bound cation. It was determined that a large-sized cation on the resin improved selectivity for perchlorate binding when combined with a less polar binding site. When strong-binding PS resins were used, it was not possible to regenerate them with brine solution (the most common regeneration method for ion exchange resins). Tetrachloroferrate was found to be successful in regenerating PS resins [1165]. Acrylic type resins, on the other hand, have a higher perchlorate capacity as well as a better regeneration efficiency [1173], however, they have low perchlorate selectivity and prefer sulfate over perchlorate and nitrate. Sulfate is a frequent companion in groundwater and would tie up active sites that were intended for perchlorate.

Perchlorate selectivity, capacity, and the thermodynamic properties of resins using commercially available ion exchange resins were measured and computer models using equilibrium multi-component chromatography theory were developed and compared to experimental results [1178]. Three treatment approaches emerged as viable options for reducing perchlorate concentrations to below proposed maximum permissible limits: **(1)** partial exhaustion-regeneration using polyacrylic resins, with a process similar to current nitrate treatment techniques, **(2)** partial exhaustion-regeneration using PS resins with elevated temperature regeneration, and **(3)** use of highly perchlorate-selective resins with resin replacement following exhaustion.

New regenerable resins based on additional Lewis acid/base forces between the ligands and the ions were developed specifically for perchlorate removal from contaminated water [1179]. For this resin, sorption kinetics improved and regeneration was pH-dependent. This resin, however, included bound copper ions which were found to leach out of the resin under unfavorable conditions. A standard strong-base anion and a weak-base anion exchange resin, a bifunctional resin (A-530E), a class of polymeric ligand exchangers and ion-exchange fibers were compared with respect to perchlorate sorption capacity, kinetics, and regenerability [1180]. While A-530E offered the greatest perchlorate capacity and selectivity, practically acceptable capacity was also

observed for the other candidates. The bifunctional resin (A-530E) was least regenerable. In contrast, polyacrylic resins offered much lower perchlorate capacity. The greater capacity of styrenic resins was attributed to enhanced ion-pairing and Lewis acid-base interaction due to the hydrophobic nature of PS matrices and lower hydration energy of perchlorate. Another ion exchange demonstration project was started at Edwards Air Force Base in California [1181].

8.9.1.1 Tradeoff: Regenerable Versus Non-Regenerable Ion Exchange Resins

There are three primary types of perchlorate-removal treatment systems:

- Non-regenerable fixed bed
- Regenerable (ISEP[®]) moving bed
- Regenerable fixed bed (not yet in commercial use).

Non-regenerable systems offer the advantages of simplicity. They can be installed quickly: Modular systems enable complete package delivery of vessels, piping, instrumentation, and resin with six weeks. Systems can be running within a week after delivery – they only need to be set on a level surface, such as a concrete pad or railroad ties. They also have few moving parts, require less operator intervention and expertise, and provide the convenience of resin replacement (by the supplier), rather than regeneration. The disposable anion exchange resins used in non-regenerable systems have a much higher selectivity for perchlorate than regenerable resins. Because these resins continue to remove perchlorate long after all other anionic species have reached breakthrough, they can be online for weeks or months before they are saturated. After a complete breakthrough of perchlorate is detected, the spent resin is removed from the system and incinerated. Fresh resin is filled to replace the spent resin. Resin incineration, with certificates of destruction, allows absolute mitigation. There is no concern about the disposal of regeneration brines like those that carry away the perchlorate from regenerable resins [1182].

Regenerable moving bed systems are favored at higher flow rates (due to economics) and when the water has a high ionic load (due to other pollutants – nitrates, sulfates, and some bicarbonate – that also need to be removed).

Calgon Carbon's ISEP[®] regenerable moving bed system uses a more easily regenerable acrylic resin with a brine regeneration (a standard sodium chloride solution similar to that used in a home water softener system). The technology has the advantage of maximizing the performance of the system through reduced regenerate usage, reduced resin requirement, and steady-state operation. As of 2002, 3.6 mgd of groundwater were treated with ISEP[®] technology, with more than 21.6 mgd of the additional capacity expected to come online in the following year. The operating system at La Puente Valley County Water District in California has been operating at less than 4 ppb perchlorate; treated water samples at Calgon's analytical lab were registering less than 2.5 ppb. Regenerable moving bed systems have more moving parts and the resins require regeneration after a matter of hours online. Nonetheless, by minimizing

the volume of waste brine and the amount of regenerate needed, the ISEP[®] technology delivers lower operating expenses than a non-regenerable system.

Regenerable fixed-bed (FXB) systems use the same ion exchange technology as regenerable ISEP[®] systems. However, current operating costs are higher due to lower brine regeneration efficiencies and higher waste volumes. The FXB technology has yet to be proven.

Another approach to remove perchlorate from water is to use a dendritic anion host. Dendrimers are repeatedly branched, roughly spherical large molecules, and can carry perchlorate-binding functional groups at the tips of the hydrocarbon chains. Dendrimers are typically symmetric around the core and often adopt a spherical three-dimensional morphology. It was suggested that dendrimers can improve the selectivity of perchlorate uptake in the presence of sulfate [1183]. It was also hypothesized that the capacity of these resins is larger, thus improving regeneration as well. Large dendrimers are still rather expensive.

Dendrigrraft ion exchange resins have binding sites throughout the volume of the resin particle (not only on the surface) resulting in large capacity. Branched dendrigrrafts with perchlorate binding sites were synthesized [1184]. Crosslinking was performed with poly(ethylene glycol) (PEG) to strengthen the resin and reduce biofouling. This technology is expected to be implemented as a fixed bed system with NaCl regeneration. Both uncrosslinked, water-soluble dendrigrrafts and PEG-crosslinked, water insoluble dendrigrrafts were investigated. Resins were tested in the presence of high perchlorate concentrations to ensure that even in the presence of high nitrate and sulfate concentrations, the capacity for perchlorate would still be high. The highest perchlorate capacities, up to 325 meq/g, were found in the soluble dendrigrrafts. These dendrigrrafts are regenerable with a lower concentration brine. It was found that dendrigrrafts are an effective way to produce high perchlorate capacity and regenerable resins with good selectivity towards perchlorate.

8.9.2 AP Removal by Using Bioremediation

Biological treatment (also known as bioremediation) is a micro-biological process that uses micro-organisms to break down perchlorate into other components. The underlying science is biodegradation, which looks at processes in natural environments. Human-engineered biodegradation applied to a specific contamination problem is often called *bioremediation*. This involves trying to accelerate and control naturally occurring processes and actively monitor their outcome. In this process, water is treated in a tank (*ex-situ*) using micro-organisms that thrive on perchlorate, or in the ground (*in-situ*) using native organisms or bacteria bred to maximize perchlorate conversion. The current section describes fundamental studies applicable to either method, and more detailed sections dealing specifically with *ex-situ* and *in-situ* treatments will follow. Small amounts of carbon sources, such as alcohol, glycerin or corn syrup, are also placed in the water as nutrients. The micro-organisms then convert the perchlorate

and carbon into two primary components: Carbon dioxide and chloride. The bacteria reduce perchlorate to chlorate and chlorite [1185]. The chlorite subsequently disproportionates into chloride and oxygen under the influence of chlorite dismutase [1121].

Perchlorate-reducing anaerobic heterotrophic bacteria were first identified in the 1960s as a byproduct of the search for nitrate-reducing bacteria. The results remained a scientific curiosity for 30 years until clean-up of the widespread perchlorate pollution in the US began and when other parts of the world required clean-up techniques that would require less chemicals and less energy. The process was initially developed for industrial wastewaters with relatively high perchlorate concentrations in stationary treatment reactors [1104]. However, it was later extended to less concentrated aqueous solutions and *in-situ* underground treatments.

Biological reactors have been used in Europe with good results for the removal of nitrate from drinking water using ethanol or hydrogen gas as the electron donor. Other bioreactors have used acetate as the electron donor. Different types of bioreactors, such as completely mixed stirred constant flow reactors, plug flow reactors (PFR), FBRs, and rotating biological reactors (RBC) were modeled and optimized for perchlorate bioremediation [1186]. In many fixed-film reactors, the biofilm is attached to a substrate (e.g., sand, granulated activated carbon).

The presence of large amounts of nitrate will prevent the reduction of perchlorate because bacteria like to feast on both (nitrate and perchlorate) and compete for the electron donor. However, it was demonstrated that in an enrichment culture from municipal anaerobic digester sludge (ADS) (perchlorate digestion is not mediated by nitrate reductase, but rather by its own reductase enzyme. A mixed bacterial culture capable of reducing perchlorate stoichiometrically to chloride under anaerobic conditions was enriched using municipal digester sludge. The reduction of 10 mM perchlorate resulted in the oxidation of the medium and cessation of perchlorate reduction. The activity was revived by the addition of a reducing agent. The addition of air to the culture during perchlorate reduction immediately killed the process and continued aeration for 12 hours, thus permanently destroyed the ability of the culture to reduce perchlorate again in the future. The culture also reduced nitrite, nitrate, chlorite, chlorate, and sulfate. The presence of 10 mM nitrite or chlorite completely inhibited perchlorate reduction, whereas the same concentration of chlorate decreased the reduction rate. Concentration ranges of 3000 ppm, 5600 ppm, 6500 ppm, and 8900 ppm perchlorate were shown to be treatable in an 11-L anaerobic continuous stirred tank reactor (CSTR). Sustained volumetric degradation rates of 222 mg ClO_4/h per L with 99.9% removal efficiencies were observed [1187–1190].

Bacteria strains that were trained to thrive on perchlorate were either isolated from natural habitats or cultivated in the laboratory to be used in bioremediation projects.

A bacterium coded as strain HAP-1 was isolated from a municipal anaerobic digester due to its ability to reduce >7000 ppm perchlorate in wastewaters [1191]. The organism is capable of the dissimilatory reduction of perchlorate or chlorate to chloride

for energy and growth. It is a Gram-negative, non-sporeforming, obligately anaerobic, motile thin rod. Antibiotic resistance, utilization of carbon substrates, and utilization of electron acceptors by bacterium HAP-1 were similar to *Wolinella succinogenes*. The organism's 16S rRNA sequence was only 0.75% different from that of the strain type of *W. succinogenes*. The morphological, physiological, and 16S rRNA sequence data indicated that bacterium HAP-1 is a strain of *W. succinogenes* that can utilize perchlorate or chlorate as a terminal electron acceptor.

A low-cost biodegradation process was developed that converts ClO_4^- to harmless Cl^- that can be safely released into sewage treatment plants and then to the surface waters [1192–1194]. In 1995 a continuous-flow pilot system capable of treating up to 3700 L (1000 gallons) per day of effluent was designed, fabricated, and successfully tested at Tyndall AFB, Florida. In 1996, optimization studies were accomplished to transition this process to industry. This process can reduce the ClO_4^- concentrations from above 1% to below the detection limit (<0.5 ppm). In 1997, improved analytical methods enabled ClO_4^- detection down to 4 ppb. The action level in drinking water was set at 18 ppb. A pilot-scale bioreactor using a commercially available, water-soluble yeast extract (BYF-100) was able to reduce 3000 ppm ClO_4^- to below detectable levels with residence times as short as 12 hours. The bacterium capable of reducing ClO_4^- to Cl^- was identified as *Wolinella succinogenes*. Oxygen (dioxygen) will compete with ClO_4^- as an alternate electron donor. Cheese whey is more soluble than brewer's yeast and can be obtained at a fraction of the cost. Components of an existing pilot-scale demonstration unit were modified and integrated with existing waste treatment facilities at Thiokol near Brigham City, UT, treating 1700 L/d (450 gal/d) effluents containing 3000–5000 ppm ClO_4^- . Concentrations above 6000–10000 ppm appeared to inhibit ClO_4^- reduction. Actual effluents from operational processes were analyzed and found safe for discharge into an existing domestic sewage treatment plant. A very detailed and nicely illustrated summary of operating conditions and operating results of a demo plant at Tyndall AFB and a full-scale operation at Thiokol is presented in an interim report dated June 1998 [1195]. Feed concentrations were 20000–40000 ppm and effluent concentrations were rarely above 100 ppm. The Minuteman III remanufacture program and the Titan solid rocket motor disposal program will benefit directly from this technology. It was hoped that engineering modifications would allow optimized processing of the diluted perchlorate feed stream at four to eight hours residence time and reduce treatment costs to as low as \$0.15 per gallon of brine or \$0.85 per pound of perchlorate destroyed.

Although the fact that microbes reduce perchlorate or chlorate has been recognized for more than 50 years, only six organisms that can obtain energy for growth by this metabolic process were reported until 1999. As part of a study to investigate the diversity and ubiquity of micro-organisms involved in the microbial reduction of (per)chlorate, (per)chlorate-reducing bacteria (PRB) were identified in very diverse environments, including pristine and hydrocarbon-contaminated soils, aquatic sediments, paper mill waste sludges [1196], and farm animal waste lagoons [1197]. In all

of the environments tested, the acetate-oxidizing PRB represented a significant population. Sizes ranged from 2.31×10^3 to 2.4×10^6 cells per g of sample. Thirteen different PRB were isolated from these environments. All of these organisms could grow anaerobically by coupling complete oxidation of acetate to reduction of (per)chlorate. Chloride was the sole end product of this reductive metabolism. All of the isolates could also use oxygen as a sole electron acceptor, and most (but not all) could use nitrate. Alternative electron donors included simple volatile fatty acids, such as propionate, butyrate, or valerate, as well as simple organic acids, such as lactate or pyruvate. Washed cell suspensions of all of the PRB isolates could dismutate chlorite, an intermediate in the reductive metabolism of (per)chlorate, into chloride and molecular oxygen. Chlorite dismutation was a result of the activity of a single enzyme. The results of this study significantly increased the limited number of microbial isolates that were known to be capable of dissimilatory (per)chlorate reduction. This demonstrated the (until then) unrecognized phylogenetic diversity and ubiquity of the microorganisms that exhibit this type of metabolism.

In searching for bacteria that are capable of reducing perchlorate, and finding them already existing in perchlorate-contaminated aquifers, an interesting question has arisen: "Have these bacteria mutated to feed on the new oxygen donor only after the area was polluted by anthropogenic perchlorate, or did they exist before that time? If they previously existed, what else did they feed on?" [1198]. Many perchlorate-reducing bacteria can also use nitrate as an alternative electron acceptor. Phylogenetic analysis of DNA sequences of perchlorate-reducing bacteria placed them in the beta subdivision of proteobacteria.

Studies on the ubiquity and diversity of microbial (per)chlorate reduction done up until 2001 resulted in the isolation of 20 new strains of dissimilatory PRB. In-depth phylogenetic analysis revealed that all of the isolates were actually members of the Proteobacteria, with representatives in the alpha-, beta-, and gamma-subclasses. The majority of the new isolates were located in the beta-subclass and were closely related to each other and to the phototrophic *Rhodocyclus* species. An in-depth analysis of these organisms, which form two distinct monophyletic groups within the *Rhodocyclus* assemblage, revealed that two new genera, *Dechloromonas* and *Dechlorosoma*, can be proposed for these beta-subclass lineages which represent the predominant PRB in the environment [1199]. The type species and strains for these new genera are *Dechloromonas agitata* strain CKBt and *Dechlorosoma suillum* strain PST, respectively. In the end, it was found that more perchlorate-reducing bacteria occurred naturally in groundwaters than anyone had expected ten years earlier [1200].

An unusual perchlorate-respiring and hydrogen-oxidizing bacterium that grows with carbon dioxide as the sole carbon source was identified as *Dechloromonas sp. strain HZ* [1201]. Strain HZ is a Gram-negative, rod-shaped facultative anaerobe that was isolated from a gas-phase anaerobic packed-bed biofilm reactor treating perchlorate-contaminated groundwater. The ability of strain HZ to grow autotrophically with carbon dioxide as the sole carbon source was confirmed by demonstrating that

biomass carbon was derived from CO₂. Chemolithotrophic growth with hydrogen was coupled with the complete reduction of perchlorate (10 mM) to chloride. Strain HZ also grew using acetate as the electron donor and chlorate, nitrate, or oxygen (but not sulfate) as an electron acceptor. Phylogenetic analysis of the 16S rRNA sequence placed strain HZ in the genus *Dechloromonas* within the β subgroup of the Proteobacteria. The discovery of this novel perchlorate-reducing bacterium may lead to new and safer technologies for removing perchlorate from drinking water.

As part of a study to elucidate the environmental parameters that control microbial perchlorate respiration, the reduction of perchlorate by the dissimilatory perchlorate reducer *Dechlorosoma suillum* was investigated under a diverse set of environmental conditions [1202]. The tests demonstrated that perchlorate reduction via *D. suillum* occurred only under anaerobic conditions and was dependent on the presence of a trace of molybdenum. Perchlorate reduction was dependent on the presence of the enzyme chlorite dismutase, which was induced during metabolism of perchlorate. Anaerobic conditions alone were not enough to induce expression of this enzyme. Dissolved oxygen (DO) concentrations less than 2 mg/L were enough to inhibit perchlorate reduction via *D. suillum*. Similarly to oxygen, nitrate also regulated chlorite dismutase expression and repressed perchlorate reduction via *D. suillum*. Some bacteria can reduce nitrate simultaneously with perchlorate while others cannot. These studies demonstrated that microbial respiration of perchlorate is significantly affected by environmental conditions and that perchlorate reduction is directly dependent on the presence or absence of competing electron acceptors. A microbial treatment strategy can achieve and maintain perchlorate concentrations below the recommended regulatory level, but only in environments in which the variables can be controlled (preferably in an *ex-situ* bioreactor above ground).

Soil samples exhibited significant decreases in respiration activity in the presence of 100 or 1000 ppm perchlorate, simulating the dispersal of unburnt rocket propellant following a launch mishap [1137]. It is possible that the excess deposition of perchlorate to coastal soils following a flight abortion could decrease the rate that material is decomposed in soil, which could adversely affect the recycling of nutrients and eventually impact plant growth. The extent of this effect is controlled by the amount of propellant deposited, the average surface-to-volume ratio of deposited particles, and the number of particles deposited per area unit. Perchlorate dissolution data suggested that 100-ppm concentrations could be achieved in solutions in which volumes are restricted, and this may occur in stagnant soil water adjacent to dissolving chunks of propellant.

As of 2002, two full-scale *ex-situ* FBR systems were already treating perchlorate-contaminated groundwater in California and Texas [1203, 1204]. A third full-scale treatment system was scheduled for start-up in early 2002. The *in-situ* treatment of perchlorate was based on the addition of specific electron donors to groundwater and quickly evolved as a viable bioremediation technology. Earlier studies suggested

that perchlorate-reducing bacteria actually widely occur in nature, including in groundwater aquifers, and that these organisms can be stimulated to degrade perchlorate to below the current analytical reporting limit ($<4\text{ }\mu\text{g/L}$).

Some bacteria can use perchlorate as an electron acceptor while oxidizing a large range of electron-donating substrates. Scientists now recognize that perchlorate-reducing bacteria (PRB) are widely distributed in the environment and can be found at perchlorate-contaminated sites or in municipal sewage treatment plants. The pathways by which PRB degrade perchlorate are now well understood and biological treatment processes have been developed to remove perchlorate from contaminated water sources. Alternate electron acceptors in the water, such as oxygen and nitrate, compete with perchlorate removal. Until the year 2000, biological treatment systems using PRB had only been proven on the bench scale. After 2003 all pilot-scale tests were successful. A perchlorate bioreactor biological treatment was judged as a suitable method for soil remediation and water treatment of perchlorate-contaminated water [1205].

Perchlorate-reducing organisms were found to be ubiquitous in both uncontaminated and contaminated environments based on Most Probable Number determinations [1206]. The ability to stimulate and/or accelerate *in-situ* perchlorate degradation through donor addition has been studied in microcosm experiments. Acetate, molasses, canola oil, and oleate all served as successful electron donors. The interference of sulfate during perchlorate bioremediation is a concern. It was determined that the effect of sulfate on perchlorate degradation is dependent on both the relative concentrations of perchlorate and sulfate and on the microbial community composition at a site. Perchlorate-reducing organisms were isolated from several sites and studied with respect to characteristics that may affect *in-situ* biodegradation of perchlorate. All organisms isolated were facultative aerobes. All but two can reduce nitrate and none can reduce ferric iron or sulfate. Growth kinetic parameters were similar for all the isolates tested.

ClO_4^- reductase is the key enzyme in the pathway of ClO_4^- breakdown. ClO_4^- reductase from cell-free extracts of the ClO_4^- -respiring bacterium *perclace* was purified ten-fold by using ion-exchange and molecular exclusion fast protein liquid chromatography [1207]. The ClO_4^- reductase catalyzed the reduction of ClO_4^- . ClO_4^- reduction was achieved in the temperature range of 20 to 40 °C and with optimum activity at 25 to 30 °C and pH 7.5 to 8.0. Amino acid sequences of 22 tryptic peptides of the 35 kDalton ClO_4^- reductase subunit were obtained by using electrospray mass spectrometry. Comparison to GenBank protein analysis of the amino acid sequences revealed some similarity to reductases, dehydrogenases, and heme proteins.

The success of natural, *in-situ*, or controlled *ex-situ* perchlorate remediation is dependent on the presence and activity of dissimilatory (per)chlorate-reducing bacteria (DPRB) within a target site. To detect DPRB in the environment, two degenerate primer sets targeting the chlorite dismutase (*cld*) gene were developed and optimized [1208]. A nested PCR approach was used in conjunction with these primer sets to increase

the sensitivity of the molecular detection method. Screening of environmental samples indicated that all products amplified by this method were cld gene sequences. These sequences were obtained from pristine sites as well as contaminated sites from which DPRB were isolated. The use of these primer sets represents a direct and sensitive molecular method for the qualitative detection of PRB in the environment, thus offering another tool for monitoring natural attenuation. Sequences of cld genes isolated in the course of this project were also generated from various DPRB and provided the first opportunity for a phylogenetic treatment of this metabolic gene.

An extensive microcosm survey of perchlorate-contaminated sites was undertaken to assess the ability of indigenous micro-organisms to degrade perchlorate [1209]. Samples from 12 contaminated sites and from one pristine location were analyzed. Perchlorate was degraded to below detection limit in all electron donor-amended microcosms. Perchlorate-reducing micro-organisms (PRMs) were numerous at most of these sites. Sixteen distinct PRMs were isolated that were phylogenetically related to either *Dechloromonas* in the Beta Proteobacteria (9/16 isolates) or to *Azospirillum* in the Alpha Proteobacteria (7/16 isolates). The majority of previously isolated PRMs are in the Beta Proteobacteria related to *Dechloromonas* or *Dechlorosoma*. This study indicated that PRMs of the genus *Azospirillum* may be more prevalent at contaminated sites than the current record of isolates suggests. Cell yields, electron donor to perchlorate ratios, and maximum specific growth rates were similar among the isolates, which is similar to previously published values. The surprising finding is that microbial perchlorate reduction is ubiquitous, even at highly contaminated sites, and can be harnessed effectively for controlled and targeted bioremediation.

Surprisingly, bacteria are able to reduce perchlorate using metallic iron Fe(0) as the electron donor. Perchlorate was reduced reproducibly by using a mixed bacterial culture over a pH range of 7.0–8.9. Similar rates of perchlorate reduction were observed between pH 7.0 and 8.5, whereas significantly slower reduction occurred at pH 8.9. The addition of iron metal, Fe(0), to the mixed bacterial culture resulted in slower rates of perchlorate reduction [1210]. Only negligible perchlorate reduction could be achieved under abiotic conditions with Fe(0) alone in a reducing anaerobic medium. The addition of Fe(0) resulted in a rise in pH, as well as precipitation of Fe minerals that appeared to encapsulate the bacterial cells. The encapsulation of bacteria by Fe precipitates contributed to the inhibition of the bacterial activity independent of the effect of pH on bacteria. These results provide the first evidence linking the accumulation of iron precipitates at the cell surface to the inhibition of environmental contaminant degradation in the field. Fe(0) was not a suitable amendment to stimulate perchlorate-degrading bacteria. The bacterial inhibition caused by precipitation of reduced Fe species may be important in other combined anaerobic bacterial-Fe(0) systems. Furthermore, the inhibition of bacterial activity by iron precipitation may have significant implications for the design of *in-situ* bioremediation reactors for the treatment of perchlorate plumes.

In spite of problems with Fe(0) reported by previous investigators, experiments with microbial reduction of perchlorate with zero-valent iron (ZVI) continued in both batch and column reactors [1211, 1212]. Iron-supported mixed cultures completely removed 65 mg/L of perchlorate in batch reactors in eight days. The removal rate was similar to that observed with hydrogen gas (5%) and acetate (173 mg/L) as electron donors. Complete removal of perchlorate by iron-supported anaerobic cultures was also achieved in a bench-scale iron column with a hydraulic residence time of two days. Iron as an electron donor is inexpensive, safe to handle, and does not leave organic residuals in the treated water.

Genetic analyses and DNA sequencing have offered the first glimpse into the enzyme encoding genes which make the perchlorate-eating bacteria “tick” [1213, 1214]. The genomic analysis has offered tools for detecting, breeding, genetically engineering, and monitoring bacteria that are even more active than the ones we have been working with up to this time. The perchlorate reduction pathway consists of two key enzymes: perchlorate reductase and chlorite dismutase. Chlorite is very toxic and if it was not immediately removed as soon as it had formed, the perchlorate reduction process would come to a grinding halt.

It is now common knowledge that bacteria need a nutrient and an electron donor to effectively reduce perchlorate. A novel approach is to add a reversible redox chemical as a mediator to the bioreactor and two electrodes with DC current flowing between them. At the cathode, the redox chemical is reduced and the bacteria is converted to its oxidized state so it can be electrolytically reduced again. The reduction of perchlorate in the cathodic chamber of a bioelectrical reactor demonstrated that *Dechloromonas* and *Azospira* bacteria readily reduced 90 mg/L perchlorate with 2,6-anthraquinone disulfonate (AQDS) as a mediator [1215]. No perchlorate was reduced in the absence of cells or AQDS or in an open-circuit control. The results of these studies showed that biological perchlorate remediation can be facilitated through the use of a cathode as the primary electron donor.

We have seen that perchlorate-reducing bacteria can use elemental hydrogen or iron as electron donors, but the discovery of perchlorate-reducing bacteria that consume elemental sulfur added a new twist to the story of bioremediation [1216]. Sulfur pellets are inexpensive and can serve as excellent packing material for both *in-situ* and *ex-situ* bioremediation. The use of sulfur as an electron donor has the additional advantage that autotrophic bacteria tend not to produce high levels of matrix-clogging biomass. In both batch cultures and bioreactor systems, the microbial community thriving on elemental sulfur could reduce both high (5 ppm) and low (100 ppb) ClO_4^- concentrations to less than 4 ppb. Culture samples indicated a dominant perchlorate-reducing strain that is most closely related to *Dechloromonas* sp. strain JM (a member of the beta-proteobacteria).

A quantitative real-time PCR assay targeting the *pcrA* gene, encoding the catalytic subunit of perchlorate reductase, detected *pcrA* genes from perchlorate-reducing bacteria in three different genera and from soil microbial communities [1217, 1218]. Partial

pcrA sequences indicated differences in the composition of perchlorate-reducing bacterial communities following exposure to different electron donors.

The response behavior of three dissimilatory perchlorate-reducing bacteria to different electron acceptors (nitrate, chlorate, and perchlorate) was investigated using two different assays [1219]. The observed response was species-specific, dependent on the prior growth conditions, and was inhibited by oxygen. The bacteria were attracted toward nitrate when *Dechloromonas aromatica* strain RCB and *Azospira suillum* strain PS were grown with nitrate. When *D. aromatica* and *Dechloromonas agitata* strain CKB were grown with perchlorate, both responded to nitrate, chlorate, and perchlorate. When *A. suillum* was grown with perchlorate, the organism responded to chlorate and perchlorate but not nitrate. A gene replacement mutant in the perchlorate reductase subunit (pcrA) of *D. aromatica* resulted in a loss of the attraction response toward perchlorate but had no impact on the nitrate response. This demonstrates the unique ability of these organisms to distinguish between structurally analogous compounds, nitrate, chlorate, and perchlorate, and respond accordingly.

Bioremediation of perchlorate started with modest beginnings, first with *ex-situ* then with *in-situ* treatment. However, over the past two decades, it has grown into a substantial industry supported by numerous scientific publications. There are even several books published on this subject which provide a lot of detail for further study and with regards to the design of clean-up projects [1083–1086].

A 2001 report listed 65 contaminated sites where various decontamination techniques were being tested on a small experimental scale; 45 of these relied on bioremediation. The following discussion is subdivided into *ex-situ* and *in-situ* treatment efforts. While various abiotic and biotic processes have been utilized for *ex-situ* perchlorate clean-up, the *in-situ* perchlorate remediation has depended entirely on finding the right combination of bacteria and nutrients. Nutrients are needed that do not leave a residue in water that is intended for human consumption.

A mathematical model was developed to describe the biodegradation kinetics of perchlorate in the presence of nitrate and oxygen as competing electron acceptors [1220]. The rate of perchlorate degradation is described as a function of the electron donor (acetate) degradation rate, the concentration of competing electron acceptors, and rates of biomass growth and decay. The kinetics of biomass growth can be described using a simplified model, and inhibition factors can be incorporated to describe the influence of oxygen and nitrate on perchlorate degradation. Model predictions were compared to laboratory data obtained using *Azospira suillum*, a perchlorate-degrading strain isolated from groundwater. This strain is capable of utilizing oxygen, nitrate, or perchlorate as terminal electron acceptors. Combined with appropriate groundwater transport models, this model can be used to predict perchlorate biodegradation during *in-situ* remediation efforts.

Most of the publications summarized here deal with dilute perchlorate solutions. To treat wastewater containing much higher concentrations of perchlorate, a perchlorate reducing-bacterial consortium was obtained from enrichment cultures

grown on high-strength perchlorate (1200 mg/L) feed medium. This was characterized in a sequence batch reactor during a long-term operation [1221]. The consortium removed perchlorate in the batch reactor with high reduction rates ($35\text{--}90\text{ mg L}^{-1}\text{ h}^{-1}$) and stable removal efficiency over 200-day operations. The maximum specific perchlorate reduction rate ($q_{\max}$), half-saturation constant (K_s), and optimal pH range were $0.67\text{ mg-perchlorate mg-dry-cell-weight}^{-1}\text{ h}^{-1}$, $193.8\text{ mg-perchlorate/L}$, and pH 7–9, respectively. The perchlorate reduction yield was $0.48\text{ mol of perchlorate/mol of acetate}$. A clone library prepared using the amplicons of *cld* gene encoding chlorate dismutase showed that the dominant (per)chlorate reducing bacteria in the consortium were *Dechlorosoma sp.* (53%), *Ideonella sp.* (28%), and *Dechloromonas sp.* (19%).

Although ion exchange is a promising non-selective and incomplete disposal process, the disadvantage is that it merely transfers perchlorate from water to the resin. The perchlorate-laden spent resins require regeneration producing concentrated brine (6–12% NaCl) or caustic waste streams. On the contrary, biological reduction completely degrades perchlorate into O_2 and innocuous Cl^- . Numerous unique dissimilatory perchlorate-reducing bacteria have been isolated and detailed studies pertaining to their micro-biological, biochemical, genetics, and phylogenetic aspects have been undertaken, as summarized in a review article [1222].

The effects of nitrate and sulfate on the degradation behavior of perchlorate (ClO_4^-) in soils and sediments of natural environments were investigated [1223]. The lag time of both ClO_4^- and NO_3^- degradation was site-specific and depended on environmental conditions such as the content of organic substrate, NO_3^- concentration, initial ClO_4^- concentration, and prior ClO_4^- exposure. The lag time of ClO_4^- degradation at an initial concentration of 5 mg/L ranged from one-and-a-half to 34 days, depending on environmental conditions, and its rate constant ranged from 0.003 d^{-1} to 0.094 d^{-1} . The lag time of NO_3^- degradation ranged from half a day to 16 days, and its rate constant ranged from 0.017 d^{-1} to 0.179 d^{-1} , indicating that NO_3^- degradation rate is relatively higher than that of ClO_4^- . Nitrate does prolong the lag time of ClO_4^- degradation, which may account for the persistence of ClO_4^- in the environment. The results revealed that micro-organisms can degrade ClO_4^- in sediments and soils, and that the degradation efficiency is influenced by the availability of an organic substrate.

Bioremediation of perchlorate-contaminated water by a heterotrophic perchlorate reducing bacterium creates an electron acceptor-donor system. The perchlorate reduction activity by *Azospira sp. KJ* was tested at multiple pH levels and with different electron acceptor and donor systems [1224]. Perchlorate reduction was drastically inhibited at the pH 6.0 and the maximum reduction of perchlorate by *Azospira sp. KJ* was observed at a pH value of 8.0. Perchlorate reduction was completely inhibited by the additional O_2 in the $\text{ClO}_4^-/\text{O}_2$ acceptor system. The reduction proceeded sequentially with ClO_3^- first, ClO_4^- later, and NO_3^- last.

8.9.3 AP Removal via *Ex-Situ* Bioremediation

Aerojet operated the Rancho Cordova site near Sacramento, CA, producing rocket propellants for nearly 60 years. There had been perchlorate releases at various propellant processing installations on the 8500-acre site. In the late 1980s, Aerojet was the first company to begin perchlorate clean-up operations. They designed a packed bed recycle reactor. Approximately ten years later, Aerojet designed and built the first full-scale, above-ground treatment facility using a fluidized-bed reactor [1225]. Ethanol was used as the electron donor. As of 2008, the FBR was still in operation at the site, treating 10 million gallons of groundwater daily. Aerojet tested microbes collected from various areas for their perchlorate reducing ability. One type of microbe was able to work with starting concentrations as high as 100 mg/L using the ethanol or manure as electron donor. Another experiment used ethanol or molasses as the electron donor.

As of 2006, full-scale fluidized bed *ex-situ* bioreactors were working at five different locations, removing perchlorate from 30 million liters of groundwater every day. In addition to this, two full-scale suspended growth bioreactors were used to treat higher-concentration industrial wastewater at rocket propellant installations. With the addition of electron donors (lactate, acetate, citrate, ethanol, vegetable oil, or hydrogen gas), the bacteria are able to reduce the perchlorate concentration from several hundred ppm to below the legal limit in effect at the time (4 µg/L). *In-situ* bioremediation demonstrations were lagging behind the *ex-situ* processes because they are more difficult to control in remote areas underground and under the influence of a variety of environmental factors that are difficult to control (soil conditions, climate, precipitation).

Perchlorate removal using anaerobic bioreactors has been proven for on-site stationary applications and at the pilot-plant level.

The results of prior lab studies at Tyndall AFB were used to design, fabricate, and demonstrate a pilot-scale complete AP biodegradation bioreactor system using actual effluent from the demilitarization of Minuteman stage 2 propellant washout supplied by Aerojet's Propulsion Division [1192, 1226]. Using an anaerobic 6000-L (1600 gal) reactor in conjunction with the HAP-1 micro-organism discovered at AFRL, it was demonstrated in both tests at both Tyndall AFB and Thiokol-Morton (Utah) that the virtually complete destruction of AP in wastewaters was possible. The operating costs for the bioreactor system revealed that fixed costs (electricity, maintenance, and labor) were at a minimum for 2000–4000 ppm perchlorate concentrations.

A bacterium, *perclace*, has been shown to reduce perchlorate to less than the detection limit of 0.004 mg/L when grown in a bioreactor on acetate under anaerobic conditions [1227]. In batch studies, the presence of nitrate did not significantly hinder the reduction of perchlorate. The ability of *perclace* to remove nitrate and perchlorate from groundwater in a flow-through system was studied in Celite-packed 300 mL columns. At a flow rate of 1 mL/min, perchlorate was removed from 0.738 mg/L to less than detectable levels. When the flow rate was 2 mL/min, 92 to 95% of the perchlorate

was removed. Analysis of bacterial biomass at the completion of the study revealed that most of the bacterial growth was concentrated in the inlet area of the column. A circulating pump was added with the idea that passing the groundwater multiple times through the bacterially active zone might increase the efficiency of the column. In this experiment, perchlorate in groundwater was reduced from 0.550 mg/L to non-detectable levels at a flow rate of 1 mL/min within several days.

Two different stationary perchlorate bioreactors were compared as part of a design study: a heterotrophic, acetate-fed consortium of bacteria and an autotrophic, hydrogen-utilizing consortium of bacteria [1228]. The heterotrophic system was assumed to use *perclace* while the autotrophic system was assumed to use a consortium of five different organisms. Both systems would be capable of removing nitrate and perchlorate simultaneously. The bacteria were tested in a bench reactor with water pumped from two contaminated wells in the San Gabriel Valley in California. One contained 200 µg/L and the other contained 550 µg ClO_4^- /L. The autotrophic system has the advantage that the electron donor (hydrogen gas) is easy to meter in, whereas accidental overdosing of organic carbon sources may cause biofouling and may require additional clean-up of the effluent.

Abatement and remediation of perchlorate in soil and groundwater were achieved using a biological permeable reactive barrier system at the McGregor, Texas Naval Weapons Industrial Reserve Plant [1229]. A biological FBR installed at the LHAAP in Karnack, Texas, has successfully reduced perchlorate levels in groundwater at the site to below the detection limit (<4 ppb) [1082]. Biological FBR are being used to remove perchlorate, with a 99.99% efficiency from contaminated groundwater at the Kerr-McGee site in Henderson, Nevada [1097].

Bioremediation of perchlorate-contaminated water was tested at several locations in pilot-scale demonstration projects. Suspended growth, fixed bed, and fluidized bed bioreactors have been used to degrade perchlorate at influent concentrations ranging from 0.13 to 7750 ppb [1089]. The biological degradation of perchlorate was examined using a laboratory-scale, autotrophic, packed-bed biofilm reactor [1230]. The reactor was operated in unsaturated-flow mode and continuously fed water containing perchlorate and a gas mixture of hydrogen (5%) and carbon dioxide at a retention time of 1.5 minutes. In the absence of nitrate, perchlorate removal rate in the reactor was found to be first order with respect to perchlorate concentration. Perchlorate removal rates in the hydrogen feed were found to be comparable to rates measured by others using organic electron donors such as acetate. When nitrate was present in the water, similar perchlorate removals were achieved despite nitrate concentrations three orders of magnitude higher than perchlorate concentrations. Perchlorate was removed by an average of $25 \pm 5\%$ per passage from a typical perchlorate-contaminated groundwater containing 73 ppb of perchlorate and 21 ppm of nitrate. Research in this area was very active for several decades and continues to grow [1231]. Perchlorate can be reduced in a hydrogen-based membrane biofilm reactor [1122, 1232, 1233].

The use of GAC as a biofilm support medium was compared to that of sand for perchlorate bioremediation in acetate-fed FXB bioreactors [1234–1236]. GAC can physically adsorb perchlorate. Perchlorate was reduced in sand column bioreactors from 20 mg/L to below the detection limit ($<4\text{ }\mu\text{g/L}$) at empty-bed contact times (EBCTs) as low as 43 minutes (detention time of 18 minutes). GAC-packed columns performed similarly for the first ten days, however, after the column was backwashed to redistribute biofilm-coated particles in the reactor, reactor efficiency was substantially reduced due to perchlorate desorption. Increasing the concentration of acetate in the feed partially restored reactor performance. It was concluded that fixed-film reactors for perchlorate-contaminated waters should contain non-perchlorate-adsorbing packing in the reactor.

Instead of packed-bed columns, the same support media (GAC or sand) can also be used in fluidized bed bioreactors [1237]. GAC FBR's achieved a higher level of perchlorate reduction than sand-filled FBR's. Ethanol/methanol mixtures worked better as electron donors than methanol by itself (see [1238–1240] also).

The clean-up of groundwater from many military proving grounds and firing ranges is complicated by the fact that the water contains not only perchlorate but also RDX and other explosive residues [1241]. The *ex-situ* remediation of both perchlorate and explosives in groundwater at the Camp Edwards Training Area on the Massachusetts Military Reservation was using a biological fluidized bed reactor (BFBR). Perchlorate and RDX were present in the groundwater at concentrations up to $300\text{ }\mu\text{g/L}$ and $200\text{ }\mu\text{g/L}$, respectively. This case presents challenges for treatment at significantly lower concentrations and for groundwater commingled with explosives such as RDX. The challenges for the BFBR treatability studies were to remediate groundwater in the operable units to less than $1.5\text{ }\mu\text{g/L}$ for perchlorate and to show significant degradation of RDX.

A bioreactor was operated continuously in a remote field location for more than two years with a stable ecosystem of indigenous organisms and was following discovery that they are capable of removing perchlorate (14 to $27\text{ }\mu\text{g/L}$) and nitrate (48 mg/L) from contaminated groundwater [1242]. Total community DNA was extracted and purified from 10-g sediment samples. Analysis by denaturing gradient gel electrophoresis of short, 16S rDNA, polymerase-chain-reaction products was used to identify dominant micro-organisms. Of the 17 dominant bands sequenced, most were gram-negative and capable of aerobic or anaerobic respiration with nitrate as the terminal electron acceptor (*Pseudomonas*, *Acinetobacter*, *Halomonas*, and *Nitrospira*). Isolates were identified from the Proteobacteria class. This is known for its ability to reduce perchlorate. Initial bacterial assessments of sediments confirmed the prevalence of facultative anaerobic bacteria capable of reducing perchlorate and nitrate *in-situ*.

The operation of bioreactors can be improved by recirculating part of the effluent for a second pass. The effect of partial effluent recirculation on perchlorate reduction in a nominally plug-flow fixed biofilm reactor was studied for two different

influent concentrations of ten and 400 $\mu\text{g/L}$ at low hydraulic loading rates (1.9 and 37.5 $\text{m}^3 \text{m}^{-2} \text{d}^{-1}$ without and with recirculation, respectively) and after a step increase in perchlorate concentration to 1000 $\mu\text{g/L}$ at the higher hydraulic loading rate (5 and 100 $\text{m}^3 \text{m}^{-2} \text{d}^{-1}$ without and with recirculation, respectively) [1243]. Complete perchlorate reduction was sustained for influent concentrations of 400 and 10 $\mu\text{g/L}$ in both flow regimes at the lower hydraulic loading rates. The recirculation bioreactor adjusted itself more rapidly to increased hydraulic and perchlorate mass loading rates while maintaining significantly lower effluent perchlorate concentrations compared to the PFR: This was 16 $\mu\text{g/L}$ versus 46 $\mu\text{g/L}$, respectively, although complete perchlorate removal was not achieved in either flow regime following 21 days of acclimation to the higher loading.

When ion exchange or membrane technologies are used to remove perchlorate from water, the question remains of how to get rid of the brine. Feeding the brine to stationary bioreactors can increase the overall attractiveness of ion exchange or membrane processes by eliminating the need to dispose of a concentrated perchlorate/brine solution.

Inhibition of the biodegradation of concentrated perchlorate (200, 500, 1100, 1700, and 2400 mg/L as ClO_4^-) solutions by increasing salinity was investigated using two microbial cultures, return activated sludge (RAS) and ADS, both isolated from a domestic wastewater treatment plant [1244]. Experiments were performed in wastewaters containing various sodium chloride concentrations ranging from 0 to 4% (w/v) NaCl (ionic strength: 0.14–0.8 M, TDS: 5.3–42 g/L) at near-neutral values of pH (6.7–7.8). Perchlorate biodegradation was sustained through stepwise acclimation to increasingly higher salinity until it failed. The ADS culture was capable of reducing perchlorate at salinities up to 4% NaCl, while the RAS culture exhibited complete inhibition of perchlorate degradation at 4% NaCl as the result of either a toxic effect or enzyme inactivation of the perchlorate-reducing microbes. It was concluded that biological reduction of concentrated perchlorate wastewaters using either RAS or ADS acclimated cultures is feasible up to 3% or 4% NaCl, respectively.

Autohydrogenotrophic bacteria were cultured in a membrane reactor and were capable of removing 3.6 mg/d of perchlorate in the presence of excess hydrogen (99% removal) [1245]. The reactor was successful in treating average influent perchlorate concentrations of 532 $\mu\text{g/L}$ down to the level of 3 $\mu\text{g/L}$. Perchlorate removal ranged from 100 to 50% per pass. The kinetic rate of perchlorate degradation was 1.62 h^{-1} . The significant degradation of perchlorate in these samples indicates the ubiquity of perchlorate-reducing organisms. Nitrate was simultaneously removed (greater than 90% removal). The unwanted growth of sulfate-reducing organisms in the reactor adversely affected perchlorate removal efficiency.

The influence of backwashing on biological perchlorate reduction was evaluated in two laboratory scale FXB biofilm reactors using 1- or 3-mm glass beads as support media [1246]. Perchlorate concentration in the feed was 50 $\mu\text{g/L}$ and 2 mg/L acetate was added as the electron donor. Perchlorate removal was evaluated at various influ-

ent DO concentrations. The immediate effect of backwashing depended on influent DO concentrations. With influent DO concentrations of 1 mg/L, backwashing resulted in a brief (<12 h) increase of effluent perchlorate concentrations up to 20 µg/L but with DO = 3 mg/L, perchlorate reduction ceased altogether.

The former Bermite site north of Los Angeles, CA, was used to manufacture various explosives, pyrotechnics, and igniters containing perchlorates, spilling some in the process. Remediation of perchlorate in soil and groundwater was performed to allow planned redevelopment activities to proceed [1247]. The general approach to perchlorate remediation of shallow soil at the site included excavation of affected soils followed by *ex-situ* bioremediation. Glycerin was chosen for use as an electron donor because of its stability, safety, low cost, and regulatory acceptance. However, full-scale bioremediation operation with glycerin initially resulted in inconsistent results despite consistent perchlorate biodegradation observed in treatability study microcosms. To eliminate the inconsistency and optimize the biotreatment process, additional studies were performed in the field on parallel tracks to determine crucial factors that influence the inconsistent breakdown of perchlorate in site soils. Total Kjeldahl nitrogen was determined to be a significant factor limiting perchlorate biodegradation. The addition of di-ammonium hydrogen phosphate resulted in consistent and complete perchlorate removal, generally within two weeks of incubation, and with a median destruction rate of about 200 µg kg⁻¹ d⁻¹. Soil processing rates were gradually increased over the year, and eventually ~2000 to 2500 tons of soil were being processed per day. The total unit treatment cost for the process was approximately \$35/ton.

Batch experiments were conducted to investigate the kinetics of perchlorate reduction by heterotrophic and mixed perchlorate-reducing bacteria [1248]. Substrate-utilizing and cellular maintenance models were employed to fit the experimental data for microbial perchlorate reduction. The half-saturation constant, K_s , obtained in this study was below 0.1 mg/L, which indicated that perchlorate-reducing bacteria are effective at utilizing low concentrations of perchlorate. A study of the effect of pH on the kinetics of microbial perchlorate reduction showed that perchlorate reduction occurred throughout the pH range from 5.0 to 9.0. The rates of perchlorate removal using a unit mass of bacteria were significantly different at various pH values with a maximum rate at pH 7. The variation of $q_{\max}$ with pH was described well with a Gaussian peak equation. This equation is expected to be applicable for practical purposes when pH effects need to be considered.

Two other chlorate- and perchlorate-reducing bacteria strains were isolated from a swine waste lagoon and grown with acetate as the sole electron acceptor [1249]. Even though the two strains differ morphologically, their physiologies are very similar and optimum growth is observed on short-chain fatty acids.

On closer examination, it was noted that novel perchlorate-reducing bacteria are discovered all the time, in this case from enrichments conducted under conditions different from all those previously tested [1250]. The use of perchlorate and other electron

acceptors distinguished strains MPT and CR from *P. limicola* physiologically. Strain LT-1T had differences in electron donor utilization and optimum growth temperatures from *A. caeni*. Strains LT-1T and MPT are the first bacteria to be described in the Betaproteobacteria outside of the *Dechloromonas* and *Azospira* genera. On the basis of phylogenetic and physiological features, strain LT-1T represents a novel genus in the *Rhodocyclaceae*; strain MPT represents a novel species within the genus *Propionivibrio*.

In February 2007, a ten-month demonstration study was initiated in Rialto, CA, to treat perchlorate-contaminated groundwater using FXB bioreactor technology [1251]. Two first-stage parallel FXB bioreactors (F120 with a 3.9-ft bed depth and a 2-ft diameter, and F130 with a 4.7-ft bed depth and a 2-ft diameter) treated groundwater to remove perchlorate. Effluent from these reactors was dosed with hydrogen peroxide to reoxygenate and oxidize residual organics and hydrogen sulfide. The reoxygenated water was then passed through a FXB biofilter (F150) to oxidize any remaining organics and sulfide and to remove turbidity. Chlorine was then dosed to the effluent of the biofilter as a final disinfection step. A bench-scale FXB bioreactor was also constructed to test operating conditions of a bioreactor on a smaller scale. Experience gained during the demonstration study formed the basis for the design and operating cost estimate of a full-scale unit [1252].

Denitrifying packed-bed bioreactors fed with perchlorate and nitrate allowed for the examination of the impact of a variety of salinity conditions (up to 10 wt.-% NaCl) on the complete perchlorate and nitrate removal capacity of the reactors using activated sludge taken from a municipal wastewater treatment plant [1253]. Based on the evaluation of the microbial community in the bioreactor using cloning analysis, *Clostridium* sp. and a *Rhodocyclaceae* bacteria were identified as the dominant population. This suggests that they may be tolerant to high salt concentrations and can reduce both nitrate and perchlorate under such conditions.

Denitrifying up-flow packed-bed bioreactors can simultaneously remove nitrate and perchlorate from ion-exchange regenerant brines. A continuous-flow reactor, which was inoculated with denitrifying bacteria obtained from a municipal wastewater plant, completely removed perchlorate as well as nitrate in adverse conditions with up to 10% salinity [1254]. Variables that affected the rate of contaminant removal were acetate (as an electron donor) and sulfate (as a competing electron acceptor) concentrations, which were both added at different salinities. Lower carbon loading decreased the nitrate and perchlorate reductions. However, increased sulfate loading did not decrease the reductions of nitrate and perchlorate.

Electron acceptors such as nitrate or sulfate ions may competitively inhibit the reduction of perchlorate in brine in continuous up-flow packed bed bioreactors. A study of the effect of pH and hydraulic retention time (HRT) on the reduction of perchlorate at high salinity revealed that the reduction of perchlorate was only moderately influenced by nitrate (under 163 mg NL^{-1}), implying that there was no significant microbial competition for electron acceptors [1255]. As a result of microbial diversity,

there were few differences between microbial communities fed with a variety of media, suggesting that most nitrate-reducing bacteria are able to reduce perchlorate at high salinity. Reduction of perchlorate was almost complete at relatively high sulfate levels (1000 mg L^{-1}), neutral pH (6–8) levels, and relatively long HRTs (>10 hours).

8.9.4 AP Removal Using *In-Situ* Bioremediation

Active *in-situ* bioremediation techniques involve the continuous pumping and metering of soluble electron donors underground to sustain the ongoing perchlorate reduction. Now we even have a book devoted exclusively to the *in-situ* bioremediation of perchlorate in groundwater [1086]. This book contains 11 chapters, all of which are individually referenced in the current book at hand, including a chapter on active bioremediation [1256]. Semi-passive systems inject soluble electron donors only periodically and rely on natural diffusion and downgradient motion to catch up with the contaminant to be reduced [1257]. Similar to an active system, groundwater is recirculated between an injection and extraction well, but only for a short time (several days) to distribute the electron donor. Following this, the pumps are turned off and the system is left to its own devices for a longer time (several weeks to several months). Injection and extraction wells can be arranged so as to create a biologically active barrier perpendicular to the groundwater flow. The equipment needed for a semi-passive system can be mobile and can be moved from well bore to well bore to serve a larger area. Semi-passive systems require fewer injection wells and are not as susceptible to biofouling as active systems. One of the recommended soluble electron donors for active or semi-passive systems is sodium lactate which does not leave any residue. Passive systems install slow-release electron donors in trenches, well bores, or direct-push situations without pumping any liquids. Some of the passive systems have used emulsified edible vegetable oils through grid injection [1258] or installed a barrier ditch filled with wood chips [1259] or mulch [1260] as a permeable biologically active barrier perpendicular to the direction of groundwater flow. The vegetable oil will slowly hydrolyze, releasing glycerol and long-chain fatty acids which are good electron donors. A passive system has low operational and maintenance costs but may not be the fastest approach to get an unacceptable situation under control. Because the organic substrate must be distributed in the contaminated strata, this method is limited to the treatment of shallow plumes.

At the Naval Surface Warfare Center, Indian Head, MD, the Navy had demilitarized rocket motors. This was accomplished via washout using water for several decades. Some of the wastewater had escaped into the ground. This site was selected to conduct the first *in-situ* perchlorate bioremediation field test by connecting a water recirculation design to distribute lactate solution in a shallow aquifer at the site [1261, 1262]. Two field plots were installed, each consisting of two injection wells and two extraction wells. Groundwater was amended with lactate and pH buffer and reinjected into the ground. The initial perchlorate concentration was 171 mg/L . Over the course

of a few months, the perchlorate concentration in eight of the nine wells decreased by more than 95% from the original value. Five wells reached perchlorate levels below 1 mg/L and two wells below 5 µg/L. Nitrate levels were also reduced very effectively and dropped to non-detectable levels in seven weeks.

Recirculation of the contaminated water, bringing it to the surface and reinjecting it into the ground, requires a substantial amount of pumping energy. If one attempts to inject the nutrient and electron donor solution directly into the aquifer holding the contaminated perchlorate solution, the vicinity of the injection well often develops competing bacterial flora. Biofouling may require frequent cleanout of clogged passages or the drilling of a new injection well at a different location. A better understanding of the competing bacteria is required to optimize the process [1263, 1264] (see [1265] also).

Perchlorate degrading bacteria are actually ubiquitous at most perchlorate-contaminated underground sites. They just lack the proper nutrients to propagate and to do a better job at reducing the perchlorate level *in-situ*. One of the objectives of ongoing *in-situ* remediation studies is to find the proper nutrients to keep the perchlorate-eating bacteria happy and working [1225, 1266].

Bacteria depend on electron donors (reductants) to be able to reduce perchlorate. Electron donors have to be present to accelerate biodegradation and bioremediation of perchlorate. If the natural environment (plants, decaying organic material, swamp gas) does not provide any of these, the soil in sites undergoing perchlorate clean up must be amended with electron donors. Electron donors tested at various *in-situ* bioremediation sites include hydrogen gas, or solutions or suspensions of acetate, lactate, corn syrup, ethanol, vegetable oil, citric acid, cow manure, and chicken manure.

Poplar trees are being tested for phytoregeneration of perchlorate-contaminated soil. Root homogenate from poplar trees stimulated perchlorate degradation in microcosms of soil and water samples collected at a perchlorate contaminated site (the LHAAP, located outside Karnack, Texas) [1267]. Perchlorate-degrading bacteria were able to thrive when given root products as the sole exogenous source of carbon and electron donors. The ability of root products to drive perchlorate respiration by using bacteria is vital for the successful achievement of perchlorate rhizodegradation in conjunction with phytoremediation.

In another clean-up project at LHAAP, active and semi-active *in-situ* bioremediation approaches were demonstrated and compared for cost and efficiency [1268, 1269].

It was discovered that the addition of hydrogen gas greatly enhances the ability of bacteria to reduce perchlorate. Two hydrogen-utilizing perchlorate-degrading bacteria have been isolated following discovery that they are capable of using inorganic carbon for growth. These are the first perchlorate-degrading autotrophs isolated from a perchlorate-contaminated site [1270]. These autotrophic bacteria are within the genus *Dechloromonas* and are the first *Dechloromonas* species that are microaerophilic and incapable of growth at atmospheric oxygen concentrations. Measured hydrogen thresholds were higher than for other environmentally sig-

nificant, hydrogen-utilizing, anaerobic bacteria (e.g., halorespirers). The chlorite dismutase activity of these bacteria was greater for autotrophically grown cells than for cells grown heterotrophically on lactate. These bacteria were fed fumarate as an alternate electron acceptor, which is the first report of growth on an organic electron acceptor by perchlorate-reducing bacteria.

A unique method for perchlorate or nitrate bioremediation in the vadose zone is a combination of an *in-situ* bioreactor with reducing (electron donor) gas injection to facilitate the action of anaerobic bacteria feeding on perchlorate and nitrate [1271]. The use of gaseous instead of liquid reductants has the advantage that they diffuse better through low-permeability soils and any excess disperses without a trace. This technique is called *Gaseous Electron Donor Injection Technology* and is an anaerobic variation of petroleum hydrocarbon bioventing. It involves injecting electron donor gases or vapors, such as hydrogen or ethyl acetate, into the vadose zone to stimulate biodegradation of nitrate and perchlorate. In lab studies, nitrate removal was best promoted by ethyl acetate. Up to 39% perchlorate removal was achieved with ethanol but this was limited by insufficient incubation time. Hydrogen, 1-hexene, ethyl acetate, and liquefied petroleum gas were tested as electron donors at different soil moisture conditions. Under high soil moisture (16 wt.-%) conditions, complete or partial perchlorate degradation was achieved with all of the tested electron donors except for ethyl acetate. Hydrogen was the most promising of the tested electron donors, achieving complete perchlorate degradation with first-order rate constants ranging from 0.13 to 0.20 d⁻¹ and reducing concentrations to non-detectable levels within 35 to 42 days [1272]. Aerojet has rehabilitated the inactive 8500-acre Rancho Cordova, CA, site by injecting a mixture of hydrogen (electron donor) with propane, nitrogen, and carbon dioxide through a specially configured injection well. After eight months of continuous treatment, final soil samples proved that this process successfully remediated contaminants at the site. The amount of perchlorate in the soil was reduced by 93% and nitrate was reduced by 94%.

A field demonstration was conducted to evaluate the *in-situ* bioremediation treatment of perchlorate using a horizontal flow treatment well system to mix electron donor into perchlorate-impacted groundwater [1273, 1274]. The objectives of this project were to demonstrate that *in-situ* biological perchlorate treatment is feasible in the field using electron donor addition and that perchlorate concentration can be lowered down to 4 µg/L. Related problems are that biofouling must be effectively controlled by measures that are easily implemented and that co-contaminants, including nitrate and trichloroethene, can be treated using the same technology.

In-situ bioremediation has many advantages, such as reduced costs and time for clean up, as compared to pump-and-treat [1256]. Alternatives for active *in-situ* bioremediation of perchlorate are (a) natural attenuation (dilution), (b) passive system using mulch biowall to intercept plume, (c) passive biobarrier using an injection of semi-soluble electron donors such as vegetable oil, and (d) an active or semi-passive system

with injection of soluble electron donors in recirculated groundwater extracted from downgradient [1275, 1276].

In the end, it may be the cost of installing and operating an *in-situ* bioremediation system that decides which system should be used [1277]. This includes not only the initial capital investment but also the operational and maintenance expenses for which a budget must be set up. Because this is a relatively new technology, the experience base is quite limited.

8.9.5 AP Removal via Phytoremediation

Phytoremediation, which refers to the use of plants and their associated microbes and root exudates for environmental cleanup, has gained acceptance in the past 20 years as a cost-effective, non-invasive alternative or complementary technology for engineering-based remediation methods. The selective revegetation of a disturbed and contaminated site with plants that have the ability to reduce perchlorate to chloride is another environmentally friendly method for bioremediation. Some plants (e.g., willows) have the ability to reduce perchlorate to chloride [1278]. Hydroponically grown woody and aquatic plants were observed to remove perchlorate from aqueous solutions via two mechanisms: an initial slow uptake and transformation of perchlorate in the plant tissues (phytodegradation) followed by very rapid removal of perchlorate from solutions in the root zone (rhizodegradation) with substantial contributions by bacteria living in the root zone [1279]. Exudates secreted from the plant roots supplied nutrients for the perchlorate-reducing bacteria.

Two types of hydroponic bioreactors were used to investigate the mechanistic changes during phytoremediation of perchlorate under different root-zone conditions [1280]. The bioreactors included (1) an aerobic ebb-and-flow system planted with six willow trees and (2) individual willow trees grown in sealed root-zone bioreactors. Radiolabeled (^{36}Cl -labeled) perchlorate was used as a tracer in a subset of the sealed bioreactor experiments to quantify the contribution of phytodegradation and rhizodegradation mechanisms. Slower rates of phytoremediation by uptake and phytodegradation were observed under high nitrate concentrations and aerobic conditions, which allowed perchlorate to persist in solution and resulted in a higher fraction uptake by the plant. The results of this study indicate that the root-zone environment of plants can be manipulated to optimize rhizodegradation and to minimize undesirable processes such as uptake, temporal phytoaccumulation, and slow phytodegradation during phytoremediation of perchlorate. This can also be done in hydroponic bioreactors in greenhouses instead of in the field [1281].

The potential to use native (*Salix exigua*) and exotic (*Tamarix ramosissima*) phreatophytes to remediate perchlorate from arid riparian environments was investigated by conducting a hydroponic greenhouse experiment [1282]. *Salix exigua* and *Tamarix ramosissima* exposed to AP at concentrations of 10 mg/L and 100 mg/L removed 15 to 22% perchlorate mass from hydroponic solution, with 55 to 64% of removal

being taken up into plant tissue. Total perchlorate taken up by plants or removed from solution was not significantly different between species on a mass or oven-dry plant weight concentration basis. Significant differences in tissue specific uptake, however, were detected, with *Salix exigua* accumulating 78 to 87% of perchlorate in the leaf and *Tamarix ramosissima* exuding 84 to 87% of uptake onto leaf surfaces. Burning the dried leaf tissue resulted in no detectable perchlorate in the ashes.

The influence of biostimulation using dissolved organic carbon (DOC) on rhizodegradation of perchlorate and plant uptake was studied under greenhouse conditions using soil and hydroponic bioreactors [1283]. One set of bioreactors planted with willow (*Salix babylonica*) plants were spiked with 300 mg/L DOC in the form of chicken manure extract, whereas a second set was not treated with DOC. A similar experiment without willow plants was run in parallel to the planted bioreactors. The planted soil bioreactors amended with DOC reduced perchlorate from 65.8 to 2.7 mg/L in 21 d for humic soil (95.9% removal) and from 69 to 0.06 mg/L for sandy loam (99.9% removal) in 11 days. Non-planted DOC-treated soil bioreactors also achieved complete perchlorate removal in six and eight days for humic and sandy loam, respectively. Both planted and non-planted soil bioreactors without DOC removed >95% perchlorate within eight days. Planted soil bioreactors respiked with perchlorate repeatedly reduced perchlorate to non-detectable levels in six days. Persistence of perchlorate in the solution of planted hydroponic bioreactors without DOC amendment suggested that natural DOC from the plant exudates was not enough to biostimulate perchlorate-reducing microbes. The hydroponic bioreactor study provided evidence that DOC is a limiting factor in the rhizodegradation of perchlorate.

Radiolabeled perchlorate was used to find that, in planted systems, as much as 11.7% of the influent perchlorate mass was taken up into the tree and 82% of the perchlorate taken up was accumulated in the leaves [1284]. The plant contribution to total perchlorate removal in non-bioaugmented low organic carbon soil was 39%, with the balance of the removal being attributed to microbial reduction. In bioaugmented soil, the microbial contribution to perchlorate removal was increased. Just planting poplar trees decreased the diversity of perchlorate reducers in the soil. At the increased oxidation-reduction potential observed in planted high organic carbon soil, the non-perchlorate-reducing bacteria appear to outcompete the perchlorate reducers and perchlorate removal is decreased. This means that perchlorate remediation in high organic carbon soil does not benefit from planting hybrid poplar trees but that remediation in low organic carbon soil is stimulated by planting and bioaugmentation.

8.9.6 AP Removal via Membrane Filtration

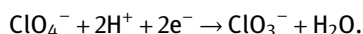
Although ion exchange and biological reduction are the most frequently used technologies for water purification, other technologies such as membrane filtration and electrodialysis may offer advantages under certain environmental

conditions [1285]. Membrane-based purification methods can be divided into three categories: **(1)** Reverse osmosis, **(2)** nanofiltration, and **(3)** electrodialysis. Reverse osmosis involves forcing water through a semiporous polymer membrane. In reverse osmosis, artificial pressure is applied on one side of the membrane, thus forcing water to migrate through the membrane wall, leaving perchlorate and most other dissolved salts behind. This technique is also used for desalination of seawater. Nanofiltration is a similar technique using membranes with slightly larger pores. However, fouling of the membrane filters remains a concern for both reverse osmosis and nanofiltration technologies. The membrane process produces two streams: the filtrate or permeate, which is nearly deionized water, and the brine concentrate, which has to be disposed of in another manner. This process could be used for point-of-use systems, such as home water purification or small-scale water treatment where sufficient electrical energy is available to drive the compressors.

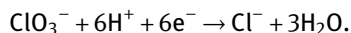
8.9.7 AP Removal via Electrochemical Reduction

Until recently, few studies had looked at the electrochemical reduction of aqueous perchlorate. As such, there is only limited data in existing literature regarding the removal of chlorate from water. Why though, when all perchlorate is produced via electrochemical oxidation, should the reaction not be reversible?

The first step of electrochemical reduction is



Further reduction of chlorate to chloride would require an elevated electrode potential:



Instead of generating oxygen at the anode, it is also possible to depolarize a catalytic anode by bubbling hydrogen gas around it, while perchlorate is reduced at the cathode like in a fuel cell.

The electrochemical reduction of perchlorate anion has been studied in an electrolysis cell with a nickel working electrode and a platinum counter electrode in concentrated solutions of HClO_4 [1286]. A significant reduction of perchlorate to chloride ions occurred on the nickel cathode in the potential region where hydrogen evolution occurs. It was found that the mechanism of this process involves platinum deposited in small amounts on the cathode as a result of oxidation of the platinum anode in the perchloric acid solution. The reduction of perchlorate was accompanied by undesirable oxidation of the nickel cathode, which was attributed to chlorate ions formed in the initial step of perchlorate reduction.

Of five different methods tested for the removal of dissolved perchlorate from water, two methods stood out as the most promising processes: a catalytic dual-

membrane system (described within this publication) and an indirect electrochemical reduction using a titanium electrode [1287].

It was attempted to develop an integrated method for simultaneous removal of perchlorate and chlorate in water by combining ZVI Fe(0) and electrochemical reduction [1288]. However, the use of Fe(0) in electrochemical processes did not produce expected results, as high pH and the presence of hydrogen gas rendered the Fe(0) ineffective for any perchlorate reduction. Electrochemical experiments for perchlorate reduction with nickel or carbon electrodes in the presence of cobalt-based catalysts did result in reaction rate constants that were three to five times higher than those achieved with Fe(0). However, these rates are still too slow for any practical application. Reaction kinetics associated with the electrochemical reduction of chlorate were comparable to that observed with Fe(0), especially at low pH. Surprisingly, bacteria are able to reduce perchlorate in the presence of Fe(0) [1212].

It is known that perchlorate can be reduced to chloride by using electrochemical reduction **or** via bacterial action, but the discovery of perchlorate remediation using bioelectrochemical reduction in a microbial fuel cell is a surprise [1289]. In such a system, not only would perchlorate be destroyed but one would gain electric energy at the same time. Microbial fuel cells (MFCs) may be a suitable method for perchlorate removal. Perchlorate reduction was obtained without the need for exogenous electron shuttles or fixed electrode potentials, achieving a maximum perchlorate removal of 24 mg/L-d and cathodic conversion efficiency of 84%.

Electrodialysis passes water through different membranes while exposing it to an electric field gradient. The electric field separates the perchlorate from the stream of treated water. This produces alternate channels of nearly deionized water (the diluate or dialyzate) and salty water (the concentrate). The diluate is used and the concentrate is discarded. The perchlorate-containing concentrated brine is then appropriately disposed of.

8.9.8 AP Removal via Selective Adsorption on Inorganic Media

Conventional adsorbents used for drinking water purification does not work for perchlorate because the ion is so highly symmetrical and is highly soluble in water. Nevertheless, modified activated carbon (charcoal) has been tested for perchlorate removal from water. In rapid small-scale column tests, cationic surfactant-tailored **activated carbons** (AC's) effectively removed perchlorate to below detection levels for up to 30 times longer than virgin AC. By pre-loading bituminous AC with cationic surfactants, 75 ppb perchlorate was removed for 27000–35000 BVs before the effluent perchlorate rose above 1 ppb. These tests employed a natural groundwater that also contained 30 mg/ LSO_4^{2-} , 26 mg/ LNO_3^- , and other ions [1290–1293]. Tailored GAC can be thermally regenerated (reactivated) and, unlike ion exchange, does not create a new disposal problem with the perchlorate-rich brine that elutes from ion exchange resins during their regeneration. Biological processes do not work well in the ppb

range where activated charcoal can remove the last traces of perchlorate from water (“polishing treatment”).

A total of ten types of commercially available activated carbons were tested for perchlorate adsorption characteristics using pH as the main variable [1294]. The activated carbons were made from different base materials such as wood, bituminous coal, and lignite coal. As such, they possessed different surface characteristics such as specific surface area and surface zero point charge, e.g. pH_{zpc} . Adsorption isotherms were obtained in the pH range of three to ten and for perchlorate concentrations from 0.01 to 1.0 mM. The adsorption isotherms followed the Langmuir type. Surface charge and **not**-specific surface area was the most important factor governing perchlorate removal. All wood-based activated carbons that had a large variation (by a factor of 3) in specific surface area (but very close pH_{zpc}) exhibited similar perchlorate adsorption capacity. On the other hand, the activated carbons with $\text{pH}_{\text{zpc}} > 8$ exhibited higher adsorption capacity than those with low pH_{zpc} of 2–3. This indicated that electrostatic forces are responsible for perchlorate adsorption. However, electrostatics alone failed to explain the better perchlorate removal compared to other anions such as sulfate or phosphate. It was demonstrated that specific chemical interactions between perchlorate and surface functional groups in combination with electrostatic forces were the major mechanism for perchlorate adsorption on activated carbon.

Perchlorate can be removed from contaminated waters using surfactant-modified zeolite [1295].

Mesoporous organosilica materials functionalized with quaternary ammonium ligands were used for the removal of perchlorate anions from aqueous solutions [1296]. The physical and chemical properties of the adsorbent were measured using nitrogen adsorption-desorption measurement, elemental analyses, XRD, and IR spectra. Equilibrium isotherms for the measurement of perchlorate adsorption capacities and kinetic performance were compared to those of organic ion exchange resins.

AP can be co-precipitated with struvite $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ [1297].

8.9.9 AP Removal via Catalytic Reduction

Of five different methods tested for the removal of perchlorate from water, two methods stood out as the most promising processes: a catalytic dual-membrane system and the indirect electrochemical system using a titanium electrode [1287]. For the former system, it was found that perchlorate was removed completely at a rapid to moderately rapid rate. Ti, Sn, Cr, Mo, Cd, and Pt are the most promising metallic catalysts for the reduction of perchlorate in diluted aqueous solutions.

The reduction of perchlorate in water via dihydrogen under mild conditions can be catalyzed by a catalyst that is prepared by using adsorption of a rhenium(VII) precursor (either ammonium perhenate or methylrhenium trioxide) onto carbon powder containing 5% palladium by weight [1298, 1299]. Under standard batch conditions of room temperature, one bar of hydrogen, and 200 ppm perchlorate (as HClO_4), reduc-

tion proceeded to less than 1 ppm in as little as five hours. Inhibition using chloride was not significant. Optimal reduction activity occurred in acidic solutions (pH ca. 3), and both the rate and extent of reaction decreased at higher values of pH. In its current form, the catalyst might best be used to destroy perchlorate in the acidic regeneration stream from selective ion exchange columns.

An electrodiallytically assisted catalytic membrane system was tested for the reduction of perchlorate in dilute aqueous solutions [1300]. The catalyst support (membrane) was a stainless steel mesh coated with specific monometallic catalysts. A total of 18 different metals covering the first, the second, and the third row of the periodical table were tested. Results indicated that the perchlorate reduction rate decreased in the order: $\text{Cd} > \text{Pt} > \text{Cr} > \text{Mo} > \text{Sc} \gg \text{Rh} > \text{Ru} \sim \text{Sn} > \text{Pd} > \text{V} \sim \text{Ti} > \text{Zn} > \text{Mn} > \text{Ni} > \text{Zr} > \text{Co} > \text{Cu} > \text{Pb}$. Tin was selected for further evaluation in spite of its moderate reaction rate. Results indicated that perchlorate reduction took place rapidly in the concentration range of 2–100 ppm at room temperature and chloride was the major end-product.

The reduction of perchlorate by using dihydrogen gas has advantages in terms of cost, ease in operation, and cleanliness. It was attempted to remove perchlorate ions from dilute solutions using dihydrogen gas assisted by metallic catalysts in a pressurized reactor at room temperature [1301]. Results indicated that perchlorate ions could be reduced to chloride by using molecular hydrogen gas. Among a total of 78 catalyst studied, only 25 showed significant or observable perchlorate reduction. The removal efficiency was about 20% in several hours at an initial perchlorate concentration of 10 ppm in the presence of catalysts. Other metallic catalysts were able to achieve about 90% removal in two weeks at an initial perchlorate concentration of 2 ppm. The most efficient system was the Ti/TiO_2 surface, which had a removal efficiency of better than 90% of the perchlorate ions in about 80 hours, even at an initial very low perchlorate concentration of 1 ppm.

8.9.10 AP Removal via Chemical Reduction

There are only a few reducing agents that will reduce perchlorate to chloride without additional treatment. One of the recommended reducing agents is titanium(III) chloride but it is not exactly the cheapest reducing agent unless one regenerates it continuously via electrolytic reduction (see Section 8.9.7).

Stabilized ZVI nanoparticles can reduce perchlorate in water or ion-exchange brine. Batch kinetic tests revealed that at an iron dosage of 1.8 g/L and at moderately elevated temperatures (90–95 °C), ~90% of perchlorate in both freshwater and in a simulated ion-exchange brine (6% NaCl) was destroyed within seven hours [1302]. An activation energy of 52.6 ± 8.4 kJ/mol was determined for the reaction. Kinetic tests suggested that Cl^{+7} in perchlorate was rapidly reduced to chloride without accumulation of any intermediate species.

Complete (99.9%) perchlorate removal was obtained in a solution containing $[\text{ClO}_4^-] = 1.0$ mM, $[\text{Ti(III)}] = 40$ mM, and $[\beta\text{-alanine}] = 120$ mM after two-and-a-half

hours of reaction at 323 K (50 °C) [1303]. The reaction is influenced by both pH and complex formation. The results revealed that, without β -alanine, the optimal pH was 2.3. The presence of β -alanine significantly increased the reduction rate of perchlorate even at near-neutral pH. This is because β -alanine formed complexes with Ti(III), which greatly improved the total soluble [Ti(III)] in the pH range between 3.5 and 6.

8.10 Other Sources of Perchlorates in the Environment

This chapter discussed sources of perchlorates in the environment other than those attributed to the industrial production of chlorates and perchlorates.

8.10.1 Natural Occurrence of Perchlorate Salts

The natural occurrence of perchlorate salts has already been discussed in Section 1.2. A current theory concerning the origin of naturally occurring perchlorate in the environment focuses on natural atmospheric processes. This theory suggests that chloride, possibly in the form of sodium chloride aerosols from seawater or land-based chloride compounds suspended in the upper atmosphere, reacts with atmospheric ozone to create perchlorate. This process occurs over much of the earth and is analogous to nitrate formation in the atmosphere. In most areas with high precipitation, the perchlorate is extracted from the soil and washed into the ocean. Only in arid areas, such as in the Atacama desert in Chile, can the perchlorate (along with the nitrate) accumulate in noticeable quantities.

Fertilizers continue to contain perchlorates even after the import of Chile saltpeter has ceased [1304, 1305] or the raw saltpeter has been treated to remove some of the perchlorate.

Cases where perchlorate pollution results from non-military and/or natural inputs need to be included in the overall environmental pollution studies [1124, 1306]. In trying to find the source of perchlorate pollution, be that human-made or naturally occurring pollution, analytical tools have been sharpened to trace the origin of perchlorates in the environment [1307]. The formation of perchlorate may be a natural process in the atmosphere [1308].

In the wake of discovering perchlorate ions in the ice of polar caps on Mars, chemists began to take a closer look at the natural occurrence of perchlorate salts on Earth [1309]. Ice and water samples were collected at remote, pristine locations where there was very little chance of industrial pollution. The possibility of naturally occurring perchlorate has only recently received significant attention. Relying primarily on domestic, agricultural, and recreational wells, a network of volunteers was enlisted to help collect 326 groundwater samples from across the coterminous US [13]. Care was taken to avoid known, US EPA-documented sites of perchlorate use or release, as well as perchlorate contamination due to disinfection

using hypochlorite. Using IC-ESI-MS and a $\text{Cl}^{18}\text{O}_4^-$ internal standard, a MDL of $40\text{ ngClO}_4^-/\text{L}$ and a MRL of 120 ng/L was achieved. Of the 326 samples, 147 (45%) were below the MDL, while 42 (13%) were between the MDL and the MRL. Of the 137 samples that could be quantified, most (109) contained 1000 ng/L perchlorates; the remaining 28 samples contained from 1000 to 10400 ng/L . These results support the notion that perchlorate occurs naturally in many groundwaters. However, unusually high concentrations (10000 ng/L) previously reported for the west-central Texas area appear to be anomalous. Perchlorate concentrations were positively correlated with nitrate levels ($P < 0.001$) but not with chloride concentrations.

Gradually the realization begins to emerge that perchlorate ion is more ubiquitous in the natural and unpolluted environment than earlier generations were aware of [14]. Forensic scientists are hunting for evidence of natural versus anthropogenic perchlorate in the environment in an attempt to try and source the cause of perchlorate pollution [1310]. Perchlorates from different origins leave fingerprints behind in the form of their isotope ratios [1311]. The isotope ratios in perchlorates have been measured and they are different for naturally occurring and synthetic perchlorates [330, 1312]. An atmospheric source for this natural occurrence is strongly implicated, and the naturally occurring isotopes of oxygen and chlorine offer considerable promise for unraveling the chemical mechanisms responsible. Perchlorates found in West Texas have isotope ratios that differ from both the Chilean Atacama minerals and from human-made perchlorate. The West Texan perchlorates have formed via a different mechanism from the South American perchlorates or they have been substantially biologically or geochemically altered and re-deposited.

The discovery of perchlorate in soil and ice from several Antarctic Dry Valleys (ADV) where concentrations reach up to $1100\text{ }\mu\text{g/kg}$ was truly surprising [1313]. In the driest ADV, perchlorate correlates with atmospherically deposited nitrate. Far away from any anthropogenic activity, ADV perchlorate provides unambiguous evidence that natural perchlorate is ubiquitous on Earth. The discovery has significant implications for the origin of perchlorate, its global biogeochemical interactions, and possible interactions with polar ice sheets. The results support the hypotheses that perchlorate is produced globally and continuously in the Earth's atmosphere, that it typically accumulates in hyperarid areas, and that it does not build up in oceans or other wet environments most likely because of microbial reduction on a global scale.

A correlation is sought between the detection of perchlorate in the ice caps of Mars and the accumulation of perchlorate in high deserts and the polar regions of Earth.

Isotopic studies indicated that natural perchlorate is produced on Earth in arid environments via the oxidation of chlorine species through pathways involving the ozone or its photochemical products. With this analogy, it was proposed that the arid environment on Mars similarly may have given rise to perchlorate through the action of atmospheric oxidants [1314]. A variety of hypothetical pathways can be proposed including photochemical reactions, electrostatic discharge, and gas-solid reactions. A preliminary study of the means to produce perchlorate was made to shed light on the

origin of Martian perchlorate. Different gas-phase pathways were investigated using a 1-D photochemical model.

Perchlorate ClO_4^- is ubiquitous in the environment. It is produced naturally by atmospheric photochemical reactions. Nitrate-enriched salt deposits of the Atacama Desert (Chile) contain high concentrations of natural ClO_4^- , which have been exported worldwide since the mid-1800s for use in agriculture. The widespread introduction of synthetic and agricultural ClO_4^- into the environment has contaminated numerous municipal water supplies. Stable isotope ratio measurements of Cl and O have been used to discriminate different ClO_4^- sources in the environment. ^{36}Cl measurements were made for further improving the discrimination of ClO_4^- sources [1315]. Groundwater and desert soil samples from southwestern areas of the US contain ClO_4^- , thus being found to have high abundances of ^{36}Cl ($^{36}\text{Cl}/\text{Cl} = 3100 \times 10^{-15}$ to 28800×10^{-15}) compared with those from the Atacama Desert ($^{36}\text{Cl}/\text{Cl} = 0.9 \times 10^{-15}$ to 590×10^{-15}). They were also found to have synthetic ClO_4^- reagents and products ($^{36}\text{Cl}/\text{Cl} = 0.0 \times 10^{-15}$ to 40×10^{-15}). In conjunction with stable Cl and O isotope ratios, ^{36}Cl data provides a clear distinction among three principal ClO_4^- source types in the environment in this geographical area.

There is a widespread presence of naturally occurring perchlorate in the high plains of Texas and New Mexico [1316]. Perchlorate concentrations measured in groundwater from remote locations in the Middle Rio Grande Basin in north-central New Mexico ranged from 0.12 to 1.8 $\mu\text{g}/\text{L}$ [1317].

UV illumination of hypochlorite solutions can lead to the formation of perchlorate. It was demonstrated that perchlorate can be formed via the conversion of chlorine precursors such as aqueous salt solutions of hypochlorite, chlorite, and chlorate exposed to UV radiation [1318]. Other experiments subjected such solutions to electric discharges. These also formed perchlorate.

Ozonization of drinking water has been widely advertised as a safer method compared to chlorination in that it avoids formation of halogenated organic compounds (chloroform) in drinking water. Only a few people have recognized that there is a potential of inadvertently forming perchlorate by ozonization of chloride ions in the incoming water [1319]. The yields and rates of ClO_4^- production from O_3 -mediated oxidation of Cl^- , OCl^- , ClO_2^- , ClO_3^- , and ClO_2 were measured as a function of reactant (O_3 and ClO_x^-) concentrations and pH [1320]. The comparative rate and efficiency of ClO_4^- production is generally greater for higher oxidation states of Cl (2.7 to 0.5% for $\text{ClO}_2^-/\text{ClO}_2$ and 0.02 to 0.005% for OCl^-/HOCl oxidation) with the notable exception of ClO_3^- , which does not react with O_3 . The very slow rate of ClO_4^- production from Cl^- ($20 \times 10^{-9} \text{ mM min}^{-1}$) even at elevated O_3 and Cl^- concentrations implies negligible potential for inadvertent ClO_4^- formation in process units of water/wastewater treatment systems that use ozonization for treatment. ClO_2 and higher oxy-chlorine radicals/intermediates (e.g., Cl_2O_6) may play a role in perchlorate formation. A similar process may take place with aerosol-borne chloride in the upper atmosphere under the influence of ozone and UV light. This may be responsible for the natural production of perchlorates.

Chlorine is known to play an important role in ozone layer chemistry, including the feared ozone destruction and formation of ozone layer holes. The same sequences of reaction can generate perchlorate, which is the most stable end-product in any series of reactions involving chlorine-oxygen species.

The frequency of detection of perchlorate in groundwater and drinking water supplies has been steadily increasing since its initial identification as a chemical of concern in 1997, however, perchlorate has also been detected in many locations in the groundwater away from any industrial pollution and human impacts (like agriculture and fertilizer). The search is on for alternative causes of widespread low perchlorate concentrations found in groundwater [1321].

Perchlorate stable isotope data ($\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$), along with other supporting chemical and isotopic environmental tracer data, were used to document groundwater ClO_4^- contamination sources and history in parts of Long Island, New York [1322]. Sampled groundwaters were oxidic and ClO_4^- were apparently not affected by biodegradation within the aquifers. Synthetic, as opposed to natural, ClO_4^- was indicated by the isotopic method in groundwater near an ordnance disposal site at a former missile base. Atacama ClO_4^- was indicated in agricultural and urbanizing areas in groundwaters with apparent ages 20 years. In an agricultural area, ClO_4^- concentrations and $\text{ClO}_4^-/\text{NO}_3^-$ ratios increased with groundwater age, possibly because of the decreasing application rates of Atacama NO_3^- fertilizers and/or decreasing ClO_4^- concentrations in Atacama NO_3^- fertilizers in recent years. Groundwater ClO_4^- with distinctive isotopic composition was a sensitive indicator of past Atacama NO_3^- fertilizer use on Long Island and may be common in other areas that received NO_3^- fertilizers from the late nineteenth century through to the twentieth century.

Stable isotope studies of nitrate deposits in various parts of the world have supported the atmospheric origin of the nitrate. The processes that form and accumulate natural nitrate can provide clues as to the origin and mechanisms of formation of naturally occurring perchlorate. Chlorine participates in many photochemical reactions in the atmosphere and global photochemical perchlorate formation in the atmosphere has been demonstrated. Thus, the question is not which areas are under perchlorate-containing rain but which geological and climate conditions allow perchlorate in some areas to be concentrated to achieve environmentally or toxicologically significant concentrations [1323]. The area where the highest amount of nitrate and perchlorate has accumulated is the Atacama desert in Chile. Isotope studies now confirmed the atmospheric origin of these anions.

Natural perchlorate is believed to be of atmospheric origin. However, until recently, no systematic study had been conducted to evaluate perchlorate deposition rate and possible seasonal or spatial variations. Perchlorate concentrations in weekly composite wet deposition samples acquired through the National Atmospheric Deposition Program from 26 sites across the continental US, Alaska, and Puerto Rico for a period of one to three years were analyzed using very sensitive analytical meth-

ods [1324]. Perchlorate concentrations varied from 5 ng/L to a high of 102 ng/L with a mean of 14.1 ± 13.5 ng/L for the 1578 total samples. The annual perchlorate flux by site ranged from a low of 12.5 (TX) to 157 mg ha⁻¹ yr⁻¹ (NE) and averaged 65 ± 30 mg ha⁻¹ yr⁻¹ for all sites. Perchlorate concentrations and flux in wet deposition were generally highest between May to August, declining to lows between December-February, which seems to correlate with sunshine hours in the northern hemisphere. Average annual perchlorate flux was correlated ($r > 0.5$; $p < 0.001$) with Ca²⁺, K⁺, NH₄⁺, NO₃⁻, Cl⁻, and SO₄²⁻ measured at the same time. Wet deposition rate of ClO₄⁻ in the conterminous US (excluding Alaska, Hawaii, and Puerto Rico) while diffuse, represents a potential annual net mass flux of 51000 kg/yr. This value is comparable to the estimated annual environmental releases from other known ClO₄⁻ sources.

The isotopic composition and stable isotope ratios of natural ClO₄⁻ indigenous to the southwestern areas of the US were measured in ClO₄⁻ ($\delta^{18}\text{O}$, $\Delta^{17}\text{O}$, $\delta^{37}\text{Cl}$) and associated NO₃⁻ ($\delta^{18}\text{O}$, $\Delta^{17}\text{O}$, $\delta^{15}\text{N}$) in groundwater from the southern High Plains of Texas and New Mexico and the Middle Rio Grande Basin in New Mexico (from unsaturated subsoil in the southern High Plains of Texas and from NO₃⁻-rich surface caliche deposits near Death Valley, California) [1325]. The data indicated that natural ClO₄⁻ in the southwestern areas of the US has a wide range of isotopic compositions that are distinctly different from those reported previously for natural ClO₄⁻ from the Atacama Desert of Chile as well as all known synthetic ClO₄⁻. ClO₄⁻ in Death Valley caliche has a range of high $\Delta^{17}\text{O}$ values (+8.6 to +18.4‰), overlapping and extending the Atacama range, indicating at least partial atmospheric formation via reaction with the ozone. However, the Death Valley $\delta^{37}\text{Cl}$ values (-3.1 to -0.8‰) and $\delta^{18}\text{O}$ values (+2.9 to +26.1‰) are higher than those of Atacama ClO₄⁻. In contrast, ClO₄⁻ from western Texas and New Mexico has much lower $\Delta^{17}\text{O}$ (+0.3 to +1.3‰), with relatively high $\delta^{37}\text{Cl}$ (+3.4 to +5.1‰) and $\delta^{18}\text{O}$ (+0.5 to +4.8‰), indicating either that this material was not primarily generated with O₃ as a reactant or that the ClO₄⁻ was affected by post-depositional O isotope exchange. High $\Delta^{17}\text{O}$ values in ClO₄⁻ (Atacama and Death Valley) are associated with high $\Delta^{17}\text{O}$ values in NO₃⁻, indicating that both compounds preserve characteristics of O₃-related atmospheric production in hyper-arid settings, whereas both compounds have low $\Delta^{17}\text{O}$ values in less arid settings. This study provides important new constraints for identifying natural sources of ClO₄⁻ in different environments by using multi-component isotopic characteristics. It also presents the possibility for divergent ClO₄⁻ formation mechanisms and (or) ClO₄⁻ isotopic exchange in biologically active environments.

Just when it seemed that isotope ratio measurement was a sure shot method to identify perchlorates from different sources, a new complication arose from the discovery that bioreduction of perchlorates proceeds at different rates depending on the isotopic makeup of the perchlorate ion. Thus, the perchlorate chlorine or oxygen isotope ratio in the inflow and outflow of a bioreactor or an underground bioreduction zone would be different depending on how long the reduction has been going on. Isotopic ratios may also be useful for identifying the extent of biodegradation of per-

chlorate, which is critical for assessing the natural attenuation of this contaminant in groundwater.

Because bacteria typically fractionate isotopes during biodegradation, stable isotope analysis is increasingly used to distinguish this process from transport or mixing-related decreases in contaminant concentrations. However, for this technique to be useful in the field to monitor bioremediation progress, isotope fractionation must be quantified under relevant environmental conditions. An *in-situ* experiment was performed in a shallow alluvial aquifer in Maryland to quantify the fractionation of stable isotopes in perchlorate (Cl and O) and nitrate (N and O) during biodegradation. During this field experiment, perchlorate concentrations decreased by 78% and nitrate concentrations decreased by 82% during the initial 8.6 hours after the injection [1326]. The observed ratio of fractionation effects of O and Cl isotopes in perchlorate ($\epsilon^{18}\text{O}/\epsilon^{37}\text{Cl}$) was 2.6, which was similar to that observed in the laboratory using pure cultures (2.5). Denitrification by indigenous bacteria fractionated O and N isotopes in nitrate at a ratio of ~ 0.8 ($\epsilon^{18}\text{O}/\epsilon^{15}\text{N}$), which was within the range of values reported previously for denitrification. However, the magnitudes of the individual apparent *in-situ* isotope fractionation effects for perchlorate and nitrate were appreciably smaller than those reported in homogeneous closed systems (0.2 to 0.6 times), even after adjustments for dilution were made. These results indicated that (1) isotope fractionation factor ratios ($\epsilon^{18}\text{O}/\epsilon^{37}\text{Cl}$, $\epsilon^{18}\text{O}/\epsilon^{15}\text{N}$) derived from homogeneous laboratory systems (e.g., pure culture studies) can be used qualitatively to confirm the occurrence of *in-situ* biodegradation of both perchlorate and nitrate, however, (2) the magnitudes of the individual apparent ϵ values cannot be used quantitatively to estimate the *in-situ* extent of biodegradation of either anion while the plume migrates through subterranean strata.

Measurements of stable isotope ratios of light elements (H, C, N, O, S, Cl) can often be used to distinguish biodegradation of organic and inorganic molecules from abiotic loss mechanisms such as adsorption, dispersion, or volatilization because of the relatively large kinetic isotope effects accompanying biodegradation. Chlorine isotope fractionation during perchlorate biodegradation via a common perchlorate-reducing bacterium, *Dechlorosoma suillum*, initially isolated from a perchlorate-contaminated groundwater source in southern California, was measured [1327]. The values of the chlorine isotopic fractionation factor α derived from two microcosm experiments were $\alpha = 0.9834 \pm 0.0001$ ($R^2 = 0.9999$) and $\alpha = 0.9871 \pm 0.0008$ ($R^2 = 0.9832$). These α values indicated that the rate of the $^{35}\text{ClO}_4$ reduction is 1.3–1.7% faster than that of the $^{37}\text{ClO}_4$ reduction. This relatively large kinetic isotope effect indicates that chlorine isotope analysis provides a sensitive technique by which to monitor the progress of *in-situ* bioremediation of perchlorate in groundwater.

The kinetic isotopic fractionations of O and Cl during perchlorate biodegradation must be known as a function of environmental variables such as temperature and bacterial species. A laboratory study was performed in which the O and Cl isotope ratios of perchlorate were monitored as a function of degradation by two separate bacte-

rial strains (*Azospira suillum* JPLRND and *Dechlorospirillum* sp. FBR2) at 283 and 295 K (10 °C and 22 °C) with acetate as the electron donor [1328]. Perchlorate was completely reduced by both strains within 280 hours at 22 °C and 615 hours at 10 °C. Measured values of isotopic fractionation factors were $\epsilon^{18}\text{O} = -36.6$ to -29.0‰ and $\epsilon^{37}\text{Cl} = -14.5$ to -11.5‰ , and these showed no apparent systematic variations with either temperature or bacterial strain. The fractionation factor ratio $\epsilon^{18}\text{O}/\epsilon^{37}\text{Cl}$ was nearly invariant in all experiments at 2.50 ± 0.04 . These data indicate that isotope ratio analysis will be useful for documenting perchlorate biodegradation in soils and groundwater. The establishment of a microbial fractionation factor ratio ($\epsilon^{18}\text{O}/\epsilon^{37}\text{Cl}$) also has significant implications for forensic studies (see [1329] also).

8.11 Pyrotechnical Sources of Perchlorates

Perchlorates and chlorates are widely used in display fireworks pyrotechnics and road flares. The combustion of these formulations is not 100% efficient. In the case of fireworks, not all stars (little cubes or balls of a pyrotechnic burning in different colors) ignite when the shell bursts and some fall to the ground unburnt.

It helps to assess the AP contamination problem by comparing it to other sources of perchlorates (mainly potassium perchlorate) in other applications such as road flares and fireworks [278]. Road flares contain 5–7% potassium perchlorate but most of it is consumed when the flare is burned as intended. Residual perchlorate in commercial products ranged from 0.094 mg perchlorate per gram material (flares) to 0.012 mg perchlorate per gram material (AN emulsion explosives). Laboratory-prepared rocket propellant formulations generated 0.014 mg of perchlorate residue per gram of material [1330]. The slag left behind by road flares was analyzed and found to contain residual perchlorates [1331].

If fireworks execute as intended, most of the perchlorate should be consumed by the time the ashes rain down on the footprint area below a fireworks display. As any pyromaniac who is seen in the early morning hours of July 5th scrounging around fireworks launch sites knows, not all the stars ignite and a certain percentage falls to the ground unburned, carrying some perchlorate with them [1332]. Studies have shown that natural perchlorate may be an important component to the general population exposure. These studies indicate that natural perchlorate is likely precipitated by atmospheric deposition. Perchlorate concentration of total (dry + wet) deposition is relatively unstudied, yet these measurements will aid in understanding natural levels in the environment. The total deposition was sampled monthly at six sites in Suffolk County, Long Island, and New York from 30 November 2005 until 5 July 2007. The mean perchlorate concentration was 0.21 ± 0.04 (standard error) $\mu\text{g/L}$ with a maximum value of $2.78 \mu\text{g/L}$. There was an 18-fold increase above the mean concentration in the July 2006 and July 2007 samples. It appears that this increase in perchlorates in the total deposition is associated with July 4th fireworks in the US.

8.11.1 Residual Perchlorates in Rocket Exhaust

For the normal operation of a solid-propellant rocket motor with an AP-based propellant, the combustion should be complete and there should be no detectable perchlorate in the exhaust.

At the very high operating temperature of rocket motors and in the immediate vicinity of combustible fuels and metals, all perchlorate would be converted to chloride. In a properly operating rocket, there should be no undecomposed perchlorate (or chlorate) in the exhaust, except toward the end when combustion has ceased, chamber pressure has dropped below the lower pressure limit, and when slivers of unburnt propellant are smoldering in the hot casing. Solid rocket boosters with thrust termination ports may contain substantial amounts of unburnt propellant at the time they impact the ocean if the thrust termination port was commanded open after the necessary ΔV was achieved.

Normal Operation

Analytical methods for the analysis of unburnt rocket propellant reactants were described in Section 4.2.4.12.

Assessment of Perchlorate Releases in Launch Operations

Static firings of AIM-7 rocket motors were conducted to measure the environmental dispersion of unburnt AP during normal operating conditions [1333]. Fifteen MK-58 motors were statically fired on a test bench to measure the residues that were expelled during combustion and collected on aluminum witness plates and aqueous traps located in the exhaust plume area. Perchlorate was detected in most of the samples collected due to the use of a very sensitive analytical method. The results obtained were consistent and reproducible. It was estimated that only 2mg of perchlorate was deposited per MK-58 motor. Considering the motor's flight range, it was concluded that their use in live-fire training does not contribute to the accumulation of perchlorate in the environment.

Launch Mishaps

The destruct charge was initiated on command after one of the boosters of a TITAN-IIIC developed a problem during launch in 1986 resulting in a shower of burning chunks of AP-containing composite propellant raining down on the landscape. A failure of a Titan-III at Vandenberg AFB on 18 April 1986, and the activation of the destruct system command released a spectacular fireworks of burning propellant fragments falling onto the coastline and into the ocean. As part of the anti-ballistic missile defense development testing, intentional intercepts of missiles during the launch phase will release unburnt propellant into the environment.

A study sponsored by the Air Force Space Missile Systems Center's Environmental Management Branch looked at the "what if?" situation after unburnt propellant from an aborted solid rocket launch is scattered over estuaries and seashore adjacent to

a launch site. Laboratory studies were conducted to determine the rates at which perchlorate is released from perchlorate-containing solid propellants and the influence of temperature and salinity on the rate of perchlorate release [1334, 1335]. The perchlorate leaching rates depend on the type of binder the AP is encased with in solid propellants. Perchlorate release rates from CTPB, HTPB, PBAN, and polyurethane (PU) solid propellants were determined in freshwater and seawater at temperatures between 278 and 303 K. HTPB is used in more recent SRMs such as Delta-IV, Atlas-V, Pegasus, and Titan-IV. PBAN was the binder used in STS SRBs and Titan-III. CTPB and PU are used in Minuteman stages and by the Quick Reaction Launch Vehicles (Taurus). Perchlorate release rates were expressed as diffusion coefficients. The diffusion coefficients for all propellant types and conditions tested were in the range of 3.6×10^{-12} to $1.1 \times 10^{-13} \text{ m}^2/\text{s}$. Diffusion coefficients were proportional to temperature and inversely proportional to salinity. The report also contains an analysis of water samples (for metals and other contaminants) in which solid propellant samples were immersed for 11 months. Soaked propellant samples assumed a sponge-like consistency.

The perchlorate leaching rates measured on laboratory samples were then combined with a launch vehicle failure model that calculates the sizes of propellant fragments and the debris stray field depending on the height, azimuth, and velocity at the time of the accident when the destruct mechanism was activated [1336].

9 Handling of Ammonium Perchlorate

A person preparing to handle larger quantities of AP or a person in charge of training new personnel about the safe handling of AP (or any other chemical) would typically start with consulting the MSDS supplied with the material from a vendor. Unfortunately, the MSDSs that were located during a recent online search were invariably of very poor quality and required updating and correcting. There are some MSDSs posted online that are outright misleading, incorrect, incomplete, and therefore useless, e.g.:

- http://www.sciencelab.com/xMSDS-Ammonium_perchlorate-9922929 (accessed 1 October 2017)
- <http://www.gfschemicals.com/msds/3MSDS.pdf> (accessed 1 October 2017)

9.1 Transportation of Ammonium Perchlorate

The transportation hazard classification for AP is Oxidizer Classification 5.1. The UN shipping identification number is UN1442. This classification was based on detonability tests conducted in accordance with TB700-2. This classification fails to limit the particle size, although it is now known that finely ground AP is detonable and should not be shipped under an Oxidizer designation.

In the wake of the incident at the PEPCON plant on 4 May 1988, the transportation classification was re-examined and subjected to a critical re-examination.

Nominal 200- μm particle size propellant grade AP in 114-L (30 gallons) DOT specification 37A-350 steel drums with bolted ring closures containing approximately 114 kg (250 lb) of material had successfully undergone shipping container safety testing in 1982 [1337]. However, the same material in 208-L (55 gallons) DOT specification 17H steel drums containing 227 kg (500 lb) of AP and aluminum bins conforming to requirements of DOT Specification 56, containing from 2045 to 2270 kg (4500 to 5000 lb) of AP, both of which were involved in the PEPCON incident, had not been subjected to the same testing. These larger containers had been approved by analogy with AP behavior in the 114-L (30 gallons) steel drums.

9.2 Storage of Ammonium Perchlorate

Under the recommendations issued by the National Fire Protection Association's (NFPA) Code for the Storage of Liquid and Solid Oxidizers [1338], coarse AP is ranked as a Class 4 oxidizer (the oxidizer class with the highest hazard rating). As such, the requirements (number and spacing of sprinklers, separation from nearest important structure, the need to use non-combustible materials of construction for storage buildings, storage bins) must be met for storing any amount of AP in excess of 4.5 kg (10 lb) in weight in one location. Finely pulverized AP with particle sizes below 15 μm is classified as an explosive.

9.3 Transportation and Hazard Classification Tests of Ammonium Perchlorate

A series of hazard classification tests were conducted on AP (nominal 200 μm size) packaged in 113.6 liters (30 gallons) DOT 37A-350, 20-gage steel drums with bolted ring closures, with each containing approximately 113.4 kg (250 lb) of material [1337]. The dimensions of the drums were 0.74 m high by 0.49 m in diameter with 0.8 mm thick walls. [Note: This is a heavier gage (20 gages versus 24 gages) drum than required for US shipment of this material.] The material was packaged inside the drum in two electrically conductive PE bags with approximately 4.5 kg (10 lb) of desiccant placed atop the AP inside the inner bag. The gross weight of the drums and contents averaged 119.5 kg (264 lb) and moisture content was approximately 0.007 mass-%. All tests were conducted in accordance with INTERREG, Transport of Dangerous Goods, 1981 Edition (<https://www.interregeurope.eu/>). A first series of type 6a single package tests were conducted on single drums of AP, each confined in all directions by 1 m (3.28 ft) of sandbags. In this test, a drum containing AP was placed on a steel witness plate (0.81 m $\times$ 0.81 m $\times$ 12.7 mm thick = 2.67 ft. by 2.67 ft. by 0.5 in.) at ground level. In all tests, the material thermally decomposed. There was no explosion, no overpressure

detected, and no rupture, splitting or fragmenting of the drum. In a second series of type 6a single package tests on single drums of AP confined in the same manner as in the first type 6a series, the initiation source was a No. 8 blasting cap. In this series, the AP also thermally decomposed and there was no explosion, no overpressure detected, and no rupture, splitting, or fragmenting of the drums. For control and information purposes, a single drum of AP was tested unconfined using an S94 squib and 56.7 g (2 oz) of FFF black powder as the ignition source. The ignition of the black powder caused the drum lid to pop off and ejected approximately one-third of the AP from the drum. The AP did not react or thermally decompose and there was no damage to the drum. The series of 6b stack tests were not conducted due to the lack of any explosive effect in either of the type 6a, single package test series. This is in accordance with paragraph 4.5.5 of the INTERREG standard. Based upon the interpretation of test results as outlined, AP nominal 200-micron particle size in 113.4 kg (250 lb) quantities in steel shipping drums does not meet the requirements for a Class I material.

Based upon laboratory test results, the West German representative to the UN Committee on the Transportation of Dangerous Goods recommended that AP of all particle sizes be classified as a Class 1.1 explosive [1339]. If this recommendation had been adopted, it would have had a drastic effect on the transportation of AP with commercial transports and military agencies. Under regulations that came into effect in 1982, only AP with a particle size less than 45 μm was considered a Class 1.1 explosive (the latest DARCOM regulation specifies 15 μm or less). Above 45 μm , AP was classified as a 5.1 oxidizer. In order to resolve this difference, a plan for conducting UN Test Series 6 for packaged AP, 200 μm size in 113-L, 113-kg (30-gallon, 250-lb) steel drums was developed in co-operation with the Joint Army Navy NASA Air Force (JANNAF) Inter-agency Propulsion Committee and US Army Development and Readiness Command (DARCOM) Safety Office.

As a result of challenges to the transportation hazard classification of AP by certain members of the United Nations' Committee on the Transport of Dangerous Goods, a test program was conducted by the US. Data was forwarded to the UN to retain a Class 5.1 designation (oxidizer) for AP, which is shipped internationally [1340]. As a follow-on to the initial team effort to conduct AP tests, the Chemical Propulsion Information Analysis Center (CPIAC) has researched existing data and compiled a matrix which catalogs test parameters and findings. These may be useful should questions of a similar nature arise in the future. Further to this, a collection of test protocols have been reviewed by a subgroup of the same UN Committee of Experts in an attempt to standardize test methods for energetic materials of all types.

Following the May 1988 explosion at Henderson, NV, some of the transportation hazard classification tests were repeated [1341]. The incident at PEPCON, Nevada, raised concern over the transportation and storage safety of 208L (55 gallons) DOT Specification 17H steel drums containing 227 kg (500 lbs) of AP and aluminum bins containing 2045 to 2770 kg (4500 to 5000 lbs) net weight AP meeting requirements of DOT Specification 56. As a result, these containers were subjected to a series

of additional transportation certification tests. Test procedures were patterned after the 1986 issue of the United Nations publication, *Recommendations on the Transport of Dangerous Goods: Test and Criteria*, (ST/SG/AC.10/11) Test Series 6, Section 41 through 44. The results of the tests for both drums and bins containing nominal 200- μ m particle size propellant grade AP confirmed the appropriate US DOT classification of AP as an oxidizer (ID number UN1442).

9.4 Recycling of Ammonium Perchlorate

Instead of open burning of AP-based solid propellants in aged missiles at the end of their useful life, water-jet cutting, and dissolving (“hogging out”) of AP-based propellants is a safer and environmentally more acceptable method of demilitarization. This provides an opportunity to recycle the AP that has been leached from the propellant.

There will be detailed chapters on the demilitarization of solid propellants in future volumes on solid propellants. This will include several AP-based propellants but will not necessarily involve recycling and re-using the oxidizer. The current chapter concentrates on recycling and re-using the washed-out AP oxidizer.

Liquid ammonia has been evaluated as a solvent system for the recovery of AP and other components from composite propellants

A solid-propellant ingredient reclamation pilot plant has been established at the Strategic Operations of Thiokol Corporation, located in Brigham City, Utah [1342]. The plant produced AP wet cake (95% AP, 5% water) for reprocessing at AP vendors. AP was extracted from two standard propellant binder systems (PBAN and HTPB as binders). Analytical work conducted at Thiokol indicated that the vendor-recrystallized AP meets Space Shuttle propellant specification requirements. One-, 5-, and 600-gallon propellant mixes were processed with the recrystallized AP. Processing, casting, curing, ballistic, mechanical, and safety properties were evaluated and compared to propellant made with fresh AP. Phillips Laboratory static-test-fired 70-lb_f and 800-lb_f Ballistic Test Evaluation Motors (BATES). The data indicated that propellant processed with reclaimed AP had nominal properties.

AP reclaimed using the water dissolving technique developed by the Thiokol Corporation was compared to two types of fresh AP in a PBAN propellant formulation [1343]. The reclaimed AP was directly substituted for the virgin AP. Side-by-side analyses of the reclaimed and virgin AP samples were performed to identify the chemical and physical properties of each. Variances for the propellant mixes were established in the areas of processing, mechanics, and ballistics. The PBAN and CTPB propellant formulations were scaled up to the 30-gallon mix size, and 70-lb BATES were cast and fired. Results revealed that reclaimed AP has the potential to be substituted for fresh material without any undue effects.

Titan-IV solid-propellant rocket motor segments were processed to recover the AP for reuse [1344]. Water used during processing was recycled in a closed-loop cycle

to save treatment costs and minimize the total volume required. The closed-loop AP recovery technology was first demonstrated during 1996 on a Minuteman Stage I solid-propellant rocket motor. After this technology was developed, byproducts from washout of solid propellant rocket motors were disposed of by open burning. The process used by Thiokol on Titan-IV solid propellant rocket motors recovered the AP from the washout refuse, thus eliminating the burn disposal. A Titan-IV rocket motor center segment was approximately ten feet in diameter and ten feet long. The weight was over 90000 lbs, which includes 70000 lbs attributed to the Class 1.3 solid propellant. Removal of propellant by hydromining and processing the removed propellant to recover AP was safely done and AP was recovered from the washed-out propellant.

Another system was designed to remove dissolved AP from the washout water by concentrating and precipitating the AP in an evaporator [1345]. The evaporator processes the 10% AP solution at 22 gallons/min and was designed to match the production rate of Thiokol's propellant washout facility. The AP slurry produced in the evaporator was dewatered by a centrifuge and automatically loaded into 55-gallon drums for reuse at the rate of 1000 lbm/h. Part of the evaporator system included equipment that sized the AP crystals. The recovered AP was 99% pure and could be reused in manufacturing new propellant. The end products of the process were crystalline AP and distilled water. The distilled water was recycled and returned to the propellant removal facility for reuse in washing out more propellant. As of the year 2000, the facility had been operating for approximately one year and had recovered 830000 pounds of AP and has evaporated 988000 gallons of AP washout water.

Among others, several (12 filament-wound segments and four unusable steel segments) Space Shuttle rocket motor segments (12 feet in diameter, 30 feet long, and over 300000 pounds each) have been washed out [1346]. The facility used high-pressure water to remove the propellant from the segments. Propellant removal rates of over 3000 lbm/h have been demonstrated. During the washout process, the majority of the AP in the propellant is leached into the process water. This water is then processed to reclaim the AP.

In addition to using water as the solvent for AP extraction from decommissioned propellant, ionic liquids have been evaluated as solvents that can serve at the same time as electrolytes for the destruction of perchlorate ions via electrochemical reduction [1347]. The electrochemical degradation of perchlorate ions and their conversion to harmless chloride during electrolysis was studied using IR and ^{35}Cl NMR spectroscopies.

Leaching AP from composite solid propellants is an internal diffusion process that is controlled by diffusion of water and AP in the propellants and the leaching-rate equation is a first-order dynamic equation [1348]. Surface topography of propellant samples before and after extracting AP with water was observed by using SEM [1349]. Results revealed that extraction time, extraction temperature, and the thickness of the specimen greatly affect the effectiveness of AP extraction while stirring speed had

little effect. The optimum extraction conditions were: An extraction time of six hours and extraction temperature of 353 K (80 °C), a mass ratio of raw materials to solution of 1:5, and a 2 mm thickness of shredded specimens. The extracting water was replaced twice. The AP recovery rate was 87%.

9.5 Disposal of Ammonium Perchlorate

The disposal of AP in aqueous solutions from propellant manufacturing processes and polluted groundwater sources has already been discussed in Section 8.9. The demilitarization of AP-based propellants and explosives poses a different problem.

Twenty years ago, a book like the one at hand would have dealt only with the industrial disposal of out-of-date propellant and of AP production waste streams. For the aged propellant, open-air burning would still have been listed as a disposal option. There are only very few facilities that can still perform open-air burning. In the meantime, the spread of perchlorate pollution has shifted the emphasis from the production wastes to those wastes that have already entered and spread throughout the environment. Consequently, environmental pollution clean-up methods have received stronger emphasis, a fact that is reflected by the number of publications cited in this book. Although the concentrations vary over several orders of magnitude, basically the same methods can be used for the destruction of perchlorate in aquifers, wastewater impoundments, and rocket motor washout effluents, including biochemical methods.

There are only relatively few publications that deal strictly with the controlled disposal of AP. After assuring the non-toxicity of AP against micro-organisms performing municipal sewage treatment, the biological reduction of AP to form inoffensive chemical species (N_2 , H_2O , Cl^-) was demonstrated using a two-step process with two ponds (lagoons). In the first one, under oxic conditions, the NH_4 was oxidized to NO_2^- and NO_3^- (nitrification). In the second the oxidized species were reduced to N_2 , H_2O , Cl^- under anoxic conditions. The overall process required carefully selected operating conditions and the addition of some nutrients [1350, 1351].

Other options for the disposal of AP production brines are concentration in solar ponds for solid-state landfill disposal or dilution with seawater and pumping it out to sea [1352].

9.6 Accident History of Ammonium Perchlorate

9.6.1 AP Production Accidents

Detailed descriptions of events leading to accidents and post-accident cause-and-effect analyses were published after the May 1988 AP explosion at PEPCON Henderson, NV [1353–1355]. The fire quickly spread through most of the facility by means of thermal radiation, firebrands, and a continuous source of fuel adjacent

to a powerful oxidizer [1356]. Two large explosions occurred during the fire, each on the order of a few hundred tons energy equivalents of TNT, claiming two lives, injuring 372 people, and damaging plant buildings as well as many buildings in nearby residential areas. During the early stages of the plant fire, a television tower maintenance crew atop a nearby mountain noticed the event and recorded most of it on videotape. The video record is unusual, spectacular, and a rare opportunity in fire/explosion investigation. It shows details of the rapid plant fire spread sequence, much of which occurred too quickly to be accurately recorded by any other means (Figure 49).



Figure 49: May 1988 AP explosion at PEPCON Henderson, NV. (From Wikipedia; AP-49-Henderson-AP-1988.jpg from https://en.wikipedia.org/wiki/PEPCON_disaster, Screenshot from a video taken by Dennis Todd, reuse licensed under CC BY 2.0.)

After the accident, an on-site accident investigation was conducted to determine the number and magnitude of explosions that occurred [1357]. Included in the investigation was the measurement of damage to many metal structures and objects throughout the plant. The locations of explosion centers were determined from craters and the direction of structural deformation. The deformation and standoff data were the basis for the calculation of blast yield for several explosions which occurred during the accident sequence.

Damages caused were surveyed and interpreted for their estimated causative air blast overpressures [1358]. Results were widely scattered by uncertainty in structural (primarily window glass) response as well as weather effects, but the total pattern of estimated overpressures versus distances generally agreed with a $1\text{ kt} = 1\text{ Gg}$ NE assumption for the airburst source strength. This would correspond to a 227 Mg HE surface burst. Since approximately 1.36 Gg AP were destroyed in the area of the largest single explosion, an HE explosive equivalence for AP appears to be about 1/6. Considering the yield-scaled response of overpressures to yield, there is no significant difference with an independent yield estimate of 454 Mg HE, made from close-in blast effects on easy-to-model structural elements (steel beams).

In the wake of this disastrous AP explosion, there was insufficient AP in storage to cover the production loss and to keep the US space program going while the cause of the accident was investigated and the plant was being rebuilt. For several decades, the US had the luxury of several AP producers. As a result of the temporary AP shortage in the US, the remaining AP had to be allocated to high-priority programs [1359].

American Pacific gained sole control of the industry in 1998 when Kerr-McGee sold its perchlorate operations to AMPAC.

9.6.2 AP Recycling Accidents

During the development of a propellant demilitarization and AP recycling process at Amtec, a mixture of AP and butanol ignited and exploded, killing two of the operators, Jim Hawke and Jerry Grimes.

On 20 February 2011, Major General Jim Rogers, Commanding General of U.S. Army Aviation and Missile Command (AMCOM) and Redstone Arsenal, announced the results of the investigation into the 5 May 2010 explosion at Building 7352, Test Area 10, on Redstone Arsenal. The investigation determined that the cause of the explosion was Amtec's operation of a particular type of decanter centrifuge to process potentially explosive materials. The investigation found that the deaths were the result of Amtec personnel conducting decanter centrifuge tests involving potentially explosive materials as an attended operation instead of running the tests remotely. Amtec was responsible for safety within Building 7352 pertaining to its operations. Amtec personnel selected, purchased, installed, and independently operated the decanter centrifuge. The investigation concluded that this type of centrifuge was unsuitable and unsafe for processing explosives. Responsible Amtec personnel did not develop safety procedures specific to the use of the centrifuge and exercised poor safety discipline. Amtec employees were working on demilitarization operations that involved AP. The goal was to develop the optimal process for achieving reclaimed dry AP at maximum recovery. To separate the AP, Amtec was using *n*-butanol as a solvent to dissolve away impurities from the AP. AP and *n*-butanol were mixed together to form a slurry. Amtec personnel were using a decanter centrifuge, which spins at high speed to remove the *n*-butanol from the AP and to dry the AP. AP wet with *n*-butanol has high chemical energy and can be explosive. During the process on 5 May 2010, friction from rotating parts inside the decanter centrifuge generated enough heat to cause a mixture of AP and *n*-butanol to ignite. The flame led to an explosion within the decanter centrifuge causing fragmentation and ultimately producing an intense fireball that engulfed personnel present in the building. The full press release may be found online [1360].

10 Explosive and Fire Hazards of Ammonium Perchlorate

The explosive properties and sensitivity of AP were determined by measuring shock and high-velocity impact sensitivities, minimum boosting requirements, the critical diameter for sustained propagation in unconfined charges, and by measuring "sensitivity" (air gap propagation or sympathetic detonation) determined in unconfined and barrel size charges [1361]. Detonation velocities and detonation pressures were also measured.

10.1 Drop Weight Impact Sensitivity of Ammonium Perchlorate

10.1.1 Drop Weight Impact Sensitivity of AP by Itself

The drop weight impact sensitivity of AP depends on the crystal size and on the humidity content. The drop weight sensitivity of AP can be reduced by coating or co-crystallizing with a few percent of ammonium tetrafluoroborate, which is isomorphous with AP and can form a solid solution at the interface [1362]. The 50% point of untreated AP was at 40 cm. By coating with 6, 10, or 20 mass.-% NH_4BF_4 , the sensitivity decreased and the drop height went up to 73, 77, or 82 cm. NH_4BF_4 has also been tested as an inhibitor in the thermal decomposition of AP.

The drop weight impact initiation of AP is related to the mechanical failure of the crystal creating hot spots. At the hot spot, the local temperature is limited by the incipient melting of the rapidly heated crystal. An investigation of the dependence of the pressure at which crystal fracture or explosion occurs as a function of the sample thickness (height, h) showed that the curves for mechanical fracture (open circle o symbols) and explosion (solid circle • symbols) connect seamlessly at a critical pressure P_{cr} level (Figure 50) [1363]. Tests were done with 10 mm and 17 mm diameter (D) samples of varying heights (h). For the 17-mm samples, the frequency of explosions as a function of D/h ratio went through a maximum. The transition from fracture to explosion takes place at a certain critical stress level of $8500 \text{ kg}_f/\text{cm}^2 = 83.4 \text{ kN}/\text{cm}^2$, indicated by a dashed line in Figure 50.

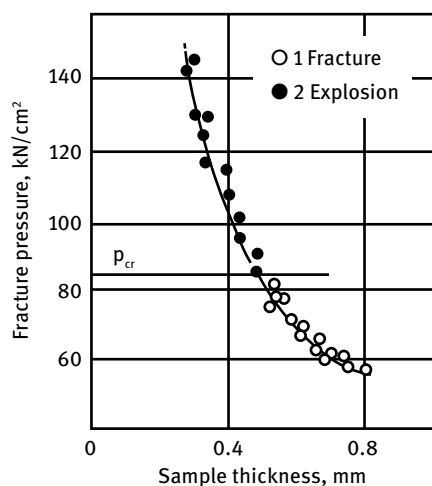


Figure 50: Pressure at which fracture (1) or explosion (2) of AP crystals occurs, 10 mm diameter samples. (Republished and modified from [1363], with permission of © 1969 Springer Nature BV; permission conveyed through Copyright Clearance Center.)

In drop-weight impact tests of a variety of materials including AP, AP ignited, coinciding with a sharp drop in its pressure-time curve, much like the behavior of RDX [1364]. This can be explained by a dislocation pile-up avalanche model to describe the local-

ized heating associated with such discontinuous load drop behavior and fracturing of the crystal as the load is released.

Following the May 1988 explosion at the PEPCON plant in Henderson, NV, an AP Management Steering Committee was established. In August 1988, a workshop was conducted at the Astronautics Laboratory, Edwards AFB, CA. The 21 experts representing government, industry, and academia attending this workshop developed a three-pronged study program. At the workshop the attendees were divided into three groups to address (1) transportation issues, (2) storage issues, and (3) fundamental properties and reactions. Each group was responsible for defining the major issues, concerns, and questions within their task area, and then for formulating a program plan to address the issues. During the workshop, and in subsequent meetings, the program became defined as the “*Determination of the Responses of AP to Thermal and Mechanical Shock Stimuli*”. In drop weight impact tests with 200 μm AP particles, the 50% threshold drop height was 100 cm, which is roughly two to three times that needed for HMX [650]. The drop height value for a co-crystallized 98:2 mixture of NH_4ClO_4 and KMnO_4 was 75 cm. When initiated by drop weight impact, AP does not propagate explosive response into adjoining material as would a high explosive. Drop weight impact threshold values for AP vary greatly depending on AP particle size and impurities. In the Bundesanstalt für Materialforschung und -prüfung (BAM) drop weight impact tester, the 50% point is at 15 Nm.

The effect of particle size of AP on impact sensitivity and friction sensitivity was systematically studied by using the Chinese standard methods GJB77A-97-601.1 and GJB77A-97-602.1 [1365]. The particle size ranged from 2.7 to 100 μm . The results demonstrated that the friction sensitivities and impact sensitivities of AP increase with the reduction of particle size. Considering that energy is consumed while breaking big particles into small ones, the small friction among the big particles and the sudden extinguishment of thermal decomposition of big particles cause big particles to be less sensitive to impact. The plastic deformation, viscous flow, and the part friction of crystals of small size particles result in an increase of friction sensitivities. The mechanisms and factors affecting mechanical sensitivity were theoretically analyzed from the point of view of physico-chemical changes of the AP ignition mechanism.

SEM, XRD, impact sensitivity, and friction sensitivity testing were done to characterize the micro-structures and mechanical sensitivity of different types of UFAP particles [1366]. The results revealed that the particles were very different in porosity, particle shape and size, crystal regularity degree, and crystal size. The mechanical sensitivity of UFAP samples is affected by so many micro-structural factors that it is difficult to establish a relation between the impact sensitivity and/or friction sensitivity and shape factors. The mechanical sensitivity of UFAP and its dependence on micro-structure can be explained by a hot-spot theory.

The effects of the particle size of AP on its impact sensitivity, friction sensitivity, and the burning rate of the propellants containing AP were investigated [66]. The relationship between particle size and critical initiation electron energy of AP particles,

which could be used to explain the change of sensitivity and burning rate with the particle size of AP, was analyzed.

Looking into what creates hot spots and makes AP crystals ignite during crushing impact, elastic, plastic, and cracking indentation measurements obtained in nano- to micro- to macro-indentation hardness tests of AP and RDX crystals were described on a hardness stress-strain basis and assessed in terms of a dislocation pileup avalanche mechanism for hot-spot generation associated with sudden crack formation [1367, 1368]. The model attempted to interpret particle size influence on the drop-weight height for 50% probability of onset of reaction, extended to include results for ϵ -HNIW crystals. Coatings and additives have been sought that would decrease instead of increase the sensitivity of AP.

10.1.2 Drop Weight Impact Sensitivity of AP Mixtures

The sensitivity of AP toward all stimuli, including drop weight impact, increases as AP becomes accidentally contaminated by or is intentionally mixed with organic combustible substances. Future volumes will contain sections of drop weight impact sensitivity of formulated composite propellants containing AP. Here we list mixtures with ingredients that are not solid propellant binders.

The mechanism of initiation by the impact of mixtures of AP with combustible additives was tested using AP and mixtures of AP with TNT or PMMA [1369]. The value of the critical stress of initiation of AP crystals was 8.5 kbar, while that of mixtures of AP with TNT or PMMA was substantially below that value depending on the AP : additive mixture ratio.

The excitation of an explosion by impact and the propagation of detonation under critical conditions differ in their physical nature but both depend on the interaction of the oxidizer and fuel components. In a study of the impact sensitivity of binary compositions containing AP, potassium perchlorate, or AN with metal powders or organic combustibles like polymers or hydrocarbons, an explanation of the role of chemical interaction between AP dissociation products and the fuel component or the products of its pyrolysis was based on examining processes at the interface between the oxidizer and combustible [1370].

Encapsulation of AP or other oxidizers protects the particles from moisture and aggregation during storage and propellant preparation and improves bonding with binders. Explosive substances like RDX, HMX, and PETN can be desensitized by encapsulation with polymers. However, this is not the case for AP. The opposite effect is observed and the sensitization makes further manipulation of propellant mixtures with coated oxidizers more hazardous. Impact sensitivities of AP coated with eight different polymers including bonding agents and binders were much higher than that of uncoated AP [81]. Coatings by encapsulation caused sensitization, while simple mixing did not lead to the same results. It is believed that the “hot spot” initiated by trapped air bubbles under impact is responsible for the sensitization since at high

polymer concentration the coated AP will recover its insensitivity. Experimental results suggest that particle size and specific heat play roles in sensitization.

A study of the impact sensitivity of two particle sizes of AP (ultra-disperse AP = UDP with particle diameter $d \leq 1 \mu\text{m}$ and nano-disperse AP = NDP with particle diameter $d \leq 0.1 \mu\text{m}$) and their mixtures with various inorganic combustible and inert materials (boron, aluminum, sulfur, carbon, fumed silicon dioxide, etc.) revealed that the mixture of AP with sulfur was the most sensitive combination tested [1371]. The sensitivity was expressed in terms of critical impact pressure σ_s at which a 50% probability of initiation was observed. The σ_s value of UDP was 175 mPa while that of NDP was 220 mPa. The relative position of these two numbers contradicts what has been written in other places about the effect of particle size on sensitivity. The critical pressure for AP/B mixtures was 127 mPa and that of an AP/S mixture was 47 mPa.

10.2 Threshold of Ammonium Perchlorate Detonations

Because AP is transported in bulk containers, the detonability of AP by itself or AP contaminated with other substances has been investigated extensively. We are discussing here only the explosion and detonation properties of AP itself.

The initiation and detonation behavior of 13- μm AP powder and pressed grains was studied at a loading density of 1.00 g/cm^3 [1372]. Steady detonation velocities were determined experimentally at three diameters and extrapolated to $3.75 \pm 0.15 \text{ mm}/\mu\text{s}$ at infinite diameter. Calculations with the Becker–Kistiakowsky–Wilson (BKW) equation of state resulted in $4.25 \text{ mm}/\mu\text{s}$, which is as good an agreement as could be expected for a low-energy chlorine-containing explosive. By introducing 24-kbar flat-topped plane shocks into pellets of various lengths, it was determined that steady full-strength detonation can be reached after about 15 mm of travel. The growth of pressure in the accelerating wave was followed approximately by means of free-surface measurements on thin Plexiglas at the top surfaces of the pellets. These measurements indicated the pressure to be $55 \pm 10 \text{ kbar}$ in the full-strength wave. Reducing the air pressure in the pressings to 5 μm Hg left the rate of pressure build-up to detonation unaffected.

The detonability of finely ground AP is dependent on particle size [1373, 1374], packing density, and charge diameter [1375]. The detonation velocity and critical density ρ_c of AP increased whereas the critical diameter decreased with decreasing particle size. The typical finite diameter D vs ρ_o curve is non-linear and exhibits a maximum in detonation velocity. The failure curve d_c (diameter) vs ρ_c (critical density) reveals a monotonic increase in D_c with ρ_c in the range $\rho_o > \text{ or } = 1.0 \text{ g/cm}^3$ and is opposite in trend to that for TNT. The detonability can be narrowed down more specifically with the card gap test. The gradient of the 50% gap pressure versus loading density curve at higher porosities is similar to that of the TNT curve.

Shock transit times in granular AP at 1.0 g/cm^3 bulk density have yielded a range of shocked states that exhibits a region of apparently positive slope in the pressure/

volume plane between three and ten kilobars and shocked specific volumes greater than the normal value of the crystal between ten and 70 kilobars [1376]. Correspondingly, the range is non-linear in the shock-velocity/particle-velocity plane. Thus, except for extremely weak shocks, AP fails to follow the collapsing aggregate model, a behavior that was ascribed to chemical reactions in initiating shocks. Because the shocked states were calculated from shock and particle velocities measured when the shock first enters the AP aggregate, it was proposed that reaction takes place in the shock front. Hot spots capable of causing such localized reactions have been photographed in large particle-sized aggregates at nominal pressures below 15 kbar.

Decomposition reactions of AP pressurized to 1.5 to 3 GPa were explosive at a heating rate of 10 °C per minute. [157]. Explosion limits were determined by heating compressed pellets of the salt at a slow and constant rate at a fixed pressure. Explosion limit curves (T against P) revealed that explosion temperatures increased with increasing pressure up to 3 GPa. The addition of small amounts of aluminum and copper chromite powders to AP and propellant reduced explosion temperatures from 10° to 60 °C, depending on the pressure.

UFAP handling, storage, and shipping properties were investigated with respect to product coatings, solid propellant formulation processing, and rocket ballistic parameters [43]. Applying hydrophobic coatings introduces combustible organic compounds into an oxidizer, resulting in an increase in the explosive sensitivity of the material. The sensitivity increases with the increasing content of coating material. Dry UFAP will detonate if confined and initiated by a blasting cap or a booster charge, although the detonation velocity may be low or tend to drop off rapidly. UFAP dust generally does not detonate, but one sample (freeze-dried with a relatively high coating content) did detonate in the dust state. AP/halocarbon-F113 suspensions, such as those encountered during the SWECO slurry grinding process, are not detonable as long as the F-113 content is at least 75 mass-%.

UFAP would have to be categorized as Explosive B for shipping purposes. It was attempted to dilute UFAP with coarse beads of an inert material for shipment that could be easily removed at the destination without contaminating the product. It was found that 10% Sorbeads (spherical shaped prills of fused silica gel) would prevent detonation at zero cards in the card gap test. Adding 30% Sorbeads as desensitizer would provide a margin for safety and avoids having to ship UFAP as Explosive B. However, not all grades of UFAP were equally desensitized. One advantage of adding Sorbeads was that they kept the humidity in the shipping container at very low levels and prevent agglomeration. Fumed silica would have the same effect [94].

In order to be on the safe side, a more accurate margin of safety in the deflagration-to-detonation transition of AP was determined [1377]. AP was placed in a sealed tube with reinforced walls and combustion was initiated at one end. The thickness of the tube and the power of the initiation stimulus were varied. AP with additives transits easily from combustion to detonation but pure AP does not do the same. In order to detonate AP, it is necessary to get a small particle size, very strong confinement, and a powerful initiation.

It is difficult to analyze the pressure profiles occurring in stationary detonation propagation in open charges of condensed explosives because of the substantial inhomogeneity. These difficulties can be eliminated by measuring the pressure profile in a wave produced in an intact confining rigid shell, which almost completely excludes lateral escape of energy. An electromagnetic method was used to measure the mass-velocity profile in the detonation of a tamped charge of AP in a strong shell [1378].

AP and AP-based HTPB composite propellant samples were subjected to shock initiation and the pressure was measured with Lagrangian gages [1379]. A pressed AP grain ($\rho = 1.7 \text{ g/cm}^3$) shocked to 4–5 GPa decomposed but did not detonate, while a similar grain shocked to 10 GPa detonated. At a modest shock pressure of 0.08 GPa, AP grains in the HTPB matrix were fractured and broken. Composite propellant containing 67% AP detonated with a velocity of 6.45 mm/s and a C-J pressure of 16 GPa.

It is surprising that 200 μm AP in large bins (with various shipping containers having capacity ranging from 114 kg to 2300 kg [250 to 5000 lbs]), when initiated with a No. 8 cap surrounded by FFF black powder, would just smolder and decompose but never transition to detonation [1341]. AP would slowly burn at one atmosphere pressure where a small mass of AP is heated to its decomposition temperature surrounded by enough insulating layers of AP so that lack of conductive heat loss allowed a slow deflagration to proceed at elevated temperatures. The black powder provided just enough heat to get a mass of AP to begin decomposing and exothermicity of AP decomposition sustained the process going to completion. The complete destruction of the AP in a 5000-lb container took an hour (see [1380] also).

10.3 Detonation Velocity of Ammonium Perchlorate Detonations

The detonation properties of AP (without additives) had been studied experimentally initially only for the (very) porous state. Andersen and Pesante [1381] reported detonation velocities of porous samples of AP and confirmed the dependence of detonation velocity on AP particle size. Their particle sizes were six and 13 μm (mean particle sizes for the various batches). Initiation of the charges to detonation was accomplished by No. 8 blasting caps and various amounts of tetryl booster, depending upon the dimensions of the AP charge. It was observed that steady-state detonation was usually established within about one charge diameter from the booster. Detonation velocities were measured over approximately the second half of the charge length, which is away from the booster and not overdriven. Unfortunately, the scatter in the measurements was significantly large such that “valid” values of D in an infinite geometry for the various densities of AP could not be extrapolated from their data. Nevertheless, they reported a summary equation, relating D and density:

$$D_i = 2688\rho + 1012$$

where D_i is the ideal detonation velocity for large diameter samples in m/s (to within ± 100) and ρ is the density in g/cm^3 . The results for a particle size of $6\mu\text{m}$ shown in Figure 51 were compared to detonation velocities as a function of charge diameter predicted by three different detonation theories: (1) nozzle theory, (2) curved-front theory, and (3) detonation-head theory but the agreement was only vague.

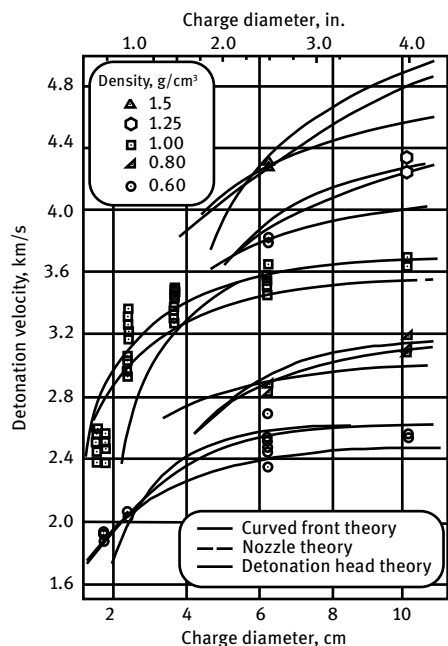


Figure 51: Detonation velocity as a function of charge diameter for different packing densities. (Reprinted and modified from [1381], © 1961, with permission from Elsevier; permission conveyed through RightsLink)

Price, Clairmont, Erkman, and co-workers [1382] built upon the 1961 work of Andersen and Pesante and took great care in preparing high-quality samples for their measurements and in documenting the particle size distributions of the AP batches. They tested a variety of batches (and hence particle sizes) of AP in their extensive studies on AP systems. Al powder was found to decrease the critical diameter when added to AP.

In their summary paper on PAP [1382] it was noted that particle size was not mentioned. Work with finely ground AP led to the infinite diameter relationship

$$D_i = 1.146 + 2.576\rho_o$$

where D_i is the detonation velocity in $\text{mm}/\mu\text{s}$ and ρ_o is the charge density in g/cm^3 over the range $0.55 \leq \rho_o \leq 1.0 \text{ g/cm}^3$. The quadratic mean error found was $0.040 \text{ mm}/\mu\text{s}$. Several computations of D_i as a function of ρ_o were summarized and compared with the experimental data. Estimated limits on the detonation temperatures were proposed [1383]. The lack of particle size information has been

found to be a deficiency in the presentation and analyses of the NOL data. In the 1968 study [1383], detonation velocity measurements were taken for AP mixtures containing 20% of HMX, PETN or 2,2,2-trinitroethyl-4,4,4-trinitrobutyrate (TNETB), indicating an oxidation-reduction reaction but for AP/HMX only. The AP in the other two mixtures contributed to the detonation velocity but the additivity rule does not seem to be applicable to mixtures of AP with organic high explosives.

The addition of fuels such as aluminum or wax will increase the energy output of AP. AP mixed with aluminum powder ("aluminized AP") or wax is a powerful explosive [255]. It could be that some solid propellant formulators would premix the AP and the Al or wax in the dry state before adding the binder but this should not be done without due precautions. Wax coatings may be used to prevent the agglomeration of AP crystals during storage.

AP by itself is not usually used as an explosive but the explosive properties of bulk quantities of AP are a matter of grave concern. In order to calculate the overpressure from accidental AP explosions, the detonation velocity must be known for various charge diameters and methods of initiation.

The detonation velocity of confined AP explosives was determined as a function of the charge diameter and the amount of nitroguanidine additive [1384]. Three particle size ranges of designated coarse (149 to 500 μm), medium (44 to 149 μm), and fine (1 to 44 μm) particles were investigated in a study of the effect of variable AP particle size upon the detonation characteristics of a typical AP composite system sensitized with 5% nitroguanidine [1385]. A decrease in AP particle size, which is already known to increase its propensity to detonate, increased the overall detonation velocity of the AP/NQ system by 5% NQ [1386].

Bulk sound speed measurements, isothermal volume compression/XRD experiments, and shock loading experiments (maximum pressure ~ 20 GPa) were performed for high initial density ($\geq 94\%$ theor. density) AN and AP [118]. The experimental data and full density Hugoniot calculated using that data suggested the presence of low-pressure, shock-induced phase transitions in both AN and AP. The AP phase transition occurs at ~ 4 GPa and exhibits characteristics of a high density to low-density phase transition but the presented data were not conclusive. The AN phase change occurs at a shock pressure of less than 3.5 GPa but the associated volume change is relatively large, indicating the presence of a previously unidentified high-pressure and high-density phase.

Published detonation velocities for AP systems have been reviewed in order to determine values for infinite diameter charges [1387, 1388]. These data have been evaluated in both the detonation velocity-density plane and the detonation velocity-reciprocal diameter plane. The interrelationship between these two planes was examined for both intermolecular and intra-molecular explosive formulations with AP. The importance of particle size in defining detonation velocities D_∞ at infinite diameter for AP-containing formulations is stressed and different interpretations of previously published data were suggested. For AP/wax systems, interesting comparisons have

been made for formulations containing 25 and 200 μm AP. Experimental data for PAP were compared to predictions of detonation velocities based on BKW parameter sets in TIGER.

Plane shock wave experiments were carried out on AP single crystals compressed along [210] and [001] orientations to peak stresses ranging from 1.2 to 6.2 GPa [123]. Quartz gauge and velocity interferometer techniques were used to measure the elastic and plastic shock wave velocities, and to record stress and particle velocity histories in the shocked samples. The measured Hugoniot elastic limit (HEL) was 0.48 ± 0.09 GPa. Above the HEL and up to about 6 GPa, the data revealed a clear two-wave structure, indicating an elastic-plastic response. Time-dependent elastic precursor decay and plastic wave ramping were discernable and orientation-dependent, but only in the low-stress data, although the orientation dependence of the peak state response was small. Data for both orientations were summarized into a single isotropic, elastic-plastic-stress relaxation model. Reasonable agreement was obtained between the numerical simulations using this model and the measured wave profiles. At a shock stress of about 6 GPa and for the time duration and crystal orientations examined, there were no features that could be identified as a sustained chemical reaction or a phase transformation.

10.4 Critical Diameter of Ammonium Perchlorate Detonations

AP of 70 ± 10 μm particle size was used for the following experiments (except the last one where the critical diameter was studied as a function of particle size) [1389]: The critical diameter of AP decreased with a sample temperature from 25 mm at room temperature to 10 mm at 473 K (200 °C), but the mode of confinement and the uncontrolled moisture content caused major variations. It was attempted to extend the experiments to higher temperatures but the AP phase change at 513 K caused the sample volume to swell and the glass tube burst before it could be detonated. Therefore, the samples were only heated to below 493 K. The critical diameter of AP is quite sensitive to the moisture content. It was noted that AP batches that were ground during different seasons of the year had different critical diameters, depending on the ambient relative humidity (winter versus summer) and the amount of moisture the material had picked up while it was ground and sifted. The squares and circles in Figure 52 identify batches processed at different times, named Batch 1 and Batch 2. The critical diameter in a glass tube increased linearly from 20 to 80 mm with a charge density of 1.1 g/cm^3 when the moisture was allowed to increase from 0.01 to 4 mass-%.

AP with 70 μm particle size was compressed to various packing densities and detonated. The critical diameter of AP detonations increased with charge density and so did the detonation velocity. The increase of critical diameter with charge density is somewhat surprising but can be explained in that the void spaces are rapidly compressed by the detonation wave and create hot spots similar to low velocity detona-

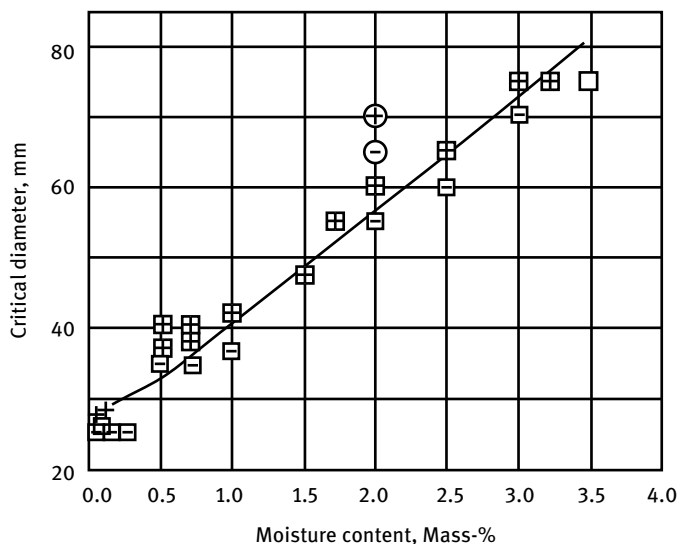


Figure 52: Critical diameter of AP explosions as a function of moisture content. (Republished and modified from [1389], with permission of © 1966 Springer Nature BV; permission conveyed through Copyright Clearance Center).

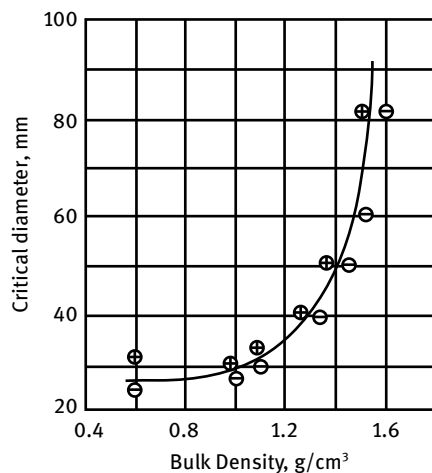


Figure 53: Critical diameter of AP explosions as a function of charge density. (Republished and modified from [1389], with permission of © 1966 Springer Nature BV; permission conveyed through Copyright Clearance Center).

tion (LVD) propagation. The circle symbols in Figure 53 indicate data from another source [1381].

The critical diameter of AP detonations decreased substantially and non-linearly with particle size, as shown in Figure 54. The charge density was 1.1 g/cm^3 , which is 56% of solid density. This illustrates the increased hazard in preparing and processing UFAP. The tests were performed with two sample geometries: eighteen to 20 cm

long cylinders with different (constant) diameters and cones with narrowing aspect diameters. The propagation in cones stopped once the critical diameter was reached. The square symbol indicates data from another source [1381]. Figure 3 on page 707 in [1381] shows the critical diameters of AP detonations for different particle sizes, packing density, and charge diameter, which is very useful information.

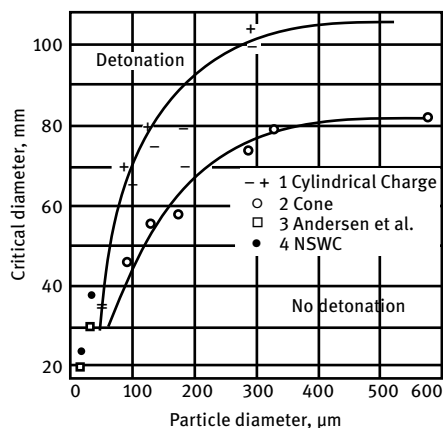


Figure 54: Critical diameter of AP explosions as a function of particle size. (Reproduced and modified from [1390].)

Other measurements indicate that even with a detonator and two ounces of FFF black powder 200-μm sized propellant grade AP cannot be detonated/exploded despite being detonable in diameters larger than four inches [1341]. The detonation velocity of 56-cm (22-in.) diameter drums of AP has been measured as being about 4 mm/μs. Lower AP detonation shock velocities have been observed at 25.4 cm (10 in.) diameter. Since detonation processes are much quicker than AP phase change, the AP orthorhombic crystal phase is the one typically involved in AP detonations (see [1390, 1374] also).

10.4.1 Modeling of AP Detonations

The detonation behavior of AP was studied to determine the effect of particle size and bulk density on the rate of energy release during detonation [1391]. A slightly divergent detonation model was used to describe the dependence of detonation velocity on charge diameter, and its results were compared to literature data. The chemical kinetic rate law resulting from parameterization of a group of data was then used to describe the heat release rate of the AP system at constant pressure. For low densities, the kinetic form agreed with the concept of hot spot formation and a grain burning reaction. At higher densities, the kinetics were found to exhibit a character more typical for thermal explosions. At any given density, the small particle material revealed a pronounced tendency toward thermal explosion. After solving the constant pressure case, additional calculations covered a pressure-dependent kinetic rate equation.

The compressibility and equation of the state of AP single crystals during shock compression normal to the (210) and (001) crystal planes was determined by velocity interferometer measurements up to 12 GPa [124]. The specific heat c_v , the coefficient of thermal pressure $(\partial P/\partial T)_V$, and the isothermal bulk modulus B_T were determined using Hugoniot and isothermal compression curves, along with available data at atmospheric pressure. It was suggested that any phase transition occurred either with a negligible change in volume or with very slow kinetics (see [227] also).

10.5 Detonation of Ammonium Perchlorate Mixtures

Small amounts of nitroguanidine (NQ) will sensitize AP so it will detonate more easily in a sympathetic detonation mode. Near-ideal detonations of NQ at densities of only 0.18 to 0.015 g/cm³ heavily diluted in AP have been achieved. The addition of NQ evidently induced a sympathetic detonation in the loosely packed AP [1384, 1392]. Amounts of NQ as low as 1% in AP will control the detonation rate of such NQ-AP composites. It appeared that the full energy of the AP is released in the detonation of these composites. It also appeared that charge diameters and confinement did not influence these results except when conditions became such that the AP itself could undergo non-ideal detonation. NQ at even lower concentrations in the vicinity of 0.01 g/cm³ detonated in an explosive composite with about 90% AP at 0.6 cm diameter in steel confinement or at 4 cm diameter in Plexiglass confinement. The detonation velocity of 5% NQ/95% AP was 2.03 km/s and the detonation velocity of 1.25% NQ/98.75% AP was 1.34 km/s. In all these studies the particle size of the AP remained unchanged, nominally 200 μ m Class C MIL SPEC AP. The effects of confinement and charge diameter on AP/NQ detonations were subsequently investigated. A study of the effect of variable AP particle size upon the detonation characteristics of an AP composite system sensitized with 5% NQ used three particle size ranges of designated coarse (149 to 500 μ m), medium (44 to 149 μ m), and fine (0 to 44 μ m) particles. This confirmed a general increase of detonation velocity with a decrease in AP particle size and also identified some anomalous behavior [1386].

10.6 Detonability of Ammonium Perchlorate Mixtures With Other Oxidizers

Occasionally AP is mixed with other oxidizers to achieve optimized performance properties of the mixture. For instance, AN-doped AP is tested as an environmentally more acceptable oxidizer since it releases less hydrogen chloride in its combustion products. However, some of these oxidizer mixtures have also been considered explosives [102, 1393]. Therefore, their safety properties must be known before production processes with such oxidizers are scaled up. Adding AP to explosives may boost their destructive power [1394].

Mixtures of AP with nitromethane are highly detonable and could be used as a two-component explosive. The propagation and extinction of detonation in heterogeneous mixtures of bead AP with mean particle diameters of 9, 35, 90, 200, and 400 μm was measured to study charge diameter effect on detonation velocity and critical diameter. The results were then graphed as a function of the equivalence ratio of the mixture and the size of particles [1395]. The reactive flow sustained by combining unburnt and burnt phases was modeled.

10.7 Explosive Yield of Ammonium Perchlorate

In the Trauzl lead block tests, the cavity volume increase of dry and densely packed AP is $195\text{ cm}^3/10\text{ g}$.

10.8 Friction Sensitivity of Ammonium Perchlorate

High purity 200 μm AP is relatively insensitive to friction with the Julius Peters Model 25 friction tester. Often a 36 kg force (the upper limit for the Julius Peters friction tester) is insufficient to reach AP ignition. AP-based propellants normally have threshold friction ignition values below 12 kg with the Julius Peters machine.

10.9 Bonfire Tests and Cook-Off of Ammonium Perchlorate

An INTERREG, Transport of Dangerous Goods, 1981 Edition, Type 6c bonfire test was conducted consisting of five drums each containing approximately 113.4 kg (250 lb) of AP that was steel-banded together and placed atop a steel crib that was approximately 1 m (3.28 ft) above the ground and surrounded by 0.5 m of lumber drenched with approximately 53 L (14 gallons) of diesel fuel and gasoline mixture (9:1 ratio) [1337]. The entire mass was ignited by two sets of electric matches and 56.7 g (2 oz) of black powder set 180 degrees apart at the base of the stack. The AP was consumed by the fire with no explosions, no overpressure detected, and no rupture, splitting or fragmenting of the drums. Additional information on solid perchlorate oxidizers can be found in [209].

11 Alkali Metal Chlorates and Perchlorates

Alkali metal chlorates have been used heavily in pyrotechnic formulations but their use is decreasing as more environmentally friendly substitutes become available. The problem with any mixture containing chlorates and fuel is their high friction and impact sensitivity. After AP, which was dealt with in the preceding section of this book, the second-most important perchlorate is potassium perchlorate. This is still used in many igniters and other pyrotechnic formulations because it has a much better thermal stability than AP and is less friction sensitive than potassium chlorate in mixtures. Sodium chlorate is mainly used for the onsite generation of OClO used in the pulp and paper industry. It is also used in emergency oxygen generating pyrotechnic formulations. Sodium chlorate is the precursor for sodium perchlorate, which is an intermediate in the production of AP and therefore its properties must be well-known. Lithium chlorate has an unusually low melting point and is very soluble in water. Lithium perchlorate is often used in mixtures with other perchlorates (AP, triaminoguanidinium perchlorate) to improve their properties. Of all the alkali metal perchlorates, LiClO₄ has the highest oxygen content (Table 24).

Table 24: Properties of alkali metal chlorates and perchlorates.

Name	Formula	CAS RN	Molecular mass, g/mol	Total oxygen, mass-%	Available oxygen, mass-%
Lithium chlorate	LiClO ₃	13453-71-9	90.397	53.08	53.08
Sodium chlorate	NaClO ₃	7790-93-4	106.445	45.08	45.08
Potassium chlorate	KClO ₃	3811-04-9	122.554	39.15	39.15
Lithium perchlorate	LiClO ₄	7791-03-9	106.392	60.14	60.14
Sodium perchlorate	NaClO ₄	7601-89-0	122.440	52.25	52.25
Potassium perchlorate	KClO ₄	7778-74-7	138.549	46.18	46.18
For comparison:					
Ammonium perchlorate	NH ₄ ClO ₄	7790-98-9	117.489	54.46	34.03

Although alkali metal and alkaline earth metal perchlorates are not used as rocket propellants, we have included some information on these salts here because they are sometimes used as additives and stabilizers or accelerators for AP and their decomposition mechanisms have been studied and compared to that of AP. The techniques now used for studying the reactivity of metal perchlorates can be later used to study the reactivity of AP and other energetic perchlorate salts, such as those derived from nitrogen bases.

The first edition of this book did not contain a separate chapter on metal perchlorates. They are not used as rocket propellants because the metal oxide thus formed as a combustion product adds to the non-condensables in the exhaust and results in poor

rocket performance. Alkali metal perchlorates are used mostly in pyrotechnic igniter mixtures and airbag gas generants. Properties of metal perchlorates are sufficiently summarized in other publications such as [1–6].

The Pearson 1969 summary in *Oxidation and Combustion Reviews* was preceded by an earlier version published as a government report [7]. The first edition of the Schumacher book was even translated into Russian in 1963. The introduction to Chapter 12 of that book contains sections on the “Environmental Effects of Perchlorates” and “Natural Occurrence of Perchlorates and Toxicity of Ammonium Perchlorate” which apply to alkali metal perchlorates as well.

11.1 Preparation of Alkali Metal Perchlorates

Sodium chlorate is mainly used for the onsite generation of OClO used in the pulp and paper industry. It is produced in a very power-intensive process where the formation of hydrogen bubbles on the cathode surface creates a circulation through the cell. Alkali metal perchlorates are prepared by electrochemical oxidation of the corresponding chlorates.

11.2 Physical Properties of Alkali Metal Perchlorates

The physical properties of alkali metal chlorates and perchlorates are summarized in Table 25. These salts form various hydrates but only the anhydrous salts are listed here.

It is difficult to determine a melting point for potassium perchlorate because of incipient decomposition and the lowering of the melting point due to the presence of decomposition products (KClO_3 and KCl). The melting point appears to be near 853 K (580 °C).

Table 25: Physical properties of alkali metal chlorates and perchlorates.

Name	Formula	Melting point		Density, g/cm ³ at 298 K
		K	°C	
Lithium chlorate	LiClO_3	400.9	127.8	2.596
Sodium chlorate	NaClO_3	521	248	2.489
Potassium chlorate	KClO_3	629–641	356–368	2.32
Lithium perchlorate	LiClO_4	509–530	236–247	2.429
Sodium perchlorate	NaClO_4	745	472	2.536
Potassium perchlorate	KClO_4	883 (dec.)	610 (dec.)	2.53

11.2.1 Solubility of Alkali Metal Perchlorates

The solubility of alkali metal perchlorates is of interest in the production and purification of perchlorates via recrystallization. It is also of interest for the recovery of perchlorates from propellants and pyrotechnic formulations that are demilitarized by leaching out the oxidizers. Environmental pollution by perchlorates has been identified as a major, long-lasting problem, and solubilities of perchlorates in water and other solvents must be known. The solubilities of alkali metal perchlorates have been summarized in Tables 26 and 27 [144].

Table 26: Solubility of alkali metal perchlorates in water.

Metal perchlorate	Solubility, g solute per 100 g of solution, at 298 K
Lithium perchlorate	37.5
Sodium perchlorate	67.8
Potassium perchlorate	2.0
For comparison:	
Ammonium perchlorate	20.0
Hydroxylammonium perchlorate	90.7

Data source: [1396]

Table 27: Solubility of alkali metal perchlorates in organic solvents.

Salt	Solubility, g salt per 100 g solvent, at 298 K		
	LiClO ₄	NaClO ₄	KClO ₄
Solvent			
Methanol	182.25	51.355	0.1051
Ethanol	151.76	14.705	0.012
1-Propanol	105.0	4.888	0.010
1-Butanol	79.31	1.864	0.0045
<i>iso</i> -Butanol	58.05	0.786	0.005
Acetone	136.52	51.745	0.155
Ethyl acetate	95.12	9.649	0.0015
Diethyl ether	113.72	insoluble	insoluble
Ethylene diamine	—	30.1	2.062
For comparison:			
Water	—	209.6	2.062

Data source: [144]

11.2.2 Thermodynamic Properties of Alkali Metal Perchlorates

The thermodynamic properties of alkali metal chlorates and perchlorates are summarized in Table 28. These salts form various hydrates but only the anhydrous salts are listed here.

Table 28: Thermodynamic properties of solid alkali metal chlorates and perchlorates.

Name	Formula	Heat capacity near 298 K		Enthalpy of formation, at 298 K		References
		J mol ⁻¹ K ⁻¹	cal g ⁻¹ °C ⁻¹	kJ/mol	kcal/mol	
Lithium chlorate	LiClO ₃	—	—	–369.0	–88.2	[1397]
Sodium chlorate	NaClO ₃	—	—	–365.8	–87.422	[1397]
		—	—	–360.3	–86.12	[1398]
Potassium chlorate	KClO ₃	100.2	23.96	–397.7	–95.06	[1397]
		—	—	–391.2	–93.66	[1398]
Lithium perchlorate	LiClO ₄	105	25.1	–380.74	–90.88	[202]
		—	—	–380.27 ± 1.21	–90.89 ± 0.29	[209]
Sodium perchlorate	NaClO ₄	111.22	26.6	–382.75	–91.5	[202]
		—	—	–382.75 ± 0.93	–91.48 ± 0.22	[209, 1398]
Potassium perchlorate	KClO ₄	110.97	26.52	–430.12	–102.8	[202, 1398]
		—	—	–431.9 ± 0.6	–103.22 ± 0.15	[1399]

The standard heat of formation of anhydrous lithium perchlorate is –383.6 kJ/mol (–91.70 kcal/mol) [1400]. The heat of solution of anhydrous lithium perchlorate and lithium perchlorate trihydrate in water (450 H₂O) at 298 K is –26.2 ± 0.1 kJ/mol (–6.25 ± 0.03 kcal/mol) and –33.1 ± 0.1 kJ/mol (–7.91 ± 0.03 kcal/mol), respectively.

11.3 Chemical Properties of Alkali Metal Perchlorates

11.3.1 Reactions of Alkali Metal Perchlorates

Anhydrous lithium perchlorate forms a stable adduct with dinitrogen tetroxide. This compound is formed if an excess of N₂O₄ is condensed onto LiClO₄ in a pressure vessel, allowed to stand at room temperature for a day or so, and the excess N₂O₄ evaporated and then pumped off at room temperature [1401]. The residue appears unchanged but it has gained weight according to LiClO₄•N₂O₄. Similar adducts can be formed with Mg(ClO₄)₂ or Ca(ClO₄)₂.

Lithium perchlorate and sodium perchlorate form hydrazinates with hydrazine [1402]. Independent of the concentrations of the starting materials, the complexes obtained were LiClO₄•2N₂H₄ and NaClO₄•N₂H₄. On grinding, the solid

complexes detonated but gentle heating in air or in vacuo in an open volume leads to the removal of the co-ordinated N_2H_4 without a detonation. IR spectra of $\text{LiClO}_4 \cdot 2\text{N}_2\text{H}_4$ revealed the presence of an ionic ClO_4^- (1100 cm^{-1}). A shift of N_2H_4 bands from the position of a free N_2H_4 molecule band indicated co-ordination to the Li^+ ion.

The dihydrazinate-perchlorate of lithium melts without decomposition but the monohydrazinate-perchlorate of sodium decomposes before melting. The alkali metal perchlorate hydrazinates are thermally not very stable and may auto-ignite upon heating [1403]. The compounds do not have a sharp melting point but gradually lose solvated hydrazine during heating before melting.

The combustion of the dihydrazinate-perchlorate of lithium and the monohydrazinate-perchlorate of sodium has been studied at 0.1–7 MPa. The oxidation of the combustible part of the complexes was incomplete. There was a clear relation between the rate of combustion and the surface temperature of the charge. The rate of combustion was determined by the oxidation of the hydrazine in the surface layer (molten) of the condensed phase [1404].

11.3.2 Thermal Decomposition of Alkali Metal Perchlorates

Good summaries on the thermal decomposition of alkali metal and alkaline earth metal chlorates and perchlorates (as well as bromates, perbromates, iodates, and periodates) are provided in [1398, 1405]. An earlier summary is now mostly of historical interest [1406]. These publications contain hundreds of literature references relating to this subject.

One of the most practical methods for the study of the decomposition of perchlorates and other energetic materials is by DTA [1407]. It has been noted that some of the energy released during exothermic decomposition of perchlorates is derived from crystallization of the higher melting chlorides as decomposition products.

When examining the rates of oxygen evolution during the decomposition of Na, K, Rb, and Cs perchlorates between 623 and 773 K, which were almost the same, it was suggested that the rate-controlling factor was a property of the ClO_4^- ion rather than the crystal lattice of the solid. This is possible if the neighboring ClO_4^- ions participate in a bimolecular interaction [1408]. The decomposition rates were determined by direct measurement of the O_2 evolution rate using a time-of-flight mass spectrometer. All four salts had nearly the same rate of decomposition below 683 K (410°C). Above 683 K (410°C) the rate of NaClO_4 was abnormally high.

A comparative study of the polymorphic transformations in ammonium and the alkali metal perchlorates using DTA developed correlations between the observed trends in the transformation temperatures and available crystallographic and thermodynamic data between these two groups of perchlorates [111]. Prior mechanical and thermal treatment resulted in a broadening of the hysteresis loops in the case of potassium perchlorate [743].

11.3.2.1 Thermal Decomposition of Lithium Perchlorate

LiClO_4 and NaClO_4 melt before they decompose. Because the activation energy of the decomposition reaction is about 270 kJ/mol, it was concluded that the rate-limiting step is the breaking of a Cl—O bond [1409]. The difference in behavior between sodium perchlorate and the other alkali metal perchlorates has been explained on the basis of the stability of the respective chlorates, formed during the LTD. This is substantiated by experiments that found that the addition of sodium chlorate to sodium perchlorate brings about a sensitization while potassium perchlorate admixed with potassium chlorate results in desensitization at high temperatures. Lithium perchlorate is stable in the melt at temperatures up to 663 K (390 °C). The degree of decomposition versus time curve of LiClO_4 exhibits an induction period and its shape is sigmoid, indicating an autocatalytic decomposition reaction.

The thermal decomposition of pure lithium perchlorate and in admixtures with lithium chloride was studied across the temperature range of 665–688 K (392–415 °C) by using constant temperature thermogravimetry [1410]. It was shown that above 520 K (247 °C) any mixture of lithium perchlorate with its decomposition product, lithium chloride, always contains the perchlorate in solution. Over the temperature range covered, the kinetics followed an autocatalytic rate law ($E_{\text{act.}} = 218 \pm 17 \text{ kJ/mol} = 52.2 \pm 4.1 \text{ kcal/mol}$) up to about 40% decomposition and then conform to first-order kinetics ($E_{\text{act.}} = 259 \pm 17 \text{ kJ/mol} = 62.0 \pm 4.1 \text{ kcal/mol}$). The point of transition between the two rate laws occurred when the decomposing melt was saturated with lithium chloride (see [1411]).

The isothermal decomposition of liquid lithium perchlorate in the presence of AgClO_4 has been studied between the temperature range of 523 and 673 K (250 and 400 °C) [1412]. The final products are primarily LiCl (precipitated as AgCl) and O_2 . Some ClO_2 and ClO_3^- is produced as an intermediate. The addition of lithium chlorate enhanced the decomposition. The relationship between this liquid melt decomposition and that of the solid alkali perchlorates [1408] was then discussed.

11.3.2.2 Thermal Decomposition of Sodium Perchlorate

Many alkali metal and earth alkaline metal perchlorates crystallize from aqueous solutions. Varying amounts of water is incorporated into the crystal lattice during crystallization. The water of hydration must be removed before the perchlorates can be used in rocket propellants and pyrotechnic formulations. In some cases, the chlorate or perchlorate may start to decompose before all water is removed. The dehydration of sodium perchlorate monohydrate proceeds in two stages corresponding to the removal of 0.2 H_2O and 0.8 H_2O per mol at 333 K (60 °C) and 423 K (150 °C), respectively [1413]. The thermal decomposition at 763 K (490 °C) was preceded by a phase transformation at 582 K (309 °C) (orthorhombic $\rightarrow$ cubic) and melting at 745 K (472 °C). Between 763 and 793 K (490 °C and 520 °C), the fractional decomposition (α) versus time (t) curves for molten NaClO_4 in vacuum were sigmoidal, thus indicating an autocatalytic process. The α , t isothermal data were best fitted by a first order autocatalytic

equation over the temperature range 763–793 K (490–520 °C). The activation energies for the two simultaneously occurring processes were 289.3 ± 5.4 and 208.9 ± 3.8 kJ/mol, respectively. The final solid product of the decomposition was sodium chloride in all cases.

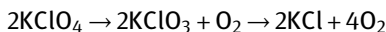
Sodium chlorate is thermally stable to well above its melting point. Decomposition starts near 673 K (400 °C). No Cl_2 or ClO_2 is formed during its decomposition. In contrast to the chlorate, the sodium perchlorate starts to decompose below its melting point. Therefore, it is difficult to determine the melting point of this chemical. In the decomposition of sodium perchlorate, sodium chlorate that is formed as an intermediate product decomposes just as fast as it is formed. Sodium perchlorate monohydrate loses water in a two-step process below 473 K and there is a phase transition between 569 and 588 K.

It is known that crystals that are undergoing decomposition often make crackling noises but very rarely have the noises been recorded and related to other evidence of decomposition that is in progress. Simultaneous measurements of acoustic emission (AE) by thermosonimetry (TS) and DTA during the thermal decomposition of KClO_4 and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ revealed that the AE technique successfully followed rapid decomposition and phase transition of these salts [1414]. In the case of KClO_4 , two extra AE signals were detected at 373–473 K (100–200 °C) and 474–573 K (200–300 °C), at which point no simultaneous thermal effect was observed on the DTA curve.

Melting and decomposition of NaClO_4 started at 723 K and continued up to 843 K. For NaClO_4 , TS curves corresponding to melting/decomposition and solidification of molten NaCl were found to consist of six peaks [1415]. During the decomposition of KClO_4 , three TS peaks appeared. The origin of these TS peaks is discussed on the basis of thermomicroscopic observations during which melting of the particles, evolution of bubbles of different sizes, the formation of solid products of varied morphologies, vigorous vibration of these solids, and precipitation of NaCl or KCl were observed.

11.3.2.3 Thermal Decomposition of Potassium Perchlorate

Potassium perchlorate, KClO_4 , underwent an endothermic phase transition from orthorhombic to cubic between 553 and 603 K. Melting and incipient exothermic decomposition starts at 858–903 K [1399]. If one plots the degree of conversion versus time, the curves for KClO_4 have a sigmoid shape and the pattern of kinetic behavior cannot be linked to a particular nucleation or autocatalyzed growth process. The acceleratory phase begins when the reactant forms a molten eutectic with its decomposition products (anions that contain less than four oxygens). The decomposition is a combination of concurrent and reverse reactions



The decomposition of KClO_4 is self-accelerating by a factor of 50 once decomposition starts.

When studying the thermal decomposition of (1) potassium perchlorate in powdered form, (2) potassium perchlorate in pelletized form, (3) potassium perchlorate recrystallized from liquid NH_3 , and (4) potassium perchlorate preheated for 24 hours at 648 K (375 °C) using DTA, it was discovered that the pre-treatment of potassium perchlorate leads to a desensitization of both endothermic and exothermic processes [1416]. The pre-treatment tends to convert the symmetric exotherm into an asymmetric exotherm due to the merging of the two exotherms. An analysis of the factors causing asymmetry in the exotherm has contributed toward understanding the mechanism of thermal decomposition of potassium perchlorate. The DTA of KClO_4 showed two endotherms, one at 573 K (300 °C) corresponding to the phase transition from orthorhombic to cubic and another around 873 K (600 °C) corresponding to melting of the eutectic mixture. The two endotherms were followed by an exothermic reaction. Other investigators found that KClO_4 has two endotherms and two exotherms. The first exotherm appeared after the melting endotherm at 879 K (606 °C). Its exothermicity decreased as it reached 909 K (636 °C). At this point, a sharp rise in exothermicity occurred, with a peak at 914 K (641 °C) followed by the rapid decay of the exotherm.

DTA was used to understand the influence of particle size on the decomposition of KClO_4 [1417]. DSC curves of KClO_4 , with different particle sizes, revealed an endothermic peak from a phase transition close to 581 K (308 °C) and a melting point at 881 K (608 °C). DTA curves produced similar results. The percentage of mass loss in the TGA curves of decomposition for the reaction of $\text{KClO}_4 \rightarrow \text{KCl} + 2\text{O}_2$ was close to the theoretical value (46.18%). The initial decomposition temperature of KClO_4 with smaller particle sizes was shifted to lower temperatures, and the decomposition activation energies of KClO_4 ranged from 231 to 269 kJ/mol.

11.3.2.4 Effects of Catalysts on Perchlorate Thermal Decomposition

The effects of catalysts, typically metal oxides known to be active as burning rate catalysts, on the thermal decomposition of AP has already been described in detail. Similar studies were performed on the thermal decomposition of alkali metal perchlorates in the presence of catalysts, and the insights gained from those tests can help in the interpretation of decomposition mechanisms of AP, which is of significantly greater practical interest than the alkali metal perchlorates. The effect of burning rate catalysts, mostly metal oxides and mixed metal oxides on the burning rate and rate of thermal decomposition of perchlorates by themselves and in propellant and gas generant compositions has been extensively investigated (See Section 4.6.8.1). In an attempt to determine if the catalysts aid in the decomposition of the ammonium ion or the perchlorate ion, many of the experiments have been repeated with alkali metal perchlorates instead of AP. Catalysts investigated included iron(III) oxide, manganese(IV) oxide, and others.

The catalytic decomposition of sodium and potassium chlorates and perchlorates was examined by TGA at low temperatures where there is practically no dissociation in the absence of a catalyst [1418–1420]. These experiments used salt crystals with a diameter of 0.14–0.20 mm mixed with 1% MnO_2 and heated. The degree of decomposition of the specimen (300 mg) was recorded by using TGA. Surface diffusion apparently plays an important role in reaction kinetics.

As observed via DTA and gas evolution measurements, KClO_4 and NaClO_4 , on heating at $4.5^\circ/\text{min}$, underwent an endothermic phase change at 579 and 577 K (306 and 304°C), melting at 848 and 741 K (575 and 468°C), respectively. They then decomposed with the liberation of two mols of oxygen gas at 893 and 834 K (620 and 561°C) [1421]. LiClO_4 did not undergo a phase change but melted at 514 K (241°C) and decomposed at 762 K (489°C). In the presence of a catalyst made of a 2:1 mixture of MnO_2 and NiO , decomposition occurred at 793, 701, and 645 K (520, 428, and 372°C) for KClO_4 , NaClO_4 , and LiClO_4 , respectively. Following a critical evaluation of literature data, the heat of formation of KClO_4 was selected as -426 kJ/mol (-101.9 kcal/mol).

The effects of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ additives on the thermal decomposition of perchlorates were investigated by means of DTA, TGA, and XRD [1422]. It was found that the oxide additives catalytically promoted the decomposition of perchlorates [NaClO_4 , KClO_4 , and $\text{Mg}(\text{ClO}_4)_2$] and resulted in a lowering of the initial decomposition temperature. When comparing the catalytic effect of twelve metal oxides, the transition metal oxides such as Cr_2O_3 , $\alpha\text{-Fe}_2\text{O}_3$, and CuO markedly accelerated the decomposition of potassium perchlorate. These oxides resulted in a solid-phase decomposition before fusion of KClO_4 . The initial decomposition temperature of KClO_4 with oxides was about $100\text{--}200^\circ\text{C}$ lower than that without catalyst. Inert oxides such as $\alpha\text{-Al}_2\text{O}_3$ and MgO resulted in a slight lowering of the temperature of the fusion and promoted the molten-phase decomposition of KClO_4 , but their effects were not as remarkable as those of the transition metal oxides. The catalytic mechanism of transition metal oxides may involve electron transfer and oxygen abstraction.

The thermal decomposition of potassium perchlorate in the presence of various metal oxides was investigated by programmed TGA and by isothermal weight loss techniques [1423]. The effect of metal oxide concentration on the temperature of initial deflection, T_i , of TGA curves of metal oxide/potassium perchlorate mixtures was determined. The Arrhenius parameters were tabulated to demonstrate the effect of metal oxide concentration on the activation energy and rate of decomposition of potassium perchlorate.

The catalytic effect of $\alpha\text{-Fe}_2\text{O}_3$ on the thermal decomposition of KClO_4 was studied using TGA and DTA methods [1424]. DTA and TGA curves showed that the addition of $\alpha\text{-Fe}_2\text{O}_3$ led to an acceleration effect on the solid-state decomposition of KClO_4 . The acceleration effect increased with a decrease in the preparation temperature and an increase in the amount of $\alpha\text{-Fe}_2\text{O}_3$ added. The decomposition rate constant, k , was estimated from TGA curves by assuming a first-order rate law. An Arrhenius plot of k demonstrated a straight line that had a sharp bend at the temperature T_B , which was

characteristic of the respective $\alpha\text{-Fe}_2\text{O}_3$ sample. It was suggested that the solid-state decomposition proceeded below T_B and the liquid-state decomposition above T_B . The activation energy of the solid-state decomposition, E_a , of pure KClO_4 was 328 kJ/mol (78.4 kcal/mol) and those of $\text{KClO}_4 + \alpha\text{-Fe}_2\text{O}_3$ mixtures were 224, 252, and 254 kJ/mol (53.6, 60.2, and 60.8 kcal/mol) for the oxide prepared at 773, 923, and 1273 K (500, 750, and 1000 °C), respectively. The activation energy of the liquid-state decomposition, E_a , for pure KClO_4 was 633 kJ/mol (151.4 kcal/mol) and those of $\text{KClO}_4 + \alpha\text{-Fe}_2\text{O}_3$ mixtures were in the range 618–642 kJ/mol (147.8–153.4 kcal/mol).

In a similar series of tests, the effect of copper/manganese oxides (MnO_2/CuO in different atomic ratios $[\text{Cu}/(\text{Cu} + \text{Mn}) = x$, where $x = 0\text{--}1]$ on the rate of non-isothermal decomposition of KClO_4 was measured. The results were interpreted assuming an electron transfer mechanism [1425]. The enhancement effect of trace Cu(II) added to the host oxide MnO_2 was attributed to an increase in the exchange capacity of manganese cations between the different oxidation states. The retarding effect associated with Cu(II) -rich samples was attributed to the trapping of the electrons required to initiate the decomposition reaction by the lattice defect holes created. On the basis of the applicability of a non-isothermal kinetic equation, it was demonstrated that two main stages are involved in the decomposition process.

The catalytic effect of chromites on the non-isothermal decomposition of KClO_4 was studied using TGA and DSC [1426]. Reactions of KClO_4 -alkaline earth chromites mixtures indicated the formation of $\text{K}_2\text{Cr}_2\text{O}_7$, through a solid-solid interaction, before accelerating the decomposition stage of KClO_4 . Such an accelerating effect became more pronounced in the case of admixing KClO_4 with some transition metal chromites. The kinetic parameters and models describing the catalyzed thermal decomposition process of KClO_4 were evaluated by using a computer program that facilitated analysis using five different methods. It was found that the adopted kinetic model for pure KClO_4 and that mixed with catalysts is a one-dimensional movement of phase boundary. On the other hand, a random nucleation mechanism was achieved in the presence of other catalysts.

12 Alkaline Earth Metal Chlorates and Perchlorates

Because alkaline earth metals are bivalent, they can carry two chlorate or perchlorate ions instead of only one as in the alkali metal salts. That gives a potentially higher percentage of oxygen in the molecule. Unfortunately, most alkaline earth perchlorates are extremely hygroscopic; so hygroscopic that magnesium perchlorate is being used as a desiccant (Anhydron[®]), which is easier to use and clean up than phosphorus pentoxide. Properties of alkaline earth metal chlorates and perchlorates are summarized in Table 29. These salts form various hydrates with water but only the anhydrous salts are listed here. The solubilities of alkaline earth metal perchlorates have been summarized in [145]. These salts also form stable complexes where ammonia or hydrazine

Table 29: Properties of alkaline earth metal chlorates and perchlorates.

Name	Formula	CAS RN	Molecular mass, g/mol	Total oxygen, mass-%
Magnesium chlorate	Mg(ClO ₃) ₂	10326-21-3	191.21	50.20
Calcium chlorate	Ca(ClO ₃) ₂	10137-74-3	206.98	46.38
Strontium chlorate	Sr(ClO ₃) ₂	7791-10-8	254.52	37.72
Magnesium perchlorate	Mg(ClO ₄) ₂	10034-81-8	223.206	57.34
Calcium perchlorate	Ca(ClO ₄) ₂	13477-36-6	238.9792	53.56
Strontium perchlorate	Sr(ClO ₄) ₂	13450-97-0	286.52	44.67
Barium perchlorate	Ba(ClO ₄) ₂	13465-95-7	336.23	38.07
For comparison:				
Ammonium perchlorate	NH ₄ ClO ₄	7790-98-9	117.489	54.46

is absorbed as the ligands. We have omitted the lowest members of this family, poisonous beryllium chlorate and beryllium perchlorate, because it is unlikely that anyone would want to use them as rocket propellants due to their toxicity. Magnesium perchlorate crystallizes with six mols of water in the hydration sphere.

12.1 Physical Properties of Alkaline Earth Metal Chlorates and Perchlorates

The physical properties of alkaline earth metal chlorates and perchlorates are summarized in Table 30. These salts form various hydrates but only the anhydrous salts are listed here.

In view of the discovery of perchlorates on Mars and their possible contributions to saturated aqueous solutions saline brine capable of surviving in underground aquifers at the low atmospheric pressure of Mars, the physical properties of alkaline earth perchlorates and their solutions have gained new significance.

Table 30: Physical properties of alkaline earth metal chlorates and perchlorates.

Name	Formula	Melting point		Density, g/cm ³ at 298 K	Enthalpy of formation kJ/mol
		K	°C		
Calcium chlorate	Ca(ClO ₃) ₂	613	340	2.71	—
Strontium chlorate	Sr(ClO ₃) ₂	393 (dec.)	120 (dec.)	3.15	—
Magnesium perchlorate	Mg(ClO ₄) ₂	524	251	2.21	−568.90 or −588.3
Calcium perchlorate	Ca(ClO ₄) ₂	543	270	2.651	−736.76
Strontium perchlorate	Sr(ClO ₄) ₂	—	—	3.02	—
Barium perchlorate	Ba(ClO ₄) ₂	778	505	3.2	−796.26 ± 1.35

Various metal (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , and Al^{3+}) perchlorate salts were studied to provide spectral and thermal data for remotely detecting and characterizing their possible presence on Mars [1427]. Spectral and thermal analyses in combination with structural analyses were needed to understand how different cations and different hydration levels affect the perchlorate mineral system in the soil. Near-IR spectral features for perchlorates are dominated by H_2O bands that occur at 0.978–1.01, 1.17–1.19, 1.42–1.48, 1.93–1.99, and 2.40–2.45 μm . Mid-IR spectral features are observed for vibrations of the tetrahedral ClO_4^- at $1105\text{--}1130\text{ cm}^{-1}$ ($\sim 8.6\text{--}9\text{ }\mu m$), $760\text{--}825\text{ cm}^{-1}$ ($\sim 12\text{--}13\text{ }\mu m$), 630 cm^{-1} ($\sim 15.9\text{ }\mu m$), $460\text{--}495\text{ cm}^{-1}$ ($\sim 20\text{--}22\text{ }\mu m$), and $130\text{--}215\text{ cm}^{-1}$ ($\sim 50\text{--}75\text{ }\mu m$). The spectral bands in both regions are sensitive to the type of cation present because the polarizing power is related to the band center for many of the spectral features. DSC data revealed variable patterns of water loss and thermal decomposition temperatures for perchlorates with different cations, consistent with changes in spectral features measured under varying hydration conditions. Results of the DSC analyses indicated that the bond energies of H_2O in perchlorates are different for each cation and hydration state.

Perchlorates found in the Martian regolith offer a new opportunity for ISRU [1428]. Mars offers an abundant source of perchlorates with confirmed measured concentrations upwards of 1% detected at two landing sites. Methods for extracting perchlorate compounds and separating them into more useable constituents are under consideration. Potential uses are *in-situ* breathing oxygen production and solid oxygen candles for astronauts. An additional and promising use would be the direct mixing of the perchlorate compounds as the solid oxidizer in a solid rocket motor configuration using a suitable binder and fuel combinations. The first settlers will have to take a small chemical factory with them to make use of this resource.

Alkaline earth metal perchlorates form energetic complexes with carbohydrazide. The crystal structures, density of states, energy gap, thermodynamic properties, impact sensitivities, and the morphology of alkaline-earth metal carbohydrazide perchlorates $[Me(CHZ)_3](ClO_4)_2$, $Me = Be, Mg, Ca, Sr, Ba$, were investigated using the DFT and crystal morphology theory [1429].

12.1.1 Thermodynamic Properties of Alkaline Earth Metal Chlorates and Perchlorates

The enthalpies of solution of N_2H_4 complexes of Mg , Ca , Sr , and Ba perchlorates in diluted HCl were related to the enthalpies of solution of the metal perchlorates in water [1430]. The standard enthalpies of formation were calculated for the complex salts $M(ClO_4)_2 \cdot 2N_2H_4$ ($M = Mg, Ca, Sr, \text{ and } Ba$) and $M'(ClO_4)_2 \cdot N_2H_4$ ($M' = Ba, Sr, \text{ and } Ca$) and similar ammonia complexes.

12.2 Properties of Specific Alkaline Earth Metal Chlorates and Perchlorates

12.2.1 Magnesium Perchlorate

Magnesium perchlorate is very hygroscopic and decomposes at above 523 K (250 °C). It is sold under the trade name Anhydron[®] or Dehydrite[®]. It is used as a desiccant to dry gas samples or to dry solid samples in a desiccator, however, it is no longer advised for use as a general desiccant due to potential hazards posed by perchlorates in contact with combustibles. It can be regenerated by applying heat at 493 K (220 °C) under vacuum. Magnesium perchlorate is stable up to 320 °C when carefully dried. In the presence of moisture, it may decompose at temperatures below 320 °C. Traces of moisture lower its melting point substantially. The heat of formation of magnesium perchlorate is -568.90 kJ/mol.

Anhydrous magnesium perchlorate forms a stable adduct with dinitrogen tetroxide. This compound is formed if an excess of N₂O₄ is condensed onto Mg(ClO₄)₂ in a pressure vessel, allowed to stand at room temperature for a day or so, and the excess N₂O₄ is evaporated then pumped off at room temperature [1401]. The residue will appear unchanged but it will have gained weight according to Mg(ClO₄)₂•N₂O₄. The density was 2.199 g/cm³ (compared to 2.21 g/cm³ for Mg(ClO₄)₂). It decomposed when heated above 344 K (70 °C) and evolved brown fumes. Similar adducts can be formed with LiClO₄ or Ca(ClO₄)₂.

12.2.2 Calcium Perchlorate

Calcium perchlorate is very hygroscopic. The most common way of keeping it in the laboratory is in the form of its calcium perchlorate tetrahydrate, Ca(ClO₄)₂•4H₂O.

12.2.3 Strontium Perchlorate

The heat capacity of Sr(ClO₄)₂ at 10–340 K was measured by using vacuum adiabatic calorimetry and the standard thermodynamic functions were derived [1431]. Strontium perchlorate is an ingredient in pyrotechnic formulations. Injection of strontium perchlorate solutions into solid propellant motor nozzles was used for thrust vector control.

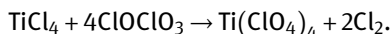
12.2.4 Barium Perchlorate

Barium perchlorate is used as the oxidizer in some igniter pyrotechnic mixtures. Barium perchlorate decomposes at 778 K (505 °C). The heat capacity of Ba(ClO₄)₂ at 10–350 K was measured via vacuum adiabatic calorimetry and standard thermodynamic functions were derived [1432]. Barium perchlorate is an ingredient in pyrotechnic formulations.

12.3 Other Metal Perchlorates

Another metal perchlorate that is frequently used for metathetical reactions in the synthesis of energetic organic amine perchlorates is silver perchlorate.

Perchlorates of polyvalent metals like titanium or chromium can form perchlorates with more than two perchlorate ions in the molecule and a correspondingly very high available oxygen content. Titanium tetraperchlorate and chromyl perchlorate can be prepared using chlorine perchlorate and the respective metal chlorides [1433, 1434].



These anhydrous metal perchlorates were found to contain bidentate perchlorato ligands. The thermal stability of $\text{Ti}(\text{ClO}_4)_4$ was examined in closed bomb tests. After one hour at 388 K (115°), the decomposition was incomplete, as evidenced by the recovery of less than the theoretical amount of oxygen in the form of O_2 and Cl_2O_7 . After four hours at 388 K (115°C), approximately half the oxygen content of the $\text{Ti}(\text{ClO}_4)_4$ was converted to O_2 and half to Cl_2O_7 .

Chromyl perchlorate is a dark red liquid with less than 1 mm vapor pressure at room temperature. Its high reactivity and low stability precluded successful transfers for property measurements. $\text{CrO}_2(\text{ClO}_4)_2$ decomposed on heating according to the equation:



AP or lithium perchlorate can form double salts with boron perchlorate or aluminum perchlorate, which might make useful solid propellant oxidizers, but they are not very stable and no applications have been reported. Very little has been published about these double salts. Properties of some of these double salts are listed in Table 31.

Ammonium or lithium perchlorate forms complex perchlorates with $\text{Al}(\text{ClO}_4)_3$ or $\text{Zn}(\text{ClO}_4)_2$ resulting in the formation of $\text{NH}_4\text{Al}(\text{ClO}_4)_4$ and $\text{LiZn}(\text{ClO}_4)_3$ [1436].

13 Nitronium (Nityl) and Nitrosonium (Nitrosyl) Compounds

It has been attempted to use the tetrafluoroborates and perchlorates of nitrosyl (NO^+ , also called nitrosonium) and nityl (NO_2^+ , also called nitronium) cations as rocket propellant oxidizers. This concept is especially attractive because not only the anion (as in traditional solid propellant oxidizers) but also the cation contributes useful oxygen. These compounds have the highest available oxygen content of any solid oxidizer known to chemists.

In organizing the vast amount of information on rocket propellant oxidizers, a decision had to be made of whether nitrosonium and nitronium oxidizer salts should be discussed under nitrogen oxides where the cation is derived from or under various chapters for the anions like perchlorate and tetrafluoroborate. A similar decision had

Table 31: Properties of perchlorate double salts.

Composition		Tetraperchlorates				Hexaperchlorates			
Formula		$\text{NH}_4\text{B}(\text{ClO}_4)_4$	$\text{NH}_4\text{Al}(\text{ClO}_4)_4$	$\text{NO}_2\text{B}(\text{ClO}_4)_4$	$\text{NO}_2\text{Al}(\text{ClO}_4)_4$	$(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$	$(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$	$\text{Li}_3\text{Al}(\text{ClO}_4)_6$	
Molecular mass, g/mol		426.688	442.848	454.656	470.816	677.842	761.746	644.542	
Density, g/cm ³		2.26	2.20	2.15	2.34	2.09	2.35	2.48	
Decomposition temperature, K		343–353	363–383	353–363	363–373	453–473	443	463	
Decomposition temperature, °C		70–80	90–110	70–80	90–100	180–200	170	190	
Enthalpy of formation, kJ/mol		–335	–845	–607	–460	–1456	–502	–795	
Enthalpy of formation, kcal/mol		–80	–202	–145	–110	–348	–120	–414	
Available oxygen, mass-%		54.4	54.4	63.3	63.3	46.0	63.0	59.6	

Data source: [1435]

to be made for the oxonium salts. It was decided to give the cations priority over the anions for the simple reason that we are used to listing the cation part of salts first and the anion part last. Perchlorates of nitrogen bases (amines, heterocyclic nitrogen bases) are discussed along the same lines in *Encyclopedia of Liquid Fuels*, under fuels, although some of them are potential oxidizers. At least the free amines from which they are derived are liquid fuels.

In the early days of nitronium (nitryl) chemistry, it was assumed that the reaction of nitric acid with perchloric acid would produce “nitracidium” perchlorates, the cation being a singly (or even doubly) protonated nitric acid. This was caused by problems with removing adhering nitric acid from the nitronium perchlorate product. This delayed the recognition of NO_2^+ as an entity of its own.

Nitrosonium and nitronium compounds are difficult to prepare and most are thermally unstable. Since none of them have found practical applications so far, we discuss them here mostly for their academic interest. They are very moisture sensitive and will hydrolyze spontaneously.

Whereas traditional inorganic oxidizers, such as potassium nitrate or potassium perchlorate, carry the alkali metal cation only as ballast and actually an oxygen sink, the nitrosonium and nitronium cations contribute useful oxygen to the overall oxygen balance of the compounds. Some nitrosonium and nitronium compounds, e.g., the fluorides and chlorides, are liquids and have more covalent bond character. Some of them have already been discussed in *Encyclopedia of Oxidizers*, chapter “Nitrogen Fluorides”. The nitrosonium and nitronium compounds discussed here have more saline character and are solids at room temperature. That is one reason why some chemists suggest that the words nitryl and nitronium should designate two different forms of NO_2 : a covalent bond bound form and an ionized salt form. The same has been argued for nitrosyl and nitrosonium.

Nitronium and nitrosonium salts can be prepared via the interaction of nitryl and nitrosyl chloride with anhydrous HF and Lewis acid fluorides [1437].

13.1 Nitronium (Nitryl) Salts

The most stable nitronium compound appears to be the nitronium tetrafluoroborate $\text{NO}_2^+\text{BF}_4^-$. This salt has been widely used to achieve nitrations, nitrosations, and diazotizations in organic chemistry. It can also be used as an intermediate in preparing nitronium perchlorate via metathetical reactions. It has also been proposed as an oxidizer in rocket propellants, however, it would be less energetic than the perchlorates.

13.1.1 Nitronium Perchlorate

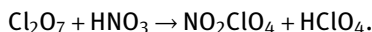
The most attractive compound as a rocket propellant in this category of oxidizers with unusual cations is nitronium perchlorate, NO_2ClO_4 , also known as nitryl perchlorate

or nitroxyl perchlorate, CAS RN [17495-81-7], which has a useful oxygen content of 66 mass-%. A very good summary of nitronium perchlorate properties is provided by Pearson [2] on pages seven through to 15.

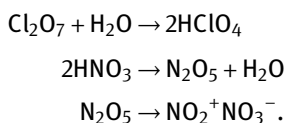
13.1.1.1 Preparation of Nitronium Perchlorate

Nitronium perchlorate was first discovered in the reaction products of concentrated perchloric acid and white fuming nitric acid. This reaction does not produce pure NO_2ClO_4 but a mixture of several compounds, including perchloric acid monohydrate and a double perchlorate $[\text{H}_3\text{O}^+][\text{NO}_2^+][\text{ClO}_4^-]_2$. The formula for the double perchlorate has also been written in the form $[\text{H}_3\text{NO}_3^{++}][\text{ClO}_4^-]_2$. For a long time, nitronium perchlorate was made by a liquid-phase reaction of dinitrogen tetroxide with perchloric acid in nitromethane as a solvent. Products from this procedure lacked thermal stability.

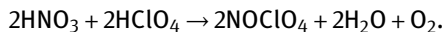
A better procedure is the reaction of dichlorine heptoxide with nitric acid. This forms a white solid, which is a mixture of anhydrides of perchloric acid and nitric acid, from which nitronium perchlorate must be sublimed under vacuum to separate it from the less volatile perchloric acid [1438]:



The unstable Cl_2O_7 is prepared via a dropwise addition of HClO_4 to P_2O_5 at 195 K (-78°C). This is a very slow reaction because the HClO_4 freezes as soon as it contacts the cold wall. The Cl_2O_7 generation takes place as the reaction mixture is left to thaw slowly. The Cl_2O_7 is not isolated as such (it is very explosive) but is distilled at a reduced pressure (1–2 mm Hg, 313 K = 40°C) directly into stirred white fuming nitric acid or red fuming nitric acid with a dehydrating agent such as P_2O_5 , while cooling the reacting mixture in a dry ice bath. The H_3PO_4 formed must then be removed via solvent extraction. Possible side reactions in this system are:

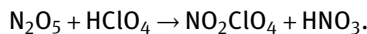


An excess of nitric acid reacts with the perchloric acid to form nitrosonium perchlorate, which may contaminate the desired product:



If the formation of nitrosonium perchlorate is undesirable, one should work with at least a 1:1 molar ratio of Cl_2O_7 and HNO_3 . Maintaining a slight excess of Cl_2O_7 , one should work in the presence of a dehydrating agent like P_2O_5 . Mixtures of nitronium perchlorate and nitrosonium perchlorate can be separated by fractional crystallization in nitromethane as the solvent.

Nitronium perchlorate with better than 99% purity can be obtained via the reaction of dinitrogen pentoxide with anhydrous perchloric acid [1439]:

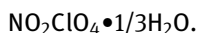
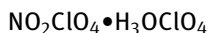
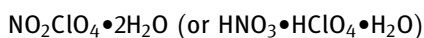


Nitrosonium perchlorate, if present as a contaminant, rarely exceeds 0.2%.

Research was initiated to produce uniform spherical particles of nitronium perchlorate in sizes up to at least 20 mesh having near perfect density. Originally, the plan was to spray-dry the nitronium perchlorate; however, it was later decided that a more promising initial approach would be to apply pan-coating techniques to the problem [1440].

Nitronium perchlorate can be obtained in higher purity and a more stable form via the reaction of dinitrogen pentoxide and chlorine trioxide in the vapor phase. Another method used nitrogen dioxide and OClO in the presence of ozone under pressure (689 kPa = 100 psig) [1441].

Studies of reactions and adduct formation in the ternary system $\text{Cl}_2\text{O}_7\text{-N}_2\text{O}_5\text{-H}_2\text{O}$ identified three compounds with increasing stability (in that order) [1442, 1443]:



Another method used a gaseous mixture of nitrogen dioxide, chlorine, and ozone and irradiated it with UV or gamma radiation in the reaction zone [1444].

Nitronium perchlorate can be made from ozonized air reacting with OClO or nitrogen dioxide in ozonized air reacting with OClO [1445]. Instead of making OClO from sodium chlorite and sulfuric acid, OClO can be prepared in a pre-reactor from dry chlorine gas and ozone. The NO_2ClO_4 thus obtained is a white solid with a density of 2.2 g/cm^3 . It decomposed at 393 K (120 °C) and had a drop-weight impact sensitivity of 120 kg-in.

Optimum yields (90%) can be obtained with ClO_2 and NO_2 gases premixed before entering the reactor, an operating temperature between 328 and 348 K (55 and 75 °C), and a $\text{ClO}_2:\text{NO}_2$ molar ratio of 1.0 to 1.3 [1446]. An improved method of synthesizing nitronium perchlorate works by oxidizing chlorine nitrate with ozone [1447].

13.1.1.2 Physical Properties of Nitronium Perchlorate

Nitronium perchlorate forms monoclinic crystals with a density of 2.25 g/cm^3 at 298 K and vapor pressure at 298 K is 10^{-4} mm Hg . Other sources reported the density as 2.220 g/cm^3 at 298 K and the standard heat of formation as $+8.7 \text{ kJ/mol}$.

Raman spectra of solid NO_2ClO_4 and several other nitronium salts confirmed the ionic structure of the crystals [1448].

IR spectra of NO_2ClO_4 were measured in the range 2–15 μ with NaCl optics in the range of 15–20 μ . CsBr optics and significant absorption bands were at 2360, 1100, 937,

625, and 570 cm^{-1} [1449]. There was no significant absorption beyond 20μ . The band at 2360 cm^{-1} is the ν_3 fundamental vibration of NO_2^+ .

The Raman spectrum of crystalline nitronium perchlorate exhibits ten well-resolved lines plus an additional weak line appearing as a shoulder [1436, 1450]. The IR spectrum consists of moderately intense absorptions at 940 and 2300 cm^{-1} and a strong broad absorption around 1100 cm^{-1} , which (on closer examination) may be resolved into three peaks. This information supports the structure of nitronium perchlorate crystals already obtained by XRD. An interpretation of these data points at the bending mode of the nitronium ion with cation-anion interaction in crystalline nitronium salts.

13.1.1.3 Thermodynamic Properties of Nitronium Perchlorate

The enthalpy of solution and hydrolysis of nitronium perchlorate was determined in an isothermal calorimeter. From that number, the enthalpy of formation of crystalline nitronium perchlorate was calculated as $+33.5 \pm 1.7\text{ kJ/mol}$ ($+8.0 \pm 0.4\text{ kcal/mol}$) [1451].

In another experiment, the heat of formation of nitronium perchlorate was determined via hydrolysis with aqueous KOH in a calorimeter and was measured as $+37.19 \pm 1.0\text{ kJ/mol}$ ($+8.89 \pm 0.25\text{ kcal/mol}$) [1452].

13.1.1.4 Molecular Structure of Nitronium Perchlorate

Early XRD examination of nitronium perchlorate confirmed that the crystal structure contains the ions NO_2^+ and ClO_4^- [1453]. The structure of nitronium perchlorate, NO_2ClO_4 , has been investigated via a three-dimensional analysis [1454]. There are four formula units in a monoclinic unit cell with the structure parameters $a = 9.16\text{ \AA}$, $b = 7.08\text{ \AA}$, $c = 7.30\text{ \AA}$, $\beta = 112.1^\circ$ and space group $C/2c$. An apparent anomaly in the electron density of one of the oxygen atoms was explained by the anisotropy of the thermal motion. After anisotropic refinement ($R = 0-13$), the bond lengths were calculated as $\text{Cl}-\text{O} = 1.464 \pm 0.007\text{ \AA}$ and $\text{N}-\text{O} = 1.10 \pm 0.01\text{ \AA}$ in ions, which are slightly distorted from the tetrahedral and linear forms, respectively. The $\text{N}-\text{O}$ distance was reported as $1.15 \pm 0.01\text{ \AA}$ in nitronium nitrate and this value was confirmed by a new refinement of the published data. Chlorine 3-D orbitals are involved in a strong π bonding system in the perchlorate ion. The nitronium perchlorate crystals are monoclinic, space group $C2/c$, with $a = 9.25\text{ \AA}$, $b = 6.99\text{ \AA}$, $c = 7.34\text{ \AA}$, $\beta = 113.5^\circ$ [1455]. It has been suggested that NO_2ClO_4 , even at ambient temperatures, has some covalent character, as substantiated by XRD, vibration spectra, and its ability to sublime.

13.1.1.5 Chemical Properties of Nitronium Perchlorate

Nitronium perchlorate is very moisture-sensitive and thermally unstable. It decomposes without melting. It begins to decompose at 323 K (50°C) and the rate of decomposition is significant above 333 K (60°C) (see next chapter). Nitronium perchlorate reacts violently with many organic compounds, causing spontaneous ignition. This limits the type of binders that can be used in combination with nitronium perchlorate

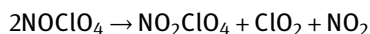
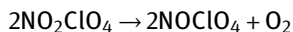
to make solid propellants. Nitronium perchlorate can be dissolved in nitromethane as a solvent and then used as a nitrating agent in organic preparative chemistry.

Dissolving nitronium perchlorate in liquid dinitrogen tetroxide converts it quantitatively to nitrosonium perchlorate. Nitronium perchlorate has been suspected as an intermediate in the thermal decomposition of AP.

Nitronium perchlorate forms complex perchlorates with $\text{Al}(\text{ClO}_4)_3$ or $\text{Zn}(\text{ClO}_4)_2$ resulting in the formation of $\text{NO}_2\text{Al}(\text{ClO}_4)_4$ and $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ [1456]. It also forms an adduct with pyridine [1457]. The composition of the white salt is $(\text{C}_5\text{H}_5\text{N})_{1.5}\text{NO}_2\text{ClO}_4$. In contrast to uncomplexed NO_2ClO_4 , the pyridine complex salt is not hygroscopic; it dissolves only slowly in water and hydrolyzes very slowly. The salt is thermally stable but only below 353 K (80 °C) and the drop weight impact sensitivity with the Olin tester is 20 kg-cm with a 2 kg weight.

13.1.1.6 Thermal Stability and Decomposition of Nitronium Perchlorate

Nitronium perchlorate is thermally unstable. It begins to decompose at 323 K (50 °C) and the rate of decomposition is significant above 333 K (60 °C). Nitrosonium perchlorate is somewhat more stable than nitronium perchlorate [1458] but when nitrosonium perchlorate is decomposed, some nitronium perchlorate can be found in the residue. The following reactions are likely steps in the NO_2ClO_4 decomposition reactions:



The thermal decomposition of solid nitronium perchlorate has been studied by measuring the rate of pressure rise in a constant volume flask over a temperature range from 343 to 385 K (70 to 112 °C) [1459]. The fractional rates of decomposition are independent of sample size. The rate constants are

$$k_{\text{initiation}} = 10^{12.6 \pm 0.5} e^{-28.5 \pm 0.8 \frac{\text{kcal}}{\text{mol}} / RT} \text{ s}^{-1}$$

and

$$k_{\text{growth}} = 10^{12.5 \pm 0.6} e^{-27.5 \pm 0.9 \frac{\text{kcal}}{\text{mol}} / RT} \text{ s}^{-1}.$$

The reaction is delayed by an induction time

$$t_{\text{induction}} = 10^{-15.0 \pm 0.9} e^{+30.7 \pm 1.5 \frac{\text{kcal}}{\text{mol}} / RT}.$$

Based on thermal decomposition studies at 373–433 K (100–160 °C) using isothermal constant volume techniques and by using mass spectrometry, the activation energy was found to be $15 \pm 1 \text{ kcal/mol}$ [1460]. This is in good agreement with the energy of photolysis derived from the absorption edge of the absorption spectrum.

Analyzing the isothermal decomposition products of a sample at 338 K (65 °C) under vacuum with a mass spectrometer shows that the initial product of decomposition is mostly oxygen [1461, 1462]. The decomposition proceeds in four stages:

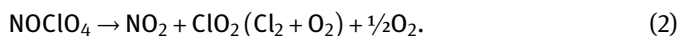
- (1) sublimate deposits on cooler parts of the system,
- (2) an induction period of 24–40 hours during which no gas evolution takes place,
- (3) an initially slow but rapidly accelerating production of oxygen which reached a maximum after being exposed to heat for 100 hours, accompanied by the appearance of a yellow condensate in a cold trap, and
- (4) gradually decreasing rate of oxygen production.

There is no residue. Products observed during the latter stages of the decomposition (NO_2 , Cl_2 , ClO_2) are attributed to the decomposition of nitronium perchlorate. If NO_2 forms at any stage of the NO_2ClO_4 decomposition, it would quickly convert it to NOClO_4 . If the NO_2 is immediately removed by keeping the sample under a vacuum, its autocatalytic effect is avoided because the NO_2 is pumped off as soon as it is formed. The isothermal NOClO_4 decomposition results of Marshall and Lewis [1461, 1462] have been interpreted such that nitronium perchlorate decomposes into nitronium perchlorate and oxygen with subsequent decomposition of the nitronium perchlorate.

The thermal decomposition of nitronium perchlorate has been studied in the range from 70 to 112 °C [1463]. A kinetic study of the overall decomposition revealed that

- (1) the decomposition is an autocatalytic process;
- (2) there is an induction period with a slow, nearly constant gas evolution (corresponding to 0.5% decomposition);
- (3) except for minor changes in the induction period, there is no variation with sample sizes;
- (4) the decomposition gives approximately 3 mols of gas per mol of nitronium perchlorate decomposed;
- (5) the maximum rate occurred when the fraction decomposed, α was approximately 0.2;
- (6) during the acceleration period, α was proportional to t^4 ; and
- (7) after the maximum, $d\alpha/dt$ showed a linear decrease with increasing α .

After the induction period, the process consists of a first-order initiation of nuclei followed by the three-dimensional growth of these nuclei. A suggested modification of the theory included a mobile equilibrium of the active sites and the interpretation that the particle size referred to a sub-crystalline unit. The decomposition can be represented by the following equations:



Moisture caused the decomposition of nitronium perchlorate and the evolution of gas. Essentially, there was more gas in a moister storage condition.

The kinetics and mechanism of the thermal decomposition of nitronium perchlorate were examined in the temperature range of 353 to 443 K (80–170 °C) using isothermal constant-volume methods and simultaneous DTA-TGA [1464]. To suppress sublimation of the salt, the study was conducted under dry He at a pressure of 100 mm Hg. DTA and TGA data revealed the presence of three distinct stepwise weight loss processes and a crystal phase change at about 429 K (156 °C). These mass loss processes were interpreted as (1) the conversion of nitronium into nitrosonium perchlorate, (2) a reversal of step (1), and (3) the destruction of nitronium perchlorate into only gaseous products. Kinetic analysis of the data indicated that stages (1) and (2) obeyed a Prout-Tompkins relation, indicating a branching-nuclei mechanism. Data from step (3) fit the contracting-cube expression $k_t = 1 - (1 - \alpha)^{1/3}$ and suggested the possibility of decomposition by ion-pair evaporation from the surface.

The thermal stability of nitronium perchlorate is usually measured by observing the pressure of an evacuated sample held in a glass bulb with an attached manometer. The stability can be changed in either direction by co-crystallization with salts containing aliovalent anions or cations (see below).

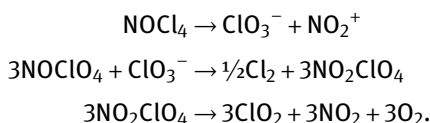
The kinetics of gas evolution from nitronium perchlorate irradiated with UV light from a high-pressure Hg arc lamp has been investigated as a function of intensity, temperature, and the duration of UV irradiation [1465]. Different gaseous products of decomposition were identified via mass spectrometry, the predominant species being O₂ and NO. The data indicated that two primary mechanisms for photolysis were operating simultaneously. The first mechanism started out rapidly, built up to a speedy rate of photolytic decomposition, and then subsided with time. The second slower mechanism then took over and was responsible for the longtime photolytic behavior. A UV absorption spectrum of a single crystal of nitronium perchlorate was also measured. The results agreed with the threshold energies for photodecomposition.

A thermobarogravimetric technique using a METTLER thermal analyzer was used to study the fundamental parameters of sublimation processes for solids that sublime and decompose simultaneously [1466]. The technique was applied to nitronium perchlorate and the resulting data has been kinetically analyzed by using the contracting volume model for sublimation. These data were consistent with models of the irreversible thermal decomposition of nitronium perchlorate. The activation energy of sublimation of nitronium perchlorate below 373 K (100 °C) was 78.2 kJ/mol (18.7 kcal/mol) and 60.2 kJ/mol (14.4 kcal/mol) between 383 and 423 K (110 and 150 °C).

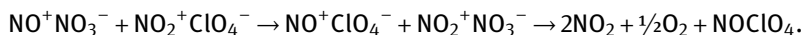
The effects of adding impurities to nitronium perchlorate were investigated using simultaneous DTA and TGA and via isothermal constant-volume decomposition with pressure measurement [1467]. The impurities were chosen to increase the number of cation vacancies and the number of anion vacancies and to produce steric hindrance effects. The thermal stability of nitronium perchlorate can be improved by the addition

of an excess of cation vacancies and ions. This produces a cation-anion interaction in the lattice and vice-versa. The thermal stability is decreased by an excess of anion vacancies.

The thermal decomposition of NOClO_4 (powder, or fragments of pressed pellets) and of NO_2ClO_4 (granules) was studied gasometrically and by XRD [1468, 1469]. During the decomposition of NOClO_4 , NO_2ClO_4 was formed as an intermediate. The following mechanism was suggested for the decomposition of NOClO_4 :



Some of the NO_2 dimerized to N_2O_4 , which can react in its ionic form. The last reaction would then be with N_2O_5 as an intermediate:



Nitronium perchlorate NO_2ClO_4 was assumed to become partly reduced to NOClO_4 during heating but others could not confirm the intermediacy of NOClO_4 . The maximum rate of oxygen evolution was at a degree of conversion of $\alpha = 0.3 - 0.4$. Independent of the composition of the initial sample, the reaction mixture will always contain both perchlorates.

The rate of decomposition of nitronium perchlorate at constant temperatures of 300 to 333 K (80 to 140 °F) was determined by measuring the weight loss of modified Kjeldahl flasks from which the accumulating decomposition products were periodically removed [1470]. The decomposition rates are based on data accumulated during tests lasting from 550 hours to 28 months. The results indicated a much slower decomposition rate than extrapolations from higher temperature data would indicate. Results also revealed that the incorporation of a fluorocarbon binder had little effect on the decomposition rate.

Stabilizers and Inhibitors for Nitronium Perchlorate

Investigations of the reactions of NO_2ClO_4 with various ligand molecules were made in an effort to increase the size of the NO_2^+ cation, and thereby improve the stability of NO_2ClO_4 [1471, 1472].

Attempts were made to improve the chemical stability of nitronium perchlorate by forming nitronium ion complexes [1473]. This approach was unsuccessful because of the general failure of NO_2^+ to form stable complexes. Pyridine was the only molecule found to produce a solid complex with NO_2ClO_4 . The pyridine complex ($\text{NO}_2(\text{py})_x\text{ClO}_4$) slowly decomposed at room temperature to a brown tar, which contained pyridinium perchlorate.

Nitronium perchlorate stabilization studies included an examination of the early stages of thermal decomposition, analysis of a contaminate, optimization of

a treatment procedure, studies on the mechanism of stabilization, and a semi-empirical additive screening study [1463]. It was attempted to prepare stabilized nitronium perchlorate by using additives, new isolating techniques, and by using new synthesis techniques starting with ultra-pure raw materials. The primary objective was the preparation of nitronium perchlorate, which had no gas evolution at 333 K (60 °C) over 100 hours. In addition to this primary goal, it was realized that the ultimate use of nitronium perchlorate is dependent on its long-term stability. Since the decomposition of nitronium perchlorate has been characterized as an autocatalytic process, the start of the accelerated decomposition phase is critical to its long-term stability. Therefore, a secondary objective of studies was to identify factors that inhibit or retard the onset of the accelerated decomposition. Decomposition studies showed that changes in the decomposition process occurred during the early stages of decomposition. Gas evolution during the induction period was unrelated to the length of the induction period.

Studies on nitronium perchlorate stabilization showed that BF_3 had a significant stabilizing effect. This initial finding was based on contacting “as received” nitronium perchlorate with BF_3 . Stabilization by boron trifluoride is only of limited utility. For some samples containing BF_3 , the treatment was equivalent to drying and resulted in lower gas evolution. For other samples, contacting with BF_3 had little if any effect. Stability tests run in the presence of BF_3 indicated lower gas evolution but BF_3 was still consumed.

Other studies indicated that the stabilizer in water-treated nitronium perchlorate is hydronitracidium perchlorate, $\text{H}_3\text{NO}_3(\text{ClO}_4)_2$, which actually is a mixed crystal system of hydronium perchlorate and nitronium perchlorate. This implies that stabilization is affected by the modification of the crystal structure of the surface layers of nitronium perchlorate. Originally, it was thought that ultra-dry nitronium perchlorate was the key to stability. Another stabilization method is the coating of nitronium perchlorate with another oxidizer. Although nitronium tetrafluoroborate no longer looked attractive as a crystal modifier, the use of ammonium tetrafluoroborate or AP was still considered.

Infrared and electron paramagnetic resonance spectroscopy was employed to measure the reactivity of nitronium perchlorate with various organic materials, including a solid propellant binder [1474]. The results indicated that compatibility between raw nitronium perchlorate and the binder system is less than satisfactory. Testing of the reactivity of simple hydrocarbons with nitronium perchlorate showed that *n*-hexane, *n*-pentane, and isooctane reacted slowly with nitronium perchlorate at ambient temperatures, and HNO_3 , NO_2Cl , N_2O , and CO_2 were the major reaction products. Methane did not appear to react. OClO is inherently present at low concentrations in dry commercial nitronium perchlorate. Concentrations are slightly higher in undried nitronium perchlorate. The formation of ClO_2 can be used as a qualitative measure of the reactivity of organic materials with nitronium perchlorate.

Nitronium perchlorate is very hygroscopic and susceptible to hydrolysis in the presence of water. Thus, is it very surprising that anyone would want to stabilize nitronium perchlorate via controlled exposure to a trace amount of water followed by evacuation to remove the reaction products after aging for several days to allow the reaction to penetrate the crystals [1475]. As an indication of improved stability, the time delay for the onset of accelerated decomposition at 333 K (60 °C) was delayed from 100 hours to 1000 hours.

It has been found that the thermal stability of nitronium perchlorate can be improved by adding an excess of cation vacancies and ions. This produces a cation-anion interaction in the lattice and vice-versa. It has been shown that thermal stability is decreased by an excess of anions [1476, 1477]. Only small mol fractions of additives, typically 10^{-2} , are required to achieve this effect due to crystal lattice defects. The addition of sulfate anions accelerated the decomposition of NO_2ClO_4 , whereas the addition of $\text{Ca}(\text{ClO}_4)_2$ or $\text{Sr}(\text{ClO}_4)_2$ stabilized the NO_2ClO_4 . Double salts like $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$ or $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ were substantially more stable than NO_2ClO_4 itself. Another way to stabilize nitronium perchlorate is to expose it to boron trifluoride gas [1478]. The sample will absorb 0.01 to 1% BF_3 to achieve this effect.

Low-melting eutectic mixtures with other perchlorates and nitrates can be melt-cast into an inert liquid to form spherical oxidizer particles. These can be coated and encapsulated with polymers (polyvinyl chloride, polyvinylidene chloride) [1444] or metalized with aluminum to protect them from moisture and to process them into solid propellants with a binder [1479, 1480]. The preferred eutectic point mixture contains 60% nitronium perchlorate and 40% lithium perchlorate and melts at 365 K (~92°C), which is below the decomposition temperature of nitronium perchlorate (Figure 55).

Another method to encapsulate nitronium perchlorate is to expose the particles slowly to an atmosphere of ammonia diluted in an inert gas [1481]. This converts a thin layer on the surface to AP, which is less hygroscopic than nitronium perchlorate.

13.1.2 Nitronium Tetrafluoroborate

Nitronium tetrafluoroborate NO_2BF_4 is easy to prepare via the reaction of nitryl fluoride with boron trifluoride. Nitryl fluoride is first prepared via the reaction of dinitrogen pentoxide with hydrogen fluoride and then saturated with BF_3 . Nitronium tetrafluoroborate is well crystallized and is an important intermediate in the preparation of other nitronium compounds or for the preparation of nitramines from their parent secondary aliphatic amines [1482].

Hypergolic propellant combinations obtained by bringing NO_2BF_4 and Lewis adducts of BF_3 with N_2O_3 , N_2O_4 or N_2O_5 in contact with organic amines, polyamines, alkyl hydrazines, or glycols have been proposed [1483]. NO_2BF_4 and Lewis adducts of BF_3 with N_2O_3 , N_2O_4 , or N_2O_5 are solids. It is therefore difficult to understand how these solid oxidizers could be combined with liquid fuels unless it is done in a reverse hybrid rocket engine. However, the ignition delays quoted in the patent

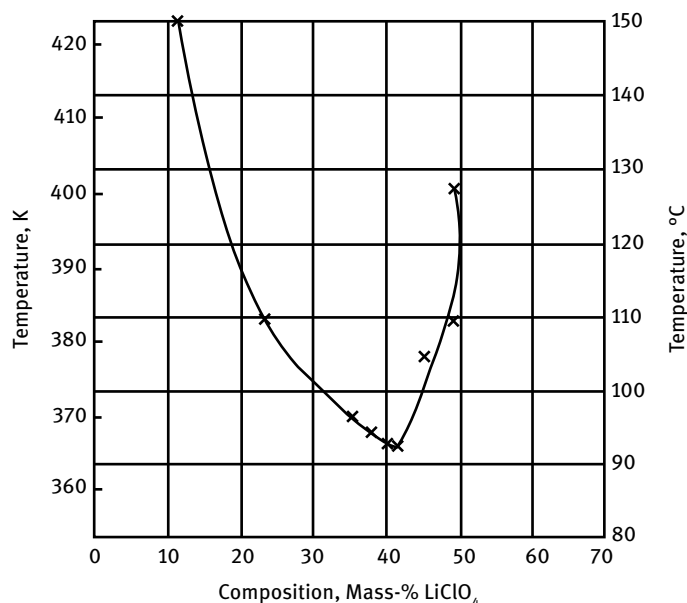


Figure 55: Melting point diagram of binary NO_2ClO_4 - LiClO_4 mixtures. (Reproduced and modified from [1480].)

(15 to 30 seconds, **not** milliseconds!) are much too long for practical applications. 1,1-Dimethylhydrazine hydrochloride was an unfortunate choice of fuel. Since it is already protonated, it would be expected to react more slowly than the free hydrazine.

13.2 Lewis Adducts of BF_3 with N_2O_3 , N_2O_4 or N_2O_5

Because the Lewis adducts of BF_3 with N_2O_3 , N_2O_4 , or N_2O_5 are closely related with NO_2BF_4 , we are discussing these compounds in a subdivision of the chapter on NO_2BF_4 . Except for the one obscure example listed in the previous section, they have not received widespread consideration as rocket propellants. The Lewis adducts of BF_3 with N_2O_3 , N_2O_4 , or N_2O_5 can be prepared by the direct addition of the Lewis base (nitrogen oxides with free electron pairs) to the Lewis acid (BF_3 with an electron gap). The 1:1 addition complex of boron trifluoride with dinitrogen tetroxide is an excellent nitrating agent. Boron trifluoride also forms a similar 1:1 complex with dinitrogen trioxide. The complex is a white, stable solid, insoluble in all solvents with which it does not react, including alkanes, nitroalkanes, and polychlorinated alkanes. It sublimates at room temperatures and does not melt in a sealed tube below 573 K (300 °C). These properties suggest that the complex is ionic in character. The

$\text{BF}_3 \cdot \text{N}_2\text{O}_3$ complex reacts rapidly with substances with which BF_3 and N_2O_3 by themselves would react as well, including water, alcohols, ethers, ketones, carboxylic acids, and amines.

13.3 Nitrosonium (Nitrosyl) Salts

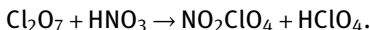
13.3.1 Nitrosonium Perchlorate

Nitrosonium perchlorate, nitrosyl perchlorate, $[\text{NO}^+][\text{ClO}_4^-]$, CAS RN [15605-28-4] is of little interest as a rocket propellant since it is thermally less stable than nitronium perchlorate and contains less oxygen. It ignites hypergolically with many amines and ammonia gas.

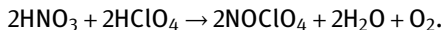
13.3.1.1 Preparation of Nitrosonium Perchlorate

Nitrosonium (nitrosyl) perchlorate can be prepared via the reaction of cold 70% HClO_4 with excess dinitrogen tetroxide in 99% HNO_3 at 268–263 K (–5 to –10 °C) [1484].

The reaction of dichlorine heptoxide with nitric acid which forms a white solid, which is a mixture of the anhydrides of perchloric acid and nitric acid. Nitronium perchlorate can be sublimed from this mixture under vacuum to separate it from the less volatile perchloric acid [1438]:



An excess of nitric acid reacts with the perchloric acid to form nitrosonium perchlorate:



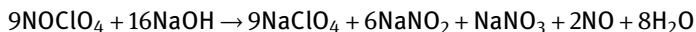
The yield of NOCIO_4 in the reaction of N_2O_4 and HClO_4 is limited by the hydrolysis of NOCIO_4 by the water formed in the reaction. Water must constantly be removed via a reaction with P_2O_5 to obtain a good yield of NOCIO_4 .

A simple method avoids the use of perchloric acid by starting with sodium perchlorate monohydrate and concentrated sulfuric acid, achieving nitrosyl perchlorate in 65% yield based on the $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ used [1485].

13.3.1.2 Physical Properties of Nitrosonium Perchlorate

Nitrosonium perchlorate forms rhombic crystals with a density of 2.169 g/cm³ at 298 K. When heated, nitrosonium perchlorate decomposes without melting.

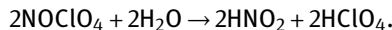
The standard enthalpy of formation of solid nitrosonium perchlorate was once estimated as –154 kJ/mol (–36.8 kcal/mol). Calorimetric measurement of the heat of reaction



resulted in a heat of formation of solid nitrosyl perchlorate as -165.7 ± 1.2 kJ/mol (-39.6 ± 0.3 kcal/mol) [1486].

13.3.1.3 Chemical Properties of Nitrosonium Perchlorate

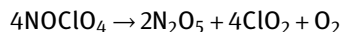
In the presence of moisture, nitrosonium perchlorate hydrolyzes to nitrous acid and perchloric acid:



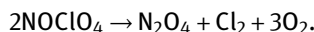
Only a few organic polymers are suitable for protective coatings of nitrosonium perchlorate to protect it against moisture. Polyvinyl chloride is compatible with nitrosonium perchlorate and can be used for this purpose. Nitrosonium perchlorate will ignite hypergolically with many amines and ammonia.

13.3.1.4 Thermal Stability of Nitrosonium Perchlorate

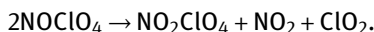
Nitrosonium perchlorate is stable at room temperature. It has no melting point but begins to decompose below 373 K to form nitrogen oxides and chlorine [1487]. The decomposition is complete at 413 K. The initial decomposition reaction may be



but these intermediate products are not stable either. The overall decomposition reaction is more like

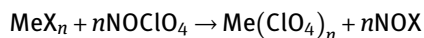


In another isothermal thermal stability test at 365 K and 3–5 mm Hg vacuum, the weight losses after three, six, nine, and 12 hours were 27, 61, 94, and 100%, respectively [1488]. At 373 K, the losses after three, six, and nine hours were 65, 80, and 99%, respectively. In similar tests at 372 K and 1 mm Hg, nitronium perchlorate was found in the solid residue [1489]. The mechanism leading to nitronium perchlorate is assumed to go by



The presence of NO_2ClO_4 in the decomposition products was verified by XRD [1490]. DTA thermograms revealed two peaks, the first at 373–398 K (100–125 °C), which was assumed to be nitrosonium perchlorate decomposition. The second was at 438–453 K (165–180 °C), which was assumed to be nitronium perchlorate decomposition [1491].

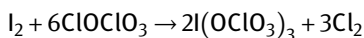
The reaction of nitrosonium perchlorate with metal halogenides is a convenient method for the preparation of metal perchlorates by a solid-solid using a metathetical reaction where the only solid reaction product is the desired perchlorate salt [1492].



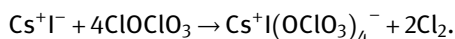
14 Other Non-Metal Perchlorates

Covalent inorganic perchlorates were prepared from chlorine perchlorate. The compound $\text{I}(\text{ClO}_4)_3$ was partially characterized and $\text{N}(\text{ClO}_4)_3$ was deduced as a short-lived primary reaction product. The one-valent iodine(I) perchlorate could not be prepared but a complex perchlorate of iodine(III), $\text{CsI}(\text{ClO}_4)_4$, was indeed synthesized [1493].

Iodine tris(perchlorate) was prepared via the low-temperature reaction of iodine with an excess ClOClO_3 [1494]. Its composition was established by quantitative synthesis:



with the material balance for all components being 99%. The compound is a white solid, stable at 228 K (-45°C). During its synthesis, no explosions were encountered. However, when exposed to a laser beam, explosive decomposition occurred even at low temperatures. It decomposed upon warming to ambient temperature. Extreme caution is advised as chlorine perchlorate is shock sensitive and samples of both $\text{I}(\text{OClO}_3)_3$ and $\text{Cs}^+\text{I}(\text{OClO}_3)_4^-$ have exploded even at low temperature while recording their laser Raman spectra. Proper safety precautions must be taken when working with these compounds. The salt $\text{Cs}^+\text{I}(\text{OClO}_3)_4^-$ was prepared according to



It is a pale yellow solid and is stable at room temperature.

Chlorine perchlorate (ClOClO_3) can be prepared using the reaction of cesium perchlorate or nitronium perchlorate with chlorine fluorosulfate or chlorine monofluoride [1495]. Bromine perchlorate (BrOClO_3) can be prepared using a similar reaction of cesium perchlorate or nitronium perchlorate with bromine fluorosulfate or via the reaction of chlorine perchlorate with elemental bromine.

Boron perchlorate $\text{B}(\text{ClO}_4)_3$ has been prepared from boron trichloride and anhydrous perchloric acid at 195 K (-78°C) [1496, 1497]. It is very unstable and can decompose explosively. It may form double salts with nitronium perchlorate or AP.

The two hydrazinium perchlorates will be discussed in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salts”.

Hydroxylammonium perchlorate will be discussed in *Encyclopedia of Oxidizers*, chapter “Hydroxylammonium Salts”.

The properties of alkylammonium perchlorates are discussed at the end of each parent amine chapter in *Encyclopedia of Liquid Fuels*, chapter “Aliphatic Amines”.

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Red Fuming Nitric Acid

Nitric Acids

Although chemically speaking there is only one nitric acid with the formula HNO_3 , we have subdivided this chapter on nitric acids into three subchapters in *Encyclopedia of Oxidizers*, dealing with four technical grades of nitric acids of different chemical composition: **white fuming nitric acid** (WFNA), **red fuming nitric acid** (RFNA), and mixed acid (MA). There are two variants of RFNA, **inhibited red fuming nitric acid** (IRFNA) and **high-density acid** (HDA).

1 Red Fuming Nitric Acid

Many of the physical properties of RFNA are like those of WFNA. Thus, if no better data are available, one can use the WFNA data in first approximation or prorate properties from mixtures of WFNA and dinitrogen tetroxide, N_2O_4 (NTO) assuming additive behavior.

1.1 Production of RFNA

RFNA can be made by simply mixing liquid N_2O_4 and HNO_3 in the appropriate ratios in a closed reactor with agitation to achieve complete mixing. The heat of mixing is exothermic. Corrosion inhibitors can be added in a subsequent operation.

1.2 Physical Properties of RFNA

Summaries of physical and chemical properties of RFNA can be found in [1] and [2]. Summaries of the physical and chemical properties of RFNA and HDA are found in [3]. The physical properties of RFNA as a function of the N_2O_4 content can be quickly looked up with the help of a nomograph [4, 5].

1.2.1 Freezing Point and Phase Diagrams of RFNA

The most effective and practically important freezing-point-depressing additive to nitric acid is dinitrogen tetroxide to form RFNA. The addition of N_2O_4 to HNO_3 not only lowers the freezing point but also improves rocket performance. In most cases, RFNA contains not only HNO_3 and N_2O_4 but may also contain an inevitable (and even desirable) trace of water.

The freezing point diagram of the binary system $\text{HNO}_3/\text{N}_2\text{O}_4$ is presented in Figure 1. A very old National Advisory Committee for Aeronautics (NACA) report contains a freezing point diagram that covers the entire composition range in the $\text{HNO}_3/\text{N}_2\text{O}_4$ binary system [6].

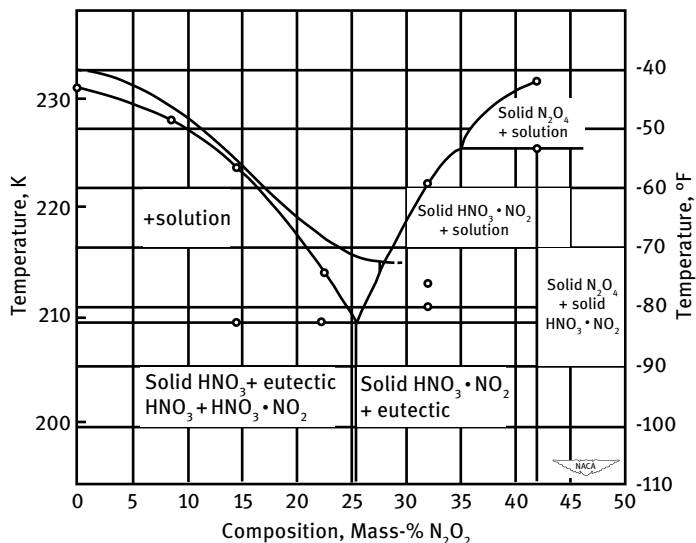


Figure 1: Freezing point of binary nitric acid-dinitrogen tetroxide system. (Reproduced and modified from [7].)

Note: This acid contained 0.4% water.

The interrelated effects of water, from 0 to 10 mass-%, and dinitrogen tetroxide, from 0 to 25 mass-%, in fuming nitric acid were investigated with respect to the freezing points of the acid mixture and the ignition delays with several hypergolic fuels [7]. An equilibrium freezing-point surface for the acids in the composition range studied is presented. A minimum freezing point of 206.2 K (−88.5 °F) occurs in a region of approximately 5% water and 17% dinitrogen tetroxide. A binary eutectic line extends from this region to nearly anhydrous acid containing 25 to 26% dinitrogen tetroxide, which freezes at 209.5 K (−82.5 °F). The freezing points of the ternary system $\text{HNO}_3/\text{N}_2\text{O}_4/\text{H}_2\text{O}$ are illustrated in Figure 2 and tabulated in Table 1. See also [8–10].

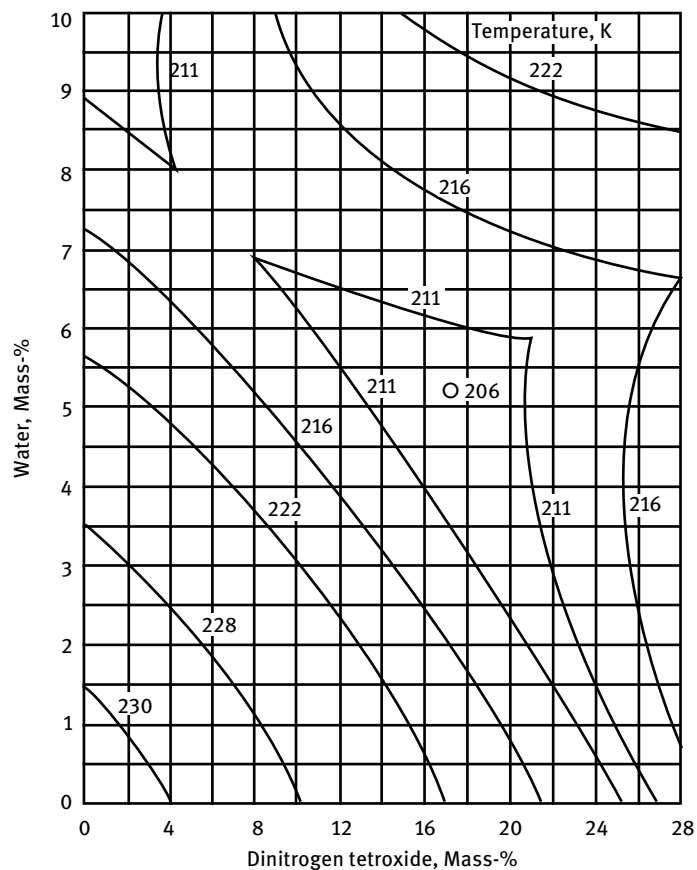


Figure 2: Curves of constant melting point in ternary system $\text{HNO}_3/\text{N}_2\text{O}_4/\text{H}_2\text{O}$. (Reproduced and modified from [7].)

Table 1: Freezing point of RFNA.

Composition	Initial freezing point, °C								
Mass fraction H ₂ O	Mass fraction NO ₂								
	0.0192	0.0513	0.0765	0.0940	0.1151	0.1308	0.1527	0.2050	0.2371
0.00	-41.7	-43.3	-44.8	-44.8	—	-48.3	-50.0	-56.6	-61.0
0.01	-42.6	-43.8	-47.7	-47.8	—	-51.2	-52.9	-62.2	-58.8
0.02	-43.8	-45.6	-51.0	-51.1	-54.9	-55.2	-56.6	-65.6	-57.9
0.03	-45.6	-48.5	-54.5	-54.6	-60.0	-59.5	-62.2	—	-58.6
0.04	-47.8	-51.9	-58.3	-58.9	-65.2	-64.6	-67.1	—	-58.3
0.05	-50.5	-55.8	-62.7	-64.1	-65.2	-66.1	-66.7	-66.2	-54.8
0.06	-54.0	-59.9	-62.7	-65.1	-65.2	-66.1	-67.0	-61.6	-51.7
0.07	-57.9	-61.1	-63.2	-64.9	-62.5	-66.5	-67.4	-57.2	-49.0
0.08	-60.0	-61.5	-60.7	-59.1	-58.3	-63.0	-57.9	-53.3	-47.1
0.09	-60.2	-62.0	-56.5	-54.5	-54.9	-58.0	-55.0	-50.2	-45.6
0.10	-60.7	-58.8	-52.6	-51.1	-51.8	-54.1	-52.3	-47.8	-44.7

Data source: [2] (see also Figure 2)

1.2.2 Boiling Point of RFNA

The boiling point of a MA with a high N₂O₄ content (54.8 mass-% HNO₃, 44.0 mass-% NO₂, 0.5 mass-% H₂O, 0.7 mass-% HF) can be extrapolated from the vapor pressure curve and was calculated as 297.8 K = 24.7 °C = 76.5 °F [11].

1.2.3 Vapor Pressure and Vapor Phase Composition of RFNA

1.2.3.1 Vapor Pressure and Vapor Phase Composition of Binary RFNA Mixtures

The high solubility of N₂O₄ in HNO₃ was already recognized very early, even before this mixture was considered as a rocket propellant, and the vapor pressure and the densities of HNO₃/N₂O₄ mixtures were measured [12]. In binary mixtures of HNO₃ and N₂O₄, if one plots the vapor pressure isotherms as a function of N₂O₄ content, as shown in Figure 17 of [13], the isotherms run flat between 35 and 95 mol-% N₂O₄ where the fluids do not mix (two-phase region) and physical properties do not change much.

Vapor pressure data for binary HNO₃/N₂O₄ mixtures are listed in Table 2. The composition of the vapor in equilibrium with binary mixtures of anhydrous HNO₃-N₂O₄-NO₂ at 273 K (0 °C) and the partial vapor pressure of the constituents of the vapor were measured with an all-glass Bourdon gauge system [14]. The composition of the liquid and vapor phases is listed in Table 3.

Table 2: Vapor pressure of RFNA (zero water content).

Mass-% NO ₂	Vapor pressure, mm Hg		Vapor pressure, kPa, at	
	0 °C	25 °C	273 K	298 K
0	15.9	62.1	2.1	8.3
5	25.2	97.9	3.3	13.0
10	28.5	111.2	3.8	14.8
15	31.5	133.1	4.2	17.7
20	37.5	167.5	5.0	22.3
25	49.2	213	6.5	28.3
30	67.5	275	9.0	36.5
35	94.3	367	12.5	48.8
40	129.5	496	17.2	65.9
44	162.5	605	21.6	80.4

Data source: [15]

Table 3: Vapor phase composition in equilibrium with binary mixtures of anhydrous HNO₃-N₂O₄-NO₂ at 273 K.

NO ₂ + N ₂ O ₄ in liquid phase (rest is HNO ₃)	Vapor phase total pressure	PHNO ₃	HNO ₃	PN ₂ O ₄	N ₂ O ₄	PNO ₂	NO ₂
Mass-%	mm Hg	mm Hg	Mass-%	mm Hg	Mass-%	mm Hg	Mass-%
0%	14.1	14.1	100%	0	0%	0	0%
8.4	17.5	13.5	71.4	3.5	26.7	0.5	1.9
9.0	13.6	11.0	76.0	2.2	22.4	0.3	1.6
15.0	19.0	11.6	53.1	6.5	43.7	0.9	3.1
17.0	—	—	52.9	—	44.0	—	3.1
24.7	34.1	9.8	22.7	21.3	72.2	3.0	5.1
33.5	62.7	6.0	7.1	49.7	86.7	7.0	6.1
41.0	(104.6 and 109.6)	(2.9 and 3.0)	3.9	(90.0 and 94.3)	89.8	(11.7 and 12.3)	6.2
47.3	—	—	0.4	—	93.0	—	6.6
48.2	(171.2 and 172.7)	(0.9 and 0.9)	—	(149.1 and 152.1)	—	(21.1 and 21.6)	—
50.0	185.0	—	—	162.1	—	22.9	—
55.0	223.2	—	—	195.6	—	27.6	—
56.0	(223.6 and 255.9)	Saturation	—	—	—	—	—
100	(254.0 and 253.3)	—	—	—	—	—	—

Data source: [14]

Another set of vapor pressure data of the binary system $\text{HNO}_3/\text{N}_2\text{O}_4$ was presented in [13], as shown in Table 4.

Table 4: Vapor pressure of binary $\text{HNO}_3/\text{N}_2\text{O}_4$ mixtures.

Composition		Temperature, K				
		263	268	273	278	283
		Temperature, °C				
		−10	−5	0	+5	+10
Mass-% N_2O_4	Mol-% N_2O_4	Vapor pressure, mm Hg				
0	0	6.94	10.07	14.16	19.63	26.73
5	3.48	7.90	11.40	16.20	22.4	30.9
10	6.96	8.95	12.9	18.40	25.9	36
15	10.80	10.75	15.58	22.15	31.2	43
20	14.63	14.40	20.40	28.60	41.15	55.3
25	18.58	20.00	28.41	40.00	55.00	74.10
30	22.73	28.27	30.8	53.60	72.3	100
35	26.90	38	52.8	73.2	100	135.4
40	31.33	54.5	75	103.2	137.5	185.5
45	35.90	78.2	106.2	143	190	245.2
50	40.50	112.2	149.2	197	257.2	323
52	42.6	129	170	222	285.1	363
54	44.55	147.9	191.7	250.8	324	407.7
Phase separation		148.1	191.9	253.5	330.9	425.2
97	95.6	148.1	192.3	254.7	333	427.2
98.5	97.82	149.1	195	258	337.2	432
100	100	149.95	198.4	262.6	344	442.5

Data source: [13]

1.2.3.2 Vapor Pressure and Vapor Phase Composition of Ternary RFNA Mixtures

At constant temperature, the vapor pressure of RFNA increases with its NO_2 concentration and decreases with increasing water content as shown in Figure 3. In this graph, the number of dashes of a line designates the NO_2 concentration, and the number of dots in the line designates the H_2O concentration (this is like trying to decipher a Morse code message), where

one dash	—	0% NO_2
two dashes	--	5% NO_2
three dashes	---	10% NO_2
four dashes	----	15% NO_2
five dashes	-----	20% NO_2
one dot	•	0% H_2O
two dots	••	10% H_2O

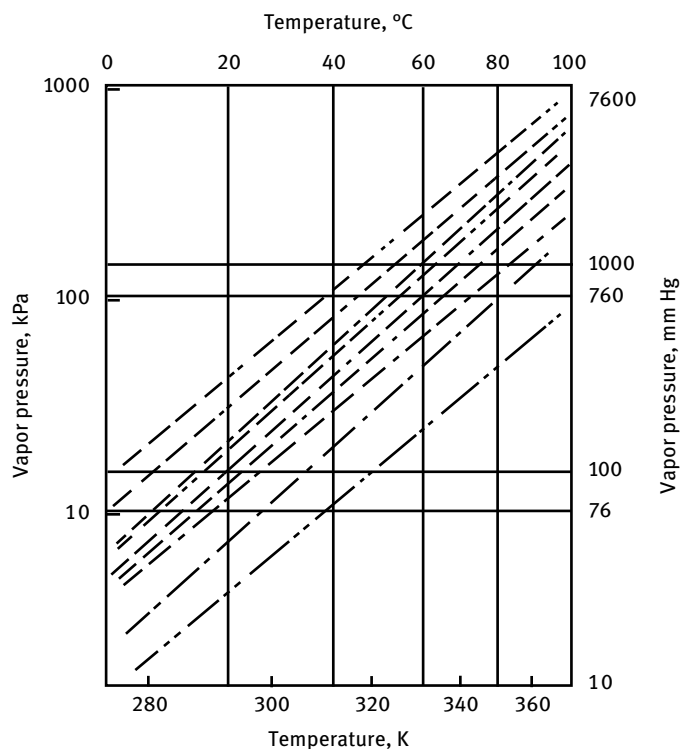


Figure 3: Vapor pressure of $\text{HNO}_3/\text{N}_2\text{O}_4/\text{H}_2\text{O}$ system. (Reproduced and modified from [9].)

It is difficult to measure the total vapor pressures of RFNA because part of the NO_2 vaporizes during the measurement and fills the void space. The vapor pressure is dependent on the ullage of the system. Total vapor pressures were measured in an isotenoscope for 16 acid mixtures of the ternary system nitric acid, nitrogen dioxide, and water within a temperature range of 283 to 333 K (10 to 60 °C) and with a composition range of 71 to 89 mass-% nitric acid, 7 to 20 mass-% nitrogen dioxide, and 1 to 10 mass-% water [16], also [17, 18]. Heats of evaporation were then calculated from the vapor pressure measurements for each sample for the temperatures 298, 313, and 333 K (25, 40, and 60 °C). Vapor pressure measurements depend on the size of the vapor space that has to be pressurized, since some NO_2 will be lost from the liquid in the process. The ullage of the apparatus used for these measurements was 0.46. Ternary diagrams showing isobars as a function of composition of the system were constructed from experimental and interpolated data for the temperatures 298, 313, 318, and 333 K (25, 40, 45, and 60 °C). Only the one for 298 K (25 °C) is shown in Figure 4 as an example of the temperature of most practical use.

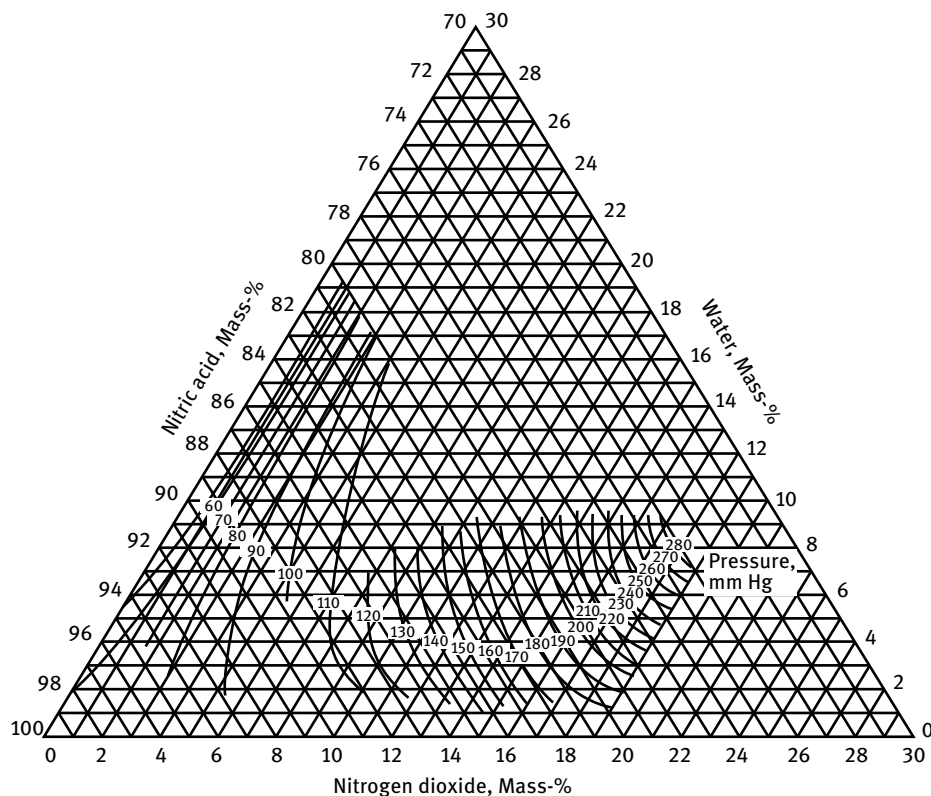


Figure 4: Total vapor pressure isobars of nitric acid, nitrogen dioxide, and water system at 298 K (25°C). (Reproduced and modified from [16].)

Vapor pressure measurements were conducted on four HDA formulations over a temperature range of 256 to 402 K (−17 to 129°C = 1 to 264°F). The resultant values were then correlated as a function of composition and temperature and resulted in the following polynomial equation covering a temperature range from 256 to 402 K (−17 to 129°C), NO₂ concentration ranges of 43.2 to 45.6% NO₂, and water ranges from 0.4 to 1.7% H₂O [11]:

$$\log p_v = 10.7662 - 4702.28/T - 5.43556 \times 10^{-2}N + 2.5549 \times 10^{-2}W \\ + 28.5036 \frac{N}{T} + 282926/T^2$$

where log is the decadic logarithm to the base of 10, p_v is the vapor pressure in atm, T is the absolute temperature in kelvin, N is the NO₂ content in mass-%, and W is the water content in mass-%, with a standard error of estimate of $\pm 4\%$ in pressure. The vapor pressure of a nominal composition of HDA is illustrated in Figure 5. The boiling point of nominal HDA would be 297.8 K (24.7°C = 76.5°F).

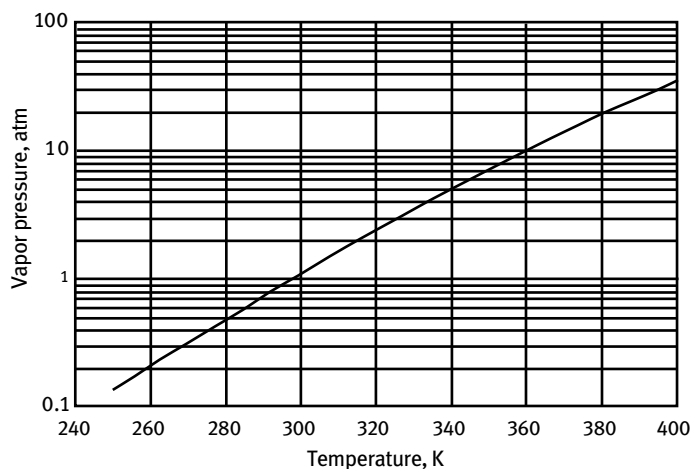


Figure 5: Vapor pressure of HDA containing 44% N_2O_4 and 1% H_2O . (Chart created by Schmidt 2020, based on data from [11].)

The vapor pressure and the vapor phase composition above RFNA is directly related to the absorption of NO_2 and/or N_2O_4 into nitric acids of various water concentrations, the reversal of evaporation and dissociation. The absorption not only would be a step in the preparation of RFNA, but is also of industrial importance in the production of WFNA. The absorption rate and mechanism of NO_2 - N_2O_4 gas mixtures diluted with nitrogen absorbing into nitric acid solutions were investigated in a wetted wall column at 298 and 308 K (20 and 30 °C) [19]. It was found that N_2O_4 , which is continuously in equilibrium with NO_2 , is preferentially absorbed into diluted nitric acid as well as into concentrated nitric acid. The absorption of N_2O_4 into diluted acid is accompanied by a rapid pseudo-first-order reaction with water. Above 63% HNO_3 the absorption was found to be purely physical. The solubility of N_2O_4 in concentrated nitric acid (63%) was derived from total vapor pressure data in the system $\text{NO}_2/\text{N}_2\text{O}_4/\text{H}_2\text{O}/\text{HNO}_3$. Henry's law was valid within the range of conditions considered.

1.2.4 Density and Partial Molar Volumina of RFNA

1.2.4.1 Density of Binary RFNA Mixtures

The density of binary mixtures of HNO_3 and N_2O_4 was measured as a function of N_2O_4 content at 288 K (15 °C) [20]. Interpolated and measured density data are summarized in Tables 5 and 6. The density showed a maximum at 40% N_2O_4 (Figure 6). That figure shows densities of mixtures below and above the miscibility gap. That same report also contains data on partial molar volumina, heat of mixing, and chemical potentials of $\text{HNO}_3/\text{N}_2\text{O}_4$ binary and $\text{HNO}_3/\text{N}_2\text{O}_4/\text{H}_2\text{O}$ ternary mixtures.

Table 5: Interpolated density data for HNO₃/N₂O₄ mixtures at 288 K.

% N ₂ O ₄	Density, g/cm ³
0	1.5240
5	1.5442
10	1.5612
15	1.5860
20	1.6049
25	1.6203
30	1.6338
35	1.6420
40	1.6467
45	1.6442
50	1.6442
52	1.6412
54	1.6376
95	1.4633
97	1.4614
98.5	1.4593
100	1.4575

Data source: [13]

Table 6: Density of binary HNO₃/NO₂ mixtures under conditions of chemical equilibrium.

Composition, mass-% NO ₂	Density, g/cm ³ , at ____ °C	
	0 °C	25 °C
0	1.5472	1.5018
5	1.5667	1.5235
10	1.5867	1.5443
15	1.6069	1.5645
20	1.6274	1.5838
25	1.6462	1.6015
30	1.6601	1.6160
35	1.6691	1.6245
40	1.6725	1.6273
45	1.6717	1.6238
50	1.6662	1.616
55 ^a	1.657	1.605

^aSaturated solution

Data source: [15]

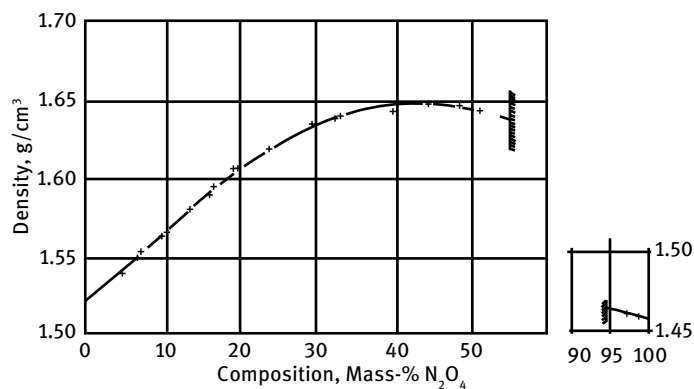


Figure 6: Density of binary mixtures of HNO_3 and N_2O_4 below and above miscibility gap at 288 K (15 °C). (Reproduced and modified from [13].)

Similar density data for the binary system $\text{HNO}_3/\text{N}_2\text{O}_4$, interpolated from a curve-fitting equation, are listed in Table 7.

Table 7: Density of binary $\text{HNO}_3/\text{N}_2\text{O}_4$ mixtures at 298 K (25 °C).

Concentration, mass-% N_2O_4	Density, g/cm^3
0	1.5010
2	1.5112
4	1.5208
6	1.5299
5	1.5384
10	1.5466
12	1.5545
14	1.5621
16	1.5696
18	1.5771
20	1.5846

Data source: [21]; water-free acid

The data in Table 7 agreed quite well with older data from [12], also for a water-free acid. The density of dinitrogen tetroxide solutions in 70.05%- HNO_3 changed rectilinearly depending on the N_2O_4 concentration in the solution and temperature.

1.2.4.2 Density of Ternary RFNA Mixtures

The density graph of ternary $\text{HNO}_3/\text{N}_2\text{O}_4/\text{H}_2\text{O}$ mixtures in Figure 7 is only for one given temperature ($273\text{ K} = 0^\circ\text{C}$):

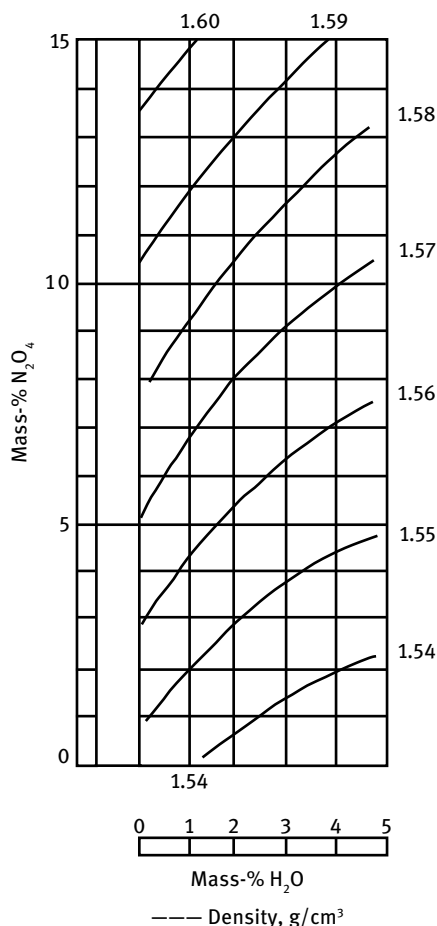


Figure 7: Density in $\text{HNO}_3/\text{N}_2\text{O}_4/\text{H}_2\text{O}$ system at 273 K (0°C). (Reprinted and modified from [22] with permission from © 1955 American Chemical Society; permission conveyed through RightsLink.)

Density data of ternary $\text{HNO}_3/\text{N}_2\text{O}_4/\text{H}_2\text{O}$ mixtures under conditions of chemical equilibrium are listed in Table 8.

The density of HNO_3 solutions containing 10–27 mass-% N_2O_4 and 0–5% H_2O was determined at 273 – 323 K (0 – 50°C) and at 213 – 273 K (-60 to 0°C) with a dilatometer with an estimated probable error of 0.002 [23]. In the concentration range of N_2O_4 , C_2 , of no higher than 26 and no lower than 5%, the following equation expressed the

Table 8: Density of ternary $\text{HNO}_3/\text{N}_2\text{O}_4/\text{H}_2\text{O}$ mixtures under conditions of chemical equilibrium.

Mass fraction		Density, g/cm ³ , at ____ °C		
NO_2	H_2O	0 °C	25 °C	40 °C
0.0000	0.0000	1.5489	1.5039	1.4569
0.0000	0.0101	1.5409	—	—
0.0000	0.0210	1.5359	1.4929	1.4679
0.0000	0.0363	1.5309	—	—
0.0000	0.0509	1.5279	1.4859	1.4609
0.0000	0.1037	1.5149	—	—
0.0480	0.0518	1.5489	1.5059	1.4789
0.0497	0.0173	1.5589	1.5169	1.4879
0.0506	0.0000	1.5689	1.5249	1.4979
0.1121	0.0563	1.5699	1.5269	1.4999
0.1163	0.0211	1.5839	1.5419	1.5149
0.1188	0.0000	1.5949	1.5529	1.5249
0.1775	0.0000	—	—	—
0.1902	0.0514	1.5929	1.5499	1.5219
0.1970	0.0174	1.6139	1.5719	1.5429
0.2005	0.0000	1.6228	1.5809	1.5529
0.2034	0.0000	1.6238	—	—
0.2496	0.0000	1.6379	—	—
0.2833	0.0000	1.6459	—	—
0.3619	0.0000	1.6448	—	—
0.4068	0.0000	1.6725	—	—
0.4235	0.0000	1.6749	—	—
0.4890	0.0000	1.6725	—	—
0.5086	0.0000	1.6699	—	—
0.9958	0.0000	1.4939	—	—
1.0000	0.0000	1.4939	—	—

Data source: [2]

experimental results:

$$\rho = 1.593 + 0.37\{[C2/(C1 + C2)] - 0.2\} - aC3 - b(t - 20)$$

where $C1$ and $C3$ are the concentrations in mass-% of HNO_3 and H_2O , respectively, t is the temperature in °C, and a and b are constants with $a = 0.00536 + 0.0072 \cdot [(C2/C1) - 0.15]$, and $b = \Delta\rho/\Delta t = 0.0016$ in the -60 to $+20$ °C interval and 0.0017 in the 20 to 50 °C interval.

Density measurements were conducted on three selected HDA formulations, one described as nominal, a second with high (1.7 mass-%) water, and a third with high (54.6 mass-%) NO_2 content using a Poole-Nyberg densitometer. All the samples

contained 0.4% HF. The results were correlated through the use of a least-squares curve-fitting computer program and resulted in the following expression of density as a function of temperature and composition [24]:

$$\rho = 1.7889 - 1.8391 \times 10^{-3}t - 5.82 \times 10^{-6}t^2 - 2.420 \times 10^{-3}N - 1.750 \times 10^{-2}W$$

where ρ is the density in g/cm^3 , t is the temperature in $^{\circ}\text{C}$, N is the NO_2 content in mass-%, and W is the water content in mass-%, with a standard error of estimate of 0.0017 g/cm^3 . This equation applies to mixtures containing 43.4 to 45.6 mass-% NO_2 and 0.4 to 1.7 mass-% H_2O . The curve-fitted data from this equation are illustrated in Figure 8.

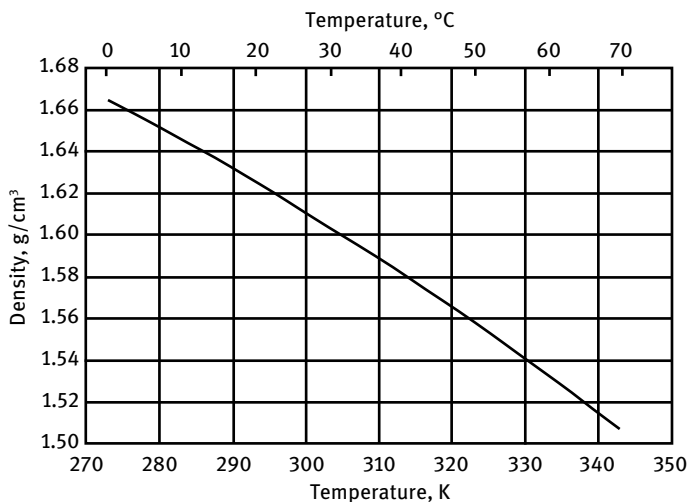


Figure 8: Density of saturated liquid HDA. (Chart created by Schmidt 2020, based on data from [11].)

Additional density data on the ternary system $\text{HNO}_3/\text{N}_2\text{O}_4/\text{H}_2\text{O}$ are in [21]. The triangular chart in Figure 9 gives lines of constant density at 308 K (35°C) for ternary mixtures of $\text{HNO}_3/\text{N}_2\text{O}_4/\text{H}_2\text{O}$ up to relatively high concentrations of either N_2O_4 or H_2O .

Determinations of the density of solutions of dinitrogen tetroxide (from 20% to boundary of separation into separate layers) in 98.2, 96.0, 94.2, and 92.2% HNO_3 at temperatures of 273, 283, and 293 K (0, 10, and 20°C) have shown that the density in the $\text{HNO}_3\text{-N}_2\text{O}_4\text{-H}_2\text{O}$ system exhibits a maximum value in the concentration range 40 to 43 mass-% N_2O_4 , whose position depends on the temperature and concentration of water in system [25, 26]. A set of equations was introduced allowing the calculation of the densities of mixtures with nitrogen tetroxide concentrations up to 10 mass-% N_2O_4 and in a temperature range of 263 to 293 K (-10 to $+20^{\circ}\text{C}$). These data can also be represented in the form of a nomograph [27].

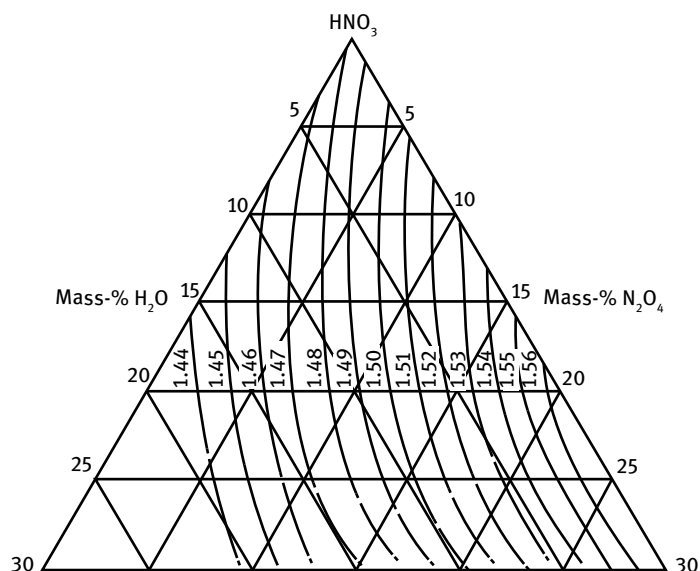


Figure 9: Density of ternary mixtures of $\text{HNO}_3/\text{N}_2\text{O}_4/\text{H}_2\text{O}$ at 308 K (35 °C). (Reprinted and modified from [21] with permission from © 1955 American Chemical Society; permission conveyed through RightsLink.)

1.2.4.3 Volumetric and Phase Behavior of RFNA

The specific volume and compressibility of $\text{HNO}_3/\text{N}_2\text{O}_4$ and $\text{HNO}_3/\text{N}_2\text{O}_4/\text{H}_2\text{O}$ mixtures have been measured repeatedly by various laboratories over a wide range of compositions, temperature, and pressure.

The volumetric and phase behavior of four binary mixtures of nitric acid and nitrogen dioxide was measured at temperatures from 344 to 444 K (160 to 340 °F) and for pressures up to 34.4 MPa (5000 psia) [28–30]. All the data were taken at both physical and chemical equilibrium. In most cases the specific volume was determined as a function of pressure at chemical and physical equilibrium at six temperatures above 344 K (160 °F). Experimental results of one of the four mixtures are presented in Figure 10 for a HDA containing 0.4607 mass fraction nitrogen dioxide. The results presented are typical of the experimental data obtained for the other three mixtures.

These binary system data were then remeasured with improved accuracy and expanded to include up to 15% water in ternary systems [31–36].

The densities of the $\text{N}_2\text{O}_4/\text{H}_2\text{O}/\text{HNO}_3$ system with N_2O_4 mol fractions from 0 to 0.15 and H_2O mol fractions from 0.08 to 0.33 were measured at 278.15, 283.15, 288.15, and 293.15 K [37]. Figure 11 shows the density of $\text{HNO}_3/\text{N}_2\text{O}_4$ mixtures as a function of N_2O_4 content, with a constant water mol fraction of 0.02.

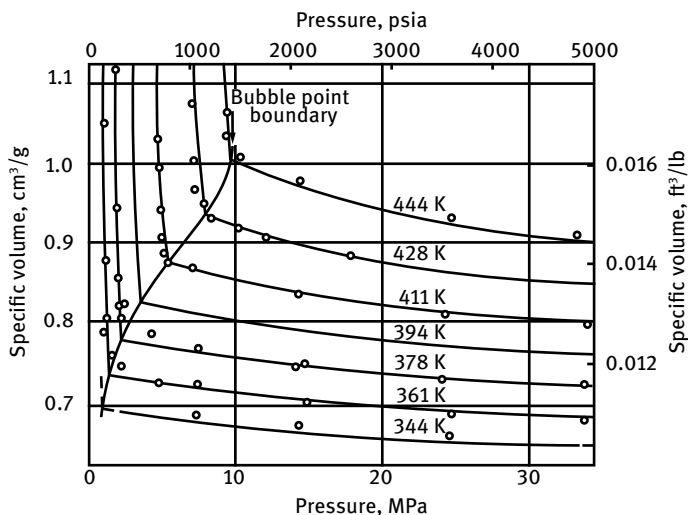


Figure 10: Specific volume of a HDA containing 0.4607 mass fraction nitrogen dioxide. (Reproduced and modified from [28].)

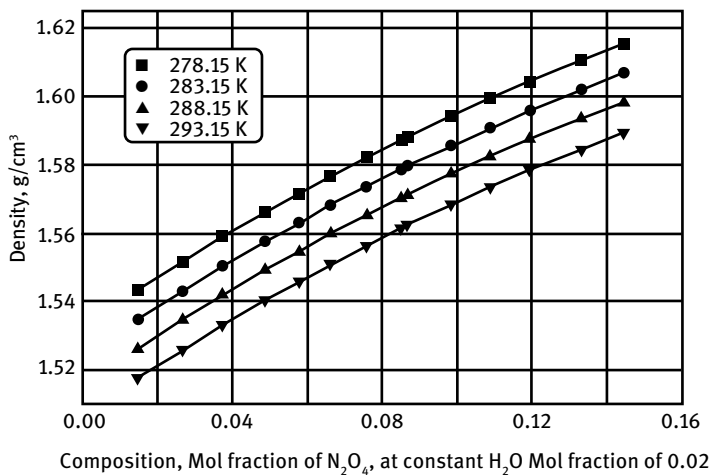


Figure 11: Density of HNO₃/N₂O₄ mixtures as a function of N₂O₄ content, with a constant water mol fraction of 0.02. (Reprinted and modified from [37], with permission from © 2011 American Chemical Society; permission conveyed through RightsLink.)

A similar graph exists for density as a function of H₂O mol fraction with a constant N₂O₄ mol fraction of 0.07. A combination of the two graphs was used to create a 3-D density graph with the N₂O₄ mol fraction plotted on the X_1 -axis and the H₂O mol fraction on the X_2 -axis (Figure 12). The excess molar volumes at 293.15 K were obtained

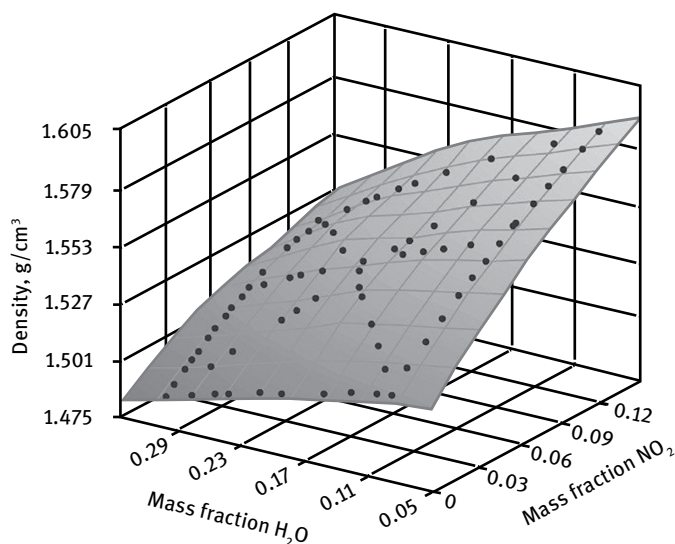


Figure 12: Experimental density of $\text{N}_2\text{O}_4/\text{H}_2\text{O}/\text{HNO}_3$ ternary mixtures at 293 K. (Reprinted from [37], with permission from © 2011 American Chemical Society; permission conveyed through RightsLink.)

from the experimental results for this ternary system. The experimental results were then correlated using an empirical equation. The average absolute deviations between the calculated values and experimental data were moderate. These data were obtained in support of electrochemical N_2O_5 synthesis methods to enable organic chemistry nitrating reactions (explosives synthesis) without the use of sulfuric acid.

1.2.5 Critical Point Properties of RFNA

It is very difficult to determine the critical point parameters of a mixture like RFNA or HDA because nitrogen oxide can exist in the form of either NO_2 or N_2O_4 . The critical point parameters were extrapolated from other measurable data of the constituents (Table 9) [11].

Table 9: Pseudocritical constants of HDA.

Constant	N_2O_4 present as N_2O_4	N_2O_4 present as NO_2	Extrapolated values
P_c , atm	97.4	97.1	97.2
T_c , K	524	555	540
Compressibility factor	0.235	0.235	0.235
$Z = PV/RT$, Z_c			
V_c , $\text{cm}^3 \text{mol}^{-1}$	104	110	107

Data source: [11]

1.2.6 Compressibility and Velocity of Sound of RFNA

The velocity of sound of a nominal RFNA composition at room temperature is 1404 m/s. Sonic velocity measurements were made in three different HDA formulations over a temperature range of 274 to 333 K (1 to 60 °C = 34 to 140 °F) under saturated liquid conditions. The resulting data were curve-fitted and resulted in the following expressions of sonic velocity as a function of temperature and composition [11]:

$$c = 2180.0 - 3.523t - 1.45 \times 10^{-2}t^2 - 14.977N - 40.6W$$

where c is the sonic velocity in m/s, t is the temperature in °C, N is the NO₂ concentration in mass-%, and W is the water concentration in mass-%. The standard errors were ±6.3 m/s. From the equation

$$\beta = \frac{1}{\rho c^2}$$

where β is adiabatic compressibility of the liquid, ρ is the density of the liquid, and c is the velocity of sound in the liquid, one can calculate the adiabatic compressibility of HDA as follows:

$$\begin{aligned} \beta = & 6.097 \times 10^{-7} - 2.9506 \times 10^{-7}t + 9.126 \times 10^{-10}t^2 + 1.718 \times 10^{-11}t^3 + 5.7924 \times 10^{-7}N \\ & + 1.727 \times 10^{-6}W + 9.808 \times 10^{-9}Nt + 2.84 \times 10^{-8}Wt \end{aligned}$$

where β is the compressibility in atm⁻¹, t is the temperature in °C, N is the NO₂ content in mass-%, and W is the water content in mass-%, with a standard error of estimate of 8.7×10^{-8} atm⁻¹.

The N₂O₄ Handbook AFRPL-TR-76-76 in the chapter “Sonic Velocity in Red Fuming Nitric Acid” listed the velocity of sound as 1379.0 m/s (4525.0 ft/s) in a sample of RFNA whose composition was 77.5% HNO₃, 20% N₂O₄, and 2.0% H₂O [3]. No temperature was given. The same value has been quoted by other sources.

1.2.7 Viscosity of RFNA

As illustrated in Figure 13, the kinematic viscosity of RFNA decreases with increasing NO₂ content in a range of 0 to 20 mass-% NO₂ and increases with increasing water content in a range of 0 to 5 mass-% H₂O. See also [22, 38].

The dynamic viscosity of two different types of RFNA is listed in Table 10. Both kinematic and dynamic viscosity data for a wide range of RFNA compositions with NO₂ content up to 51% and water content up to 5.6% at three different temperatures are presented in Table 11.

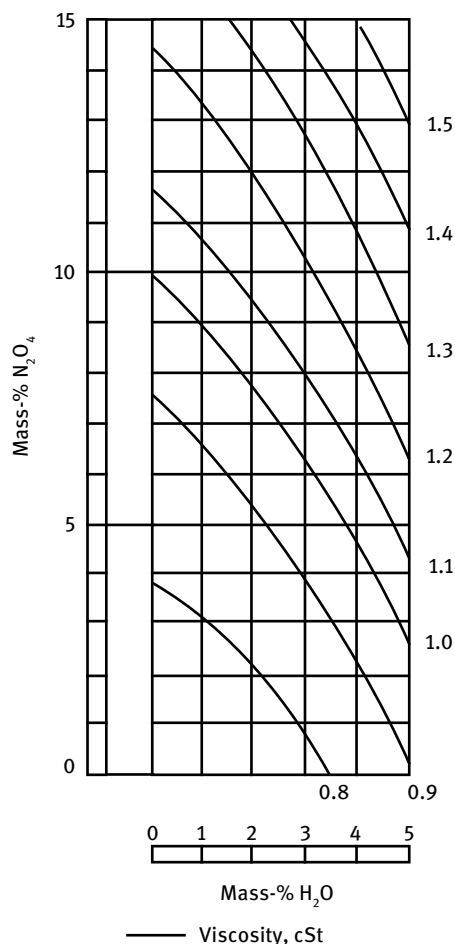


Figure 13: Kinematic viscosity in $\text{HNO}_3/\text{N}_2\text{O}_4/\text{H}_2\text{O}$ system at 273 K (0°C). (Reprinted and modified from [22] with permission from © 1955 American Chemical Society; permission conveyed through RightsLink.)

Viscosities in the $\text{HNO}_3\text{-N}_2\text{O}_4\text{-H}_2\text{O}$ system were determined for 98.2, 96.0, 94.2, and 92.2% HNO_3 at 293, 283, and 273 K (20, 10, and 0°C) [40]. The viscosity increased initially up to a maximum with an increase of N_2O_4 concentration (in the range of 39 to 43 mass-% N_2O_4) and decreased slightly with any further increase of N_2O_4 concentration. The location of the viscosity maximum was related to association processes in the mixture and varied with temperature and water concentration in the ternary system.

The viscosity of nitrogen tetroxide solutions in 70% HNO_3 remained practically unchanged (within limits of determination accuracy) with a change in N_2O_4 concen-

Table 10: Dynamic viscosity of RFNA.

Temperature		RFNA ^a	RFNA ^b
K	°C	Dynamic viscosity cPs	
283	10	2.040	1.013
293	20	1.635	0.875
303	30	1.350	0.758
313	40	1.105	0.651
323	50	0.925	0.585
333	60	0.785	0.520
343	70	0.670	0.457
353	80	0.570	0.435
363	90	0.490	0.408
373	100	0.425	0.391
383	110	0.370	0.386
393	120	0.315	0.385

^aInitial composition: 83.3 mass-% HNO₃, 14.3% NO₂, 2.4% H₂O^bInitial composition: 94.2% HNO₃, 4.0% NO₂, 1.8% H₂O

Data source: [39]

tration in the solution. When the temperature dropped, the viscosity of the system rose irregularly [41]. A set of equations was introduced, allowing the calculation of the viscosities of mixtures with nitrogen tetroxide concentrations up to 10 mass-% N₂O₄ and in the range of temperatures of 263 to 293 K (–10 to +20 °C). These data can also be represented in the form of a nomograph [42].

Viscosity measurements were made on three HDA formulations over a temperature range of 274.2 to 327.5 K (1.1 to 54.4 °C = 34 to 130 °F) using a Zhukov capillary viscometer. The resulting kinematic viscosity data were correlated as a function of temperature and composition through the use of a least-squares curve-fitting computer program. The correlation included conversion to absolute viscosity using a density polynomial equation and can be represented by the following equation [11]:

$$\log \eta = 0.27546 - 470.89/T + 216430/T^2 - 1.7017 \times 10^{-2}N - 4.6580 \times 10^{-2}W$$

where $\log$ is the decadic logarithm to the base of 10, η is the absolute viscosity in centiPoise, T is the absolute temperature in kelvin, N is the NO₂ content in mass-%, and W is the water content in mass-%, with a standard error estimate of 1.6%. The absolute viscosity of a nominal HDA (44% N₂O₄, 1% H₂O) as a function of temperature is graphed in Figure 14.

Table 11: Viscosity of $\text{HNO}_3/\text{NO}_2/\text{H}_2\text{O}$ mixtures.

Mass fraction		Temperature, °C					
NO_2	H_2O	0		25		40	
		Kinematic viscosity, cSt	Dynamic viscosity, cPs	Kinematic viscosity, cSt	Dynamic viscosity, cPs	Kinematic viscosity, cSt	Dynamic viscosity, cPs
0.0000	0.0000	0.705	1.092	0.496	0.746	0.418	0.617
0.0000	0.0101	0.704	1.085	—	—	—	—
0.0000	0.0210	0.731	1.123	0.513	0.766	0.435	0.639
0.0000	0.0363	0.804	1.231	—	—	—	—
0.0000	0.0509	0.878	1.342	0.591	0.878	0.492	0.719
0.0000	0.1037	1.300	1.969	—	—	—	—
0.0480	0.0518	1.086	1.682	0.705	1.062	0.571	0.845
0.0497	0.0173	0.874	1.363	0.603	0.915	0.499	0.743
0.0506	0.0000	0.834	1.309	0.572	0.873	0.480	0.720
0.1121	0.0563	1.413	2.220	0.860	1.313	0.676	0.980
0.1163	0.0211	1.148	1.818	0.755	1.163	0.608	0.921
0.1188	0.0000	1.053	1.680	0.700	1.087	0.572	0.873
0.1775	0.0000	1.290	2.08	—	—	—	—
0.1902	0.0514	1.766	2.81	1.022	1.584	0.779	1.188
0.1970	0.0174	1.548	2.50	0.941	1.479	0.731	1.128
0.2005	0.0000	1.425	2.31	0.893	1.412	0.707	1.099
0.2202	0.0000	1.540	2.51				
0.2403	0.0000	1.634	2.67				
0.2504	0.0000	1.695	2.74				
0.2805	0.0000	1.858	3.06				
0.3003	0.0000	1.977	3.26				
0.3505	0.0000	2.24	3.73				
0.4002	0.0000	2.49	4.16				
0.4235	0.0000	2.62	4.39				
0.4516	0.0000	2.65	4.44				
0.5000	0.0000	2.63	4.39				
0.5191	0.0000	2.58	4.30				
0.9958	0.0000	0.365	0.545				
1.0000	0.0000	0.359	0.536				

Data source: [22]

Viscosities and surface tensions of solutions of N_2O_4 or N_2O_5 in HNO_3 were determined at 278–293 K (5–20 °C), 0–10 mass-% N_2O_4 , or 0–20 mass-% N_2O_5 [43]. The data were fitted to empirical equations as functions of composition and temperature.

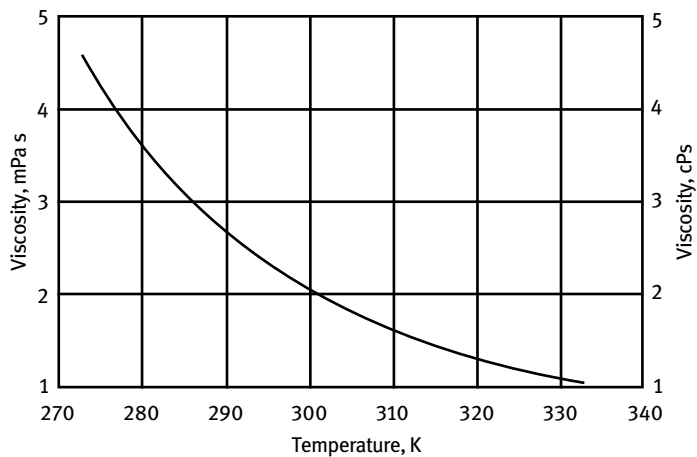


Figure 14: Absolute viscosity of saturated HDA. (Chart created by Schmidt 2020, based on data from [11]).

1.2.8 Surface Tension of RFNA

The change in surface tension with the temperature of a nominal HDA is illustrated in Figure 15. See also [44].

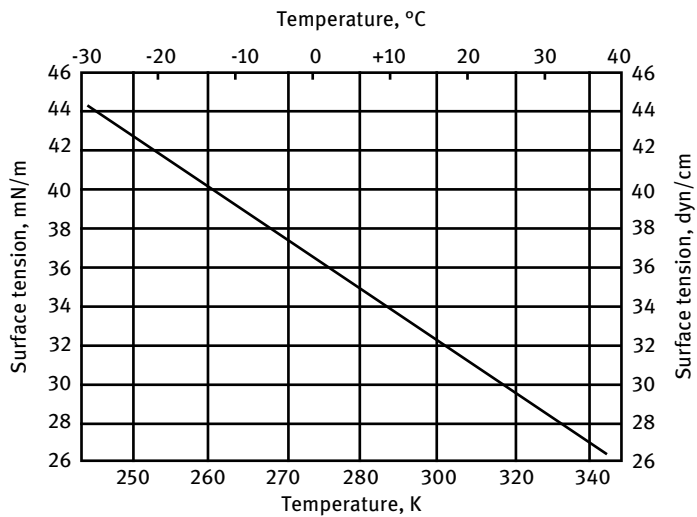


Figure 15: Surface tension of HDA. (Reproduced and modified from [11].)

1.2.9 Heat Transfer Coefficient of RFNA

Attempts to measure the heat transfer properties of RFNA were plagued with experimental difficulties because the heat transfer surface became coated with an insoluble residue soon after the start of the experiments and heat transfer decreased as the surface became progressively fouled [45–47]. The few data points obtained prior to this premature interruption indicated that the heat transfer to RFNA can be expressed by equations very similar to those used for WFNA [48, 49].

RFNA is not suitable as a regenerative coolant for rocket engines, but the heat transfer coefficient at the upper limit to nucleate boiling was measured and compared to that of other rocket propellants (Table 12) [50].

Table 12: Heat transfer coefficient of RFNA compared to other rocket propellants.

Coolant liquid	Heat transfer coefficient q_{ul} at 2.07 MPa = 20.4 atm, 9.1 m/s, and 310.9 K = 37.8°C inlet temperature		Heat capacity at 310.9 K = 37.8°C	
	kW/cm ²	BTU in. ⁻² s ⁻¹	J g ⁻¹ K ⁻¹	cal g ⁻¹ °C ⁻¹
RFNA	43.39	265.5	1.76	0.42
N ₂ O ₄	29.38	179.8	1.64	0.393
NH ₃	15.95	97.6	4.89	1.17
JP-3	28.73	175.8	1.82	0.435
Corporal-Fuel ^a	51.64	316	2.09	0.50
N ₂ H ₄	79.10	484		

^aThe fuel used in the Corporal ballistic missile consisted of 80 mass-% aniline and 20 mass-% furfuryl alcohol.

Data source: [50]

The effect of iron impurity levels up to 100 ppm as Fe₂O₃ on HDA heat transfer was studied in 30 tests using resistance-heated, circular, 1/8-in.-diameter Al-6061-T6 tubes [51]. The effects of iron impurity level, propellant inlet temperature, and simulated engine shutdown were established. Coolant conditions, velocity, and pressure were characteristics of the AGENA thrust chamber tests. The chamber is regeneratively cooled with HDA. Results showed that normal nucleate boiling did not occur with either of the HDA compositions. The experimental forced convection heat transfer coefficients were unaffected by iron impurity level and exhibited increased values with increased bulk temperature. As the heat flux was increased the tube wall temperature increased much above the saturation temperature of 411 K (280 °F). Film boiling cooling was apparent up to wall temperatures of about 755 K (900 °F) when tube failure occurred. As the wall temperature increased above 422 K (300 °F), heat transfer was adversely affected by both HDA compositions at all levels of iron impurity. Tubes that had previously been operated at wall temperatures above 422 K (300 °F) with shutdown generally exhibited increased thermal resistance during the

subsequent test. This increased thermal resistance was attributed to scale formed on the inner surface of the tube. Qualitative analysis of the scale from a sectioned tube showed its composition to be inorganic sulfates and nitrates, with aluminum as the major metallic component. Test with modified HDA showed that increased thermal resistance was exhibited at each of the iron impurity levels of 10, 50, and 97 ppm. Comparison of results showed that the modified HDA exhibited about 10% lower forced convection heat transfer coefficients but somewhat higher heat flux at tube destruction than standard HDA.

1.2.10 Thermodynamic Properties of RFNA

There is substantially more need for the thermodynamic properties of RFNA than those of WFNA. Unfortunately, the thermodynamic properties of RFNA are dependent on so many variables that there are few reliable data in the literature. A detailed analysis of the enthalpies and entropies of mixing in the $\text{HNO}_3/\text{H}_2\text{O}$ and $\text{HNO}_3/\text{N}_2\text{O}_4$ systems is presented in [52].

1.2.10.1 Heat Capacity of RFNA

Heat capacity data for RFNA in Table 13 were copied from a second-hand source, but the original source of these data and the temperature range in which they are valid is not known.

Table 13: Heat capacity of RFNA.

Composition Mass-% N_2O_4	Heat capacity	
	$\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$	$\text{J g}^{-1} \text{ K}^{-1}$
0	0.410	1.715
5	0.412	1.724
10	0.413	1.728
15	0.416	1.741
20	0.417	1.745
30	0.421	1.761
40	0.424	1.774
50	0.428	1.791

Data source: [53]

The heat capacity of RFNA in the range 300–422 K (80–300 °F) was determined by calorimetric measurements because it was needed to calculate the regenerative cooling capability of this oxidizer in a rocket engine [54].

1.2.10.2 Enthalpy of Formation of RFNA

The thermodynamic properties of RFNA are dependent on so many variables that there are few reliable data in the literature. In most cases the enthalpy of formation of RFNA is extrapolated from the enthalpy of formation of the pure ingredients and their heat(s) of mixing. The heat evolved when dissolving liquid N_2O_4 in HNO_3 was measured near 273 K over a range of compositions with 0 to 50 mass-% NO_2 in a Dewar flask modified for use as a calorimeter [55, 56]. Isobaric heat capacities were obtained as a side benefit while measuring the heat of solution and were found to increase from 1.71 to $1.80 \text{ J g}^{-1} \text{ K}^{-1}$ (0.41 to $0.43 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$) when the N_2O_4 content was increased from 0 to 50%. The differential heat of solution of N_2O_4 in the $\text{HNO}_3/\text{N}_2\text{O}_4$ system was about 247 J/g (59 cal/g) when starting with WFNA and then dropped to 16.7 J/g (4 cal/g) when the solution was nearly saturated at 50 mass-% N_2O_4 . The integral heat of solution for making a solution of 50% N_2O_4 in HNO_3 was about 66.9 J/g (16 cal/g) of solution. The enthalpies of formation of $\text{HNO}_3/\text{NO}_2/\text{H}_2\text{O}$ mixtures containing 0 to 50 mass-% NO_2 at 273 K (0°C) were tabulated [57].

The heat of solution of N_2O_4 in HNO_3 was estimated to be near -6.53 kJ/g-mol (-1.56 kcal/g-mol) N_2O_4 . The small amount of HF that is also added as corrosion inhibitor has only a minor effect on the heat of formation of the IRFNA or HDA mixture.

One undocumented secondary source of data listed the standard enthalpy of formation of RFNA (84% HNO_3 , 14% N_2O_4 , 2% H_2O , average molecular mass 75.016 g/mol) (ΔH_f^{298}) as $-638.1 \text{ cal/g} = -47.868 \text{ kcal/mol}$.

The heat of formation of HDA (with a nominal composition of 54.8% HNO_3 , 44.0% N_2O_4 , 0.5% H_2O , 0.7% HF) was estimated using the additive heats of formation of the components and their heats of solution with each other and gave $+181.2 \pm 3.3 \text{ kJ/100 g}$ ($+43.3 \pm 0.8 \text{ kcal/100 g}$) [11]. The empirical formula of such a mixture would be $\text{N}_{1.82606}\text{H}_{0.96015}\text{O}_{4.54953}\text{F}_{0.03499}$.

Red fuming acid data listed in PEPCODED.DAT with 14% NO_2 have the gross formula $\text{H}_{151}\text{N}_{165}\text{O}_{471}$ and an enthalpy of formation of $-654 \text{ cal/g} = -2736 \text{ J/g}$ and a density of $0.0567 \text{ lb/in.}^3 = 1.569 \text{ g/cm}^3$ [58]. A similar acid with 20% NO_2 has the gross formula $\text{H}_{85}\text{N}_{114}\text{O}_{314}$ and an enthalpy of formation of $-544 \text{ cal/g} = -2276 \text{ J/g}$. The related data file JPLCODED.DAT (1988) uses an RFNA with the gross formula $\text{H}_{1.56470}\text{N}_{1.63390}\text{O}_{4.72100}$ and an enthalpy of formation of $-638.1 \text{ cal/g} = -2667 \text{ J/g}$.

1.2.10.3 Heat of Evaporation of RFNA

The heat of evaporation of RFNA or HDA is difficult to determine because vapor pressure is mostly due to the NO_2 , and the composition of the vapor phase would change with increasing temperature. To predict the heat of evaporation, one needs to know vapor-phase composition measurements for the vapor space above RFNA or

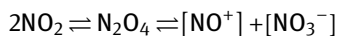
HDA. The heat of evaporation can be calculated from vapor pressure measurements using the Clausius-Clapeyron equation, but it would be valid only for evaporation at the boiling point at atmospheric pressure. Approximating calculations yielded a value of 7.00 kcal/mol vapor at the normal boiling point 297.8 K (24.7 °C = 76.5 °F) assuming the vapor is mostly NO₂.

The heats required to vaporize 1 mol of the equilibrium vapor mixtures from infinite amounts of the liquid samples were estimated from the slopes of vapor pressure curves. The differences in these heats of evaporation among samples of different composition at the same temperature were not very large; the heats ranged from 36.0 to 42.1 kJ/mol (8.6 to 10.07 kcal/mol) at 298 K (25 °C) and from 34.8 to 40.7 kJ/mol (8.320 to 9.740 kcal/mol) at 333 K (60 °C) [16–18].

1.2.11 Optical, Electrical, and Magnetic Properties of RFNA

1.2.11.1 Raman Spectra of RFNA

The Raman spectra of solutions of dinitrogen tetroxide in nitric acid led to the conclusion that the dinitrogen tetroxide molecule, in dilute solution in nitric acid, is almost completely disassociated, partly homolytically, but chiefly heterolytically, as follows [59]:



The frequency of the nitrosonium ion is usually found at about 2300 cm⁻¹, though the value varies slightly with the conditions of solvation. The value 2240 cm⁻¹, obtained in nitric acid, is, however, outside the usual range of variation, and it is shown to arise from a modification of the nitrosonium ion by some specific molecular interaction. The nitrogen dioxide molecule is assumed to form a molecular compound NO⁺•NO₂, held together by a partly homopolar but mainly electrostatic one-electron bond.

A Raman spectral study of solutions of N₂O₄ and N₂O₅ in anhydrous and aqueous HNO₃ provided a more detailed knowledge of the species present in these solutions and to assess the applicability of Raman spectroscopy as an analytical measurement technique [60]. Solutions of N₂O₄ in HNO₃ showed evidence of the presence of the associated species, 3NO⁺•NO₃⁻ (also written N₄O₆⁺²), which had been identified previously in a solid compound. The effects of H₂O on the spectra of these solutions were also examined.

The Raman spectra of HNO₃-containing NO₂ have been analyzed on liquid and solid surfaces. The Raman spectra of HNO₃ solutions containing N₂O₄ have been partly reinterpreted in terms of contributions from HNO₃•N₂O₄ and N₂O₄•NO₃⁻ adducts [61]. Some of such adducts may form in highly polluted atmospheres.

1.2.12 Electrical Conductivity of RFNA

The electrical conductivity of the binary system HNO_3/NO_2 is dependent on the NO_2 content. At 273 K and atmospheric pressure, nitrogen dioxide (dinitrogen tetroxide) is miscible with nitric acid only above 0.48 mass fraction HNO_3 . Below 0.48 mass fraction HNO_3 , a second liquid phase appears containing less than 0.1 mass-% HNO_3 . The specific conductance of this latter phase is small, being less than $7 \times 10^{-6} \text{ Ohm}^{-1} \text{ cm}^{-1}$ at 273 K. Between 0.72 and 1.00 mass fraction HNO_3 the conductance of the system decreased with increasing concentrations of acid [62]. This behavior agrees with studies of Raman spectra of solutions of nitrogen dioxide in nitric acid where nitrosonium ions (NO^+) and nitrate ions (NO_3^-) have been identified. The dinitrogen tetroxide undergoes homological dissociation and ionizes to give these ionic species according to the reaction equation



This ionization caused the increase in conductance observed when nitrogen dioxide was added to HNO_3 . At mass fractions of HNO_3 below 0.72, a decrease in HNO_3 concentration resulted in a decrease in conductance until the phase boundary was reached (Figure 16).

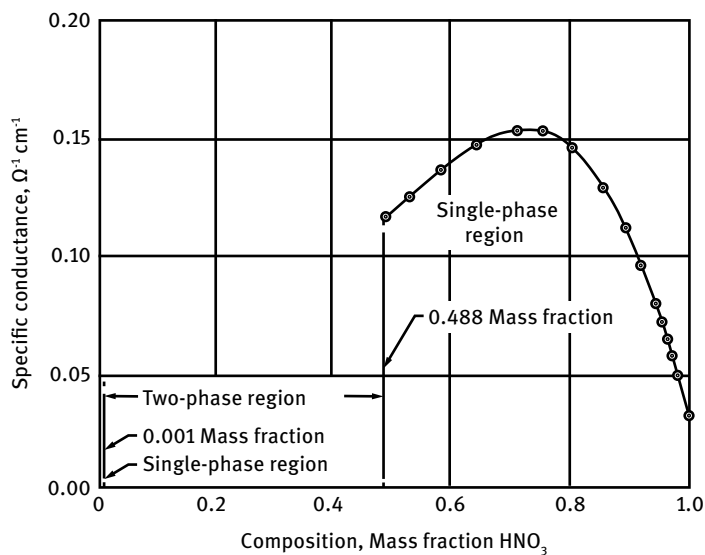


Figure 16: Specific conductance of nitric acid/nitrogen dioxide at 273 K and atmospheric pressure. (Reproduced and modified from [63].)

Table 14: Electrical conductivity of anhydrous RFNA at 273 K (0 °C).

Mass fraction		Specific electrical conductivity, $\text{Ohm}^{-1} \text{cm}^{-1} \times 10^2$
NO_2	HNO_3	
0.144	0.856	12.9
0.200	0.800	14.6
0.249	0.751	15.2
0.293	0.707	15.3
0.358	0.642	14.7
0.419	0.581	13.6
0.471	0.529	12.5
0.511	0.489	11.7
0.548	0.452	10.7

Data source: [63]

The electrical conductivity of the ternary system $\text{HNO}_3/\text{NO}_2/\text{H}_2\text{O}$ is dependent on both NO_2 and water content (Table 14). Electrical conductance measurements present a possible analytical tool for determining the composition of RFNA or WFNA. It is necessary to determine the concentration of only one species in the system by another physicochemical method such as the measurement of transmittance with a spectrophotometer. The nitrogen dioxide or water concentration can be determined by transmittance measurements in the visible region or the IR region, respectively. These measurements together with the conductance measurements bracket no more than two values of composition. Figure 17 shows smoothed curves of constant specific conductance as a function of composition for nitric acid weight fractions greater than 0.80 in a ternary composition diagram.

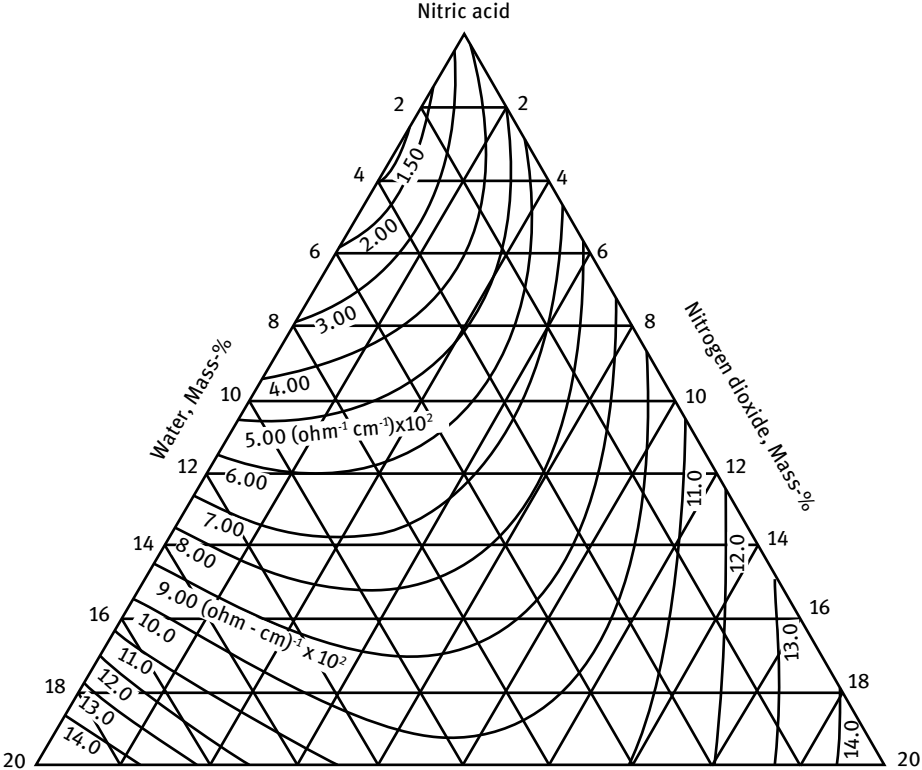


Figure 17: Curves of constant specific conductance in nitric acid-nitrogen dioxide-water system at 273 K and atmospheric pressure. (Reproduced and modified from [63].)

Table 15, which gives a very detailed list of electrical conductivity of $\text{HNO}_3/\text{NO}_2/\text{H}_2\text{O}$ mixtures at 273 K and 101 kPa, is suitable for the quick look-up of data to accurately correlate composition and conductivity.

Table 15: Electrical conductivity of HNO₃/NO₂/H₂O mixtures at 273 K and 101 kPa.

Mass fraction HNO ₃	Specific electrical conductivity, Ohm ⁻¹ cm ⁻¹ × 10 ²																
	Mass fraction NO ₂																
	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	0.11	0.12	0.13	0.14	0.15	
1.00	3.77	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.99	2.18	4.50	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.98	1.51	3.2	5.22	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.97	1.31	2.7	3.9	5.95	—	—	—	—	—	—	—	—	—	—	—	—	—
0.96	1.40	2.3	3.4	4.8	6.68	—	—	—	—	—	—	—	—	—	—	—	—
0.95	1.69	2.3	3.2	4.0	5.7	7.38	—	—	—	—	—	—	—	—	—	—	—
0.94	2.07	2.7	3.2	3.9	5.0	6.4	8.07	—	—	—	—	—	—	—	—	—	—
0.93	2.55	2.9	3.4	4.0	4.8	5.9	7.3	8.74	—	—	—	—	—	—	—	—	—
0.92	3.10	3.3	3.8	4.2	4.9	5.7	6.9	8.1	9.38	—	—	—	—	—	—	—	—
0.91	3.75	3.9	4.2	4.6	5.0	5.7	6.7	7.7	8.8	10.0	—	—	—	—	—	—	—
0.90	4.52	4.7	4.8	5.0	5.3	5.9	6.6	7.4	8.3	9.5	10.6	—	—	—	—	—	—
0.89	5.36	5.3	5.3	5.4	5.7	6.1	6.7	7.3	8.1	9.0	10.0	11.2	—	—	—	—	—
0.88	6.24	6.1	6.0	6.0	6.1	6.4	6.9	7.3	8.0	8.8	9.7	10.7	11.7	—	—	—	—
0.87	7.10	6.9	6.7	6.6	6.6	6.8	7.1	7.5	8.0	8.7	9.3	10.2	11.1	12.1	—	—	—
0.86	8.00	8.0	7.6	7.2	7.1	7.2	7.4	7.7	8.2	8.7	9.2	9.9	10.8	11.7	12.6	—	—
0.85	9.5	9.0	8.6	8.2	8.0	7.9	7.9	8.1	8.3	8.8	9.2	9.8	10.4	11.3	12.1	13.0	—
0.84	10.7	10.0	9.6	9.1	8.8	8.6	8.4	8.4	8.7	8.9	9.3	9.7	10.3	11.0	11.8	12.6	—
0.83	11.9	11.1	10.6	10.0	9.7	9.3	9.1	9.0	9.0	9.1	9.4	9.7	10.2	10.8	11.4	12.1	—
0.82	13.2	12.4	11.7	11.0	10.6	10.1	9.8	9.6	9.4	9.4	9.7	9.9	10.2	10.7	11.2	11.8	—
0.81	14.7	13.8	13.0	12.1	11.5	11.0	0.6	10.2	10.0	9.9	9.9	10.1	10.3	10.7	11.1	11.7	—
0.80	15.9	15.0	14.2	13.5	12.8	12.0	11.4	11.0	10.7	10.4	10.3	10.2	10.3	10.7	11.0	11.4	—

Data source: [62, 63]

1.2.13 Solubility and Miscibility with Mixtures of RFNA

Solubility data are for gaseous or solid compounds that dissolve in nitric acid. Miscibility data are for other liquids that are added to nitric acid to improve its properties as a rocket propellant.

Solubility and miscibility are a chemical phenomenon, but solubility numbers for various compounds in HNO_3 should be summarized under physical properties. Some phase diagrams indicate compound formation. Not all mixtures lead to HNO_3 -based oxidizers with more desirable properties than pure HNO_3 .

1.2.13.1 Miscibility in $\text{HNO}_3/\text{H}_2\text{O}$ Binary System

Inevitably, whether or not one wants it, WFNA will contain varying amounts of water as a byproduct carried over from its production, moisture absorbed from the atmosphere, or water formed during decomposition of HNO_3 .

1.2.13.2 Miscibility in HNO_3/NO_2 Binary System

Freezing-point measurements in the system $\text{HNO}_3/\text{N}_2\text{O}_4$ indicate that at a molar ratio of $\text{N}_2\text{O}_4 : \text{HNO}_3 = 1 : 2$ a solid additive compound is formed. Nitric acid and dinitrogen tetroxide at 273 K are miscible only in the composition range from 0 to 52 and 99.6 to 100 mass-% N_2O_4 [15]. In between there exists a miscibility gap that limits the choices of RFNA compositions for various propulsion applications.

As shown in Figure 18, the mixtures in a range between these numbers separate into two immiscible phases, which would be highly undesirable for the use of RFNA as a rocket propellant. A critical mixing temperature exists at 334 K (61 °C) and 68.6 mass-% N_2O_4 . Above this point the two liquids are miscible over the entire range of mixture ratios (although the system must be pressurized to prevent boiling).

The temperature for the phase separation of N_2O_4 was measured in $\text{HNO}_3\text{-H}_2\text{O}$ systems containing 69.9–99.99% HNO_3 [64]. The critical phase separation (“demixing”) temperature changes with the proportion of N_2O_4 in the mixture and reaches a maximum value. This critical value changes with the HNO_3 concentration in the $\text{HNO}_3\text{-H}_2\text{O}$ system and reaches a minimum value of 315 K (42 °C), with the eutectic containing 90.5% HNO_3 .

The ternary system $\text{HNO}_3/\text{NO}_2/\text{H}_2\text{O}$ has a eutectic point at a composition of 4% H_2O and 17% NO_2 with a freezing point of 195 K (–78 °C).

The liquid-liquid and solid-liquid equilibrium phase boundaries and liquid-liquid and solid-liquid equilibrium data for the $\text{N}_2\text{O}_4/\text{HNO}_3$ system were measured by a cloud point method at 258.2–281.2 K [65, 66]. The critical points and the solubility of dinitrogen tetroxide in nitric acid and the solubility of nitric acid in dinitrogen tetroxide showed that with an increase in temperature, the two-phase area shrank and the solubilities of dinitrogen tetroxide in nitric acid and nitric acid in dinitrogen tetroxide increased, as expected. The addition of dinitrogen pentoxide to RFNA would create an even more powerful oxidizer. Addition of dinitrogen pentoxide affects the miscibility gap between N_2O_4 and HNO_3 .

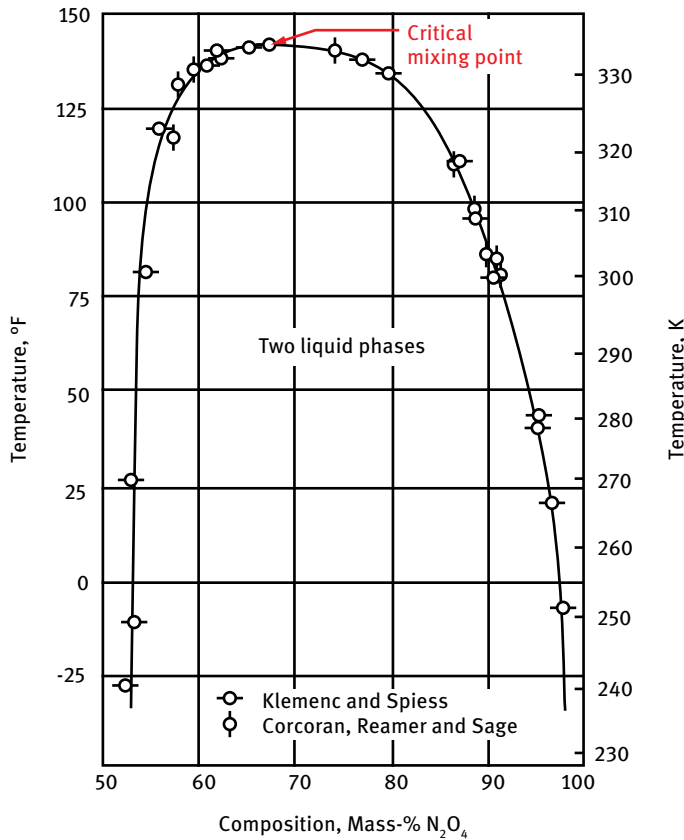


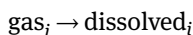
Figure 18: Miscibility of nitric acid and dinitrogen tetroxide. (Reproduced and modified from [29, 15].)

Dissolving N_2O_4 in HNO_3 is not only a physical solution process but involves shifting some of the equilibria that otherwise would lead to the decomposition of HNO_3 [67].

1.2.13.3 Solubility of Gases in RFNA

The solubility of gases in RFNA is of practical interest for several reasons: **(1)** oxygen may have formed as a result of continuing decomposition of HNO_3 , although the addition of H_2O and NO_2 to the equilibrium mixture will suppress further decomposition, and **(2)** pressurant gases will dissolve in the oxidizer and cause cavitation during pumping or loss of performance.

Although dissolving a gas (here identified by the subscript i) in a liquid solvent (identified by the subscript j) is a physical process where no chemical changes are involved, the process



can be expressed by an equilibrium constant like those used for chemical reactions:

$$K = \frac{\text{ppm}_i}{P} = 10^6 M_i \frac{X_i}{M_j} P_i$$

where M_i and M_j are the molecular masses of the gas and the solvent, X_i is the mol fraction of the gas in the solution, and P_i is the pressure above the solution (in units of atmospheres). K is temperature dependent, and a plot of $\log K$ vs. $1/T$ gives a linear correlation like an Arrhenius curve:

$$\log K_i = \frac{A}{T} + B$$

where A and B are dimensionless constants tabulated in Table 16 [68].

Table 16: Gas solubility equation constants for gases dissolving in IRFNA.

Gas	A	B	Solubility at 1 atm (ppm)	
			at 273 K	at 298 K
He	-232	0.7121	0.7	0.8
N ₂	-1364	6.3730	24.0	62.8
CO ₂ ^a	+787	1.241	13300	7600

^a Estimated by similarity method

Data source: [68]

1.2.13.4 Solubility of Oxygen in RFNA

The solubility of O₂ in HNO₃ mixtures was determined from 308 to 343 K (35 to 70 °C) and for pressures up to 2.13 MPa (21 atm). The solubility increased with the temperature. Contrary to the solubility trend of oxygen in other solvents, the solubility of oxygen in nitric acid increased with temperature, as indicated by the change in Henry's law coefficient

$$\text{CO}_2 = \alpha \text{PO}_2$$

The solubility of oxygen in nitric acids of varying compositions is summarized in Table 17.

Table 17: Solubility coefficient of oxygen in nitric acid and mixtures containing water and/or nitrogen dioxide.

Constituents	Composition	Temperature		Solubility coefficient α
	Mass fraction	K	°C	
HNO ₃	1.00	310.8	37.7	5.55
HNO ₃	1.00	327.5	54.4	5.80
HNO ₃ /NO ₂	HNO ₃ 0.85/NO ₂ 0.15	310.8	37.7	3.60
HNO ₃ /NO ₂	HNO ₃ 0.85/NO ₂ 0.15	310.8	37.7	3.78
HNO ₃ /NO ₂	HNO ₃ 0.85/NO ₂ 0.15	327.5	54.4	3.84
HNO ₃ /NO ₂	HNO ₃ 0.85/NO ₂ 0.15	327.5	54.4	3.86
HNO ₃ /H ₂ O	HNO ₃ 0.94/H ₂ O 0.06	310.8	37.7	4.16
HNO ₃ /H ₂ O	HNO ₃ 0.94/H ₂ O 0.06	327.5	54.4	4.26
HNO ₃ /H ₂ O	HNO ₃ 0.94/H ₂ O 0.06	344.2	71.1	4.98
HNO ₃ /H ₂ O	HNO ₃ 0.94/H ₂ O 0.06	360.9	87.8	5.63

Data source: [69,70]

1.3 Chemical Properties of RFNA

Calculations were performed to determine the structures, energetics, and spectroscopy of atmospherically relevant complexes that might also occur in RFNA, such as (HNO₃)•(NO₂), (HNO₃)•(N₂O₄), (NO₃⁻)•(NO₂), and (NO₃⁻)•(N₂O₄) [71]. The binding energies indicated that three of the four complexes are quite stable, with the most stable (NO₃⁻)•(N₂O₄) possessing a binding energy of almost 58 kJ/mol (14 kcal/mol). Vibrational frequencies were calculated for use in detecting the complexes by IR and Raman spectroscopy. An attenuated total reflectance-Fourier transform infrared (ATR-FTIR) experiment showed features at 1632 and 1602 cm⁻¹ that were attributed to NO₂ complexed to NO₃⁻ and HNO₃, respectively. The electronic states of (HNO₃)•(N₂O₄) and (NO₃⁻)•(N₂O₄) were investigated using an excited state method, and it was determined that both complexes possess one low-lying excited state that is accessible through absorption of visible radiation. Evidence for the existence of (NO₃⁻)•(N₂O₄) was obtained from UV/vis absorption spectra of N₂O₄ in concentrated HNO₃, which showed a band at 320 nm that was blue-shifted by 20 nm relative to what is observed for N₂O₄ dissolved in organic solvents.

1.3.1 Analysis of RFNA

Analytical methods are needed for the determination of HNO₃ assay and H₂O, NO₂, HF contaminants and additives in IRFNA [72]. In the United States, RFNA for rocket propellant applications must meet the requirements of Military Specification MIL-PRF-7254G – Propellant, Nitric Acid [73], but there is no specification for WFNA. The WFNA

that is used to make RFNA is not covered by a specification of its own. There are three types of RFNA called out in that specification (Table 18). In Type IIILS, the LS stands for limited storage. The HDA Type IV was added to the specification as an amendment in 1972 and made permanent in 1997. The N_2O_4 used for making Type IV HDA must meet the requirements of MIL-PRF-26539F – Propellants, Dinitrogen Tetroxide, MON-1.

Table 18: Composition of RFNAs as specified by MIL-PRF-7254G.

Constituent	Unit	Type of IRFNA				Test method
		Type IIIA	Type IIIB	Type IIILS	Type IV High Density	
HNO_3	Mass-%	81.6–84.9	81.7–84.9	83.7–86.4	52.7–57.4	By difference
NO_2	Mass-%	14 ± 1	14 ± 1	14 ± 1	44 ± 2	Cerimetric titration
HF	Mass-%	0.7 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	Fluoride-specific ion electrode
H_2O	Mass-%	1.5–2.5	1.5–2.5	0.5 max.	0.5 max.	IR spectrophotometric at $1.4 \mu\text{m}$
Fe_2O_3	Mass-%	not specified	not specified	0.0015 max.	0.002 max.	Colorimetric at 248 nm, in HCl-dissolved solids residue
Solids, max. as nitrates	Mass-%	0.10	0.04	0.04	0.04	Gravimetric
Specific gravity, at 289 K = 60 °F	g/cm ³	1.564–1.575	1.564–1.575	1.572–1.582	1.642–1.652	Hydrometer

The chemical composition of RFNA can change slowly with extended storage, although the changes are not as fast or as dramatic as with WFNA. Nevertheless, it is important to analyze RFNA at the point of delivery and again before it is filled in a rocket propulsion system. Since RFNA has been fielded in several prepackaged missiles, selected units are returned from the field as a regular surveillance program to determine the useful lifespan under real-life conditions. The main parameters analyzed are the water and NO_2 content, since these will affect the ignition delay with hypergolic fuels. See also [74–76].

1.3.1.1 Determination of Water Content in RFNA

A method for determining water in WFNA or RFNA is volumetric titration using Karl Fischer reagent [77, 78]. This method can be used in RFNA containing up to 15% NO_2 , and the standard deviation is 0.052% absolute.

Simplified go/no go indications of RFNA samples can be obtained by electric conductometric methods. One of these methods [79, 80] measured the conductivity at constant temperature, one sample as is and a second sample after saturating it with potassium nitrate.

The electrical conductivity of the ternary system $\text{HNO}_3/\text{NO}_2/\text{H}_2\text{O}$ is dependent on both NO_2 and water content [62]. Thus, the method by itself cannot give both the NO_2 and H_2O content. The method must be combined with another method to obtain both numbers.

The water analysis method recommended in MIL-PRF-7254G first obtains the absorption spectrum of the sample between 1500 and 1350 nm versus CH_2Cl_2 , both contained in 5-mm cells, then measures the absorption at 1404 nm, which is specific for water, while the absorption at 1440 nm is mostly that of HNO_3 . A calibration curve is generated from solutions of water in acetonitrile with known H_2O concentrations.

1.3.1.2 Determination of NO_2 Content in RFNA

The NO_2 content of RFNA can be determined spectrophotometrically at 425 or 500 nm in a thermostatted spectrophotometer as long as there are no other colored contaminants [81–83]. A calibration curve can be best prepared from freshly prepared samples with known NO_2 contents. Water contents must be kept similar for both calibration and actual samples. The photometric method has also been used to determine the degree of dissociation of NO_2 and HNO_3 in RFNA.

The optical absorbance of solutions of nitrogen dioxide in nitric acid was measured at 273 K (0 °C) and 1 atm using light at a wavelength of 425 nm to study the ionization occurring in solutions [82–84]. The results indicated that in nitric acid solutions containing less than 1% nitrogen dioxide, the nitrogen dioxide is about 70% ionized into nitrosonium ion NO^+ , whereas the nitric acid is about 5% ionized into nitronium NO_2^+ ions.

A dual-band spectrophotometer has been developed especially for RFNA analysis that can analyze both H_2O and NO_2 : First the H_2O absorption at 1.423 μm and then the NO_2 absorption at 480 nm is measured and compared to absorption values obtained from calibration curves [85]. The accuracy is $\pm 0.064\%$ for water and $\pm 0.25\%$ for NO_2 . The sample must be free of iron nitrate or other colored contaminants that might interfere with NO_2 determination.

For the determination of N_2O_3 , NO_2 , and HNO_2 in nitric acid by volumetric methods, one can first titrate total acid acidimetrically and then titrate the oxidizable species by manganometric titration [86].

The method for nitrite analysis recommended in MIL-PRF-7254G dissolves an IRFNA sample in excess of 0.5-N NaOH under exclusion of air, then reacts an acidified aliquot with an excess of 0.1-N acidic ceric ammonium hexanitrate solution sufficient to react the nitrite ion, and then back-titrates with acidic 0.05-N ferrous ammonium sulfate solution with potentiometric end point indication.

Mass spectrometric analysis of WFNA or RFNA may be very accurate and identify many species, but it is not practical for field use [87]. This method would be used only to identify unusual contaminants or for kinetic studies. For other analytical methods for RFNA see also [88–92].

The addition of dinitrogen pentoxide to RFNA creates a more powerful oxidizer and nitrating agent, so its composition must be analyzed before additional testing is done with this oxidizer [93]. The concentrations of N_2O_4 and N_2O_5 in nitric acid can be measured by chemical titration or NMR [94]. Both methods are in agreement and accurate. N_2O_4 assay titrations using cerium(IV) sulfate as the oxidant were more accurate than those using potassium permanganate as the oxidant.

Some chemical supply companies offer RFNA described as “ HNO_3 , >90%, 5–10% dissolved oxides as N_2O_3 .” This description may not be accurate because if the acid contained N_2O_3 instead of $\text{NO}_2/\text{N}_2\text{O}_4$, it would be blue-green and not red.

1.3.2 Thermal Stability and Decomposition of RFNA

The thermal stability of RFNA during sudden heating (as in a regenerative cooling jacket in a rocket engine) is sufficiently high and will not cause any chemical changes between the start of the heating and injection into the combustion chamber. Concern is only for the liquid that may remain trapped in the cooling jacket after the engine shuts down and heat soaks from the hot wall into the remaining structure of the engine. In this regard, RFNA is more stable than WFNA because it is already close to the equilibrium composition in the $\text{HNO}_3/\text{NO}_2/\text{H}_2\text{O}$ system [95, 96].

Dinitrogen tetroxide and/or water has been added to WFNA to retard the troublesome oxygen evolution and potential overpressurization of tanks during storage. The equilibrium decomposition pressure of samples of $\text{HNO}_3/\text{H}_2\text{O}$ mixtures containing 2.5 and 5.0 mass-% water and of HNO_3/NO_2 mixtures containing 7.5 and 15.0 mass-% nitrogen dioxide were determined between 358 and 423 K (85 and 150 °C) and at vapor volume to total apparatus volume ratios varying from 0.05 to 0.8 [97]. The decomposition measurements were carried out in a glass tube in a high-pressure apparatus under isochoric conditions and with continuous stirring. The experimental data were then presented graphically a) as plots of equilibrium pressure vs. ratio of vapor volume to total volume, V_G/V , at constant temperature and b) as plots of the equilibrium pressure vs. the specific volume of the mixture at constant temperature. By appropriate cross plots of the data, a series of diagrams showing the equilibrium pressure vs. temperature at constant V_G/V ratios for integral values of initial water and nitrogen dioxide content were prepared and high-temperature data were extrapolated to 298 K (25 °C). The kinetics of decomposition of nitric acid was studied by analyzing available pressure-time rate data for different V_G/V values and in a temperature range of 349 to 373 K (76 to 100 °C). Rate measurements were also carried out in the presence of excess nitrogen dioxide and water for different V_G/V values at 358 K (85 °C) and with excess

oxygen at an initial pressure of 3.1 MPa gauge (454 psig) and at 349 K (76 °C). Under the conditions of the investigation, the decomposition of nitric acid was believed to be a homogeneous liquid-phase reaction. The rate of decomposition can be represented satisfactorily by the equation

$$\frac{dP}{dt} = Ae^{B(P_{\infty} - P)}$$

where P_{∞} = equilibrium pressure, t = time, e = base of natural logarithms, and A and B are constants. This equation held accurately over 80% of the reaction. The initial fast rate was followed by a slower apparent-first-order rate with respect to time. The initial rates were (a) unaffected by addition of up to 15% nitrogen dioxide or by excess oxygen at an initial pressure of 3.1-MPa gauge (454 psig) at 349 K (76 °C) and (b) lowered considerably by the addition of small amounts of water. The specific first-order rates were increased by excess nitrogen dioxide and oxygen but were lowered by added water. The experimental energy of activation was found to be 125.5 kJ/mol (30 kcal/mol), independent of the V_G/V ratio. The preexponential factor for the Arrhenius equation was 10^{14} s^{-1} .

Later experiments confirmed that (1) the pressure, which is primarily due to the oxygen formed as a result of the decomposition, increased with an increase in temperature and with a decrease in the V_G/V ratio, (2) the pressure was markedly reduced by the addition of nitrogen dioxide and (or) water, particularly at the lower temperatures, and (3) the V_G/V ratio had a very great influence on the value of the equilibrium pressure of mixtures high in nitric acid content, but this influence diminished with the addition of nitrogen dioxide and water and became relatively insignificant in mixtures containing more than 20% of additive (nitrogen dioxide plus water). On a weight basis, water was more effective in reducing the pressure than nitrogen dioxide.

Thermal stability tests starting with WFNA and RFNA with widely varying compositions showed that the ternary diagram can be subdivided into three stability regions:

- A. Decomposition with resulting pressure increase due to oxygen evolution
- B. Stable, but only while maintaining increased oxygen pressure
- C. Stable under most conditions

The compositions of the liquid phase at physicochemical equilibrium at 358 K (85 °C) and the three regions of (in)stability were plotted on a triangular diagram (Figure 19) [98]. None of the equilibrium mixtures contained more than about 91% nitric acid, indicating that acids of this strength and above were unstable and would decompose spontaneously at this temperature. On the other hand, ternary mixtures containing 80% nitric acid and more than 6% water were found to be stable. Compositions between these two extremes were stable only under an oxygen pressure of 0.34 to 10.3 MPa (50 to 1500 psia).

The ultimate decomposition pressures at equilibrium if WFNA or RFNA with low N_2O_4 and H_2O contents is stored at 358 K (85 °C) in a hermetically closed system

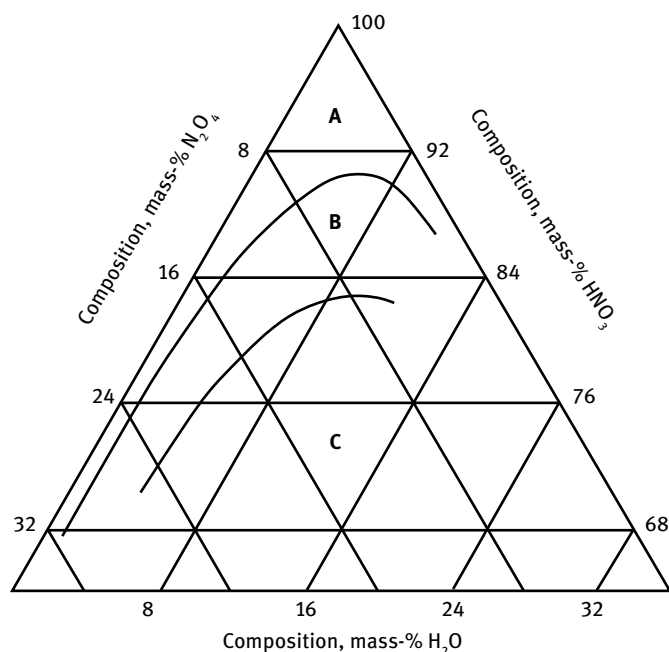


Figure 19: Stability regimes of RFNA at 358 K (85 °C). (Reproduced and modified from [98].)

with only 15% ullage were calculated and displayed in a ternary diagram, Figure 20 [96–99]. As shown in this graph, the decomposition pressures developed at the end of the test can be quite destructive.

The saturation pressure of NO_2 dissolved in HNO_3 with 3% H_2O reaches atmospheric pressure once the NO_2 concentration is increased beyond 16% NO_2 . For this reason, it is not practical to increase the NO_2 concentration beyond 16% NO_2 because the composition of the acid would change each time the liquid is transferred from one container to another or the vapor space is vented. The NO_2 saturation pressure could be decreased slightly by adding more water, but that is not desirable because it causes a loss of rocket performance of the resulting oxidizer mixture. These calculations are of interest not only in the handling and storage of nitric acid but also in the manufacture of concentrated nitric acid from liquid nitrogen dioxide, water, and oxygen under pressure, where the same equilibrium is approached from the other side.

The addition of HF as a corrosion inhibitor to RFNA to make IRFNA does not change the thermal and storage stability of the acid, other than preventing the leaching of contaminants that might catalyze the decomposition reaction. The thermal stability of IRFNA is discussed in Section 2.3.2.1.

A maximum-density HDA that is stable enough to survive the sterilization heating of interplanetary spacecraft may contain 43.9% NO_2 and 56.03% HNO_3 [100]. The

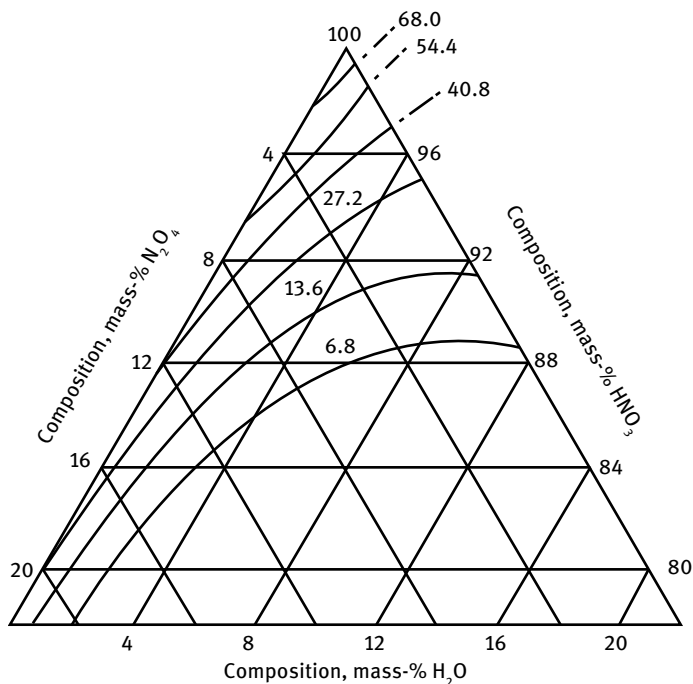


Figure 20: Decomposition pressure (in atm) of $\text{HNO}_3/\text{NO}_2/\text{H}_2\text{O}$ mixtures at 358 K (85 °C) in a container with 15% ullage. (Reproduced and modified from [99].)

addition of 0.1–1% HF may reduce the corrosion of metals. This composition was also called maximum-density fuming nitric acid (MDFNA).

1.4 Compatibility with and Corrosion of Materials in RFNA

Several metals and alloys were tested to determine their rates of corrosion in two types of RFNA and one type of MA [101]. Several stainless steels and Duriron exhibited good resistance to corrosion by concentrated nitric acids; aluminum alloys were more extensively attacked, Haynes-Stellite alloys and chromium were only slightly corroded, and tin, gold, and tantalum exhibited very good resistance to corrosion, even at elevated temperatures. Corrosion rates in MA were lower than in the other nitric acids for most of the metals tested (Table 19). In general, corrosion rates in 16 and in 6.5% NO_2 RFNA were similar. A limited number of experiments with WFNA (containing less than 0.5% NO_2) indicated further that the corrosion rates of metals were not significantly different in fuming nitric acids with various concentrations of nitrogen dioxide.

Table 19: Corrosion rates by nitric acids at two different temperatures.

Material	Corrosion rates, mm/year					
	Temperature 283–300 K (10–27 °C = 50 to 80 °F)			Temperature 394–422 K (121–149 °C = 260 to 300 °F)		
	RFNA 16% NO ₂	RFNA 6.5% NO ₂	Mixed acid ^a	RFNA 16% NO ₂	RFNA 6.5% NO ₂	Mixed acid ^a
SAE-1020	0.25	0.76	0.025	203	140	0.61
AISI-302	—	0.015	—	—	—	—
AISI-303	—	—	0.025	56	—	0.2
AISI-304	0.01	0.01	0.015	33	30	2.0
AISI-316	—	0.018	—	—	63	—
AISI-321	—	—	0.038	—	—	2.0
AISI-347	—	—	0.038	—	—	0.61
AISI-410	—	0.025	—	—	127	—
AISI-414	0.051	0.101	—	—	89	—
AISI-416	0.101	0.076	0.0076	127	76	0.076
AISI-420	—	—	—	89	—	—
AISI-430	0.0125	—	—	20	—	—
AISI-440	0.51	—	—	63	—	—
AISI-446	0.0125	—	—	7.6	—	—
Stainless Steel W	—	0.015	—	—	101	—
Worthite	—	<0.0001	—	—	12.5	—
Iron SAE 4130	—	—	0.101	—	—	3.8
Haynes Stellite No.1	—	<0.0001	0.023	—	7.6	1.5
Haynes Stellite No.6	—	—	—	—	51	—
Aluminum 2S	0.10	—	0.25	152	—	1.0
Aluminum 17-ST	—	0.05	0.15	178	101	0.5
Aluminum 24-ST	—	0.025	0.18	76	155	0.76
Alcoa 43	0.076	—	—	170	—	0.5
Alcoa 61-S	0.23	—	—	203	—	0.5
Alcoa 195	0.05	—	—	210	—	—
Alcoa 214	0.25	—	—	480	—	—
Alcoa 355	0.10	—	—	—	—	—
Alcoa 356	0.125	<0.0001	0.25	84	115	0.5
Chrome coating	—	0.012	0.0076	—	17.8	0.5
Tin	—	0.0025	0.0051	—	0.18	3.3
Tantalum	—	—	—	—	<0.001	0.02

^a Mixed acid = 88 parts of 95% HNO₃ + 12 parts of fuming sulfuric acid H₂SO₄ containing 20% SO₃

Data source: [101]

Table 20: Stagnant corrosion rates of CRES-304 in 6.5% NO₂ RFNA

Temperature		Corrosion rate	
K	°F	mm/year	in./year
299.8	80	0.010	0.0004
327.6	130	0.18	0.007
353.1	176	5.1	0.2
370.4	207	7.6	0.3
383.1	230	12.7	0.5
394.3	250	30	1.2

Data source: [101]

Table 20 gives the stagnant corrosion rates of CRES-304 in 6.5% NO₂ RFNA for six different temperatures.

The primary advantages of Type IIIA acid with regard to storage stability, low freezing point, and less corrosion were sufficient to justify its use in rocket propulsion systems slated to be developed in the US shortly after World War II for tactical use. The use of 17-7PH with Type IIIA acid was considered questionable [102]. Most rocket engine construction materials are equally adaptable to Types I and IIIA acids. Design criteria (combustion, injection, pumps, and cooling jackets) appear to be equally adaptable to Types I and IIIA acid. The differences in vapor pressure, density, and heat capacity must be considered in systems design.

The corrosion, ignition reactions, and stress-corrosion cracking of titanium and its alloys resulting from storage in fuming nitric acid were studied [103]. The metal samples were stored in the liquid and vapor phases of various concentrations of the HNO₃-NO₂-H₂O system for periods of time ranging from 1 h to 90 d at temperatures ranging from room temperature to 344 K (71°C). The susceptibility to ignition reactions, the tendency toward stress-corrosion cracking, and the corrosion rates of the metal were studied as a function of the chemical composition and temperature of the fuming nitric acids. In particular, the corrosion-time relationships of two titanium alloys in anhydrous RFNA (20% NO₂) over a temperature range of 298 to 344 K (25 to 71°C) were determined. The corrosion rates of Ti-6Al-4V in RFNA with 0, 10, or 20% NO₂ after 1 week at 327 K (54°C) were 8.16, 20.76, or 96.83 mil/year (1 mil = 0.001 in.). The samples in 10 or 20% NO₂ RFNA were sensitive to ignition when scratched, but those in 0% NO₂ = WFNA were not. The addition of 1 to 2% water significantly reduced the corrosion rates. The addition of hydrofluoric acid did not change the corrosion behavior of titanium in RFNA [104, 105].

Tests on A70 commercial titanium and Ti-7% Mn alloy C110M indicated that sporadically rapid attack in RFNA may be associated with limited air supply in the test container. Evidence was found indicating that sporadically observed rapid attack on titanium in RFNA may, in some cases, be associated with a limited air/oxygen supply

in the test container [106]. Additions of air, oxygen, and certain salts resulted in noticeable corrosion inhibition. Attack in the uninhibited acid was found to be largely intergranular. In the case of a two-phase alloy, the beta phase was removed preferentially, leaving a finely divided pyrophoric deposit of the alpha structure. A commercial grade of RFNA was used that had a specific gravity of 1.59 to 1.60 g/cm³ and a nominal composition of 20% NO₂, 78% HNO₃, and 2% H₂O. The WFNA consisted of 90% HNO₃ and 10% H₂O and had a specific gravity of 1.49 to 1.50 g/cm³. A possible mechanism was proposed for the observed breakdown in passivity.

Storage tests to determine the effectiveness of inhibition by oxygen indicated no inhibition of titanium corrosion by oxygen but confirmed the inhibiting effect of water content of 1 to 2 mass-% in fuming nitric acid [107]. The addition of water alleviates the tendency of titanium, when exposed to anhydrous RFNA, toward ignition reactions and stress cracking. In these tests, which lasted 28 d at 303 K (30 °C), the samples investigated were 1/2-in. squares (0.020 in. thick) of commercially pure (CP) titanium (75A) and a binary 8%-manganese alloy (C110M). When analyzing for leached metals in solution, the Ti concentrations in the acid offloaded from the Ti CP were very small (0.01–0.15% Ti), but in the Ti-Mn alloy, both metals were leached in substantial quantities (0.07–0.88% Ti). The metal after corrosion in anhydrous RFNA (20% NO₂) was pyrophoric.

Static corrosion tests were performed to evaluate candidate materials being considered for use with standard HDA [108, 109]. HDA contained 53–54% HNO₃, 44–45% NTO, 0.2% H₂O, and 0.7% HF. The NTO used for making HDA contained 1 mass-% NO and was green, so it should have been designated as MON-1. The tests were performed at temperatures and times representative of anticipated service conditions for each material. Fifty-nine candidate rocket engine materials were screened through corrosion tests with standard HDA. This included 19 tests for a total of 7 d at 322 K (120 °F), 5 tests for a total of 6 h at 378 K (220 °F), and 38 tests for a total of 60 d at 305 K (90 °F). In addition to studying duration and temperature effects, the tests provided comparisons between parent metals, welds, and galvanic couples. In most cases, data were obtained for exposure to liquid and vapor. With few exceptions, S/V (surface of metal/volume of acid) was 1.0, which is intermediate between conditions in large tanks and small lines. The objective of these analyses was to provide an explanation for current test results and a basis for future tests with inhibitors other than HF. Measurements and observations were made both for changes in the acid and the material. This included chemical analyses and corrosion rates calculated from changes in mass. Based on the results, the materials were ranked in one of four categories, ranging from satisfactory for general use to unsatisfactory. Class I materials were considered satisfactory for general use in contact with the propellant tested. Other classes were restricted in usage. Several aluminum alloys fell in the former category. Stainless steels appeared good for limited use. Only three stainless steel samples exhibited a Class I rating, and this only at 305 K (90 °F). Results are shown in Table 21, where X denotes an acceptable

Table 21: Satisfactory materials for general use with standard HDA.

Materials	Service at (temperature)		
	305 K 90 °F	322 K 120 °F	378 K 220 °F
Aluminum alloys			
356A cast	X		
356-T6	X		
5086		X	
5086 welded		X	
5454-0		X	
5454-H32		X	
5454-1132 welded		X	
6061-T6	X	X	
6061-T6 welded		X	
300 Series stainless steel			
304L	X		(II)
316 spring wire	X		
347	X	(III)	
Other metals			
17-4 PH H1025	X		
17-7 PH fully annealed, Cond. A	X		
17-7 PH spring wire	X		
17-7 PH torque tube	X	(II)	
PT-CO alloy		X	
Non-metals			
Rulon 123	X	(II)	

Data source: [109]

operating condition for 7-d use and the Roman numerals indicate marginal material classes. It was recommended that compounds containing fluorine and phosphorus be evaluated as inhibitors.

A study of the influence of dissolved corrosion products from CRES-347 or Al-6061 on the phase separation in HDA, containing 52.7–57.4 mass-% HNO_3 and 44 ± 2 mass-% N_2O_4 showed that the presence of two liquid phases could be responsible for flow irregularities, particularly if one of these phases is of high viscosity as a result of a high concentration of dissolved corrosion products [110]. For any given amount of corrosion products in solution, it is important to determine the exact liquid composition at which a second phase appears. In searching for the best method for detection of phase separation in $\text{HNO}_3/\text{N}_2\text{O}_4$ mixtures, changes in electrical conductivity were found to provide a sensitive and accurate method. Experiments showed a considerable decrease in corrosion rate by uninhibited HDA as the concentration of N_2O_4 was increased (Figure 21).

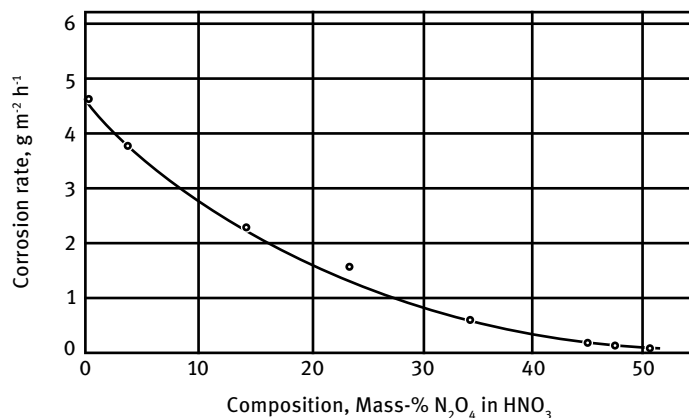


Figure 21: Dependence of corrosion rate of CRES-321 on N_2O_4 concentration in HDA. (Reproduced and modified from [110].)

The selection of materials for the safe handling of RFNA requires special considerations, in particular for welded stainless steels, where the heat-affected zone becomes more susceptible to corrosion due to carbide precipitation [111]. See also [112].

The corrosion rate of nickel-silicon alloys in RFNA as a function of the silicon content was shown to have two extreme points: a maximum at a Si content of 5% and a minimum at 10% Si [113]. Alloying of Ni-15% Cr alloys with silicon monotonically lowered their corrosion rate. Corrosion rates were correlated to the electrochemical potentials of Ni/Cr and Ni/Cr/Si alloys.

A procedure for corrosion investigation of stainless steels and heat-resistant alloys in RFNA at high temperatures was developed and corrosion rate data were obtained for stainless steels and heat-resistant alloys at 323–723 K (50–450 °C) [114]. Corrosion rate data were obtained for (Russian designations) EI654, 12Kh18N10T, Kh28VI, 15Kh18N12S4TYu, and 95Kh18 steels and EI703 alloy. It was found that the corrosion rate increased sharply with the temperature while the system was in the liquid phase. Then at 573–723 K (300–450 °C) the corrosion rate slowed down, and scale coated the metal surface. The apparatus for studying electrochemical behavior of metals in a corrosive medium at high temperatures consisted of glass with metal electrodes. Anodic potentiostatic curves of stainless steel in RFNA showed that the rise in temperature reduced the passive area, decreased the potential of repassivation, and increased the current in the passive area.

The corrosion resistance of 28 metals and 2 metalloids to RFNA was examined, and the effect of alloying iron and nickel with corrosion resistant elements on their electrochemical properties was measured [115].

The corrosion resistance of type 28 steel specimens in RFNA was investigated, with variations depending on the steelmaking method, heat treatment, manganese, and carbon contents and additional alloying [116]. It was shown that intergranular corrosion (IGC) of 128 type steel can be prevented by alloying it with niobium or titanium provided that carbon and manganese content are limited. It was also found that the quenching and tempering of 428 type steel affect its IGC in RFNA, contrary to the known effects on its IGC in other corrosive media.

1.4.1 Corrosion Products in RFNA

Corrosion products in nitric acids can settle as a sludge at the bottom of a tank and become entrained in feed lines to the rocket engine, eventually clogging injector orifices and causing engine failures. The analysis of corrosion products may also give a hint as to which component in a propulsion system is failing due to inadequate compatibility. Aluminum nitrate, a corrosion product often encountered in WFNA or RFNA stored in aluminum tanks, is not very soluble in nitric acid [117]. The effect of iron impurity levels up to 100 ppm as Fe_2O_3 on HDA heat transfer was studied in 30 tests using resistance-heated, circular, Al-6061-T6 tubes [51]. The experimental forced convection heat transfer coefficients were unaffected by iron impurity level.

1.4.2 Protective Coatings for Metals in RFNA

Attempts have been made to develop protective linings of polytetrafluoroethylene (PTFE) and similar materials in RFNA storage tanks, but with limited success. N_2O_4 dissociates to produce NO_2 , which quickly permeates thin layers of polymers and leads to the delamination of the lining from the substrate metal. No coating materials will effectively protect steel or aluminum from RFNA where atmospheric moisture may also have access to the metal [118, 119].

1.4.3 Lubricants for RFNA Service

The only lubricants acceptable for WFNA or RFNA service are chemically inert perfluorinated hydrocarbons or chlorofluorocarbons. Examples of recommended lubricants are Fluorolube, Kel-F oil, Krytox 240AC, or Nordcoseal-147-S. Similar lubricants are used for N_2O_4 service. Conventional hydrocarbon greases and oils must be avoided because they constitute an explosion hazard if mixed with RFNA [120]. One particular lubricant was made from perfluorinated $\text{C}_4\text{-C}_6$ trialkylamines mixed with PTFE powder [121].

1.4.4 Accidental Ignition of Metals in RFNA

Titanium is generally considered to be compatible with either WFNA or RFNA. However, in several instances, exceptionally high rates of attack were observed in RFNA. In these cases, the rate of attack ranged from 10/1000ths to 100/1000ths of an

inch per year and frequently adherent but pyrophoric corrosion deposits formed. The corrosion product was found to be sensitive to heat, shock, and electric sparks, and in two cases it exploded with violence, causing severe injuries and one fatality to attending personnel [122, 123]. The titanium involved in the accident was commercially pure titanium in various stages of metals processing (cold-rolling, annealing, welding). In another incident, several test specimens of a titanium-8% manganese alloy reacted with RFNA, showering a chemist with corrosive liquid.

1.5 Toxicity and Safe Handling of RFNA

1.5.1 Toxicity of RFNA

RFNA contains typically 3 to 16 mass-% NO_2 or N_2O_4 , which substantially increases the vapor pressure of the liquid and readily evaporates as soon as the liquid is exposed to ambient air, creating an inhalation toxicity hazard. The toxicity hazard of accidental inhalation of the red fumes from RFNA is substantially higher than the problems faced when handling WFNA [124]. The occupational hazard with RFNA may actually be higher than that of liquid N_2O_4 because liquid N_2O_4 and mixed oxides of nitrogen (MON) are always handled and transferred in hermetically closed containers under pressure, while RFNA can be poured from one container into another at atmospheric pressure while exposed to the air and thus more likely to be spilled [125–128]. The toxicity of NO_2 escaping from RFNA is essentially the same as that of NO_2 escaping from dinitrogen tetroxide, the other very widely used storable rocket propellant oxidizer. In Volume 1, *Encyclopedia of Oxidizers*, the chapter “Dinitrogen Tetroxide” contains a detailed account of the toxicity of NO_2 .

1.5.2 Protective Equipment for Safe Handling of RFNA

Whereas a gas mask with a filter for acidic fumes may suffice for handling WFNA or MA, handling of RFNA requires a special filter for NO_2 or even a supplied air breathing apparatus to provide adequate respiratory protection of propellant handlers. The red fumes do not provide enough of a visual warning regarding the presence of NO_2 . It is better to rely on special monitoring and warning apparatus.

Serious injury by concentrated nitric acids is not infrequent, accounting for a significant number of cases of disability and death from spills of hazardous chemicals. Toxicologically, the two major forms, WFNA and RFNA, may be regarded as identical, since they are both extremely corrosive and since both emit dangerous fumes. The literature contains reports about fatal RFNA accidents [129, 130].

Protective clothing for propellant handlers in contact with RFNA must be made from RFNA-resistant materials [131]. Several materials for gloves, boots, aprons, and splash shields were evaluated in permeation tests with hydrazine, unsymmetrical dimethylhydrazine (UDMH), and IRFNA [132–134].

1.5.3 Handling, Transportation, Storage, and Disposal of RFNA

1.5.3.1 Safe Handling of RFNA

A 20-page summary on the hazards of handling IRFNA and HDA is provided in Chapter 15 of [135]. The CPIA/M4 Unit 17 (Mar 1976) is 40 pages long and deals with both RFNA and WFNA. It has a materials compatibility list where materials are ranked in four compatibility classes. See also [136].

1.5.3.2 Transportation and Storage of RFNA

The transportation and storage of RFNA would be easier than the storage and transportation of WFNA because no excessive oxygen pressure buildup is expected during storage as long as the NO_2 and H_2O concentrations are kept in the optimum range [137].

1.5.3.3 Disposal of RFNA

At the end of the Cold War, large quantities of RFNA were stored in Russia and the former Soviet republics. As part of the SALT disarmament agreements, the missiles and their support facilities had to be decommissioned and large quantities of this toxic and corrosive material had to be demilitarized. A brief Internet search revealed numerous pieces of information, but they could not be independently verified, and the following survey may not be complete. Numerous international conferences have been devoted to the subject of cleaning up contaminated former military sites so that the areas can be returned to civilian use [138]. Most of the concern at these conferences was about spilled halogenated solvents, transformer oils, and hydrocarbon fuels that have permeated into the ground and aquifers. Some reports list RFNA in one breath with problems in the disposal of plutonium and chemical warfare agents. The problem of RFNA disposal is dwarfed by problems associated with the disposal and accountability of these other chemicals. Some reports discuss RFNA disposal in connection with the disposal of other liquid rocket propellants, such as UDMH (code name: Heptyl), Samin (a mixture of xylydine and triethylamine) or dinitrogen tetroxide (code name: Amyl) [139]. Unfortunately, the storage conditions were not carefully controlled and some of it had already leaked into the ground. The abandoned storage magazines constituted a hazard to the surrounding communities [140]. Various weapon systems used RFNA (“*Melanj*”) and had to be demilitarized [141]. The amounts stored in two military depots at Alyat and Mingechevir in Azerbaijan may have amounted to nearly 2000 metric tons, and similar quantities were found in other locations.

The compositions of RFNA (*Melanj*) were analyzed, and apparently there were different grades, also designated as *azotnaya kislota* (nitric acid), or AK with designations like AK-20k, AK-27p, and AK-27i [142]. *Melanj* AK-20f, AK-20i, and AK-20k contained 17.5–22.5% NO_2 . *Melanj* AK-20f, AK-20k, and AK-27p contained 0.1–1.3% phosphoric acid. *Melanj* AK-20f, AK-20k, and AK-27p were IRFNA and contained 0.3–0.8% anhydrous hydrofluoric acid. One of these mixtures may contain up to 7.5% sulfuric acid in addition to dinitrogen tetroxide and nitric acid. Several methods were evalu-

ated to convert the unwanted rocket propellant oxidizer to commercially useful products, such as fertilizer.

Besides abandoned propellants in Azerbaijan, additional tanks filled with Melanj had to be disposed of in Moldova [143]. Several different methods were evaluated to not only dispose of but also to convert the abandoned and unwanted rocket propellants, including Samin and Melanj, into commercially useful products, such as fertilizer or plastics [144–148]. Ukraine had planned to dispose of all its remaining toxic rocket fuel, most of it known as Melanj, by 2013.

2 Inhibited Red Fuming Acid

Development work during the 1950s revealed that corrosion by $\text{HNO}_3/\text{N}_2\text{O}_4$ mixtures can be greatly reduced by the inclusion of small concentrations of fluoride in the form of hydrogen fluoride. This has usually been achieved by adding liquid hydrogen fluoride (0.7 mass-%) to the oxidizer. The mechanism of passivation appears to be the formation of an impervious coating of insoluble metal fluoride on the surface of the metal. The presence of the fluoride corrosion inhibitor can reduce the rate of attack (in terms of loss of section) on steel and aluminum alloys to acceptable levels, but it also causes a secondary problem due to the formation of significant quantities of low-solubility corrosion products. These corrosion products are troublesome because they do not remain adhered to the walls of the propellant tanks but tend to form semicolloidal suspensions in the liquid or settle as a sludge in the bottom of the oxidizer tank. In either case such material is dangerous since it has the capacity to cause clogging of the propellant feed system, thereby affecting the performance of the rocket engine.

This section on IRFNA includes data on inhibited HDA, which contains more N_2O_4 than IRFNA. The AGENA upper stage propulsion system started operating in 1957. Between 1957 and 1972, several engine modifications and propellant changes were made to increase performance. Notable among the latter was a change from IRFNA to standard HDA (HDA). Hydrogen fluoride was added to both oxidizers as a corrosion inhibitor. Experience showed HF to be less effective in HDA than in IRFNA, and a search was launched for an alternate corrosion inhibitor that would extend the useful life of either of the two oxidizers. Under Contract F04611-72-C-0026 Bell Aerospace Textron developed a superior corrosion inhibitor, phosphorus pentafluoride, which promised long-term storability and extended mission life. The new oxidizer was named modified HDA. Extended storage tests completed under Contract F04611-73-C-0069 showed that the new oxidizer could be stored for 2 years in aluminum and stainless-steel tanks with insignificant corrosion. Under Contract F04611-76-C-0054, the corrosiveness of standard HDA and modified HDA toward a variety of materials in AGENA and integrated secondary propulsion system (ISPS) engines was compared. Modified HDA was found to be significantly less corrosive than standard HDA. Additional data were obtained

concerning the analysis and some of the properties of the two acids. There was no adverse effect on substitution of one corrosion inhibitor for the other. Although HDA is a more energetic propellant than RFNA, experience suggests that it is also more susceptible to problems with corrosion products than IRFNA, and this is one factor that may have restricted the use of HDA.

2.1 Preparation of IRFNA

IRFNA can be prepared from RFNA by the addition of a measured amount of anhydrous hydrogen fluoride ("hydrofluoric acid", HF). In Russia, the following IRFNA compositions were in use:

- AK20 Russian formulation consisting of 80% nitric acid + 20% N_2O_4 (AK = *azotnaya kislota* in Russian = nitric acid)
- AK20F Russian formulation consisting of 80% nitric acid + 20% N_2O_4 + fluorine passivating agent
- AK20I Russian formulation consisting of 80% nitric acid + 20% N_2O_4 + iodine passivating agent
- AK20K Russian formulation consisting of 80% nitric acid + 20% N_2O_4 + unknown additive
- AK27I Russian formulation consisting of 73% nitric acid + 27% N_2O_4 + iodine passivating agent
- AK-27P Russian formulation consisting of 73% nitric acid + 27% N_2O_4 + unknown additive.

2.2 Physical Properties of IRFNA

The physical properties of IRFNA are essentially the same as those of RFNA. The presence or absence of a small percentage (<0.5 mass-%) HF does not make that much of a difference. Some of the physical properties reported in other sections of this book may actually have been for IRFNA instead of plain RFNA.

2.2.1 Freezing Point and Phase Diagrams of IRFNA

The addition of 0.5–0.7 mass-% HF did not significantly alter the freezing point of IRFNA compared to that of RFNA.

2.2.2 Boiling Point of IRFNA

The addition of 0.5–0.7 mass-% HF did not significantly alter the boiling point of IRFNA compared to that of RFNA.

2.2.3 Vapor Pressure and Vapor Phase Composition of IRFNA

Eight modified HDA solutions containing high and low concentrations of 41 and 45% NO_2 , 0.4 and 1.0% H_2O , and 0.5 and 0.7% PF_5 were prepared for vapor pressure measurements in Teflon-lined aluminum vessels [149]. The NO_2 concentration was bumped up 1% above nominal because some NO_2 was lost when admitting the liquid to the evacuated apparatus and filling the vapor space above the liquid. It was necessary to separate the decomposition pressure component of equilibrium pressure from the vapor pressure component, at a fixed temperature. The decomposition pressure arose from the generation of dioxygen gas by the decomposition of nitric acid and the relatively low solubility of oxygen in modified HDA. The vapor pressures for two compositions bracketing the range of compositions studies are graphed in Figure 22.

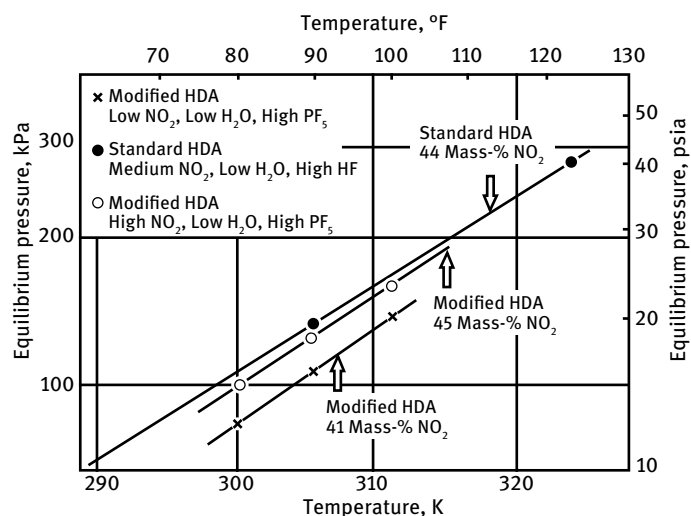


Figure 22: Vapor pressure of modified HDA in comparison to standard HDA. (Reproduced and modified from [150].)

2.2.4 Density and Partial Molar Volumina of IRFNA

Nine batches of modified HDA containing three levels (42, 44, and 46%) of NO_2 content and three levels of water content (as received, 0.5, and 1.0% H_2O) were prepared to measure the density of HDA containing 0.5% PF_5 instead of 0.7% HF as inhibitor [149]. The composition of the nine acids is given in the legend to Figure 23. No water was deliberately added to the first three blends. The variations in water content reflected minor differences in the starting materials. Calculated amounts of water were added prior to nitrogen dioxide addition during preparation of the other blends to bring the final water content up to 0.5 or 1.0%. Large enough batches were prepared in each

case so that density measurements could be made on portions of the same stock solution. The density was measured in a capillary pycnometer in a thermostatted bath. As shown in Figure 23, all curves have the same slope, allowing extrapolation from one temperature to another within the limits of the graph. Interpolation between curves is less reliable. The curves fall in three families with three different water contents. Density at a given temperature for a given NO₂ content increased with a decrease in water content. Maximum density, at a given temperature and water content, is associated with blends containing 44 mass-% NO₂. The type and amount of inhibitor had only a negligible effect on HDA density (Table 22).

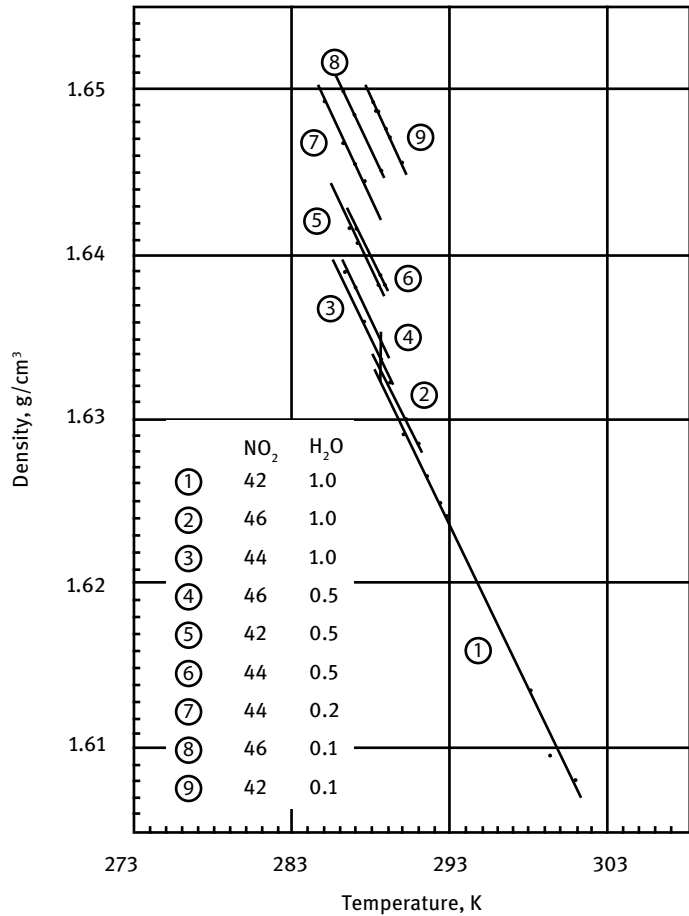


Figure 23: Density of modified HDA as a function of temperature. (Reproduced and modified from [150].)

Table 22: HDA density as a function of corrosion inhibitor

Corrosion inhibitor	Temperature			Density
	°F	°C	K	g/cm ³
None	60.0	15.6	288.7	~1.6492
0.8 mass-% HF	60.0	15.6	288.7	~1.6445
0.4 mass-% HF	60.0	15.6	288.7	~1.6385
0.5 mass-PF ₅	60.0	15.6	288.7	1.6485

Data source: [150]

2.3 Chemical Properties of IRFNA

2.3.1 Analysis of IRFNA

It is important to maintain the correct amount of HF inhibitor in IRFNA. If the HF concentration is too low, the metals are insufficiently protected. If the HF content is too high, additional corrosion will occur. Various instruments are available that can analyze for HF in IRFNA under field conditions or in the laboratory [151]. One method for determining nitrogen dioxide consists of measuring the nitrogen pressure that develops when fuming nitric acid reacts with sulfamic acid solution. Water is determined by measuring the hydrogen pressure that develops when the water content of an acid sample reacts with calcium hydride. Hydrofluoric acid was estimated colorimetrically through bleaching of the color of an iron salicylate solution. See also [152–154].

In another method, the sample is treated with hydrogen peroxide, neutralized with sodium hydroxide, and then titrated with standardized aluminum chloride solution with a methyl red indicator [155].

One technique for directly measuring fluoride-ion concentrations in IRFNA involves the use of fluoride-selective ion electrodes, where the concentrations are determined by measuring the potential developed between this electrode and a reference electrode [156]. A special procedure involving a buffer solution was devised for weighing the inhibited nitric acid before neutralization, dilution, and measurement. The results were more accurate than those obtainable by the commonly used, and more complex, indirect methods. It works with samples as small as 1 g.

2.3.2 Thermal Stability and Decomposition of IRFNA

2.3.2.1 Storage Stability of IRFNA

The pressure rise in hermetically sealed storage tanks containing inhibited white fuming nitric acid (IWFNA) or IRFNA is basically the same as that observed in WFNA or RFNA without any addition of inhibitor already described in *Encyclopedia of Oxidizers*, chapter “White Fuming Nitric Acid” and Section 1.3.2 above.

Measurements of the pressure rise in sealed aluminum-61S-T6 containers, which had been filled at 294 K (21 °C) leaving only 10% ullage, as a function of the initial com-

position of the acid showed that the equilibrium pressure was achieved after 4 weeks of storage at 327 K (54 °C) [10]. The highest decomposition pressure (7.57 MPa = 75 atm) was observed if the test was started with pure nitric acid containing hardly any H₂O or N₂O₄ (Figure 24).

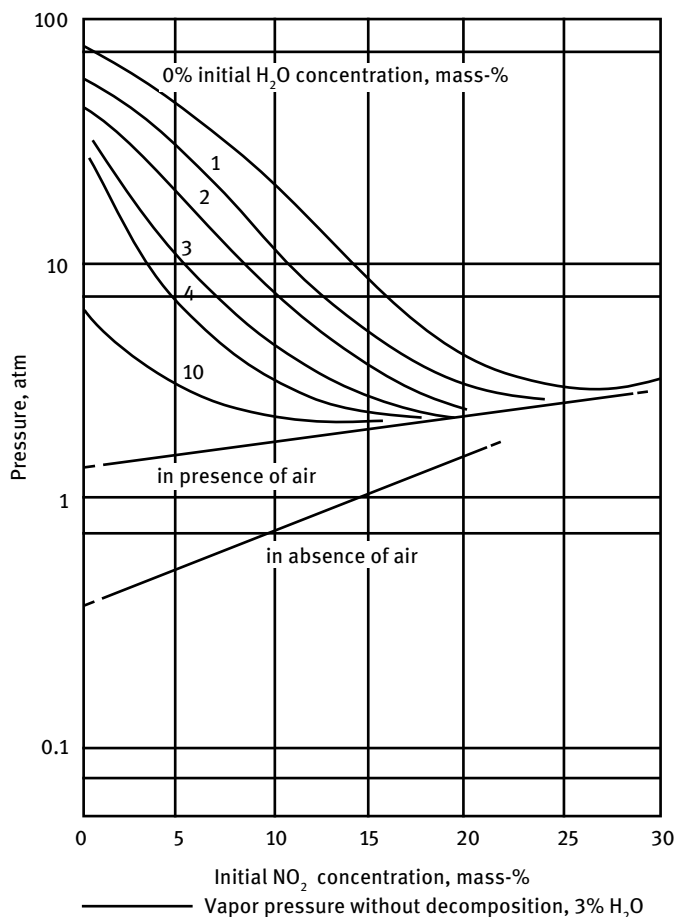


Figure 24: Maximum decomposition pressure in Al 61S-T6 aluminum drums filled at 294 K with 10% ullage and stored at 327 K (54 °C) for 4 weeks. (Republished and modified from [10], with permission of © 1956 American Institute of Aeronautics & Astronautics; permission conveyed through Copyright Clearance Center Inc.)

All acid samples in the aforementioned experiment contained 0.5% HF as a corrosion inhibitor. If the acid contained 12 to 16% NO₂ and/or 2 to 3.5% H₂O (in addition to 0.5% HF) to start with, the equilibrium decomposition pressure achieved after storage at 327 K (54 °C) for 4 weeks was only on the order of 505 kPa (5 atm). Nitric acid in this

initial near-equilibrium mixture decomposed only to the extent of 0.5%, whereas pure nitric acid decomposed to the extent of 19%, resulting in a mixture of about 9% NO_2 and 1 to 2% H_2O . If the tank was vented during storage, the degree of decomposition progressed even further, because after each venting more HNO_3 decomposed until the new equilibrium was again attained. These decomposition experiments served to select an almost stable and storable RFNA composition containing 2 to 3% H_2O and 13 to 15% NO_2 .

2.4 Compatibility with and Corrosion of Materials in IRFNA

2.4.1 Inhibitors to Prevent Corrosion of Metals in IRFNA

The corrosion of aluminum and other metals in RFNA can be reduced substantially by the addition of hydrogen fluoride. An investigation of the effect of small amounts of hydrogen fluoride in inhibiting corrosion by fuming nitric acid revealed that corrosion rates of 6061-T6 aluminum and Type 347 stainless steel were generally reduced by a factor varying from about 10 to 100, when an initial HF content of approximately 0.75% by mass was used [157]. No further reduction in corrosion rate was obtained by increasing the HF content to 2.0%. A HF concentration of 0.75% was selected as the optimum inhibitor concentration for further tests. The effect on the metals of exposure to the inhibited acids was determined in crevices and in stressed specimens, at weld zones, in galvanic couples, in containers with different ullages and with different sizes of vent holes, with various ratios of metal area to acid volume, with acids containing varying amounts of solid matter, and with acids flowing through orifices and impinging against metal at various velocities. Analytical methods for determining HF content and for determining other constituents of acids were also investigated. Similar methods are described in [158, 159].

The rate of corrosion of welded and unwelded Uniloy 19-9DL and 19-9DX steels and welded CRES-321 by fuming nitric acid in liquid and gas phases at 328 and 344 K (130 and 160 °F) during 35-d tests was measured with and without hydrofluoric acid added as corrosion inhibitor [160, 161]. Because of their ease of fabrication by welding, high strength-to-weight ratio, and relatively good corrosion resistance, these steels were used in guided missiles for the construction of pressure vessels that were to contain fuming nitric acid. Stainless steels 19-9DL and 19-9DX are predominantly austenitic steels containing nominally 19% chromium and 9% nickel with molybdenum, tungsten, and carbon added to increase strength at room and elevated temperatures. Alloys of the general type of 18% chromium and 8% nickel with relatively high carbon content are susceptible to IGC. When the metal had previously undergone IGC by exposure to uninhibited fuming nitric acid, subsequent exposure to HF-inhibited acid resulted not in passivation but extremely severe corrosion. The effect of heat treatment on corrosion, in particular of welded seams,

was of special concern. Only 0.6 mass-% HF in fuming nitric acid already inhibited corrosion.

Measurements were made at 328 K (130 °F) of the extent of corrosion of several metals exposed to the liquid and the gas phase of thermally stable nitric acid containing 11–13% NO₂ and 2–4% H₂O with and without HF added as a corrosion inhibitor [162]. Liquid-phase corrosion of the following metals was readily inhibited by hydrofluoric acid in fuming nitric acid of this composition: aluminum alloys 2S-0 (1100), 14S-T6 (2014-T6), 17S-T4 (2017-T4), 24S-T4 (2024-T4), 61S-T6 (6061-T6), and 75S-T6 (7075-T6); aluminum 2S-0 welded to 356; and chromium-nickel steels 302, 303, 304, 321, and 347, Armco 17-7PH, and Uniloy 19-9DL and 19-9DX. Inhibition of gas-phase corrosion was found to occur readily in the case of the following metals tested: steels 303, 410, 430, and 446 and aluminum 61S-T6, but gas-phase corrosion of steels 4130 and 1020 was usually aggravated by hydrofluoric acid. Exposure of aluminum 61S-T6 and stainless steel 347 to fuming nitric acid with a repeated cycling of temperature between 294 and 344 K (70 and 160 °F) was found not to impair the inhibiting effect of hydrofluoric acid on gas- and liquid-phase corrosion of these metals.

Attempts have been made to explain the mechanism of inhibition by hydrogen fluoride by the fact that the fluorides that form a surface coating on the metals are even less soluble in nitric acids than the corresponding nitrates [163]. Inhibition by hydrogen fluoride is effective in the liquid phase as well as in the vapor phase corrosion of metals exposed to the vapor phase above inhibited WFNA or RFNA. In general, the addition of only 0.1 to 0.5 mass-% HF is sufficient to achieve lasting inhibition and passivation. Only in very rare cases was the inhibitor concentration increased to 0.7%. Such a small amount of additive does not significantly affect the performance of nitric acids as rocket propellants or the ignition delay in hypergolic combinations. The inhibiting effect of HF in RFNA on the liquid-phase corrosion of aluminum alloys and iron alloys was found to be dependent primarily on the formation of a protective layer of a tenacious, insoluble fluoride compound of aluminum or iron, respectively, on the surface of the metal [164].

In acids containing no fluorides the weight loss of aluminum was approximately 1/5 that of stainless steel. Addition of 1% fluoride ion to the acid reduced the weight loss of both metals to practically zero even after 26 d of exposure to the acid at 350 K (170 °F) [165]. The minimum quantity of fluoride ion required to inhibit corrosion was found to be approximately 0.25 and 0.5% for aluminum and stainless steel, respectively, in WFNA and 0.5 and 1% for aluminum and stainless steel, respectively, in RFNA (18% NO₂).

Addition of up to 5% HF to RFNA containing 20% NO₂ will lower the freezing point, reduce corrosion and lower the rate of gas evolution and pressure buildup during storage [166]. The addition of small amounts of HF in either the anhydrous form or 52% HF aqueous solution form to RFNA will lower the freezing point from 216 K (−70 °F) to 194 K (−110 °F). If anhydrous HF is used, a low melting (310 K = −99 °F) eu-

tectic forms with only 0.85% HF in the RFNA. If uninhibited RFNA with 18% NO₂ is stored at 347 K (+165 °F) for two months, the pressure in the drum will rise to 1.31 MPa (190 psig), but an IRFNA with 5 vol-% of a 52% HF solution added will show a pressure rise of only 0.86 MPa (125 psig) after three months.

In an effort to develop a corrosion inhibitor for fuming nitric acids that has corrosion-inhibiting and scale-and-sludge formation properties superior to those of hydrogen fluoride, optimum inhibitor concentrations in Types I and III fuming nitric acids, and inhibitor depletion rates for eight inhibitors including hydrofluoric acid (Table 23) were determined, and effects on the mechanical properties of welded specimens of selected aluminum and stainless steel alloys were measured [167, 168]. Storage tests were conducted for 58 d at 294, 322, and 344 K (70, 120, and 160 °F) with three selected inhibitors. The results showed that ammonium hexafluorophosphate provided better inhibition of the corrosion of 6061-T6 aluminum alloy and 17-7PH and A.I.S.I. Type 304L stainless steels than hydrofluoric acid. Measurements of the mechanical properties of the welded specimens after subjection to the liquid and vapor phases of eight inhibited acid systems for 30 d at 322 K (120 °F) indicated that no significant change in properties was caused by these exposure conditions.

Table 23: Optimum inhibitor concentrations

Compound	Formula	Optimum concentration, mass-%
Hydrofluoric acid	HF	0.7 as HF
Potassium fluoride + HF	1 mol KF ± 2.3 mols HF	0.75 as HF
Ammonium acid fluoride	NH ₄ F•HF	0.5 as HF
Lithium iodate + HF	LiIO ₃ + HF	0.3 LiIO ₃ + 0.6 HF
Potassium periodate + HF	KIO ₄ + HF	0.5 KIO ₄ + 0.6 HF
Trisodium phosphate + HF	Na ₃ PO ₄ + HF	0.4 as H ₃ PO ₄ + 0.6 HF
Orthophosphoric acid + HF	H ₃ PO ₄ + HF	0.4 as H ₃ PO ₄ + 0.60 HF
Ammonium hexafluorophosphate	NH ₄ PF ₆ •NH ₄ F	0.3 as HF

Data source: [167]

Evaluation of the inhibited systems showed that only ammonium hexafluorophosphate provided an inhibited system free of corrosion products and scale in Types I and III acid. Except for a microfilm on the aluminum, the exposed test specimens showed no indication of having been immersed in the acid. The trisodium phosphate and orthophosphoric acid-hydrofluoric acid combinations approximated ammonium hexafluorophosphate. An evaluation of inhibited Types I and III fuming nitric acid systems at optimum inhibitor concentration was performed on welded 6061-T6 aluminum alloy, 17-7PH, and A.I.S.I. Type 304L stainless steels exposed to the liquid and vapor phases for 30 d at 322 ± 0.3 K (120 ± 0.5 °F). The ammonium hexafluorophosphate inhibited-acid systems produced the greatest pressures under both sets of conditions. The hydrofluoric acid produced the least pressure when contained in the stainless-

steel test vessels. The phosphoric acid plus HF system produced the least pressures when contained in aluminum test vessels. All the acid-inhibitor systems provided good inhibition with a minimum of scale and corrosion products at ambient temperature. At 322 K (120 °F), the phosphoric acid and ammonium hexafluorophosphate with 0.6% HF were better than HF by itself. At 344 K (160 °F), the ammonium hexafluorophosphate provided the best inhibition. A spot-check of the concentration of inhibitor remaining in the storage test vessels after 58 d at 322 and 344 K (120 and 160 °F) for both acids showed that ammonium hexafluorophosphate suffered the smallest losses. The HF and the phosphoric acid plus HF inhibitors suffered approximately the same loss ratio in the Type I acid medium at 322 K (120 °F). Zinc salts have been proposed as corrosion inhibitors for nitric acids [169]. Some of the Russian IRFNA modifications contained iodine as a corrosion inhibitor.

Three additives were evaluated as potential replacements for HF in inhibited HDA [170]. The compounds were ammonium hexafluorophosphate, phosphorus pentafluoride and monofluorophosphonic acid. Comparison was based on results from 30-d 305-K (90 °F) static immersion tests with Al-6061 and CRES-347. The inhibitors were tested at three different concentration levels and the metals were exposed separately to acid liquid and vapor. Best results were with ammonium hexafluorophosphate or phosphorus pentafluoride when used in the concentration range 0.4–0.6 mass-%. These two inhibitors performed better than HF in 7-d tests with additional metals at 322 K (120 °F). A major improvement was with stainless steels which were much more compatible with HDA when the replacement inhibitors were used instead of HF.

Several other fluorides and phosphorus compounds such as PF_5 , HPO_2F_2 , and P_4O_{10} have been evaluated as inhibitors in RFNA and WFNA [110–173]. HF is less effective as a corrosion inhibitor in HDA than in RFNA. Phosphorus(V) pentafluoride has been evaluated as an alternate inhibitor for HDA. NMR spectroscopy was used to elucidate the nature of the interaction of PF_5 , HPO_2F_2 and P_4O_{10} with the solvent system 44% N_2O_4 in 100% HNO_3 (HDA) [174]. PF_5 generated the species PF_6^- , HPO_2F_2 , and HF (with some $\text{H}_2\text{PO}_3\text{F}$ present as a minor product). HPO_2F_2 gave rise to $\text{H}_2\text{PO}_3\text{F}$ and HF (with smaller amounts of PF_6 also present).

2.4.2 Corrosion of Steels in IRFNA

Tests were conducted to determine the corrosion behavior of Armco 17-7PH and AISI-1050 stainless steel alloys in RFNA containing various amounts of hydrofluoric acid as an inhibitor [175]. It was found that hydrofluoric acid additions to RFNA markedly reduced the corrosion rate of the alloy. Inhibition was obtained in both liquid and vapor phases at 322 and 344 K (120 and 160 °F), for periods of up to 42 d. It was found that a hydrofluoric acid concentration of 0.25% by weight was marginal for good inhibition, and that a hydrofluoric acid concentration of 0.75% was near optimum. The electrochemical potentials of aluminum and stainless-steel electrodes were observed in

fuming nitric acids with various nitrogen dioxide and water contents, and with added fluoride. It was found that water additions shifted the potential of both aluminum and stainless steel in the anodic direction. Nitrogen dioxide content up to 30% did not produce a significant change in the potential of either electrode. Fluoride additions caused a definite anodic shift in the stainless steel potential and had a tendency to shift the aluminum potential in the cathodic direction.

The corrosion rates of cold reduced and annealed plain carbon steel AISI 1020 tubing in RFNA were obtained by measuring the change in the electrical resistance of the tube with time [176]. Corrosion rates decreased with increasing NO_2 concentration in RFNA in a range of 0 to 14% and decreased with increasing H_2O content in the range from 0 to 3.5 mass-% H_2O . This behavior indicated the possibility that NO_2^+ ion or N_2O_5 were the rate-controlling species in RFNA.

The inhibiting effect of fluoride on the corrosion of AISI-321 (CRES-321) stainless steel by RFNA has been investigated with regard to the influence of the N_2O_4 content of the mixture and the nature of the solid corrosion products formed in such systems [177]. The effectiveness of fluoride inhibition in these mixtures decreased with increasing N_2O_4 content and, for one of these N_2O_4 mixtures (HDA), with increasing water concentration. Investigation of the surface film formed on CRES-321 in the latter mixture has shown it to consist primarily of an oxide layer but some fluoride was also incorporated. The long-term storage of fluoride-inhibited HNO_3 - N_2O_4 mixtures in contact with CRES-321 resulted in the eventual precipitation of an insoluble corrosion product that was later identified as a hydrate of iron(III) fluoride.

2.4.3 Corrosion of Aluminum Alloys in IRFNA

The corrosion of six welded aluminum alloys containers and weight-change specimens immersed in IRFNA for 40, 100, 180, and 360 d at 239, 300, 319, and 339 K (−30, 80, 114, and 150 °F) was measured [178]. The corrosion resistance of tungsten inert gas (TIG)-welded specimens from the base metal/filler metal combinations: Al-3003/1100, 2014/4043, 5052/5052, 1100/1100, 5154/ 5154, and 6061/4043 was determined by the change in weight of specimens suspended in IRFNA and by the effect of the acid on the tensile strength of specimens machined from the walls of the containers at the conclusion of the tests. The corrosion of the welded alloy combinations exposed to IRFNA progressed with time except when exposed at 239 K (−30 °F) where no corrosion occurred at that temperature. The corrosion rates of all the welded combinations, except 5154/5154, were higher at 300 and 319 K than at 339 K. At the highest temperature (339 K), the corrosion rates of the welded combinations, except Al-5154/5154, were retarded due to the formation of protective films. The tensile strengths of the welds and base material were not adversely affected by contact with IRFNA for 1 year at the temperatures investigated. The corrosion rates of the 3003/1100 and 5052/5052 combinations increased, whereas that of the 2014/4043 combination decreased as the water concentration of the IRFNA was increased to 7.5% H_2O . The Al-5052/5052 combination

exhibited the highest corrosion resistance of the three combinations investigated over a range of water concentrations from 3.5 to 7.5% H₂O.

Aluminum alloy Al-2014, which may contain 3.9–5% copper and 0.4–1.2% manganese, suffers intergranular attack in RFNA [179]. The corrosion mechanism was examined by electrochemical impedance spectroscopy.

If an aluminum alloy contains copper, there is a chance that locally galvanic corrosion will occur in an electrolyte like RFNA. The effect of dissolved Cu²⁺ ions and over-and-above-specification levels of water content on the corrosion rate of aluminum alloy Al-2014 (3L65) in IRFNA and the effects of variations in IRFNA composition on the corrosion rates in IRFNA were studied potentiometrically in an electrochemical cell where the potential vs. time was recorded for 200 d [180]. There was an order-of-magnitude increase in corrosion rates after the addition of water. Also, the effects of surface pretreatment (F₂/HF for 24 h) on the surface film composition was analyzed by Auger spectroscopy.

Corrosion rates have been measured for Al-2014 (3L65) aluminum alloy, either untreated or subjected to certain surface pretreatments, in contact with IRFNA, gelled IRFNA (IRFNA + SiO₂ + LiNO₃), and these media containing some added P₂O₅ [181, 182]. The temperature dependence of the corrosion reaction in gelled IRFNA has also been studied electrochemically. The lowest corrosion rates determined by weight change occurred when the alloy had been pretreated with gaseous ClF₃ before immersion in gelled IRFNA or gelled IRFNA containing 0.5 mass-% P₂O₅. This medium gave a low corrosion rate even without ClF₃ pretreatment. Pretreatment with a gaseous HF/F₂ mixture or by electropolishing and anodizing conferred no advantage as judged electrochemically. See also [183].

Addition of gelling agents such as fumed silica to IRFNA does not significantly change corrosion behavior in aluminum alloys [184–189]. The compatibility of gelled IRFNA with aluminum alloys was examined using electrochemical methods, weight loss, and surface observation studies [190]. Comparisons were presented between liquid IRFNA and gelled IRFNA with and without added inhibitor (P₄O₁₀). The Al-1100 and Al-2014 alloys behaved in a similar fashion when exposed to gelled IRFNA, based on weight loss measurements. The addition of phosphoric oxide is beneficial with the Al-1100 systems according to the electrochemical results. However, the weight loss data suggested that the gels were satisfactory even without added P₄O₁₀, especially when compared to a liquid IRFNA system. The XPS data showed that the fluorine from the hydrofluoric acid inhibitor in IRFNA was not consumed entirely by the silica gelling agent and remained available to passivate the metal surface. Aluminum, silicon, and phosphorous will compete for the fluorine present in systems with added HF inhibitor.

2.4.4 Corrosion of Titanium in RFNA

Severe corrosion was observed on two types of chemically pure titanium immersed in RFNA with 8–22% NO_2 . One of the samples held in a stoppered Erlenmeyer flask exploded when the chemist tried to vent eventual overpressure after only a few days of immersion, destroying (triggering similar explosive reactions in) adjacent flasks and spattering acid over the operator and the entire laboratory [122–191].

The powdery corrosion product removed from commercially pure titanium after exposure to 20% NO_2 RFNA was found by XRD and chemical analysis to be titanium metal [192]. Metallographic observations indicated that the possible mechanism of corrosive attack of RFNA on titanium and titanium alloys is through IGC of the all- α or all- β titanium alloys. Similar observations of the mixed α - β alloy indicated a possible galvanic or electrochemical mechanism of the attack by liquid-phase RFNA.

The corrosion of commercially pure titanium in RFNA followed a power law that was not interpretable in terms of any one single mechanism [193]. The effects of stress relief and galvanic action on corrosion rates were determined. The influence of acid composition as well as heat treatment of the metal samples on stress corrosion cracking was further investigated.

Corrosion tests of commercially pure titanium and an 8% manganese alloy in the liquid and vapor phase of anhydrous RFNA (20% NO_2) were conducted at 327 and 344 K (54 and 71 °C) [194]. The exponents in the power laws for the corrosion of the two metals were essentially independent of temperature between 327 and 344 K (54 and 71 °C). Stress corrosion tests of 180° bent and clamped samples of the commercially pure titanium and the 8% manganese alloy in both the stressed and stress-relieved condition at 303 and 344 K (30 and 71 °C) exposed the samples to more serious conditions.

A study showed that the sensitivity of titanium alloys toward ignition with RFNA depended on the presence of a dark coating on the metal surface that was identified as finely divided, powdery titanium metal formed as a corrosion product [195]. Stress corrosion cracking occurred with greater than 6.5% NO_2 and less than 0.7% H_2O in RFNA. Corrosion vs. time relationships of two titanium alloys in anhydrous RFNA (20% NO_2) were determined. See also [196].

2.4.5 Corrosion Products in IRFNA

Three experiments were performed in which CRES-321 stainless steel was exposed to IRFNA at ambient temperature (20–25 °C) [197]. These tests may be outlined as follows:

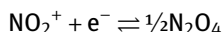
- (a) a mixture of 56/44 by mass ratio $\text{HNO}_3/\text{N}_2\text{O}_4$ (i.e., HDA) stored in a small steel tank for a period of 150 d;
- (b) a mixture of 70/30 by mass ratio $\text{HNO}_3/\text{N}_2\text{O}_4$ stored in a thick-walled PTFE vessel with two stainless-steel specimens (bar, 18 mm diameter, 14 mm long) for a period of 300 d; and

- (c) 100% HNO_3 , stored in a PTFE vessel with steel specimens as in item (b) above, for a period of 220 d.

The tests were terminated when visual inspection of samples of the liquid revealed the presence of particulate matter in suspension. Attempts were then made to isolate the solid product by expelling the liquid from the test vessel and passing it through a PTFE filter (pore size 100 μm). These results clearly indicated the corrosion product to be a form of iron(III) fluoride, but although both the IR and XRD data showed that the material was hydrated, most likely $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, the only form of iron (III) fluoride known to be green, is the anhydrous form. The corrosion of 18/8 stainless steel by the nitric acid-based propellants IRFNA and IHDA resulted in the formation of a solid reaction product, which may be formulated as $\text{FeF}_3 \cdot x\text{H}_2\text{O}$ ($0 < x < 1$). This compound is very hygroscopic and rapidly converts to $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ if exposed to atmospheric moisture.

2.4.6 Test Methods for the Study of Corrosion of Metals in IRFNA

Electrochemical studies demonstrated that the electrode reaction



occurred on the surface of a rhodium electrode [198]. Platinum could also be used as a reference electrode, although its performance was slightly inferior to that of rhodium. Electrochemical studies indicated that stainless steels corrode in $\text{HNO}_3/\text{N}_2\text{O}_4$ mixtures by a mechanism involving transpassive layer breakdown. This breakdown can be prevented by cathodic polarization or by the addition of hydrogen fluoride or phosphorus pentafluoride. The results were consistent with fluoride functioning as an anodic film-forming inhibitor. Sulfuric acid can also function as an inhibitor, but its performance was less satisfactory than that of fluoride.

The solubility of corrosion products in modified HDA was found to be relatively independent of temperature and initial nitrogen dioxide or water content, but highly dependent on the specific species present in the acids, from competing corrosion reactions [149]. Metal couples typical of those in propellant containment devices were exposed to modified HDA to obtain further corrosion product solubility data and to test for passivation of the metals with time. No passivation was noted within 1 month. Corrosion took place at a relatively constant rate.

2.4.7 Tank Storage Tests with IRFNA

Tanks that had held IRFNA and were stored in a controlled storage environment at 303 K (85 °F) and 85% relative humidity for 4–6 years were emptied, cleaned, and dissected for metallurgical analysis [199]. The corrosion effects of the stored propellants on the internal metal surfaces were negligible, with no serious degradation of strength or structural integrity occurring. Corrosion occurred primarily due to pitting, gas- and

liquid-phase interactions occurring during storage, manufacturing defects, and at the manifold tubing welds.

Thousands of Bullpup missiles using Type III-A IRFNA per MIL-N-7254C as the oxidizer was fielded during the 1960s, and several were examined for corrosion after they were decommissioned and unloaded after 10–12 years in the field. No leakage of the missile tanks had occurred during the 10-year storage period [200]. Analysis of the residues removed from the oxidizer tank indicated only slight metal attack and dissolution. The degree of corrosion that did occur was considered insignificant and would not have affected the functional capability of the missile system. Some slight corrosion of stainless-steel components present in the oxidizer tank was noted but should present no serious problems.

2.4.8 Other Compatibility Problems in IRFNA

Ignition of titanium in RFNA has been the cause of severe accidents [122].

One of the main applications of IRFNA in the upper stages of launch vehicles was in AGENA [150]. Numerous material compatibility studies were performed in support of that upper stage program.

A spontaneous explosion of a missile tank of a target drone containing IRFNA was reported some time ago in a tropical, hot-climate country such as the Philippines. Preliminary results from failure analysis indicated that the major cause for the explosion was probably due to the overpressure from the oxidizer tank containing the IRFNA. It was concluded that the burst tank was negligently overfilled when originally loaded with IRFNA. Based on these findings, the shelf life of the units filled with the acid was reduced to no more than 2 years. Because a 2-year limit had operational and logistical implications, it was then proposed to quantify the rate of reaction of oxidizer with tank metals by taking microcalorimeter measurements and extrapolate to a safe shelf life from there [201]. The reaction of nitric acid with metals is exothermic and can be detected by a microcalorimeter.

2.4.9 Filter Screens for IRFNA Service

The inlets to propellant valves are usually protected by filters to retain particles that might get lodged on the valve seat and cause the valve to leak when it is commanded shut. The screen material on the filters must be compatible with the propellant, which in the case of IRFNA or NTO is a difficult task. The nitrate film growing on the thin metal wires might cause a narrowing of the passages and increase the pressure drop or embrittle the wires. Similar wire mesh is used in surface tension propellant management devices in propellant tanks for 0-g operation. The long-term effects of propellant immersion on fine micronic stainless-steel wire cloth were studied for IRFNA and nine other propellants [202]. Immersion time histories reported in the literature ranged from 3 months to 7 years.

2.5 Toxicity and Safe Handling of IRFNA

The toxicity and precautions for the safe handling of IRFNA are essentially the same as those for RFNA. The addition of hydrofluoric acid would aggravate any skin injuries if IRFNA instead of RFNA is accidentally spilled on skin.

2.6 Disposal of IRFNA

Disposal and demilitarization of IRFNA is complicated by the presence of corrosion inhibitors such as HF and H_3PO_4 . In addition, some of the Russian IRFNA modifications that needed to be demilitarized after the SALT agreements contained some iodine. Disposal and spill cleanup of IRFNA has been practiced for many decades, and there exists a good database on available methods for safe handling of this oxidizer, for instance Chapter 4 in [203].

Techniques used for demilitarization of IRFNA would vary depending on whether it is disposed of simply to get rid of it at any cost whether more economical disposal methods are needed, where some of the nitric acid is recovered in sufficient purity that it can be used for other commercial purposes, such as nitration reactions of organic compounds for WFNA or fertilizer for concentrated or dilute HNO_3 .

In the US, demilitarization of decommissioned LANCE intermediate-range ballistic missiles posed a problem in the disposal of IRFNA and UDMH propellants off-loaded from these missiles [204]. Some of the decommissioned LANCE missiles were later used as practice targets for antiballistic missile interceptor field tests.

One method for the recovery of useful products such as 100% HNO_3 involve first filtering the IRFNA to remove particulate contamination, then distilling or sparging out the NO_2 , and then distilling the HNO_3 after adding additional H_3PO_4 in an amount at least five to six times that of HF [205]. The same equipment can also be used to regenerate contaminated, aged RFNA or to convert IFRNA to RFNA if these oxidizers are returned from the field after long storage times and after they no longer meet the MIL-SPEC requirements.

3 Gelled Nitric Acids

Gelled propellants are non-Newtonian fluids and therefore exhibit a non-linear relationship between the stress and deformation rate. Depending on the gelling agent used, gelled propellants may also have a finite yield stress. Stresses applied to the fluid below the yield stress will not cause the fluid to flow, but they deform like a solid. Numerous rheological models exist for non-Newtonian fluid mechanics, and the choice of rheological model for a particular fluid depends on how well they match experimental data.

One of the potential benefits of gelled liquid fuels is that gelled liquid fuel propulsion systems in missiles can meet insensitive munitions (IM-LOVA) safety criteria, while many of the solid propellant missiles currently in service cannot. Extensive safety testing, in particular cook-off behavior, has been done with gelled propellant propulsion systems.

Like efforts with other rocket propellants, nitric acids have been gelled as a method to prevent or slow down leakage during storage or sloshing in a rapidly moving missile. Most of the gelling effort has been devoted to RFNA and IRFNA, but few investigators have attempted to produce WFNA gels. In either case, the selection of gelling agents for nitric acids is limited by the reactivity of most organic gelling agents with nitric acid. Organic gelling agents like those used for gelling fuels would rapidly be destroyed in fuming nitric acids. That leaves mostly inorganic gelling agents, which have the necessary chemical resistance but will not improve the rocket performance properties of WFNA or RFNA. Inorganic gelling agents like fumed silica will add inert ballast to propellants, will form troublesome residues in places where they interfere with the operation of the rocket engine, and may settle out during long-term storage. Despite half a century of research and development of gelled hypergolic bipropellants, substantial amounts of money invested in demonstration programs, these gelled propellants have not found any practical application and have not yet flown in a fielded, mass-produced missile.

3.1 Gelled RFNA

NO₂ from spilled gelled RFNA would evaporate more slowly and constitute less of a hazard than spilled ungelled RFNA. The main gelling agent tested for RFNA is fumed silica, also known under the brand names of Cab-O-Sil and Aerosil [206]. The compatibility of gelled IRFNA with aluminum alloys is not much different from that of ungelled IRFNA [189]. The fumed silica that is used as the gelling agent absorbs and removes part of the HF inhibitor, but enough HF remains in solution to passivate the metal surfaces. Another gelling agent is finely divided lithium nitrate [207]. RFNA has been gelled using 4.25 mass-% sodium silicate [208].

The rheological properties of gels prepared from water, RFNA, and UDMH with aerogel silica were investigated over a wide range of gelling agent concentrations [209].

Fumed silica is hygroscopic, and it absorbs water readily from the surrounding environment. The amount of moisture absorption on the fumed silica surface correlates directly with the ambient humidity and can reach 12% by weight at an atmospheric relative humidity of 90%. The silica intended for gelling propellants must be dried in a vacuum drying oven at 383 K (110 °C) and a pressure of <138 mbar for at least 4 h prior to use to ensure the silica has minimal water content.

RFNA gels are usually produced using fumed silica as the gelling agent with concentrations from 3 to 5% by mass. Measurements of the viscosity of 3 to 5 mass-% silica/IRFNA gels were plotted over a range of viscosity measurements on a common plot, although no distinctions were made between different gellant concentrations and the viscosity variation for a single gellant concentration [210]. Thixotropy and yield stress measurements were performed to further classify the behavior of the gel propellants. IRFNA and hydrogen peroxide oxidizers, gelled with silica, were characterized as yield thixotropic fluids with significant shear yield stress. Creep tests were conducted on two rheological types of gels with different gellant contents, and the results were fitted by a viscoelastic constitutive model. The effect of temperature on the rheological properties of gel propellant simulants was also investigated. A general rheological classification of gel propellants and simulants was proposed. The hydroxypropylcellulose/methylhydrazine (MMH) gels were classified as shear-thinning, time-independent fluids with low yield stress values.

RFNA gels were mixed containing 3, 4, and 5% fumed silica by mass [211]. The variation of rheological properties for different silica concentrations and effect of age on the gel rheological properties were measured and compared to model predictions. The RFNA gels were thixotropic, leading to large variations in viscosity and yield stress measurements. Pre-shearing the samples allowed for more repeatable results that should be more representative of the fluid conditions entering a rocket injector. Other factors, e.g., thixotropy, influencing the rheological properties were considered. A series of aging tests were performed to determine whether the rheological properties of the RFNA/SiO₂ gels changed with time. Two 4% silica/RFNA gels were made, and the shear-thinning behavior and yield stress of these gels was measured the day of the mix, 4 d after the mix, 9 d after the mix, and 14 d after the mix. No discernible trend was observed for the yield stress or consistency index for both 4% gel mixes, but the 4% silica/RFNA gels showed a decrease in the power law (PL) index over the 2-week measurement period. The increased shear-thinning behavior suggested that the silica-silica hydrogen bonds were being weakened over time.

Despite the availability of viscosity data, knowledge of the viscosity of a gel like IRFNA gel is not sufficient to predict the pressure drop across an injector in a rocket engine. The discharge coefficient is assumed, and hardware must be fabricated and tested to verify the validity of the assumed discharge coefficient. The propellant formulator does not know the impact on the injector design when the viscosity profiles of gel fuels and oxidizers are altered. Without information about the impact of viscosity on the injector design one cannot distinguish between hardware design problems and propellant formulation problems.

Fumed silica with a mean particle size of 12 nm was evaluated as a gelling agent for IRFNA [212]. A mixing time of 30 min was sufficient for preparing the gel. Operating at different temperatures, gelling was possible in a temperature range of 269 to 308 K (−4 and 35 °C), but 298–308 K (25–35 °C) was more appropriate. The gel with 3–4% SiO₂ needed to age 24 h. During this period the gel viscosity increased up to

30% compared to the viscosity of the gel immediately after its preparation. The gel had good stability in a temperature range of 221 to 337 K (−52 to +64 °C). The prepared gel retained its desirable rheological properties for at least 6 months. Mechanical stability test under acceleration of 500 g for 30 min showed that the prepared gel had suitable mechanical stability. The gel had desirable rheological properties, such as shear thinning, thixotropic behavior, and hysteresis.

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White Fuming Nitric Acid

Nitric Acids

Although chemically speaking there is only one nitric acid with the formula HNO_3 , we have subdivided the chapter on nitric acids into three subchapters in *Encyclopedia of Oxidizers*, dealing with four technical grades of nitric acids of different chemical composition: **White Fuming Nitric Acid** (WFNA), **Red Fuming Nitric Acid** (RFNA), and **Mixed Acid** (MA). There are two variants of RFNA, one called **Inhibited Red Fuming Nitric Acid** (IRFNA) and another called **High Density Acid** (HDA), both of which are included in the RFNA chapter.

1 White Fuming Nitric Acid

Pure nitric acid, HNO_3 , CAS RN [7697-37-2] in the freshly prepared state is a colorless liquid which forms white fumes in moist air and solidifies at 231.5 K (−41.6 °C) forming colorless crystals. In practice, it does not stay colorless very long, because a slow, un-stoppable decomposition leads to its visible contamination by a decomposition product, nitrogen dioxide, which stains it yellow. For several reasons, pure nitric acid is hardly ever used as rocket propellant. In most cases, physical and chemical properties of the pure compound are only determined in laboratory experiments for academic reasons and to use it as a standard reference substance in the analysis for other grades of nitric acid containing additives or contaminants. Additives serve the purpose of reducing the rate of decomposition and reducing the rate of corrosion of metals in the acid. Contaminants come from the acid decomposition itself, are absorbed from the atmosphere if the acid is exposed to air during transfer, or are leached from container materials.

1.1 Nomenclature

The English language literature often abbreviates **White Fuming Nitric Acid** as WFNA. For practical applications, WFNA is not really 100% HNO_3 , but depending on its age, it will contain up to 2% H_2O and up to 0.5% NO_2 , which causes the yellow discoloration of the liquid. Already a small percentage of NO_2 suffices to color the liquid yellow.

Nitric acid containing more than 10% NO_2 is generally called **Red Fuming Nitric Acid**, abbreviated RFNA, and will be described in a separate chapter in this volume devoted exclusively to this rocket propellant oxidizer.

If RFNA contains a small percentage of hydrofluoric acid (hydrogen fluoride) as a corrosion inhibitor, it is called **Inhibited Red Fuming Nitric Acid**, abbreviated as IRFNA.

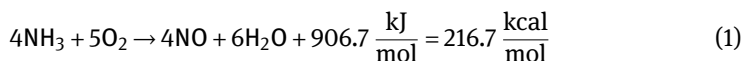
In the distant past, NASA and other government agencies in the United States commonly used abbreviations which designated the nominal composition of nitric acid oxidizers. For WFNA, the digit following the abbreviation designated the water content, e.g. WFNA-7 contained 7 mass-% H_2O . For RFNA, the first of the two numbers following the abbreviation designated the water content and the second and third digit designated the NO_2 content. For instance, RFNA-3-14 would have been an oxidizer containing 3 mass-% H_2O and 14 mass-% NO_2 .

1.2 History of Nitric Acid Usage as a Rocket Propellant

Nitric acid was first used as a rocket propellant in various German missiles during World War II. The German code names were *S-Stoff* for 90% nitric acid/10% sulfuric acid or nitric acid/ferric chloride and *SV-Stoff* or *Salbei* for 85% nitric acid/15% sulfuric acid or nitric acid/dinitrogen tetroxide. Some versions of *Salbei* contained iron(III) nitrate or iron(III) chloride as ignition catalysts. In the US arms inventory, small missiles using nitric acid oxidizer were the BULLPUP air-to-ground missile, surface-to-air anti-aircraft missiles were several generations of NIKE, starting with NIKE-AJAX, and a tactical IRBM missile was the LANCE. All these are now only of historical interest, and there are no missiles active on the US side that still use nitric acid as the oxidizer. Launch vehicles using nitric acid were the highly successful AGENA which has flown as a second stage on numerous first stage launch vehicles (THOR, ATLAS, DELTA, TITAN). Third world countries continue to use nitric acid as a storable rocket propellant. Nitric acid/unsymmetrical dimethylhydrazine (UDMH) propellant combinations have flown in second stages of Russian launch vehicles, such as the S-3 stage with more than 400 flights. SCUD was the first tactical ballistic missile developed by Russia using storable propellants. SCUDs have gone through several development and improvement changes in Russia and were copied by several third world countries. Several SCUDs were flown by the US Army and used as targets for development of anti-missile rockets in the ballistic missile defense program. Later some decommissioned LANCE missiles were used as targets because the plume signature was similar to that of SCUDs. Although WFNA is not currently used as a rocket propellant, we are summarizing its properties here because it may be used for making RFNA or IRFNA or nitrate ester rocket propellants and plasticizers. Sometimes WFNA is used for laboratory ignition delay tests with candidate hypergolic fuels.

2 Production of White Fuming Nitric Acid

Nitric acid is an important bulk chemical product of the chemical industry, mostly the fertilizer industry. It is an important intermediate in the synthesis of many other chemicals. Nitric acid is produced by catalytic oxidation of ammonia with air or oxygen over a gauze of platinum or platinum/rhodium wire mesh



If ammonia and oxygen (air) were allowed to react under equilibrium conditions, nitrogen and water would be the only products, worthless products. There are various variations of this three-step process, which differ mostly in the operating pressure. For instance, the Berlin-Anhaltische Maschinenbau A.G. (BAMAG) combination process operated at 1, 4, and 8 atm pressure for steps 1, 2, and 3. Because reaction step 1 is a highly exothermic combustion process, the catalyst loss may amount to 44 mg of platinum per ton of nitric acid produced. Quite often, the intermediate nitrogen dioxide/dinitrogen tetroxide is not produced in industrial plants devoted exclusively to the production of this rocket propellant oxidizer but is diverted from an existing nitric acid production stream and later purified to meet rocket propellant specification purity criteria.

An unwanted by-product of this process is nitrous oxide, N_2O , which until recently was just vented to the atmosphere since there were only few other uses for it. Typical nitric acid plants produce 2–9 kg N_2O per metric ton of HNO_3 produced. Only after N_2O was recognized as a “greenhouse gas” contributing substantially to global warming, has the industry taken steps to minimize emissions of this by-product [1, 2]. Recently, within the last 20 years, the interest of rocket propellant chemists has been expanded to include nitrous oxide, and the rocket people would dearly like to see the N_2O captured and made available to rocket propulsion companies at a reduced price. Government-imposed N_2O -emission restrictions are likely to increase the price of nitric acid in the future [3].

The most common form of nitric acid in commercial trade is weak nitric acid, which is the azeotrope which contains only 69.2 mass-% HNO_3 and boils at 394.9K (121.8 °C). Most nitric acid production facilities take the product concentration only to this level, leaving 30% water in the product. Weak nitric acid is of insufficient strength to be used as an oxidizer in rocket propellants. Weak nitric acid is still called “concentrated nitric acid” in many publications.

Anhydrous WFNA is prepared from concentrated nitric acid in a subsequent process by distillation from a dehydrating chemical (concentrated or fuming sulfuric acid, phosphorus pentoxide, magnesium nitrate) or by a high-pressure $\text{NO}_2 + \text{O}_2$ reaction

method developed by the German chemical company Pintsch Bamag in Berlin. That process and a similar process by DuPont essentially takes RFNA and heats it with additional dioxygen at higher temperature and pressure, then removes the excess $\text{NO}_2/\text{N}_2\text{O}_4$.

99% nitric acid can be obtained from a 71% aqueous solution of nitric acid by electrolysis in the anode section of a diaphragm cell [4]. The net result of electrolysis is the decomposition of some of the water and a consequent increase in the concentration of the nitric acid.

2.1 Production Statistics of Nitric Acid

The industrial base of the chemical industry in any country is based on its ability to produce ammonia and, as the next step by combustion of ammonia, nitric acid, and ammonium nitrate. Both are important fertilizers for the agricultural industry to feed a growing domestic and world population and to produce food exports if the soil and weather conditions permit. The only known strong nitric acid plant in the US (LSB Industries Inc., El Dorado, AR, USA) uses the direct strong nitric (DSN) acid Uhde process. The amount of nitric acid and dinitrogen tetroxide (NTO) diverted during HNO_3 production used as a rocket propellant is an insignificant fraction of the total HNO_3 production in any country. Even if we include the fraction used for production of nitrocellulose and double-base propellants, the amount is still very small. Another small fraction is or was used to produce the traditional dynamite made by soaking glycerol trinitrate in kieselguhr. In the USA about 65% of the nitric acid produced is consumed in the manufacture of fertilizers, for example, ammonium nitrate. In 2007, 76% of total US nitric acid production was converted at the production site to ammonium nitrate. We are listing here only production capacity numbers to give the reader a perspective

Table 1: World output of nitric acid.

	1962–1963	1965–1966
Millions of metric tons, based on 100% HNO_3		
USA	3.4	4.7
USSR	2.5	3.7
West Germany	2.2	2.55
France	1.73	2.2
Italy	1.05	1.3
Norway	1.0	1.25
Netherlands	0.7	0.95
United Kingdom	0.6	0.90
Rest of the world	5.12	5.85
Total	18.30	23.40

Data source: [5]

Table 2: Historical and projected US nitric acid production.

Year	Nitric acid produced, thousand metric tons
Actual	
2006	6447
2007	6866
2008	7072
2009	7284
2010	7502
2011	7000
2012	6790
2013	6730
2014	6460
2015	6650
2016	6780
2017	7050
2018	7130
2019	7200

Data source: [6]

of the ease of diversion of such chemicals for rocket propellant and explosives manufacturing. Nitric acid is used in the manufacturing of nitrocellulose and nitrate esters for double-base propellants. Table 1 and 2 give nitric acid production statistics for the World and for the USA.

Approximately 3/4 of US nitric acid production is consumed in making ammonium nitrate, while adipic acid manufacture (for Nylon and other polyamides) consumes about 9%.

2.2 Purification of Nitric Acid

Many of the physical properties reported for nitric acid are of dubious value because the investigators may not have used truly pure nitric acid. In many cases, the nitric acid already decomposed while the measurement was in progress.

Attempts to prepare pure nitric acid by fractional crystallization of 98.5% nitric acid were partially successful [7]. The highest concentration attained by this method was 99.67–99.79% HNO_3 . The product was a white crystalline solid which formed a straw-colored liquid when melted. This led the investigators to believe that pure nitric acid is stable only below its freezing point. Actually, pure nitric acid can be kept at 273 K (0 °C) for many hours without visible signs of decomposition.

Aged nitric acid that has turned yellow by partial decomposition can be purified by bubbling ozonized oxygen (5% O_3 in O_2) through the solution [8]. After bubbling

ozonized oxygen through the acid for about 5 minutes, the yellow color disappeared and the acid was a clear colorless liquid like water.

3 Physical Properties of White Fuming Nitric Acid

Published physical properties for nitric acid HNO_3 vary widely, depending on the purity of the sample used for the physical property determination. In particular, older data are often plagued by inaccuracies due to the lack of purity of the acid used. The problem arises from the fact that pure nitric acid is not stable and will slowly decompose (See Section 4.4, Decomposition of Nitric Acid), even while the measurements of physical properties, in particular measurements at elevated temperatures, are in progress. Sometimes the acid needs to be analyzed once at the start of the physical property measurement and again after the measurement has been completed.

Although pure nitric acid is not used as a rocket propellant, we have assembled here a fairly complete summary of its physical properties because it would be even more difficult to determine these properties for mixtures of WFNA with other oxidizers, such as RFNA or IRFNA. In many cases the properties of HNO_3 -containing mixtures must be interpolated or extrapolated from other data, starting with WFNA. For rocket applications, most of the nitric acid goes into nitrating organic compounds, such as cellulose, glycerol or ethylene glycol. In designing process equipment for the production of these solid propellant ingredients, the physical properties of nitrating acid must be known. Spent nitrating acid from industrial nitrating processes is often reprocessed to recycle the nitric acid and use it for other purposes. The design of equipment for the recovery of nitric acid from spent acid will depend on a complete knowledge of the properties of pure nitric acid.

When referencing sources of physical data, one must always specify if the data were obtained with freshly prepared, chemically pure nitric acid or if they were obtained with a technical grade of “white fuming nitric acid”. Because pure nitric acid must be freshly prepared immediately prior to the measurement, only few experimenters have gone through the extra trouble of using freshly prepared, chemically pure nitric acid. Even if the freshly prepared acid was stored in the frozen state to preserve it, it may still have some impurities that evolved when it was thawed. The data for the pure nitric acid are only of academic interest, because acid this pure would rarely be used as a rocket propellant. The data for the technical grade WFNA are of more practical importance. Both are summarized in this chapter of this book.

Summaries of physical and chemical properties of WFNA nitric acid are found in the following publications: [9–14]. The summary published by Stern, Mullhaupt, and Kay in *Chemical Reviews* in 1960 is a very thorough compilation of good data. We wished summaries like that were available for all chemicals in this book.

The molecular mass of nitric acid is 63.0128 g/mol equivalent to 15.8698 mols/kg [15].

3.1 Freezing Point and Phase Diagrams of WFNA Mixtures

Literature data on freezing point of pure nitric acid are summarized in Table 3. The data from various sources are fairly consistent.

Table 3: Literature data on freezing point of pure nitric acid.

Freezing point		Authors	Year	References
K	°C			
230.6–232.1	–41.0 to –42.5	Biltz and Huelsmann	1932	[16]
232.0	–41.1	Miskidzhyan and Trifonov	1947	[17]
231.85	–41.3	Sage	1957	[18]
231.6	–41.5	Briner, Suesz, and Favarger	1935	[19]
231.56	–41.59	Forsythe and Giauque	1942a	[20]
231.5 ± 0.01	–41.6 ± 0.1	Antipenko, Beletskaya, and Krylova	1958	[21]
231.55 ± 0.05	–41.60 ± 0.05	Kay and Stern	1955	[22]
231.53 ± 0.05	–41.62 ± 0.05	Dunning and Nutt	1951	[23]
231.3	–41.8	Potier	1953	[24]
231	–42	Weast	1984	[25]

The freezing point diagram of the binary system $\text{HNO}_3/\text{H}_2\text{O}$ in Figure 1 shows two distinct maxima which can be attributed to the formation of stoichiometric hydrates of nitric acid, ($\text{HNO}_3 \cdot \text{H}_2\text{O}$ and $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$) [18]. For the application of WFNA as a rocket propellant we are only interested in nitric acid containing less than 10% H_2O . The freezing point diagram illustrates the fact that the freezing point cannot be taken as an indication of acid concentration. For instance, an acid sample freezing at 228 K (–45°C) might contain 85 or 94 mass-% HNO_3 .

Figure 2 is a more detailed representation of the high-concentration end of the diagram in Figure 1. The NACA report has a much nicer, more detailed diagram of this system covering the entire range of compositions [26].

Table 4 contains measured raw data for the freezing point of WFNA with up to 20 mass-% water.

Even a small percentage of water causes the freezing point of WFNA to go down noticeably (Table 5).

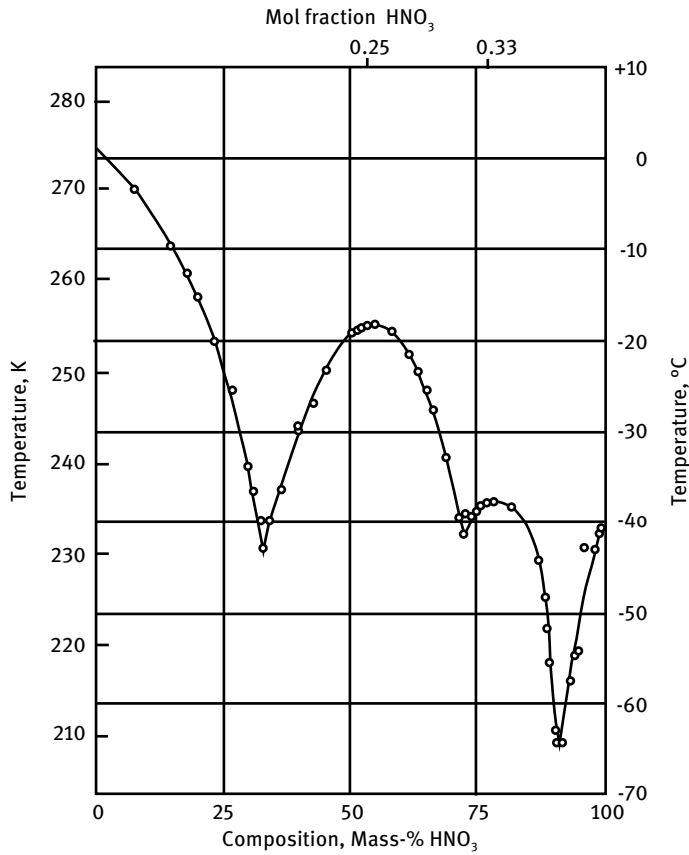


Figure 1: Freezing point diagram in the system HNO₃/H₂O. (Reproduced and modified from [18].)

Table 4: Freezing point of technical grade nitric acid.

Mass fraction		Freezing point	
HNO ₃	H ₂ O	K	°C
1.000	0.000	231.85	-41.3
0.956	0.044	230.85	-42.3
0.953	0.047	230.35	-42.8
0.907	0.093	228.75	-44.4
0.808	0.192	219.85	-53.3
0.800	0.200	218.15	-55.0

These data were extracted from [18]; See also Figure 1.

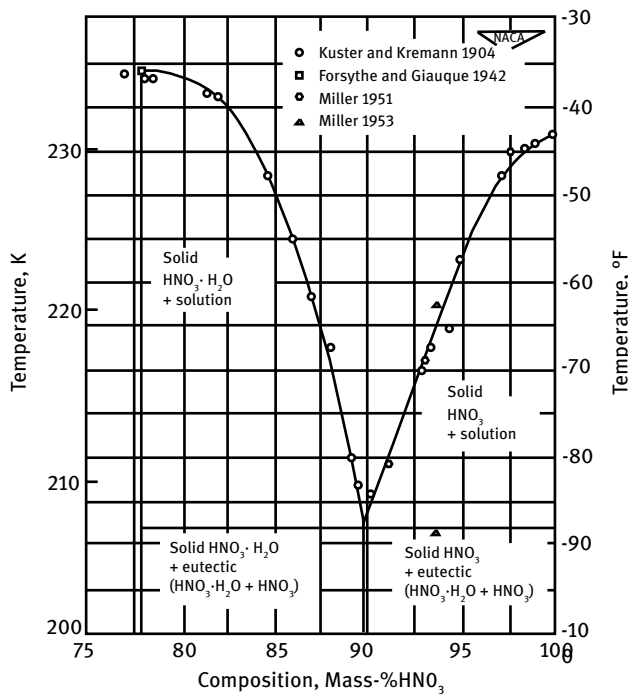


Figure 2: Freezing point of the nitric acid-water system. (Reproduced and modified from [27].)

Table 5: Freezing point of WFNA with low water contents

Composition, mass-%		Freezing point		
HNO ₃	H ₂ O	K	°C	°F
100	0	231.5	-41.6	-42.9
99.94	0.06	231.4	-41.7	-43.1
99.83	0.17	231.3	-41.8	-43.2
99.74	0.26	231.2	-41.9	-43.4
99.65	0.35	231	-42.1	-43.8

Data source: secondhand data from [28, p. 157]

Nitric acid hydrate crystals have been observed in polar stratospheric clouds in polluted atmospheres. Therefore, the HNO₃/H₂O binary liquid/solid phase diagram in the region of nitric acid trihydrate and nitric acid dihydrate was investigated using highly sensitive DSC and IR spectroscopy of thin films [29]. There are several eutectic transitions in the region of nitric acid trihydrate, dihydrate, and monohydrate. A new solid phase was found that undergoes a transition at ~228 K for samples in the range 54–75 mass-% HNO₃. Phase diagrams of more dilute nitric acids in the mole fraction

range below $\chi \text{HNO}_3 = 0.25$ are of interest mostly for atmospheric chemistry and not so much as rocket propellants [30]. Various phases, including a possible pentahydrate, were examined by XRD and IR spectroscopy.

3.2 Boiling point of WFNA

The thermal instability of nitric acid makes an accurate determination of its normal boiling point very difficult. For this reason, the accuracy of experimentally determined values of the boiling point is often questionable. Literature data on boiling point of pure nitric acid are summarized in Table 6.

Table 6: Literature data on boiling point of pure nitric acid.

Boiling point		Authors	Year	References
K	°C			
355.9 ± 0.2	82.6 ± 0.2	Potier	1953	[24]
356	83	CRC Handbook Chem. Phys. 64 th Ed.	1984	[25]
357.05	83.90	Duisman and Stern	1969	[31]
357 (calculated)	84 (calculated)	Egan	1945	[32]
357.2 (calculated)	84.1 (calculated)	Stern, Mullhaupt, and Kay	1959	[14]
358.4 (756 mmHg)	85.3 (756 mmHg)	Miskidzhyan, Trifonov, and Balandina	1949	[33]

3.3 Vapor Pressure and Vapor Phase Composition of WFNA

3.3.1 Vapor Pressure of WFNA

The vapor pressure of nitric acid at room temperature is sufficiently high, 50 mmHg at 293 K (20 °C), to release noxious fumes which make the handling of this oxidizer a hazardous operation. In moist air the vapors will form a white mist which is an acute inhalation hazard. In addition to splash protection, respiratory protection is required when transferring WFNA from one container to another container by pouring it in open air.

It is difficult to measure vapor pressure of WFNA at temperatures above room temperature because the acid will start to decompose.

Vapor pressure measurements of pure nitric acid in the narrow temperature range between 263 and 293 K are shown in Figure 3 and can be expressed by the equation

$$\log_{10} P = 8.986 - \frac{2141}{T}$$

where P is the pressure in mmHg and T is the temperature in kelvin [34, 35].

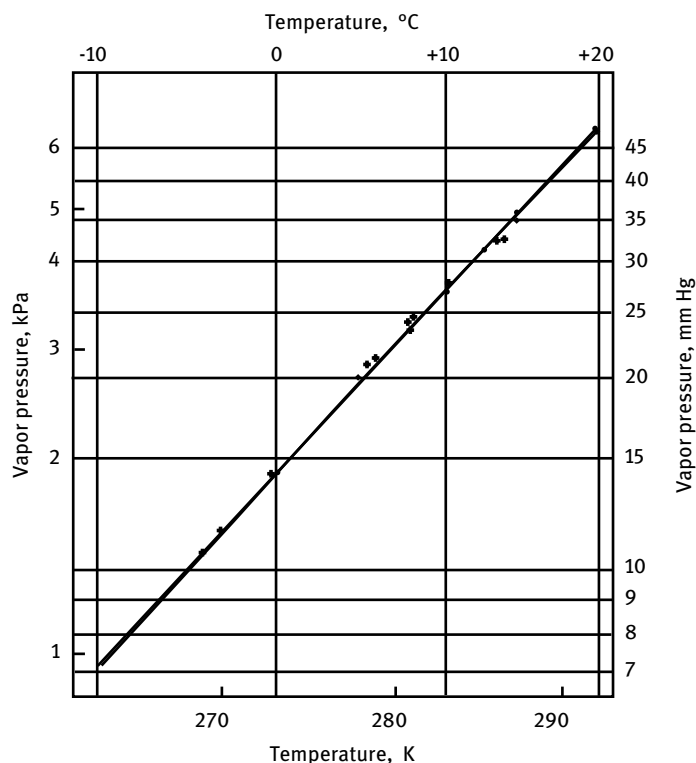


Figure 3: Vapor pressure of pure nitric acid. (reproduced and modified from [36].)

Legend: + Experimental points, • Extrapolated from isotherms, -- Interpolated, - - - Least squares fit

The vapor pressure of pure nitric acid can be calculated from the equation

$$\log p_v = 7.61628 - 1486.238/(t + 230)$$

where p_v is the vapor pressure in mmHg and t is the temperature in °C. The vapor pressure calculated from thermodynamic data agreed well with experimental data in Table 7. See also [31].

Droplet evaporation experiments were performed with single drops of WFNA and of aniline on a hot surface in the temperature range 573–1373 K (300–1100 °C) [37]. These drops showed initial evaporation periods, during which the diameter of the drops did not diminish. The influence of bubble-inflation on the course of the evaporation, and on the total time of evaporation for a given initial diameter was studied. The evaporation times were exponential functions of the temperature of the hot surface. It was demonstrated that, for a constant temperature, the evaporation times per 1 mg of drops can be longer or shorter for nitric acid than for aniline depending on the actual value of the temperature.

Table 7: Vapor pressure of pure nitric acid.

Temperature		Vapor pressure	
K	°C	mmHg	kPa
273.15	0	14.4	1.919
277.6	4.44	19.0	2.533
283.1	10.0	26.6	3.546
288.7	15.6	36.8	4.905
294.2	21.1	50.7	6.758
299.8	26.7	68.3	9.104
305.3	32.2	91.0	12.13
310.9	37.8	120.0	16.00
327.1	54	250.0	33.32
344.1	71	487.2	64.94
361.1	88	876.6	116.8

Data source: [32]

3.3.2 Vapor Phase Composition of WFNA Mixtures

The vapor phase composition as a function of liquid phase composition and temperature must be known if one wants to concentrate dilute nitric acid by distillation. Nitric acid and water do form an azeotrope, which is why WFNA (100% HNO_3) cannot be made by simple distillation of 68% HNO_3 .

The azeotrope formation in the HNO_3/H_2 system is evident from the vapor pressure curves as a function of acid composition, which show a minimum near 35 mol-% HNO_3 (depending on the temperature) (Figure 4).

Measured values of the partial pressures of H_2O and HNO_3 above nitric acid solutions with 50–100 mass-% HNO_3 at 273 and 293 K (0 and 20 °C) were used to calculate the heat of evaporation of nitric acid [38].

Very concentrated solutions of HNO_3 contain free molecules of HNO_3 , H_2O , and the ions NO_3^- and H_3O^+ , and a hydrate ($\text{H}_2\text{O} \cdot \text{NO}_2\text{OH}$) which has no vapor pressure. Calculations involving the partial vapor pressures of pure HNO_3 and H_2O and the coefficient of ionization, which was determined spectrographically, confirmed the existence of a monohydrate between 75 and 100 mass-% HNO_3 [39]. The rate of evaporation of nitric acid droplets is an important design criterion for injectors in rocket engines, see [37]. See also [40, 41].

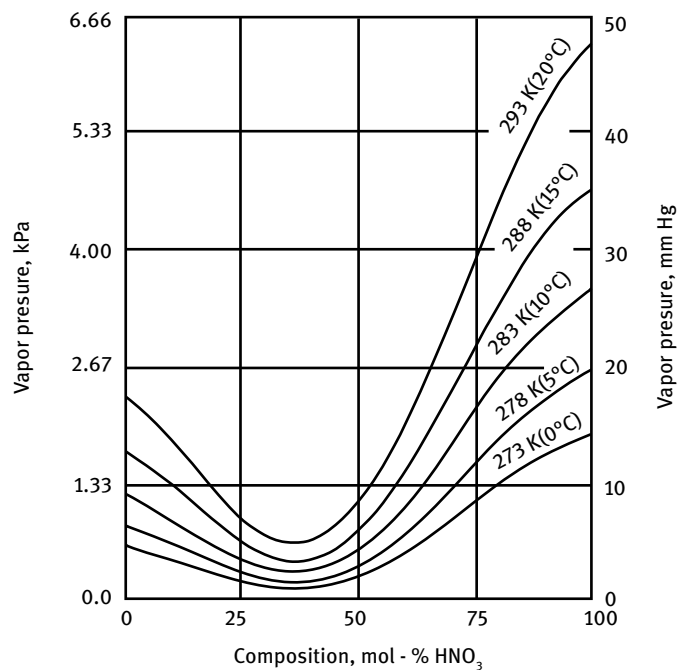


Figure 4: Vapor pressure isotherms in the HNO₃/H₂O system. (reproduced and modified from [36].)

3.4 Density and Partial Molar Volume of Nitric Acid

3.4.1 Density of Pure Liquid Nitric Acid

Density data for liquid nitric acid are summarized in Table 8.

Table 8: Single-point density data for pure nitric acid from the literature.

Temperature		Density	Authors	Year	References
K	°C	g/cm ³			
283	10	1.5310	Intl. Critical Tables, Vol. 3, p. 59	1928	[42]
273	0	1.5492	Mason, Petker, and Vango	1955	[43]
298	25	1.5037	Mason, Petker, and Vango	1955	[43]
283	10	1.5310	Antipenko, Beletskaya, and Krylova	1958	[21]
273	0	1.5492	Fine	1962a	[44]
298	25	1.5027	Weast, CRC Handbook Chem. Phys. 64 th Ed.	1984	[25]

The density of the pure nitric acid as a function of temperature can be calculated by the equation [44, 45]:

$$\rho = 1.5492 - 0.00183t$$

where ρ is the density in g/cm^3 and t is temperature in $^{\circ}\text{C}$. Densities calculated from this equation have been tabulated in Table 9 for convenience.

Table 9: Temperature dependence of density of anhydrous nitric acid.

Temperature		Density	Remarks
$^{\circ}\text{C}$	K	g/cm^3	
0	273	1.5492	Freezing point of water
5	278	1.5401	
10	283	1.5310	
15	288	1.5219	
20	293	1.5128	
25	298	1.5037	Standard reference temperature
30	303	1.4946	
40	313	1.4764	
50	323	1.4582	
60	333	1.4400	
70	343	1.4218	Upper limit for military specifications
71	344	1.4200	
80	353	1.4036	Boiling point
83	356	1.3981	

Data source: [21]

A similar equation for the density of pure nitric acid as a function of temperature, obtained in a narrow temperature range from 16 to 32°C is

$$\rho = 1.54918 - 0.001809t$$

where ρ is the density in g/cm^3 and t is the temperature in $^{\circ}\text{C}$, with a standard deviation in the density of 0.00028 g/cm^3 [46].

Density data in Table 10 for nitric acid with low water content have been gathered from secondary sources and the original source of these data is not known. The densities of pure nitric acid with 0–4% water were measured at 288 K (15°C) and are summarized in Table 11. See also [16]. The coefficient of thermal expansion of nitric acid can be derived from density data Table 12.

Table 10: Density of pure nitric acid, multiple literature data.

Composition		Temperature		Density
HNO ₃ , Mass-%	H ₂ O, Mass-%	K	°C	g/cm ³
100	0	283	10	1.52
100	0	293	20	1.513
100.0	0.0	268	−5.0	1.558
100.0	0.0	278	+5.0	1.540
100.0	0.0	288	15.0	1.522
100.0	0.0	298	25.0	1.504
100.0	0.0	313	40.0	1.477
99.0	1.0	268	−5.0	1.550
99.0	1.0	278	+5.0	1.533
99.0	1.0	288	15.0	1.514
99.0	1.0	298	25.0	1.497
99.0	1.0	313	40.0	1.472
98.0	2.0	268	−5.0	1.545
98.0	2.0	278	+5.0	1.528
98.0	2.0	288	15.0	1.519
98.0	2.0	298	25.0	1.492
98.0	2.0	313	40.0	1.468

Data sources: [47, 28]

Table 11: Density of pure nitric acid with 0–4% water at 288 K.

Nitric acid, mass-%	Density, g/cm ³
100.0	1.5241
99.81	1.5216
99.70	1.5204
99.67	1.5200
99.66	1.5199
99.43	1.5176
99.07	1.5152
98.86	1.5137
98.74	1.5129
98.52	1.5122
98.38	1.5112
98.13	1.5100
97.86	1.5089
97.76	1.5086
97.36	1.5075
95.91	1.5038
95.90	1.5037

Data source: [36]

Table 12: Coefficient of thermal expansion of nitric acid.

Physical state	Temperature range °C	Coefficient of thermal expansion 1/°C
Liquid	4.0–14.2	1.274×10^{-3}
Liquid	14.2–24.2	1.240×10^{-3}

Data source: [28]

3.4.2 Density of Frozen Nitric Acid

The density calculated from XRD measurements, which were obtained at the freezing point of the acid (−41.6 °C), is 1.895 g/cm³ [48].

3.4.3 Pressure Dependence of the Specific Volume (Isothermal Compressibility)

The volumetric behavior of pure HNO₃ was determined at chemical and physical equilibrium between 344 and 444 K (160 and 340 °F) and for pressures up to 34 MPa (5000 psi) [49]. At 344 K (160 °F), approximately 30 h were required to reach chemical equilibrium under isochoric conditions, whereas only about 5 h were required at 361 K (190 °F). The bubble-point pressure varied from about 13.8 MPa to more than 17.2 MPa (2000 psi to more than 2500 psi). At 294 and 311 K (70 and 100 °F), the volumetric behavior of pure HNO₃, at physical equilibrium in the liquid phase, was determined for pressures up to 34 MPa (5000 psi). Data for the pressure dependence of the specific volume of nitric acid (isothermal compressibility) are listed in Table 13.

Table 13: Pressure dependence of the specific volume of nitric acid (isothermal compressibility).

Pressure, atm	Specific volume, cm ³ /g	
	at 21.1 °C	at 37.8 °C
13.609	0.661164	0.674149
27.218	0.660166	0.672963
40.828	0.659167	0.672276
54.437	0.658293	0.671402
68.046	0.657294	0.669779

Data source: [50]

Density data for pressures up to 340 atm from the same source are summarized in Table 14.

Table 14: Density of nitric acid at high pressures.

Pressure		Temperature	
		294.2 K (21.1 °C)	310.9 K (37.8 °C)
atm	MPa	Density, g/cm ³	
13.6	1.37	1.5124	1.4833
27.2	2.75	1.5147	1.4859
40.8	4.12	1.5170	1.4874
54.4	5.49	1.5190	1.4894
68.1	6.88	1.5213	1.4910
85.1	8.60	1.5241	1.4930
102.1	10.31	1.5264	1.4948
119.1	12.03	1.5286	1.4967
136.1	13.75	1.5308	1.4983
153.1	15.46	1.5327	1.5000
170.1	17.18	1.5344	1.5016
187.1	18.90	1.5361	1.5029
204.1	20.61	1.5377	1.5042
238.2	24.06	1.5405	1.5063
272.2	27.49	1.5432	1.5081
306.2	30.93	1.5454	1.5094
340.2	34.36	1.5470	1.5100

Data source: [50]

3.4.4 Partial Molar Volume of Nitric Acid Mixtures

As shown in Figure 5, the specific volume of nitric acid as a function of water content is not a linear function [46, 51]. The excess specific volume is initially positive and becomes negative above a water mass fraction of 0.017.

The positive values of the excess volume suggest that at low concentrations, water behaves as a simple non-electrolyte, showing neither association nor attractive interaction with the solvent nitric acid.

The volumetric behavior of the system $\text{HNO}_3/\text{H}_2\text{O}$ under equilibrium conditions showed a distinct deviation from the behavior of ideal solutions [34, 52–54]. This included measurements of the specific volume at temperatures from 360.9 to 444.3 K (190 to 340 °F), for pressures up to 34.5 MPa (5000 psia) for 3 mixtures of water and nitric acid.

Data for the specific volume of nitric acid/water mixtures under conditions of chemical equilibrium are listed in Table 15.

For additional data on specific volume of nitric acid-water mixtures see also [18].

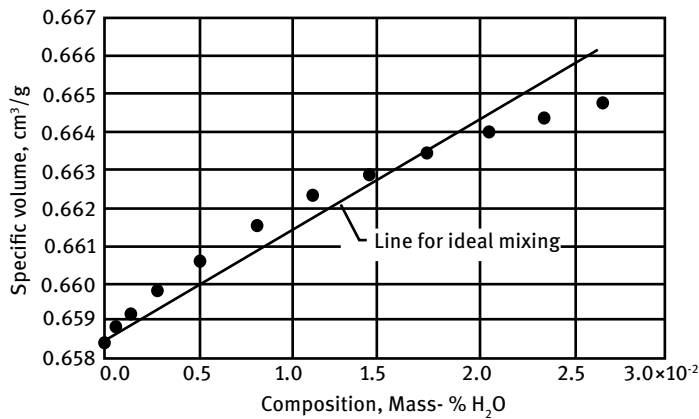


Figure 5: Specific volume of nitric acid with small water contents. (reproduced and modified from [46].)

Table 15: Specific volume of binary nitric acid/water mixtures under conditions of chemical equilibrium.

Concentration, mass-% H ₂ O	Specific volume, cm ³ /g						
	Temperature, K						
	273.1	277.59	283	288.7	294.2	299.8	305.3
	Temperature, °C						
	0	4.44	10.0	15.6	21.1	26.7	32.2
5	0.6518	0.6542	0.6592	0.6642	0.6698	0.6748	0.6792
10	0.6580	0.6611	0.6655	0.6698	0.6748	0.6792	0.6848

Data source: [55]

3.5 Compressibility and Velocity of Sound of WFNA

3.5.1 Compressibility of WFNA

Data on the temperature dependence of the specific volume (isochoric compressibility) of nitric acid are listed in Table 16.

The following data on the isothermal compressibility of liquid nitric acid are only from a secondary source and the original source of these data could not be located (Table 17).

Table 16: Temperature dependence of the specific volume (isochoric compressibility) of nitric acid.

Temperature		Specific volume
K	°C	cm ³ /g
277.54	4.44	0.648866
283.1	10.0	0.653111
288.7	15.6	0.657544
294.2	21.1	0.660852
299.8	26.7	0.666346
305.3	32.2	0.670841
310.9	37.8	0.675335 (extrapolated)

Data source: [56]

Table 17: Isothermal compressibility of liquid nitric acid.

Pressure		Isothermal compressibility, 1/atm	
MPa	atm	at 21.1 °C at 294.5 K	at 37.8 °C at 310.9 K
2.76	27.2	130.6×10^{-6}	110.4×10^{-6}
5.51	54.4	107.6×10^{-6}	86.4×10^{-6}
8.62	85.1	93.3×10^{-6}	76.3×10^{-6}

Data source: [28]

3.5.2 Velocity of Sound in WFNA

The velocity of sound in liquid nitric acid can be used to calculate the adiabatic compressibility of this liquid (Table 18).

Other sources reported a velocity of sound of 1425 m/s at 289 K = 16 °C.

Table 18: Velocity of sound and specific heat ratio of technical grade nitric acid.

Composition, mass-%	Velocity of sound, m/s	Adiabatic coefficient
97.08% HNO ₃ , 0.22% NO ₂ , 1.91% H ₂ O, 0.79% Fe(NO ₃) ₃	1239.2	1.31
97.52% HNO ₃ , 0.28% NO ₂ , 2.11% H ₂ O, 0.09% Fe(NO ₃) ₃	1239.7	1.26

Data source: [57]

3.6 Viscosity of WFNA

One must differentiate between dynamic viscosity and kinematic viscosity. The SI physical unit of *dynamic viscosity* is the Pascal-second ($\text{Pa} \cdot \text{s}$), equivalent to $(\text{N} \cdot \text{s})/\text{m}^2$, or $\text{kg m}^{-1} \cdot \text{s}^{-1}$. The cgs physical unit for dynamic viscosity is the *poise*, abbreviated as Ps.

$$1 \text{ Ps} = 0.1 \text{ Pa} \cdot \text{s}$$

$$1 \text{ cPs} = 1 \text{ mPa} \cdot \text{s} = 0.001 \text{ Pa} \cdot \text{s}.$$

The SI unit of *kinematic viscosity* is m^2/s . The cgs physical unit for *kinematic viscosity* is the *stokes*, abbreviated as St. It is sometimes expressed in terms of centistokes (cSt).

$$1 \text{ St} = 1 \frac{\text{cm}^2}{\text{s}} = 10^{-4} \frac{\text{m}^2}{\text{s}}$$

$$1 \text{ cSt} = 1 \frac{\text{mm}^2}{\text{s}} = 10^{-6} \frac{\text{m}^2}{\text{s}}.$$

The following conversion factors are useful when bringing viscosity data from different sources to a common denominator:

$$1 \text{ cPs} = 1 \times 10^{-3} \text{ N s m}^{-2}$$

$$1 \text{ cPs} = 1 \text{ mPa} \cdot \text{s} = 0.001 \text{ Pa} \cdot \text{s}$$

$$1 \text{ cSt} = 1 \text{ mm}^2 \cdot \text{s}^{-1} = 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$$

The kinematic viscosity is the ratio of the dynamic (absolute) viscosity μ to the density of the fluid ρ . It is usually denoted by the Greek letter nu (ν). It is a convenient parameter when analyzing the Reynolds number which expresses the ratio of the inertial forces to the viscous forces.

The agreement among various viscosity data reported for pure nitric acid in the literature is not very good. In many cases the investigators (negligently or ignorantly) used a nitric acid of dubious purity. Quite often the acid decomposed extensively during the viscosity measurements. Table 19 is a random sampling of viscosity data reported in the literature, arranged by increasing temperature (not by year of publication as some of the other tables).

From an examination of the available data and of the work of Chanukvadze [63] on the nitric acid-water system up to 99.5% HNO_3 , it appears that the values of Briner, Suesz, and Favarger [19], of Naumova [59], and Mason, Petker, and Vango [43] (Table 20) are the most representative for the viscosity of pure nitric acid.

Table 19: Literature summary of dynamic viscosity data of nitric acid.

Temperature		Dynamic viscosity	Author(s)	Year	References
°C	K	$\mu \times 10^3$ Ps			
0	273	12.23	Miskidzhyan and Trifonov	1947	[58]
0	273	11.00	Naumova	1949a	[59]
0	273	10.92	Mason, Petker, and Vango	1955	[43]
10	283	10.37	Bingham and Stone	1923	[60]
10	283	10.3 ^a	International Critical Tables	1929	[61]
20	293	8.780	Bingham and Stone	1923	[60]
20	293	8.98 ^a	International Critical Tables	1929	[61]
20	293	9.46	Miskidzhyan and Trifonov	1947	[58]
24.9	298.05	7.61	Briner, Suesz, and Favarger	1935	[19]
25	298.15	7.33 ^b	Taylor, Lyne, and Follows	1951	[62]
25	298.15	7.46	Mason, Petker, and Vango	1955	[43]
40	313	6.798	Bingham and Stone	1923	[60]
40	313	6.80 ^a	International Critical Tables	1929	[61]
40	313	7.15	Miskidzhyan and Trifonov	1947	[58]
40	313	6.17	Mason, Petker, and Vango	1955	[43]

^a Reported as relative viscosities and converted to cgs units using the viscosity of water at the stated temperature

^b Extrapolated from viscosity data of mixture of nitric acid and nitrogen

Data source: [14]. Not all references in this table are in our database and identified in this book.

Table 20: Dynamic viscosity of pure anhydrous nitric acid.

Temperature		Dynamic viscosity	
°C	K	cPs	Pa · s
0	273.15	1.092	1.092×10^{-3}
4.44	277.59	0.865	0.865×10^{-3}
10.0	283.15	0.746	0.746×10^{-3}
15.6	288.7	0.687	0.687×10^{-3}
21.1	294.2	0.655	0.655×10^{-3}
26.7	299.8	0.637	0.637×10^{-3}
32.2	305.3	0.625	0.625×10^{-3}
37.8	310.9	0.618	0.618×10^{-3}

Data source: [43, 64]

Dynamic viscosity data of a technical grade nitric acid containing 95–97.5% HNO₃ and <2% H₂O are listed in Table 21.

Table 21: Dynamic viscosity of technical grade nitric acid (95–97.5% HNO₃, <2% H₂O).

Temperature		Dynamic viscosity	
°C	K	cPs	Pa · s
–34.3	238.8	2.46	2.46×10^{-3}
–17.8	255.3	1.73	1.73×10^{-3}
10	283.1	1.08	1.08×10^{-3}
37.8	310.9	0.726	0.726×10^{-3}
65.6	338.7	0.525	0.525×10^{-3}
93.3	366.4	0.397	0.397×10^{-3}
121.1	394.2	0.314	0.314×10^{-3}
148.9	422.0	0.254	0.254×10^{-3}

Data source: [65]. Same data are shown in [10]

The viscosity of a technical grade of WFNA illustrated in Figure 6 is based on data similar to those in Table 21.

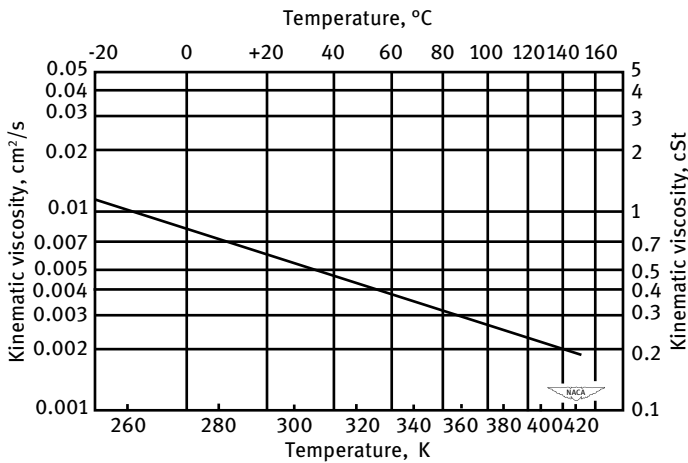


Figure 6: Kinematic viscosity of technical grade WFNA. (Reproduced and modified from [10].)

Conversion factors: 1 cm²/s = 100.5 cSt; 1 ft²/s = 9.2927 × 10⁴ cSt

Dynamic (absolute) viscosity data for 99.51% HNO₃ from an unidentified source are tabulated in Table 22.

Table 22: Dynamic viscosity of 99.51% HNO₃.

Temperature			Dynamic viscosity	
K	°F	°C	mPa s	cPs
277.6	40.0	4.4	1.101	1.101
294.3	70.0	21.1	0.863	0.863
310.9	100.0	38.0	0.683	0.683
344.2	160.0	71.0	0.465	0.465
377.6	220.0	93.0	0.389	0.389

Data source: [28], p. 158

The temperature dependence of the viscosity of nitric acid between 291 and 343 K (18 and 70 °C) has been expressed by the following equation [66]:

$$\log \mu \times 10^3 = -0.9004 + 550.0/T$$

where μ is the viscosity in poise and T is the temperature in kelvin. The acid decomposed extensively during the viscosity measurements. The composition was not stated, but the acid appears to have contained excess nitrogen dioxide and possibly also water. The viscosity of HNO₃ at 273 K (0 °C) is 12.23 mPs [67].

Temperature dependency (293–353 K = 20–80 °C) of the viscosity of aqueous HNO₃ shows a maximum at 33 mol-% HNO₃, suggesting strong interaction and formation of the HNO₃•2H₂O dihydrate [68]. The dynamic viscosity of aqueous nitric acid as a function of HNO₃ concentration and temperature can be expressed by the equation

$$\log \eta = -1.6964 - 2.748(1 - c) + 2.719(1 - c)^2 + [457.39 + 1471.5(1 - c) - 1669.3(1 - c)^2]/T$$

for the concentration range $0.60 < c < 0.97$ mass fraction HNO₃ and by

$$\log \eta = -1.5712 + [235.98/(t + 130)] + 0.387c + 0.273c^2$$

for the concentration range $0 < c < 0.60$ mass fraction HNO₃, where c is the HNO₃ mass fraction, η is the viscosity in cPs, t is the temperature in °C, and T is the temperature in K. The viscosity increases with HNO₃ concentration and decreases with temperature. As illustrated in Figure 7, there is something wrong with these two equations because they do not connect at $c = 0.6$. They may connect at a mass fraction somewhat below 0.6. The average error in these equations is 5%.

The viscosity η of pure HNO₃ with a freezing point of 231.9–231.6 K (–41.2 to –41.5 °C) and a density of $d_0 = 1.5495 \text{ g/cm}^3$ was determined in the temperature range from 233 to 348 K (–40 to 75 °C) [69]. The viscosity η vs. temperature function was a straight line. The extrapolated values of η and the density data previously given

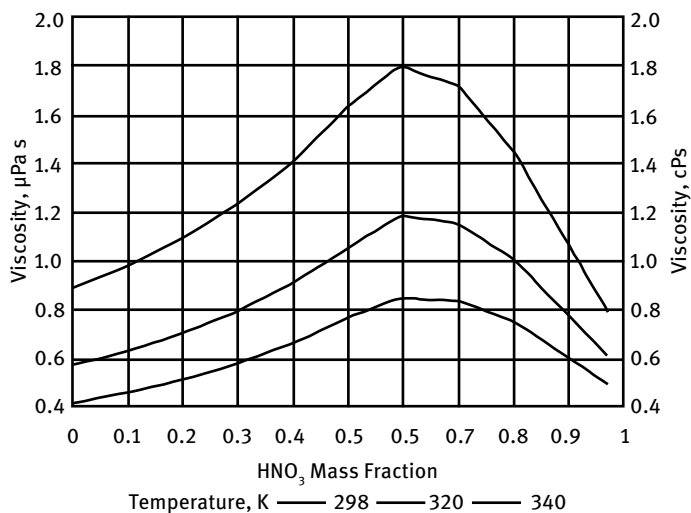


Figure 7: Dynamic viscosity of nitric acid solutions (image created by Schmidt 2019, based on data from [68])

were used in an attempt to determine the effect of temperature on the dissociation equilibrium of HNO_3 . Bachinski's equation

$$\eta = A/(t + \alpha)^3$$

gave a linear function with breaks at 243, 263, and 298 K (−30, −10, and 25 °C) and that of Frenkel,

$$\eta = Ae^{U/KT}$$

gave a linear function with breaks at −30 and −10 °C. The plots of fluidity ϕ vs. specific volume, and that of specific volume V vs. temperature were curved lines, the curvature of which increased with temperature. This behavior was attributed to the decomposition of solvate ions of HNO_3 .

3.7 Surface Tension of WFNA

Surface tension data for WFNA are listed in Table 23. The surface tension of pure HNO_3 at 293 K (20 °C) is 41.15 dyn/cm [71]. The surface tension of aqueous nitric acid as a function of HNO_3 concentration and temperature for the range $0 < c < 0.9$ can be expressed by the equation

$$\sigma = 72.75 - 5.57c - 24.55c^2 - 0.166(t - 20)$$

Table 23: Surface tension of pure nitric acid.

Temperature		Surface tension	
°C	K	dyn/cm	N/cm
0	273.15	43.56	0.000436
11.5	284.6	42.7	0.00043
20	293.1	41.2	0.00041
40	313.1	37.8	0.00038
78.2	351.3	31.5	0.00031

Data source: [70], p. 153–154, based on data from Miskidzhyan and Trifonov [17]

Conversion: 1 dyn = 10^{-5} N

where σ is the surface tension in dyn/cm, c is the mass fraction HNO_3 and t is the temperature in °C [68]. The surface tension decreases with increasing HNO_3 concentration and temperature.

3.8 Thermal Conductivity of WFNA

Thermal conductivity data for WFNA, gathered from several secondary sources where the original source of data is not always known, are summarized in Table 24 through Table 27.

Table 24: Thermal conductivity of pure nitric acid.

Temperature		Thermal conductivity		
°C	K	kcal m ⁻¹ h ⁻¹ K ⁻¹	kJ m ⁻¹ h ⁻¹ K ⁻¹	W m ⁻¹ K ⁻¹
10	283	0.236	0.987	0.274
65	338	0.260	1.088	0.302

Data source: Secondhand data from [47].

Table 25: Thermal conductivity of technical grade nitric acid.

Temperature		Thermal conductivity		
°C	K	kcal m ⁻¹ h ⁻¹ °C ⁻¹	cal cm ⁻¹ s ⁻¹ °C ⁻¹	W m ⁻¹ K ⁻¹
0	273	0.231	0.000642	0.269
25	298	0.243	0.000675	0.282
50	323	0.253	0.000703	0.294
Boiling point		0.286	0.000794	0.332

Composition 99.01% HNO_3 , 0.46% NO_2 , 0.53% H_2O

Table 26: Thermal conductivity of technical grade nitric acid.

Temperature			Thermal conductivity		
K	°F	°C	BTU ft ⁻¹ h ⁻¹ °F ⁻¹	cal cm ⁻¹ s ⁻¹ °C ⁻¹	W m ⁻¹ K ⁻¹
241.4	-25	-31.7	0.146	0.00060	0.251
255.3	0	-17.8	0.150	0.00062	0.259
269.2	25	-3.9	0.154	0.00064	0.268
297.0	75	23.9	0.162	0.00067	0.280
324.8	125	51.7	0.170	0.00070	0.293
366.4	200	93.3	0.183	0.00076	0.318
455.3	360	182.2	0.199	0.00082	0.343

Data source: [28], p. 158

Composition 99.01% HNO₃.Conversion factor 1 BTU ft⁻¹ h⁻¹ °F⁻¹ = 4.13376×10^{-3} cal cm⁻¹ s⁻¹ °C⁻¹ = 0.017296 W cm⁻¹ K⁻¹**Table 27:** Thermal conductivity of technical grade nitric acid

Temperature			Thermal conductivity			Prandtl number
°F	°C	K	cal cm ⁻¹ s ⁻¹ °C ⁻¹	BTU h ⁻¹ ft ⁻¹ °F ⁻¹	W m ⁻¹ K ⁻¹	
-30	-34.3	238.8	5.99×10^{-4}	0.145	0.251	17.35
0	-17.8	255.3	6.20×10^{-4}	0.150	0.259	11.81
50	10	283.1	6.49×10^{-4}	0.157	0.272	7.05
100	37.8	310.9	6.86×10^{-4}	0.166	0.287	4.45
150	65.6	338.7	7.23×10^{-4}	0.175	0.303	3.07
200	93.3	366.4	7.56×10^{-4}	0.183	0.316	2.23
250	121.1	394.2	7.89×10^{-4}	0.191	0.330	1.71
300	148.9	422.0	8.23×10^{-4}	0.199	0.344	1.35

Composition: 95–97.5% HNO₃, <2% H₂O

Data source: [65]. Same data are shown in [10]

Extrapolating from the thermal conductivity of nitric acid/water solutions to 100% HNO₃ gave a thermal conductivity of $0.21 \text{ kcal m}^{-1} \text{ h}^{-1} \text{ °C}^{-1}$, or $5.8 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ °C}^{-1}$, for the thermal conductivity of 100% nitric acid at 290.3 K (17.2 °C) [72]. Additional data on the thermal conductivity of a lesser grade technical nitric acid are in Table 27.

A graph in a NACA report shows the thermal conductivity as a function of temperature [26].

3.9 Heat Transfer Properties of White Fuming Nitric Acid

Although most rocket engines use the fuel instead of the oxidizer for regenerative cooling, in the past, occasionally both fuel and oxidizer (WFNA, RFNA, or NTO) have been used as coolants in bipropellant engines. For these applications it is of fundamental importance to know the heat transfer properties of these fluids [65, 73].

At Reynolds numbers from 55000 to 220000, initial acid temperatures of 283–341 K (10–68 °C), and pressures from 441 to 1138 kPa (4.35–11.2 atm = 64–165 psia) with heat fluxes between 21.3 and 230 W/cm² (5.1 and 55 cal cm⁻² s⁻¹ = 21.3 and 230 J cm⁻² s⁻¹) it was concluded that the heat transfer properties follow the Colburn equation, similar to the behavior of water at very high pressures [74, 75].

$$j = \frac{h}{\frac{m^*}{A} C_p (\text{Pr})^{2/3}} = 0.023 (\text{Re}^{-0.2})$$

where j is the Colburn modulus (a dimensionless number), h is the heat transfer coefficient, m^*/A is the mass flux per unit cross-sectional area, and C_p is the heat capacity. Pr and Re are the Prandtl and the Reynolds numbers. Continued circulation of the same acid in the test apparatus reduced the heat-transfer coefficient as much as 25%. Whether this was due to scale, dissociation, corrosion, or a combination of the three is not known. When the inside surface temperature of the tube exceeded the saturation temperature of the WTNA, the heat transfer rate and the pressure drop increased above

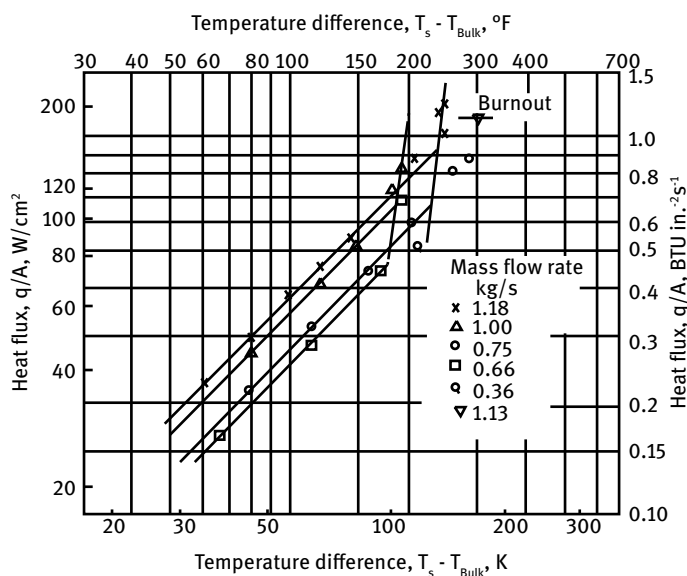


Figure 8: Heat flux density of WFNA nucleate boiling heat transfer at 0.448 MPa (65 psia) in 13.6-mm (0.537-in) I.D. Haynes 25 tube (reproduced and modified from [76]).

those predicted by the equation above. No satisfactory correlations of data could be obtained in the nucleate boiling regime. The nucleate boiling data were plotted with the heat-flux density against the temperature difference $t_s - t_{\text{bulk}}$ for constant mass flow rate in Figure 8. The curves were geometrically similar to those obtained by other investigators with fluids other than WFNA. For each mass flow rate the slope of the curve increased sharply as the surface temperature of the tube reached the saturation temperature, indicating that small increases in the surface temperature resulted in large increases in heat transfer rates. Shortly after entering a film-boiling region, the tube burned out.

A much simpler correlation for WFNA was obtained in continuation of this work [76]:

$$j = 0.030(\text{Re})^{-0.2}$$

In the same apparatus, tests with RFNA instead of WFNA resulted in much faster corrosion such that no reliable data could be obtained [77]. See also [78].

3.10 Critical Constants of WFNA

It is unlikely that measured data for the critical constants of nitric acid exist, because of the rapid decomposition of anhydrous nitric acid at elevated temperatures. Consequently, there is more than average uncertainty in the estimated values. The critical temperature of nitric acid was estimated at 624 K and the critical pressure was estimated as 94 atm by the methods of Gates and Thodos [79]. Critical compressibility is about 0.238. See also [80].

3.11 Solubility of Gases in Nitric Acid

The solubility of gases in nitric acid is of dual importance: First we need to know how much of the oxygen formed during the slow decomposition of WFNA during storage can remain in solution and how much of it will pressurize the ullage to unwanted and often dangerous overpressure. Secondly, pressurant gases dissolved in the oxidizers will affect their heat transfer coefficients in cooling jackets and cavitation in pumps in propellant feed systems. Henry's law at constant temperature may be written as

$$C_{\text{O}_2} = \alpha p$$

where C_{O_2} is the dissolved oxygen concentration in mol/L, α is the Henry's law coefficient and p is the pressure in atm. The solubility of dioxygen in WFNA or RFNA increased with temperature but decreased with increasing NO_2 or water content (Figure 9) [81, 82]. The Henry's law coefficient for solubility of dioxygen in pure nitric acid at 310.8 K (37.7 °C) was $5.55 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}^{-1}$.

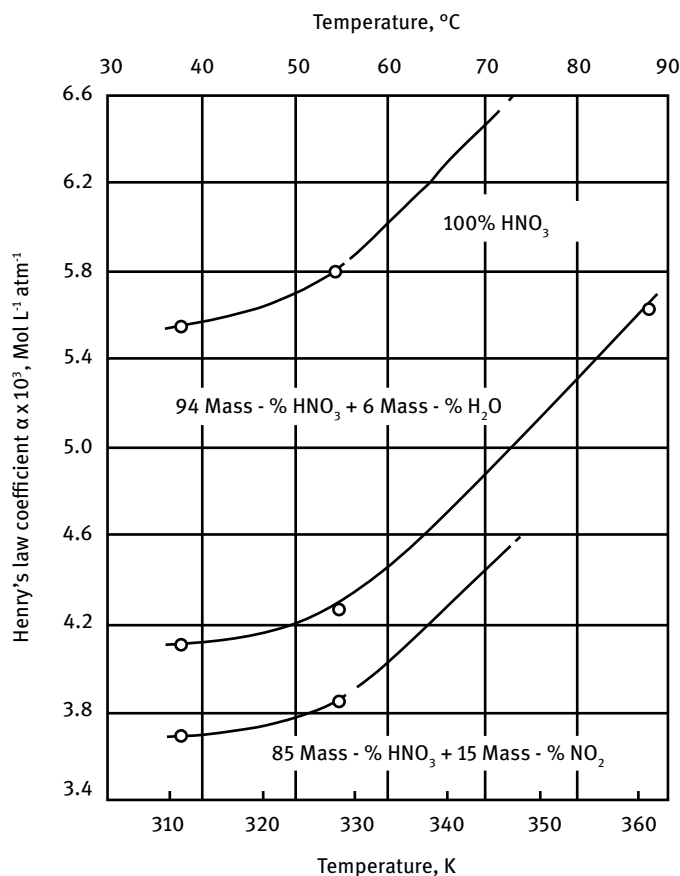


Figure 9: Effect of temperature on coefficient α in Henry's law for solutions of oxygen in nitric acid and mixtures of nitric acid with nitrogen dioxide or water (reproduced and modified from [82]).

The solubility of oxygen in 100% nitric acid at 298 K and 101 kPa was 0.0659 L gas under standard temperature (273 K) and pressure (0.101 kPa)(STP) per L of acid equal to 0.0437 L gas (STP) per g of acid [83]. The solubility decreased when water or dinitrogen tetroxide was added to the acid (Figure 10) and increased if the temperature was raised (Figure 11).

In Figure 11 the solid lines represent the same Robertson data as in Figure 9 above, while the dashed lines represent new data. Although smooth curves can be drawn as indicated by the dashed lines, it is necessary to ignore the points at 310.8 K (37.7°C) and to reverse the curvature of the solid lines. So far there is no theoretical basis for a choice of either type of curvature. It might even be a straight line; however, data for the solubility of oxygen, nitrogen, or helium in water show curvatures like the curves shown in solid lines, and therefore provide a basis for preference. While the results of

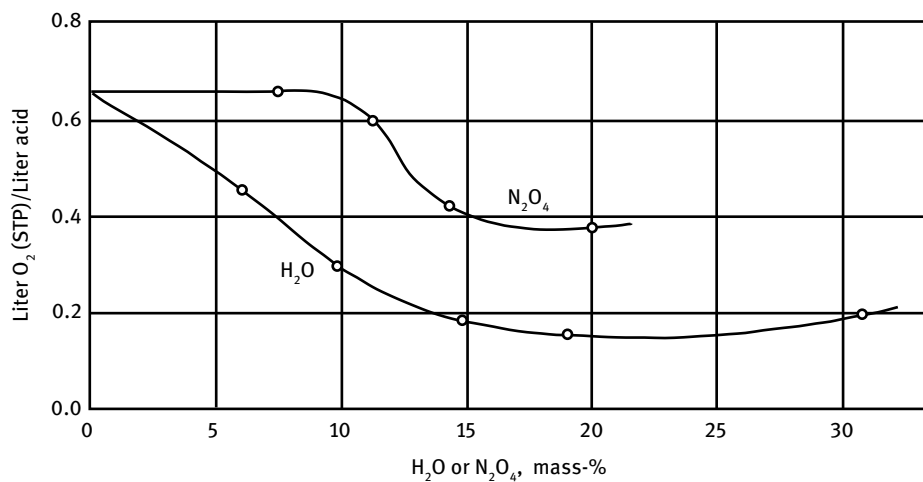


Figure 10: Solubility of oxygen in $\text{HNO}_3/\text{N}_2\text{O}_4$ and $\text{HNO}_3/\text{H}_2\text{O}$ mixtures (reprinted and adapted from [83] with permission. ©1955 American Chemical Society; permission conveyed through RightsLink)

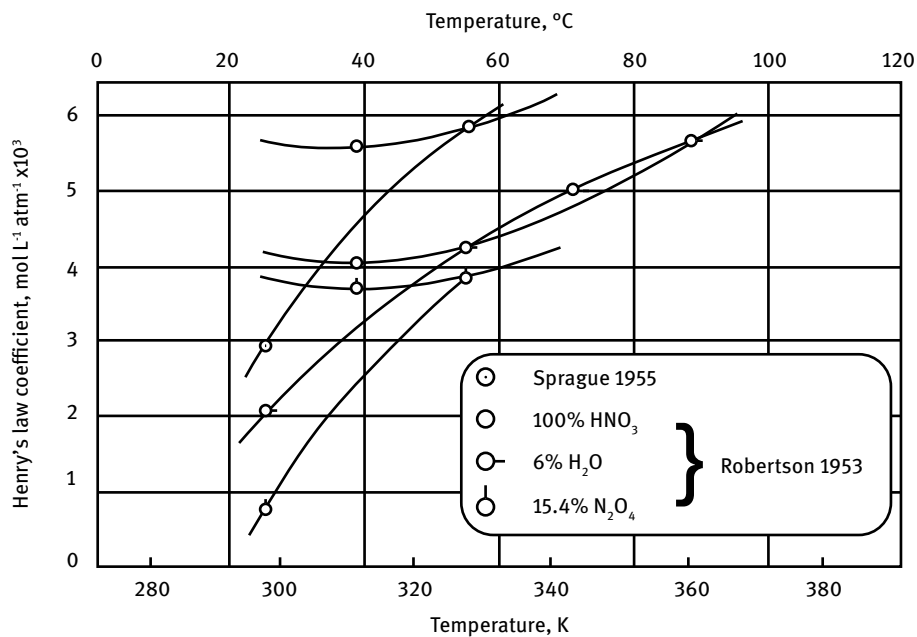


Figure 11: Solubility of oxygen in $\text{HNO}_3/\text{N}_2\text{O}_4$ and $\text{HNO}_3/\text{H}_2\text{O}$ mixtures as a function of temperature (reprinted and adapted from [83] with permission. © 1955 American Chemical Society)

Sprague (dashed lines) indicate a somewhat lower solubility than those of Robertson, there is at least an order of magnitude agreement. It is unfortunate that data were not obtained at the same temperature, so that a direct comparison could be made.

At 293–353 K (20–80 °C) and 1–6 MPa (10–60 atm) the solubility of oxygen in 0–100% aqueous HNO_3 solutions is linearly related to temperature and pressure [84]. With an increase in temperature, the solubility of oxygen in $\leq 16\%$ HNO_3 decreased. In $>16\%$ HNO_3 , a temperature increase promoted a salting in of the oxygen with increased solubility. See also [85].

3.12 Nitric Acid as a Solvent

Mixtures of nitric acid with fuels can be used as explosives. Mixtures of nitric acid with alcohols are immediately detonable and not suitable as monopropellants. Solutions of some organic amine nitrates, mostly quaternary alkylammonium salts, in nitric acid have been tested as monopropellants (CAVEA-B, see *Encyclopedia of Monopropellants*, chapter “Nitric Acid or Perchloric Acid-Based Monopropellants”). Although tributyl phosphate and nitric acid, often in intimate contact during the reprocessing of nuclear reactor fuel elements, are not miscible, their emulsions are potentially detonable. Numerous explosions have occurred in nitrating reactors in the chemical industry where the solubility of reactants was underestimated. Nitric acid, dinitrogen tetroxide, and their mixtures are useful as media for inorganic reactions [86].

It is important to know the solubility of corrosion products in nitric acid, because once their solubility is exceeded, and mostly when the propellant tanks cool down, the salts may precipitate and clog filters, valves, and injector orifices. Unfortunately, data on solubility of iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (CAS RN 10421-48-4) are available only in aqueous solutions containing from 0 to 59.9 mass-% HNO_3 at 293 K (20 °C) [87] and data for higher acid concentrations are lacking. With an increase in HNO_3 concentration, within the above range, the solubility of $\text{Fe}(\text{NO}_3)_3$ decreased sharply, dropping from 78.3–83.3 g/100 g to 13.0 g/100 g solution. At lower acid concentrations, $\text{Fe}(\text{NO}_3)_3$ had a tendency of to undergo hydrolysis.

Mixtures of nitric acid with acetic acid or acetic anhydride are often used for nitration of organic compounds where the traditional nitrating acid (nitric acid/sulfuric acid or nitric acid/oleum) would be too aggressive and result in unwanted side reactions. The properties of nitric acid/acetic acid solutions have been investigated. The melting point/concentration curve of the system $\text{HNO}_3/\text{CH}_3\text{COOH}$ is typical of a system where a compound is formed having a congruent melting point [88]. One eutectic occurs at 230.5 K (–42.6 °C), 33.3 mol-% HNO_3 , the other at 214.0 K (–59.1 °C), 80 mol-% HNO_3 . The compound, whose formula is $\text{CH}_3\text{COOH} \cdot \text{HNO}_3$, melts at 248.5 K (–24.6 °C). The viscosity-concentration curves at 273, 293, and 313 K (0, 20, and 40 °C) exhibit maxima (35.46 mPs) at 40–45 mol-% HNO_3 . The curves of surface tension σ vs.

composition of nitric acid/acetic acid mixtures were almost straight lines at all temperatures [71]. The heat of mixing of nitric acid and acetic acid goes through a maximum of 1158 cal/mol of mixture at 50 mol-% [89]. This shows chemical interaction and formation of an equimolar complex. Nitric acid and acetic acid form a low-boiling azeotrope which boils at 128.6°C and contains about 33 mol-% HNO_3 [90].

The variation of the electrical conductivity of solutions of ammonium nitrate (AN) in nitric acid and in nitric acid/dinitrogen pentoxide mixtures as a function of AN concentration was similar to that observed for many electrolytes in a variety of solvents, except when AN was dissolved in $\text{HNO}_3/\text{N}_2\text{O}_5$ solvents, where specific conductance decreased with increasing AN concentration [91]. The presence of additional nitrate anions suppressed the formation of nitronium NO_2^+ cations which are charge carriers in other nitric acid solutions. The addition of NH_4NO_3 stabilized concentrated, anhydrous HNO_3 .

3.13 Thermodynamic Properties of White Fuming Nitric Acid

The thermodynamic properties of WFNA are summarized in Table 28 through Table 34.

3.13.1 Heat Capacity of White Fuming Nitric Acid

3.13.1.1 Heat Capacity of Solid and Liquid White Fuming Nitric Acid

The heat capacity of pure nitric acid was measured calorimetrically in the temperature range 15–231.51 K (solid state) and 231.51–300 K (liquid state) [20]. The heat capacity of solid and liquid WFNA is tabulated in Table 28. These heat capacities of the liquid can be expressed conveniently by an empirical equation. The equation for the liquid represents the data in Table 28 between 230 and 300 K to better than 0.05%:

$$C_p = 25.64 + 1.427 \times 10^{-2}T - 4.090 \times 10^{-5}T^2$$

where C_p is the molar heat capacity in $\text{cal } ^\circ\text{C}^{-1} \text{ mol}^{-1}$ and T is the temperature in kelvin.

Table 29 gives heat capacity data of technical grade WFNA for a different temperature range. The isobaric heat capacities of WFNA and RFNA were determined at bubble point in a stainless-steel calorimeter, which was gold-plated for use with corrosive liquids [92]. The heat capacity measurements for WFNA were made in the temperature range from 316 to 336 K (110–145 °F). The nitric acid samples removed from the calorimeter after the heat capacity measurements showed evidence of significant corrosion. It appears that the heat capacity of liquid HNO_3 does not change much over the temperature range of interest (Figure 12).

Table 28: Heat capacity of solid and liquid pure nitric acid.

Physical state	Temperature		Heat capacity c_p	
	K	°C	J g ⁻¹ K ⁻¹	cal g ⁻¹ °C ⁻¹
Solid	22.1	-251	0.0995	0.0238
Solid	55.1	-218	0.4383	0.1048
Solid	89.1	-184	0.6260	0.1496
Solid	122.1	-151	0.7410	0.1771
Solid	155.1	-118	0.8365	0.1999
Solid	188.7	-84.4	0.9376	0.2241
Solid	222	-51.1	1.0560	0.2524
Liquid	255.3	-17.8	1.7668	0.4223
Liquid	266.43	-6.67	1.7608	0.4208
Liquid	277.54	4.44	1.7544	0.4193
Liquid	288.7	15.6	1.7446	0.4170
Liquid	299.8	26.7	1.7413	0.4162

Data source: [20]

Composition: HNO₃ with 0.01 mol% impurity**Table 29:** Heat capacity of liquid (technical grade 95–97% HNO₃) nitric acid.

Temperature			Heat capacity c_p	
K	°F	°C	cal g ⁻¹ °C ⁻¹	J g ⁻¹ K ⁻¹
238.8	-30	-34.3	0.423	1.770
255.3	0	-17.8	0.423	1.770
310.9	100	37.8	0.423	1.770
366.4	200	93.3	0.424	1.774
394.2	250	121.1	0.429	1.795
422	300	148.9	0.436	1.824

Data source: [28], p. 158

3.13.1.2 Heat Capacity of White Fuming Nitric Acid Vapor

The heat capacity of nitric acid vapor as a function of temperature can be calculated from the following polynomial Shomate equation which was obtained from NIST Chemistry WebBook [15]:

$$C_p^\circ = A + B \times \tau + C \times \tau^2 + D \times \tau^3 + \frac{E}{\tau^2}$$

where C_p is the molar heat capacity in J mol⁻¹ K⁻¹, τ is the temperature in kelvin divided by 1000 and A, B, C, D, and E are constants listed in Table 30 for two different temperature ranges. One must note that HNO₃ is unstable at temperatures above 400 K and the column for the higher temperature range 1100–6000 K is only of academic inter-

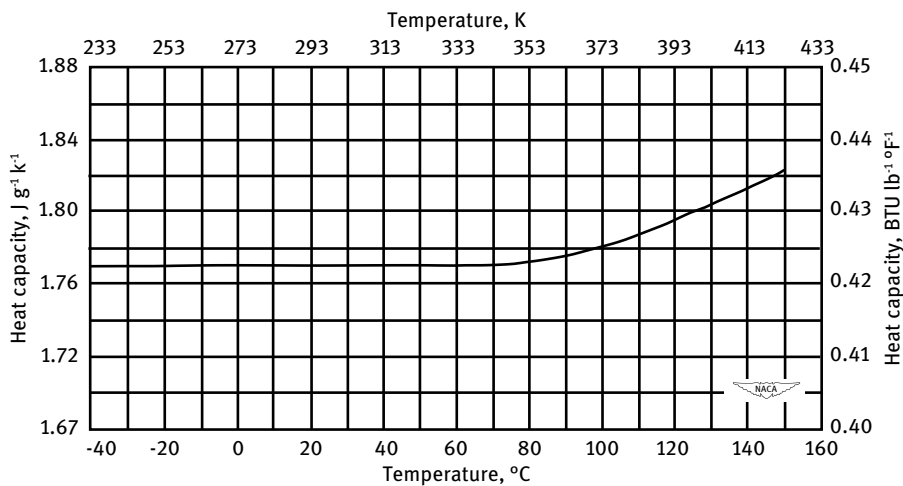


Figure 12: Heat capacity of liquid (95–97% HNO₃) nitric acid (reproduced and modified from [10])

Table 30: Thermodynamic property polynomial equation coefficients for nitric acid vapor.

Temperature, K	298–1200	1200–6000
A	19.63229	97.45959
B	153.9599	5.429577
C	-115.8378	-1.029688
D	32.87955	0.067950
E	-0.249114	-12.29314
F	-146.8818	-192.4912
G	247.7049	343.8051
H	-134.3060	-134.3060

Data source: [93]

est. It is not very practical to list thermodynamic data for a compound that is unstable at the temperature range listed. It would be much more important to have accurate thermodynamic data for the liquid mixtures of nitric acid with dinitrogen tetroxide.

Some HNO₃ vapor heat capacity data calculated with above equation are summarized in Table 31. Heat capacity data for HNO₃ vapor calculated from IR measurements can be expressed by the equation [94]:

$$C_p = 2.88 + 4.047 \times 10^{-2}T - 2.407 \times 10^{-5}T^2$$

where C_p is the molar heat capacity in cal °C⁻¹ mol⁻¹ and T is the temperature in kelvin.

Table 31: Heat capacity of nitric acid vapor.

Temperature		Molar heat capacity C_p		Heat capacity c_p		Remarks
K	°C	J mol ⁻¹ K ⁻¹	cal mol ⁻¹ K ⁻¹	J g ⁻¹ K ⁻¹	cal g ⁻¹ K ⁻¹	
221.56	-51.59	43.34	10.36	0.688	0.164	Freezing point of HNO ₃
273.15	0	50.37	12.04	0.799	0.191	Freezing point of water
298.15	25	53.31	12.74	0.846	0.202	Common reference temperature
300.15	27	53.53	12.79	0.850	0.203	
310.15	37	54.63	13.06	0.867	0.207	
320.15	47	55.70	13.31	0.884	0.211	
330.15	57	56.73	13.56	0.900	0.215	
340.15	67	57.74	13.80	0.916	0.219	
344.15	71	58.13	13.89	0.923	0.221	
350.15	77	58.72	14.03	0.932	0.223	
357.05	83.9	59.38	14.19	0.942	0.225	Boiling point of HNO ₃
373.15	100	60.87	14.55	0.966	0.231	Boiling point of water

Data source: [93]

3.13.2 Heat of Formation of White Fuming Nitric Acid

Standard enthalpy of formation (ΔH)₂₉₈ data for liquid and gaseous nitric acid are listed in Table 32.

Table 32: Standard enthalpy of formation (ΔH)₂₉₈ of nitric acid.

Physical state	Standard enthalpy of formation (ΔH_f) ₂₉₈			Data source	Year	References
	kJ/mol	kcal/mol	cal/g			
Gas	-134.31	-32.1	-509.4	NIST Chemistry WebBook	1998	[93]
Gas	-134.360 ± 0.5	-32.113 ± 0.120		Dorofeeva et al.	2003	[95]
Gas	-134.196	-32.073	-509	PEPCODED.DAF	1986	[96]
Liquid	-173.47	-41.46	-658	PEPCODED.DAF	1986	[96]
Liquid	-171.58	-41.01	-650.8	JPLCODED.DAT	1988	[96]

Molecular mass: 63.0128 g/mol [10]

In the past, the enthalpy of formation of nitric acid was determined from data on equilibria involving HNO₃. The JAN(N)AF thermochemical tables and the compilation published by Gurvich et al. [97] provide an exhaustive analysis of these experimental data, resulting in values from -129.7 to -136.7 kJ/mol for $\Delta H_f^\circ \text{HNO}_3(\text{G})$ at 298.15 K. The value adopted by [95], -134.360 ± 0.5 kJ/mol, is the average of experimental values. This value is in good agreement with the results of theoretical calculations based on *ab initio* calculation and the isodesmic reaction procedure -133.3 kJ/mol. A similar

value of -132.7 kJ/mol was calculated by the composite G3 method using the GAUSSIAN 98 system of programs.

The generally accepted standard enthalpy of formation of nitric acid vapor at 298 K is -134.31 kJ/mol [93]. The enthalpy of formation of nitric acid vapor as a function of temperature can be calculated from the following polynomial equation:

$$H^\circ - H^\circ_{298.15} = A \times \tau + \frac{B \times \tau^2}{2} + \frac{C \times \tau^3}{3} + \frac{D \times \tau^4}{4} - \frac{E}{\tau} + F - H$$

where $H^\circ - H^\circ_{298.15}$ is the excess enthalpy in kJ/mol , τ is the temperature in kelvin divided by 1000 and A, B, C, D, E, F, and H are constants listed in Table 30 for two different temperature ranges. It is disappointing that NIST WebBook [93] does not give any data for liquid nitric acid.

3.13.3 Heat of Fusion of White Fuming Nitric Acid

The heat of fusion of nitric acid is $10.472 \pm 0.008 \text{ kJ/mol} = 2.503 \pm 0.002 \text{ kcal/mol}$, determined calorimetrically [20].

3.13.4 Heat of Evaporation of White Fuming Nitric Acid

The heat of evaporation $\Delta H_{\text{evap.}}$ of nitric acid at the normal boiling point is $35.85 \text{ kJ/mol} = 8.569 \text{ kcal/mol}$ and the heat of evaporation $\Delta H_{\text{evap.}}$ at $298 \text{ K} = 25^\circ\text{C}$ is $39.13 \text{ kJ/mol} = 9.353 \text{ kcal/mol}$. Literature data on the heat of evaporation of nitric acid are summarized in Table 33.

Table 33: Heat of evaporation of nitric acid.

Temperature		Heat of evaporation		Authors	Year	References
K	°C	kJ/mol	kcal/mol			
348	75	33.05 ^a	7.90 ^a	Pascal	1921	[98]
359	86	31.73 ^a	7.584 ^a	Pascal	1921	[98]
293	20	32.64 ^a	7.80 ^a	Taylor	1925	[99]
353	80	31.38 ^a	7.50 ^a	Taylor	1925	[99]
293	20	39.12 ^a	9.35 ^a	Wilson and Miles	1940	[38]
	—	39.44 ^b	9.426 ^b	Wilson and Miles	1940	[38]
298	25	39.14	9.355	Forsythe and Giauque	1942	[20]
303	30	44.02	10.520 ^a	Berg	1954	[100]

^a Calculated from vapor pressure data

^b Average calorimetric value

In a critical review, the value of 7.80 kcal/mol at 20 °C was rejected as unreliable and 9.426 kcal/mol was considered the best data as of 1960. The heat of evaporation at 298 K could also be calculated from the differences in enthalpy of formation of the liquid and the vapor. Differences in the heat of formation data of liquid and vapor HNO_3 in Table 32 would indicate $658\text{--}509\text{ cal/g} = 149\text{ cal/g} = 9.388\text{ kcal/mol}$.

The heat of evaporation in $\text{HNO}_3/\text{H}_2\text{O}$ mixtures with $>60\%$ HNO_3 remains constant and is similar to that of pure water. Some of the vapor pressure data indicate a hydrate with the composition $2\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ [100]. The vapor pressure has a minimum at this composition. Others interpreted this as a mixture of the well-known monohydrate and trihydrate.

3.13.5 Entropy of White Fuming Nitric Acid

The structural, spectroscopic, and thermochemical properties of HNO_3 vapor have been re-examined and recalculated and revised ideal gas thermodynamic tables were published [95]. The revisions were based on new spectroscopic information and made use of improved calculation methods. Compared to previous calculations, the entropy at 298.15 K $S^\circ(298.15\text{ K})\ 266.860 \pm 0.7\text{ J K}^{-1}\text{ mol}^{-1}$ (Table 34 and 35) is unchanged for $\text{HNO}_3(\text{G})$, but the high temperature values ($T > 4000\text{ K}$) are significantly different. The original publication contains tabulated data for up to 6000 K which is only of the-oretical value because at that temperature nitric acid ceases to exist. The calculated entropy value at 298.15 K which is $266.8\text{ J K}^{-1}\text{ mol}^{-1}$ is in close agreement with the value of $S^\circ(298.15\text{ K})$ obtained from calorimetric data which is $266.2\text{ J K}^{-1}\text{ mol}^{-1}$.

Table 34: Ideal gas thermochemical properties of nitric acid vapor at standard state pressure ^a.

T , K	C_p , $\text{J K}^{-1}\text{ mol}^{-1}$	S° , $\text{J K}^{-1}\text{ mol}^{-1}$	$[G^\circ - H^\circ(\text{Tr})]/T$, $\text{J K}^{-1}\text{ mol}^{-1}$	$\Delta_f H^\circ$, kJ mol^{-1}	$\Delta_f G^\circ$, kJ mol^{-1}	$\log K_f$
298.15	54.092	266.816	266.816	-134.300	-74.059	12.975

^a At standard state pressure, p_r 0.1 MPa and temperature $T_r = 298.15\text{ K}$

Data source: [95]

Table 35: Standard entropy of formation S_{298} of nitric acid at 101 kPa.

Physical state	Standard entropy of formation (ΔS_f) ²⁹⁸		Authors	Year	References
	$\text{J K}^{-1}\text{ mol}^{-1}$	$\text{cal } ^\circ\text{C}^{-1}\text{ mol}^{-1}$			
Gas	266.39	63.67	NIST Chemistry WebBook	1998	[93]
Gas	266.860 ± 0.7	63.78 ± 0.17	Dorofeeva et al.	2003	[95]

The standard entropy of formation of nitric acid vapor at 298 K and 101 kPa is $266.39 \text{ J mol}^{-1} \text{ K}^{-1}$ [93]. The entropy of nitric acid vapor as a function of temperature can be calculated from the following polynomial equation:

$$S^\circ = A \times \ln(\tau) + B \times \tau + \frac{C \times \tau^2}{2} + \frac{D \times \tau^3}{3} - \frac{E}{2 \times \tau^2} + G$$

where S° is the entropy in $\text{J mol}^{-1} \text{ K}^{-1}$, τ is the temperature in kelvin divided by 1000 and A, B, C, D, E, and G are constants listed in Table 30 for two different temperature ranges.

Entropy data for condensed phase nitric acid are scarce. One source of information [20] lists it as $S_{298} = 155.6 \text{ J mol}^{-1} \text{ K}^{-1} = 37.19 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$ for the liquid at 298 K (25°C) and $82.37 \text{ J mol}^{-1} \text{ K}^{-1} = 19.686 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$ for the solid at melting point (231.51 K).

3.14 Molecular Properties, Structure, Dipole Moment, and Molecular Orbital Calculations

3.14.1 Molecular Structure of Nitric Acid

The analysis of electron diffraction patterns and the microwave spectrum indicated that the molecule of nitric acid in the gas phase is planar. The molecular structure of nitric acid is illustrated in Figure 13.

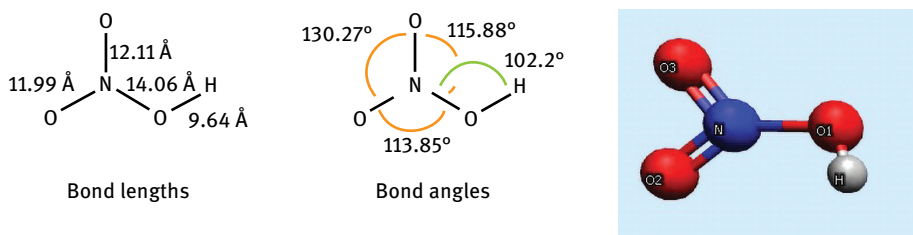


Figure 13: Molecular structure of nitric acid $1 \text{ pm} = 10^{-9} \text{ m} = 10 \text{ \AA}$

Other estimates for the atomic distances and bond angles in the nitric acid molecule based on electron diffraction measurements are $\text{N}-\text{O} 1.22 \pm 0.02 \text{ \AA}$, $\text{N}-\text{OH} 1.41 \pm 0.02 \text{ \AA}$, $\angle \text{O}-\text{N}-\text{O} 130 \pm 5^\circ$, $\angle \text{O}-\text{N}-\text{OH} 115 \pm 2.5^\circ$. Similar results were derived from XRD measurements: $\text{N}-\text{O} 1.24 \pm 0.025 \text{ \AA}$, $\text{N}-\text{OH} 1.30 \pm 0.025 \text{ \AA}$, $\angle \text{O}-\text{N}-\text{O} 134 \pm 3.5^\circ$, $\angle \text{O}-\text{N}-\text{OH} 113 \pm 5^\circ$.

Other molecular structure data from a recent review of data [95] are:

$r(\text{O}-\text{H})$	$0.9416 \pm 0.003 \text{ \AA}$	$\text{H}-\text{O}-\text{N}$ 102.660.3°
$r(\text{N}-\text{OH})$	$1.4106 \pm 0.002 \text{ \AA}$	$\text{O}-\text{N}-\text{O}$ <i>cis</i> 115.760.2°
$r(\text{N}-\text{O})$	<i>cis</i> $1.2136 \pm 0.002 \text{ \AA}$	$\text{O}-\text{N}-\text{O}$ <i>trans</i> 114.160.2°
$r(\text{N}-\text{O})$	<i>trans</i> $1.1986 \pm 0.002 \text{ \AA}$	

There may be a resonance between three possible structures I, II, and III with structure III being less likely due to the proximity of two identical charges on the two central atoms (Figure 14).

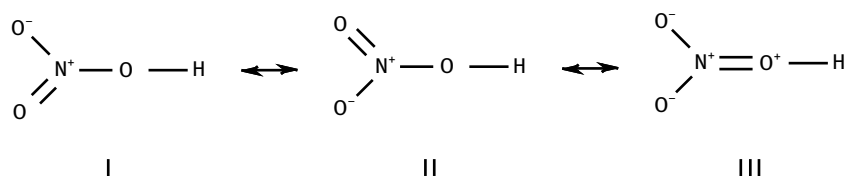
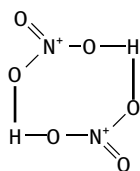


Figure 14: Resonance structures of the HNO_3 molecule

Two molecules of HNO_3 may associate in solutions or in the vapor phase, forming a dimer. Self-association was quantitatively studied by cryoscopy and infrared spectrometry at different temperature of HNO_3 solutions in CCl_4 [101]. From studies of the surface tension and parachor of liquid nitric acid, association of HNO_3 molecules was inferred, the dimers having the structure



Nitric acid dimer structure

Any valence model for nitric acid vapor must account for the large $\text{O}-\text{N}-\text{O}$ angle and the high barrier to rotation about the $\text{N}-\text{OH}$ bond. Both these facts may be explained by intramolecular hydrogen bonding. The composition $(\text{HNO}_3)_2$ would also be identical with hydrated nitronium nitrate $[\text{NO}_2^+][\text{NO}_3^-][\text{H}_2\text{O}]$ which is the active nitrating agent in anhydrous nitric acid and mixed acid. The nitric acid monohydrate $\text{HNO}_3 \cdot \text{H}_2\text{O}$ may also have the structure of an ortho nitric acid $\text{ON}(\text{OH})_3$ in analogy to phosphoric acid [100].

3.14.2 Crystal Structure of Frozen Nitric Acid

The crystal unit cell of frozen nitric acid contains 16 molecules of HNO_3 and has the dimensions $a = 16.23 \pm 0.05 \text{ \AA}$, $b = 8.57 \pm 0.03 \text{ \AA}$, $c = 6.31 \pm 0.01 \text{ \AA}$ [48]. The space group symmetry is $P2_1/a - C_{2h}^5$ in the monoclinic system, with the angle $\beta = 90^\circ$. The XRD density calculated from these values, which were obtained at the freezing point of the acid (-41.6°C), is 1.895 g/cm^3 .

3.15 Dipole Moment of Nitric Acid

Microwave measurements predicted the dipole moment of nitric acid to be $\mu = 2.17 \pm 0.02$ Debye units.

3.16 Optical Properties of White Fuming Nitric Acid

3.16.1 Infrared Absorption Spectra of Nitric Acid

Due to the troublesome formation of nitric acid as an atmospheric pollutant, most spectroscopic studies were done for nitric acid vapor and only relatively few studies were done for liquid or even frozen nitric acid.

The IR spectra of nitric acid have practical interest. They can be used to ascertain the purity of nitric acid samples and detect nitric acid as a constituent of atmospheric smog and stratospheric clouds in polluted atmospheres. Nitric acid may form and needs to be detected as an intermediate in the decomposition of organic nitrate esters, where hundreds of those compounds have been evaluated and a dozen of those are being used as rocket propellant ingredients. Spectroscopy of decomposing alkyl nitrates revealed the short-lived presence of nitric acid. The disappearance of HNO_3 can be measured by IR absorption in kinetic studies of nitration reactions that lead to nitrate esters or nitro compounds.

3.16.1.1 Infrared Spectra of Nitric Acid Vapor

The pure rotational absorption spectrum of nitric acid vapor has been measured by Fourier-transform infrared (FTIR) spectroscopy in the region $8\text{--}40 \text{ cm}^{-1}$ at a resolution of 0.05 cm^{-1} [102]. The structure of the spectrum corresponds closely to the normally forbidden perpendicular pure rotation band of a symmetric top. In the limit of a planar oblate near symmetric rotor, the band simply shows a series of equispaced sharp absorption lines.

The vibration-rotation spectrum of nitric acid of the bands ν_5 and $2\nu_9$ has been recorded between 855 and 915 cm^{-1} , with a resolution of 0.05 cm^{-1} [103].

High resolution spectra in the region of the ν_2 band of nitric acid have been obtained for selected portions of the HNO_3 spectrum using tunable diode laser techniques, showing continuous spectra from 1718.97 to 1729.57 cm^{-1} , with a spectral reso-

lution of $\leq 0.001 \text{ cm}^{-1}$ (30 MHz) [104]. The IR spectrum of the ν_2 band of nitric acid has been measured with a tunable diode laser in the wave number interval from 1690 to 1727 cm^{-1} [105]. Over 210 transitions have been measured in the millimeter and submillimeter spectral region [106]. Additional information on the IR spectra of nitric acid is found in [107–109]. The data necessary to reproduce the spectrum of HNO_3 at temperatures up to 300 K in the $1\text{--}7000 \text{ cm}^{-1}$ range has been stored in a variety of formats, including a line list in the ExoMol format [110]. The list contains transitions involving rotational quantum number J up to 70 for 9×10^6 vibration-rotation energy levels belonging to 1715 vibrational states and associated transitions probabilities. In total the line list contains about 2 billion transitions.

Isotope Studies of Infrared Spectra of Nitric Acid

Isotope substitution of hydrogen in nitric acid with deuterium allowed the assignment of fundamental vibrations in the IR spectrum of nitric acid vapor as shown in Table 36 [94]. This work also identified the barrier height against internal rotation around the N–OH axis and derived thermodynamic functions.

Table 36: Fundamental vibrations in the IR spectrum of HNO_3 and DNO_3 .

HNO_3	Wave number, cm^{-1}	DNO_3	Wave number, cm^{-1}
a'	3560	a'	2627
a'	1710	a'	1685
a'	1335	a'	1313
a'	1320	a'	1014
a'	886	a'	883
a'	765	a'	764
a'	583	a'	543
a''	680	a''	670
a''	465	a''	365

Data source: [94]

The vibrational spectra of four isotopic nitric acid molecules including ^{15}N and D isotope labeling have been obtained in the vapor and solid phases and compared to Raman spectra of normal nitric acid [111, 112]. The potential barrier against internal rotation of the hydroxyl group has been calculated to be $32.6 \pm 0.4 \text{ kJ/mol} = 7.8 \pm 0.1 \text{ kcal/mol}$ in both the H and D acids. The IR spectrum of nitric acid vapor at two different pressures, measured in a 10.2-cm path length cell, is shown in Figure 15.

A similar spectrum is available from the same source for solid nitric acid at the temperature of liquid nitrogen. See also [113].

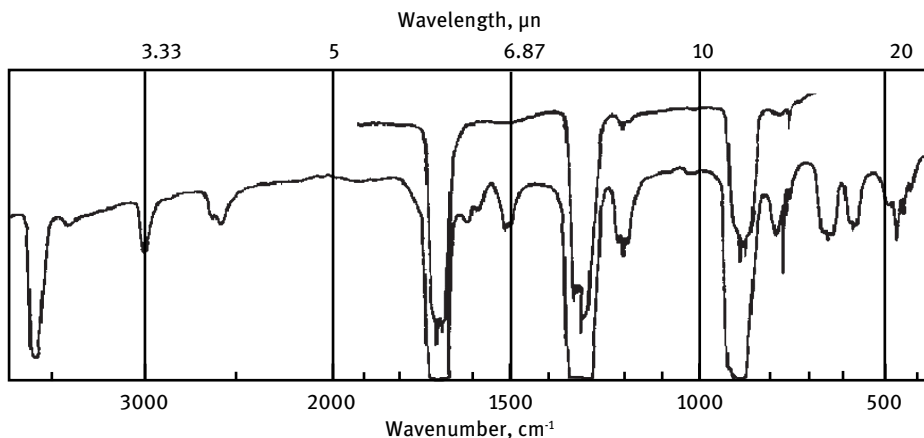


Figure 15: IR spectrum of nitric acid vapor at pressures of 20 and 50 mm Hg (from [111])

Infrared Spectra of Liquid Nitric Acid

The IR absorption spectrum of liquid 99.2% HNO_3 held between silver chloride windows with a path length of $2\mu\text{m}$ shown in Figure 16 is similar to that of nitric acid vapor [114]. There are only very few near-IR spectra published in the 1000–2000 nm range where the Military Specification for N_2O_4 measures the water content.

Table 37 is a comparison of the frequencies of IR vapor, IR liquid, and Raman liquid absorption/fluorescence spectra.

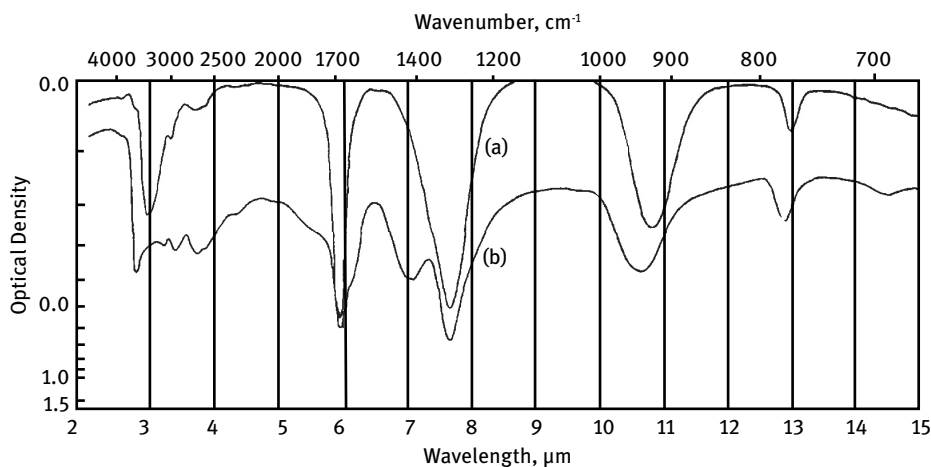


Figure 16: IR spectrum of liquid nitric acid (republished and modified from [114], with permission of © 1957 American Institute of Physics; permission conveyed through Copyright Clearance Center Inc.)
 Legend: (a) 99.2% by weight (cell path length $2\mu\text{m}$), (b) 80% by weight (cell path length $5\mu\text{m}$)

Table 37: Comparison of the vibration frequencies of nitric acid IR vapor, IR liquid, and Raman liquid.

Molecular vibration frequencies, cm^{-1}		
IR vapor	IR liquid	Raman liquid
3560m	3380m	3400 band
3390		
3000	3010w	
2627	2690w	
2585	2600w	
1710s	1680s	1675m
	1538w	1535
1335s		
1320s	1308s	1300s
1206		
886s	924	925s
765m	769	(767)b
		680m
583m	beyond NaCl region	610m
465s	beyond NaCl region	480w

s = strong, m = medium, w = weak, b = observed only as overtone

Note: Numbers in **bold** are incompletely resolved doublets

Data source: [114]

Infrared Spectra of Nitric Acid Hydrates

The freezing point curve and other physical property measurements in the $\text{HNO}_3/\text{H}_2\text{O}$ binary system indicate the formation of hydrates with various $\text{HNO}_3 : \text{H}_2\text{O}$ ratios. This is confirmed by examining the IR spectra in the liquid phase. Vibrational spectroscopy and XRD have been applied to investigate the crystallization of concentrated amorphous nitric acid ($0.5 \leq x \leq 0.95$) [115]. Crystalline nitric acid monohydrate ($\text{HNO}_3 \cdot \text{H}_2\text{O}$) is the major hydrate phase detected together with traces of metastable nitric acid dihydrate ($\text{HNO}_3 \cdot 2\text{H}_2\text{O}$) and pure crystalline nitric acid. XRD showed nitric acid monohydrate has a highly symmetrical structure, which is confirmed by IR, Raman, and inelastic neutron scattering spectra. The NIST Chemistry WebBook [93] shows only IR spectra of 14, 23.3, and 35% HNO_3 aqueous solutions, which are not very characteristic.

Infrared Spectra of Solid Nitric Acid

Ab initio calculations and IR spectroscopy have been used to study of the structure and vibrational frequencies of crystalline nitric acid [116]. The crystallographic data on the unit cell structure have been refined and the vibrational frequencies of the crystal have been determined in the calculation. In the higher frequency range, the experimental spectra showed a broad absorption band with 2 maxima at about 3100 and 2980 cm^{-1} assigned to the stretching of the $\text{O}'-\text{H}$ bond, ν_1 . Proposed assignments to the predom-

inant molecular vibrations in the range between 3487 and 426 cm^{-1} were given for the strongest absorption bands. The calculation provided an indication of the position of the H atoms in the crystal. The average O'—H bond distance is $1.013 \pm 0.009 \text{ \AA}$ and the NOH angle is $105.490 \pm 0.025^\circ$. See also [117, 118].

3.16.2 Raman Spectra of Nitric Acid

Raman spectra of the equimolecular mixture $\text{HNO}_3 \cdot \text{H}_2\text{O}$ in the liquid and glassy frozen states in the range from 4000 cm^{-1} down to 50 cm^{-1} indicated the presence of at least 4 species: **(1)** The free molecular association $\text{H}_2\text{O} \cdots \text{HONO}_2$ with $\nu\text{OH}(\text{H}_2\text{O}) = 3550 \text{ cm}^{-1}$ (3440 cm^{-1}) and $\nu\text{OH}(\text{HNO}_3) = 2930 \text{ cm}^{-1}$ (2915 cm^{-1}) in the liquid and the glassy state, respectively. **(2)** The free ionic pair $(\text{H}_2\text{OH})^+ \cdots (\text{ONO}_2)^-$ that give a splitting ($\Delta\nu = 170 \text{ cm}^{-1}$) of the $\nu_3\text{NO}_3^-$ vibration. **(3)** Free HNO_3 molecules: $\nu\text{NOH} = 940$ and 950 cm^{-1} in the liquid and the glassy state. **(4)** The nitric acid trihydrate: $\text{H}_7\text{O}_3^+\text{NO}_3^-$ with νOH between 3100 and 3300 cm^{-1} [119, 120].

At very high pressures up to 50 GPa, the association of nitric acid to form dimers and higher associates becomes more pronounced as is evident from changes in the Raman spectra [121] and nitric acid will begin to crystallize. Like common practice in identifying IR vibrations, isotope substitution allows investigators to identify Raman-active molecular vibrations and species that are in equilibrium with nitric acid as it associates or dissociates [122].

3.16.3 Ultraviolet Absorption Spectra of Nitric Acid

The UV absorption of nitric acid is difficult to determine because the molecule photolyzes even while the measurement is in progress. Quantitative measurements were made of the pure HNO_3 vapor absorption spectrum in the 1700–2636 $\text{\AA}$ wavelength interval at 295 K (22°C) [123]. Absorption coefficients were determined using 6 absorption cell lengths between 0.1 and 10.0 cm, and numerous gas pressures in the 40–6687 Pa (0.0004–0.066 atm) range. An example absorption spectrum obtained with a 5-cm cell is shown in Figure 17. The maximum of absorption is near 1800 $\text{\AA}$. The results were used to estimate the absorption of UV radiation by stratospheric HNO_3 , which is an air pollutant and smog ingredient.

The ultraviolet (UV) absorption spectra of amorphous and crystalline $\text{H}_2\text{O}/\text{HNO}_3$ films were measured in a cold cell. Pure HNO_3 films showed a broad absorption peak with a maximum absorbance at $\lambda \approx 1950 \text{ \AA}$ [124]. Figure 18 shows a comparison of UV spectra of HNO_3 in the form of a solid thin film, liquid, and vapor. The absorbances of amorphous $\text{H}_2\text{O}/\text{HNO}_3$ films were very broad and peaked at $\lambda = 1960\text{--}1980 \text{ \AA}$. The major absorbing species in crystalline HNO_3 hydrates is the nitrate ion NO_3^- .

Both nitronium and nitrate participate in ionic equilibria in the system water-nitric acid-nitrogen pentoxide at compositions near 100% HNO_3 . It was suggested that the nitronium ion might be responsible for some of the absorption at 2565 $\text{\AA}$. Since the

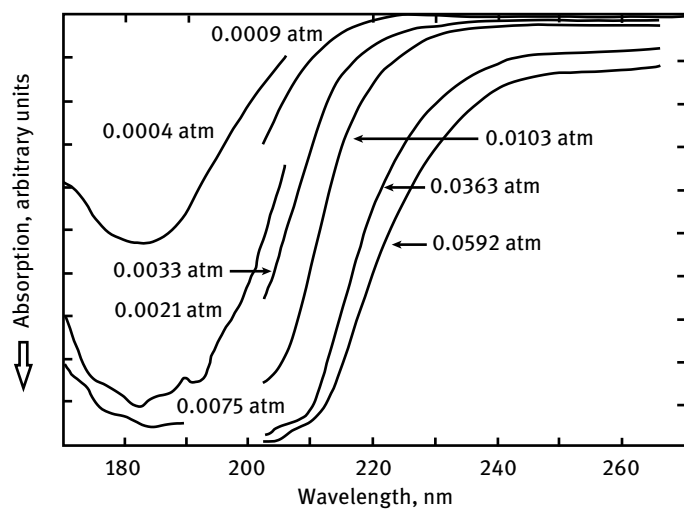


Figure 17: UV Absorption of nitric acid vapor in a 5-cm cell (reprinted and modified from [123], with permission granted by © 1974 The Optical Society)

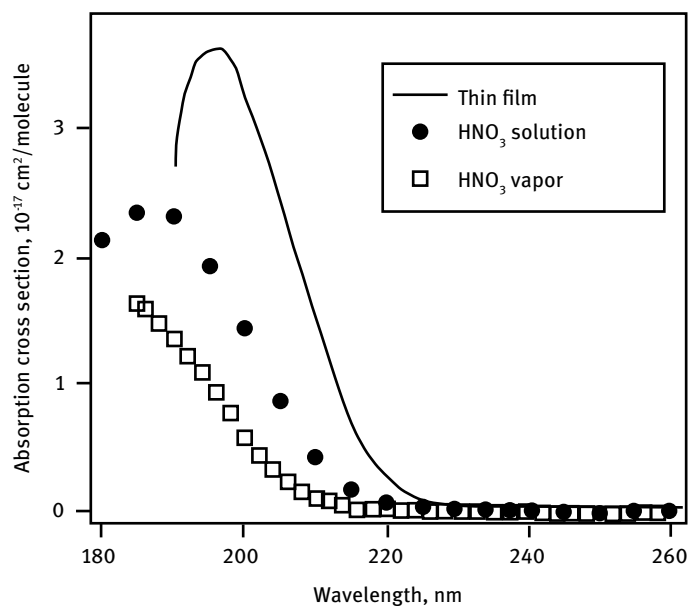


Figure 18: Comparison of UV spectra of HNO_3 in three different forms (reproduced and modified from [124])

nitrate ion is a relatively weak absorber with a maximum at 3020 Å, it would not contribute appreciably to the maximum for the pure acid.

3.16.4 Index of Refraction of Nitric Acid

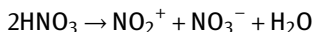
The index of refraction of 100% HNO₃ is $n_D = 1.3910$ at 308 K (35 °C) and 1.4030 at 278 K (5 °C) [71]. Another data point is $n_D = 1.3970$ at 297 K (24 °C) [90].

3.17 Microwave Absorption Spectra of Nitric Acid

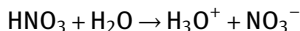
Microwave measurements dimensions indicated that the O—N—O angle is closer to 135° than the 130° value found by electron diffraction. For a symmetric or nearly symmetric rotor, the relative intensities of the *P*, *Q*, and *R* branches in the IR spectrum are known approximately for various orientations of the vibrational dipole moment of inertia. The greater O—N—O angle is more consistent with the observed band shapes and assignments in the IR spectrum of nitric acid vapor. Isotope labeling gave the following results: O—H = 0.964 Å, (H)O—N = 1.406 Å, *cis*-N—O = 1.211 Å, *trans*-N—O = 1.199 Å, $\angle$ HON = 102°9', $\angle$ *cis*-ONO(H) = 115°53', $\angle$ *trans*-ONO(H) = 113°51', and O...O (NO₂ group) = 2.184 Å. This determination clearly demonstrated a 2° tilt of the NO₂ group away from the hydrogen atom and exact planarity of the nitric acid molecule [125]. From these microwave measurements, the total dipole moment of nitric acid was predicted to be $\mu = 2.17 \pm 0.02$ Debye units.

3.18 Electrical Properties of White Fuming Nitric Acid

The chemistry and electrical conductivity of 100% nitric acid is governed by the self-dissociation equilibrium:



Solvation of the water and nitrate ion by nitric acid is strong. Clearly, addition of one of the components on the right-hand side of equation is expected to suppress the concentration of the other two. For instance, the addition of water is seen to reduce the conductivity of the nitric acid as the concentration of NO₂⁺ + NO₃[−] are reduced. A conductivity minimum is observed at ca. 4 mass-% water, and the increase in conductivity with further water addition is attributed to the production of the hydroxoniun ion according to:



As shown in Figure 19, the conductance of the HNO₃/H₂O system increased with an increase in the mass fraction of HNO₃ and reached a maximum at about 0.29 mass frac-

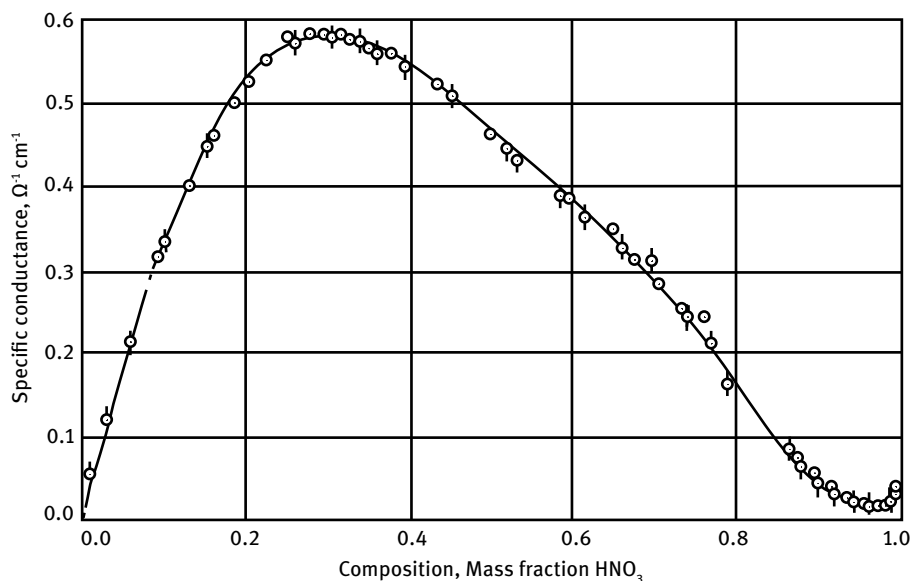
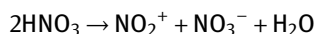


Figure 19: Specific conductance of nitric acid/water at 273 K and atmospheric pressure as a function of nitric acid content (reproduced and modified from [126])

tion HNO₃ [126, 127]. Between 0.30 and 0.97 mass fraction the conductance decreased and reached a minimum at 0.97 mass fraction HNO₃. Below 0.97 mass fraction HNO₃, hydrogen and nitrate ions are the predominant conducting species. In the range 0.97–1.00 mass fraction nitric acid, the conductance again increased. In this latter range, studies of the Raman spectra of the system indicated that HNO₃ undergoes self-ionization to yield nitronium ions (NO₂⁺) and nitrate ions (NO₃⁻) according to the equation



It is evident from this expression that the self-ionization of nitric acid is suppressed by the addition of water. Thus, the reduction of conductance of pure nitric acid upon the addition of water can be explained. Similar electrical conductivity measurements for binary HNO₃/N₂O₄ and ternary HNO₃/N₂O₄/H₂O mixtures are shown in the RFNA Chapter.

Literature data for the electrical conductivity of pure nitric acid are summarized in Table 38 and 39. All measurements are consistent in showing that the temperature dependence of the specific conductance is very small. Electrical conductivity numbers reported by [128] seem to be totally out of range when compared to other data.

Table 38: Electrical conductivity of pure nitric acid.

Temperature		Electrical conductivity	Authors	Year	References
K	°C				
		ohm ⁻¹ cm ⁻¹			
273	0	0.0377	Robertson, Mason, and Sage	1951, 1952	[126, 127]
273	0	0.0383	Sage	1957	[18]
288	15	0.0406	Sage	1957	[18]
303	30	0.0416	Sage	1957	[18]
253	-20	0.034	Lee and Millen	1956	[129]
263	-10	0.0368	Lee and Millen	1956	[129]
273	0	0.027 ^a ; 0.0322 ^b	Miskidzh'yan and Trifonov	1947	[130]
291	18	0.0317 ^b	Miskidzh'yan and Trifonov	1947	[130]
273	0	0.03279	Naumova	1949a	[59]
298	25	0.034724	Naumova	1949a	[59]
273	0	0.03558; 0.03653	Taylor, Lyne, and Follows	1951	[62]
283	10	0.03678	Taylor, Lyne, and Follows	1951	[62]
288	15	0.03703	Taylor, Lyne, and Follows	1951	[62]
298	25	0.03744, 0.03704, 0.03735	Taylor, Lyne, and Follows	1951	[62]
303	30	0.03690	Taylor, Lyne, and Follows	1951	[62]

^a After 3 h^b After 6 days**Table 39:** Electrical conductivity of technical grade nitric acid.

Composition, mass-%		Electrical conductivity, ohm ⁻¹ cm ⁻¹
HNO ₃	H ₂ O	
100.0	0.0	3.77×10^{-2}
99.0	1.0	2.18×10^{-2}
98.0	2.0	1.51×10^{-2}

Data source (second hand): [28, p. 158]

3.19 Magnetic Properties of White Fuming Nitric Acid

Nitric acid is a diamagnetic substance. The specific magnetic susceptibility of anhydrous nitric acid at room temperature measured by Pascault and Chedin [131] was -0.3168×10^{-6} cgs units and the molar magnetic susceptibility was -19.9×10^{-6} cgs units. Other magnetic susceptibility data reported in the literature were obtained in aqueous nitric acid solutions and may be less reliable.

4 Chemical Properties of WFNA

Nitric acid is a powerful oxidizer which enables spontaneous ignition of many organic substances as soon as it comes in contact with them. This property, called “hypergolic ignition” is the main reason why nitric acid has been used as a rocket propellant for a long time. In addition, nitric acid can be used as an oxidizer also with non-hypergolic fuels, such as kerosene or JP-4, but that would require a separate ignition mechanism and lacks repeated startability. The chemical properties of three types of nitric acid are discussed here: WFNA, RFNA (IRFNA), and mixed acid (MA). Chemical properties of interest for the rocket application of these oxidizers are: storage stability, thermal stability, corrosion, and methods of analysis and detection.

4.1 Reactions of WFNA

4.1.1 Reactions of Nitric Acid with Inorganic Compounds

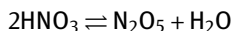
The reaction of HNO_3 with H_2O in aqueous solutions forming hydrates can barely be called a chemical reaction, but the hydrate formation is evidenced by peritectic points in the melting point diagram of the $\text{HNO}_3/\text{H}_2\text{O}$ system (Figure 1). The formation of nitric acid hydrates has already been discussed in various sections of this chapter. Occasionally additional hydrates are discovered [132]. The determination of the dissociation constant of nitric acid in diluted solutions in water is difficult because nitric acid is not completely dissociated as one would expect for a strong acid, but some of the undissociated acid is bound in the form of hydrates. The acid constant pK_a of nitric acid in 1-M solutions was estimated as -0.9 ± 0.2 .

4.1.2 Reactions of Nitric Acid with Organic Compounds

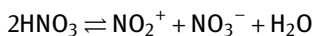
There are two types of reactions of nitric acid with organic compounds that are of importance for rocket propellants: **(1)** nitration reactions for the preparation of nitro compounds and nitrate esters (hopefully not leading to ignition in the reaction vessel), and **(2)** hypergolic ignition reaction with hypergolic fuels, mostly alkylamines, alkylhydrazines or unsaturated hydrocarbons. Nitration reactions are discussed in *Encyclopedia of Oxidizers*, chapter “Nitrate Esters” on the preparation of nitrate esters. One must keep in mind that any mixture of nitric acid with organic compounds is potentially detonable and adequate precautions must be taken when handling such mixtures.

4.2 Autodissociation of Nitric Acid

Autodissociation (self-ionization) of nitric acid is responsible for the relatively high electrical conductivity of pure nitric acid. Pure 100% nitric acid dissociates partly into dinitrogen pentoxide and water:



Dinitrogen pentoxide is completely dissociated in nitric acid solutions at low temperatures into stably solvated nitronium (NO_2^+) and nitrate (NO_3^-) ions, while the water exists mainly as a solvated molecular species. The absence of the known Raman frequencies of molecular nitrogen pentoxide demonstrates its complete dissociation into these ions. The complete self-ionization of nitric acid can consequently be expressed, apart from solvation, by the equation:

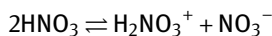


The equilibrium constant for this process, defined in terms of mol fractions and activity coefficients, was calculated for several temperatures using cryoscopic and conductance data (Table 40).

Table 40: Equilibrium constant for self-ionization of nitric acid.

Temperature		Equilibrium constant $\times 10^5$	Authors	Year	References
K	°C				
233	−40	2.44	Dunning and Nutt	1951	[23]
253	−20	1.602	Lee and Millen	1956	[129]
263	−10	0.930	Lee and Millen	1956	—
298	25	0.280	Taylor, Lyne, and Follows	1951	[62]

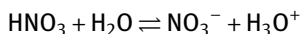
While the mechanism of the self-ionization of nitric acid is due to self-dehydration, about 10–15% of the process could be attributed to autoprotolysis



The extensive evidence available in favor of the former mechanism of self-ionization comes from cryoscopic measurements [133]. It is estimated that in analytically anhydrous nitric acid at 233 K (−40 °C), about 3–4% of the original acid is dissociated to give 1.2% of nitronium ion, 1.7% of nitrate ion, and 0.5% water.

Evidence for the presence of water in analytically anhydrous nitric acid has been obtained by finding two very weak bands in the Raman spectrum of pure nitric acid, at

2980 and 3550 cm^{-1} , which belong to a hydrogen bonded solvate of water. The ionization of water in nitric acid solutions, which could take place according to the equation:



occurs only to a small extent. This has been substantiated by the observation that the electrical conductivity of nitric acid solutions containing as much as 8–10 mass-% of water is smaller than that of the pure acid.

The addition of up to 23% of dinitrogen pentoxide to nitric acid has only a negligible effect on the total vapor pressure, a behavior suggesting that the ionic species formed by the dissociation of dinitrogen pentoxide are strongly solvated.

4.3 Analysis of White Fuming Nitric Acid

Because WFNA is in a constant state of decomposition and changes its composition during storage, it is important to analyze it periodically to make sure that the contents of the container are still what it says on the label. In addition, the acid is hygroscopic and might absorb moisture from the air or it might become contaminated by corrosion products.

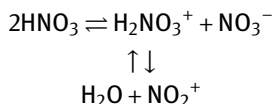
Analytical methods are needed for the determination of HNO_3 assay and H_2O , NO_2 , HF contaminants, and additives. In the United States, RFNA must meet the requirements of MIL-PRF-7254G – Propellant, Nitric Acid, but there is no corresponding military specification for WFNA. The WFNA being used for making RFNA is not covered by a specification of its own. Lesser concentrations of nitric acid are covered by Federal Specification O-N-350B, Nitric Acid, Technical (Sep 1985). The methods for analysis of NO_2 and H_2O in RFNA listed in MIL-PRF-7254G can also be used for WFNA at lower concentrations. See also [134].

4.3.1 Determination of Water Content of White Fuming Nitric Acid

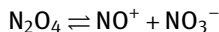
The determination of water in WFNA can be performed by IR spectrophotometric or volumetric methods.

The addition of water to pure nitric acid caused a weak absorption band to develop at 0.97 μm . The strength of the band increased with increasing concentrations of water. Absorption bands of pure liquid water at 1.92 and 3.0 μm occurred also in 95% nitric acid, almost unaffected except for a slight shift in wavelength and some peak sharpening. Liquid water has absorption bands at approximately the following wave lengths: 0.98, 1.18, 1.45, 1.74, 1.79, 1.96, and 2.79 μm . No absorption bands which can be attributed to nitrogen dioxide have been reported between 1 and 2 μm . This is important because fuming nitric acid often contains nitrogen dioxide.

One IR spectrophotometric method for determination of water content in white fuming nitric acid used the absorption band of O—H at $1.423\mu\text{m}$, but it tended to give high results, because some of water is the result of autodissociation of nitric acid [135]:



Because this equilibrium is affected by the NO_3^- content, which in turn is affected by the N_2O_4 and NO_2 concentration, by way of the equilibrium



the indicated water content is dependent on the NO_2 content of the acid. A correction must be applied that can be looked up in the following graph, unless both water and NO_2 concentrations are very small (see Figure 20). Corrections can be looked up for acids containing up to 20% NO_2 . Nitrate salts that are dissolved in the acid will also affect the water readings.

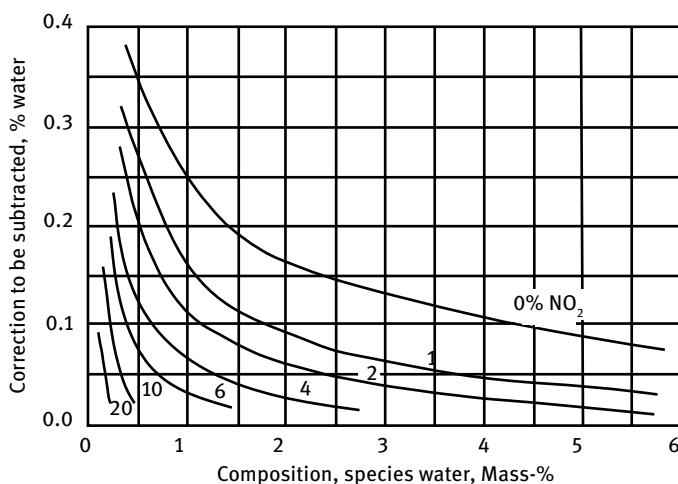


Figure 20: Correction for IR spectrophotometric determination of water in nitric acid (reprinted and modified from [135] with permission from © 1956 American Chemical Society; permission conveyed through RightsLink)

Another method for determination of water in white or red fuming nitric acid is the volumetric titration using the Karl Fischer reagent [136, 137].

In another variant of this method, the acid was first slowly neutralized by addition of a 2:1 volume ratio mixture of pyridine and dimethylformamide to avoid interfering reactions with the reagent [138]. An excess of Karl Fischer reagent was added and then

back-titrated with standard water in methanol titrant. In the absence of dissolved salts an accuracy of 1% relative could be achieved. Nitrogen dioxide concentrations up to 1.5 mass-% did not interfere.

Wet chemical methods are cumbersome and not very accurate. For acceptance tests of WFNA in the field, an electric conductometric method would be preferred. Several conductometric methods have been developed and field-tested for that purpose [139].

At a given temperature the conductance of a sample of fuming nitric acid, together with the conductance of a duplicate sample saturated with anhydrous potassium nitrate, gives enough information to determine the composition of the sample [140, 141]. Values of the specific conductance of saturated solutions of potassium nitrate in fuming nitric acid were obtained at 273 K for various fuming nitric acid mixtures, and the resulting data necessary for utilizing this conductometric method of analysis in the composition range 0–12 mass-% NO_2 , 0–10 mass-% water were presented in graphical and tabular form. By this method NO_2 can be determined to within $\pm 0.3\%$ on an absolute basis and water can be determined to within ± 0.3 mass-% in the composition range studied. These conductance values can be compared to earlier published data [142]. For other analytical methods for field analysis of WFNA see also [143, 144]. The determination of traces of NO_2 in WFNA uses the same methods as the determination of larger concentrations of NO_2 in RFNA and will be discussed in chapter “Red Fuming Nitric Acid”.

4.3.2 Analysis of Corrosion Products in WFNA

Soluble corrosion products remain after evaporating a sample of WFNA to dryness and will be weighed and can be analyzed if needed. Sometimes metal salts, in particular nitrates of transition metals, are added to nitric acids on purpose to achieve shorter ignition delays with hypergolic fuels. These salts also need to be analyzed for quality control.

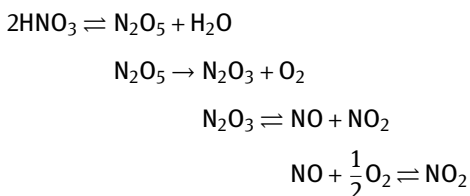
4.3.3 Analysis of Corrosion Inhibitors in WFNA

Nitric acid may contain hydrogen fluoride as a corrosion inhibitor. The fluoride content of WFNA or RFNA can be determined gravimetrically by precipitating lead chloride fluoride PbClF . Another method would be to neutralize the acid and determine fluoride volumetrically by titrating with thorium nitrate and using sodium alizarin sulfonate as the indicator. See also [145].

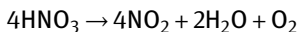
4.4 Thermal Stability and Decomposition of WFNA

4.4.1 Slow Decomposition of Nitric Acid during Storage

Pure nitric acid is not stable, but will slowly decompose to nitrogen dioxide, water, and oxygen. The decomposition of nitric acid in the heterogeneous vapor-liquid region is a kinetically complex reaction which can be explained as proceeding according to the following steps:



The summation of these steps leads to the overall stoichiometric relation



where NO_2 designates an equilibrium mixture of N_2O_4 and NO_2 . The nitrogen dioxide will stain the acid yellow. This reaction is accelerated by temperatures above 273 K (0 °C) and by light (see Section 4.6 on photolysis of nitric acid). This reaction cannot be retarded by high oxygen pressure. In an intermediate range of compositions between those of WFNA and RFNA, pressurizing the mixture with oxygen will stabilize the composition, but that is not practical. The rate of decomposition can be retarded by deliberately adding two of the decomposition products, nitrogen dioxide and water. This addition of nitrogen dioxide and water to WFNA leads to RFNA and is one of the reasons for the popularity of this oxidizer.

The slow decomposition of nitric acid has been thoroughly investigated, because it is a limiting parameter when it comes to evaluating the storability of rocket propellants. The most undesirable effect of HNO_3 decomposition is the build-up of internal pressure in storage vessels from evolution of oxygen gas, which dissolves in the liquid only to a small percentage. There have been incidents of metal drums rupturing from overpressure because they were not vented periodically during the storage of WFNA. For this reason, we are including a section on the solubility of gases in HNO_3 in this chapter (see Section 3.11). Additional data on the solubility of gases in various grades of WFNA and RFNA are included in chapter “Red Fuming Nitric Acid”, which illustrates the equilibrium decomposition pressure in a ternary diagram of $\text{HNO}_3/\text{NO}_2/\text{H}_2\text{O}$ mixtures for containers with 15% ullage.

The thermal decomposition of nitric acid vapor was studied in two glass cells of considerably different surface-to-volume ratios from 100 to 465 and the rate was followed colorimetrically as the appearance of red nitrogen dioxide [146–148]. The decomposition was ambivalent: a heterogeneous reaction at low temperatures and predominantly a fast homogeneous first-order reaction above 673 K (400 °C). The het-

erogeneous reaction was initially first order, but its rate was reduced by water or nitrogen dioxide on the surface. The heterogeneous reaction has a very low energy of activation, about 20.9 kJ/mol (5 kcal/mol). The homogeneous rate was independent of reaction products: its energy of activation was 167 kJ/mol (40 kcal/mol) or higher. A mechanism was proposed whereby nitric acid decomposed to hydroxyl radicals and nitrogen dioxide but this alternative route of decomposition via ionic intermediates which was proposed earlier was later proved wrong because it was unable to explain the kinetics of the decomposition process [149].

A detailed investigation of the decomposition process of white fuming nitric acid indicated that the decomposition proceeds via the anhydride of nitric acid, dinitrogen pentoxide, as an intermediate. The decomposition of liquid HNO_3 at temperatures of 338 and 343 K was studied by measuring the rate of dioxygen gas evolution from the system at atmospheric pressure [150]. The rate data were interpreted in terms of a unimolecular decomposition of molecular N_2O_5 , which results from the self-dissociation of HNO_3 into N_2O_5 , NO_2^+ , NO_3^- , and H_2O . The liquid phase decomposition kinetics of HNO_3 can be explained if one assumes that 3.2% of the total N_2O_5 from the self-dissociation is in the molecular form at 338 K and 5.4% is in the molecular form at 343 K.

In the later work with liquid instead of gaseous nitric acid, the thermal decomposition was studied at 328, 338, and 348 K (55, 65, and 75 °C). The rate of decomposition could be expressed in terms of the water produced by the decomposition

$$-d(\text{HNO}_3)/dt = (\text{HNO}_3)^2/[f_0^0 + S(\text{H}_2\text{O})]$$

Pseudo-activation energies were then determined for f_0^0 and S . They were -162 and -116 kJ/mol, respectively (-38.7 and -27.8 kcal/mol, respectively). The ionic mechanism previously proposed for the decomposition was found to be inadequate to explain the effects of some additives. An alternative free radical mechanism was then proposed. This mechanism was found to be more satisfactory than the ionic mechanism and gave a correlation between the liquid phase and gas phase decompositions.

A study of the kinetics of the liquid phase decomposition of HNO_3 in the temperature range from 327 to 361 K (54–88 °C) suggested that the unimolecular decomposition of N_2O_5 , which is known to exist in fuming nitric acid solutions plays a significant role in the rate-determining step [151, 152]. A rate mechanism experimentally indistinguishable from that of the N_2O_5 hypothesis involves the ionic product $[\text{NO}_2^+][\text{NO}_3^-]$. The effect of several inorganic additives, namely H_2O , N_2O_4 , N_2O_5 , KNO_3 , KHSO_4 , NOHSO_4 , H_2SO_4 and HClO_4 , on the rate of decomposition was in agreement with these postulated rate mechanisms. The inhibition of the decomposition rate by various additives tested was found to be insufficient to prevent the eventual attainment of high equilibrium pressure resulting from the decomposition of fuming nitric acid when stored in closed container for periods of about 1 month in the temperature range 327–361 K (54–88 °C). Of all the additives tested on both a molar and a weight basis, H_2O gave the most pronounced effect inhibiting HNO_3

decomposition, but of course it would also detract from its performance as a rocket propellant.

The rate of pressure increase in hermetically sealed WFNA containers with 25% ullage increased with increasing temperature (Figure 21).

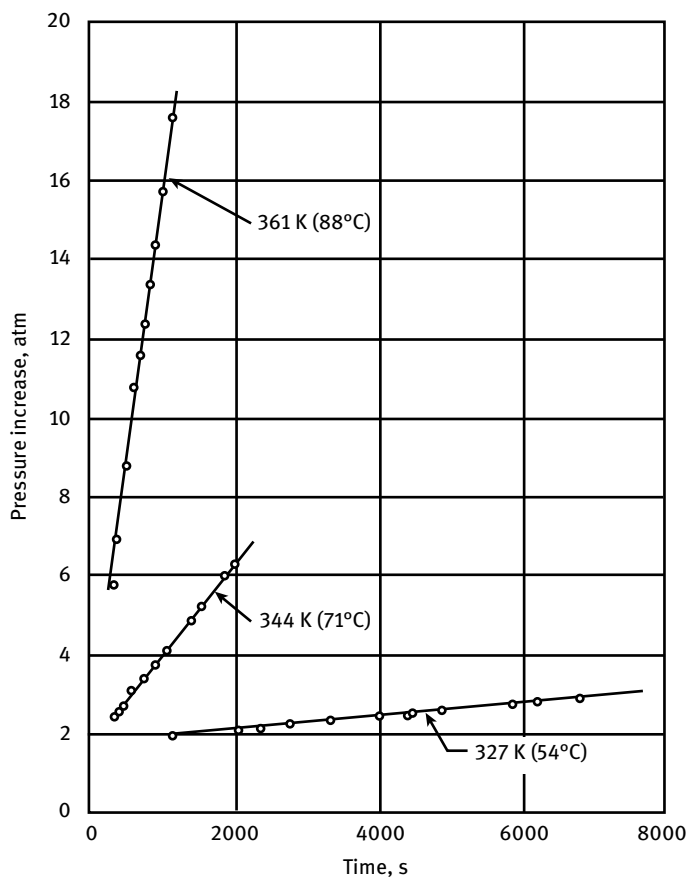


Figure 21: Decomposition pressure of HNO_3 as a function of time and temperature (from Contract AF33(038)10381)

The equilibrium composition is achieved after 33 h at 344 K (71°C) or 6 h at 361 K (88°C). If the logarithm of the rate of decomposition is plotted versus the reciprocal absolute temperature, the curve is nearly a straight line, in accordance with the Arrhenius function.

Other experiments showed that the equilibrium achieved in a hermetically filled container with 11% ullage is achieved after 20 h at 347 K (76 °C) [22, 153] Figure 22.

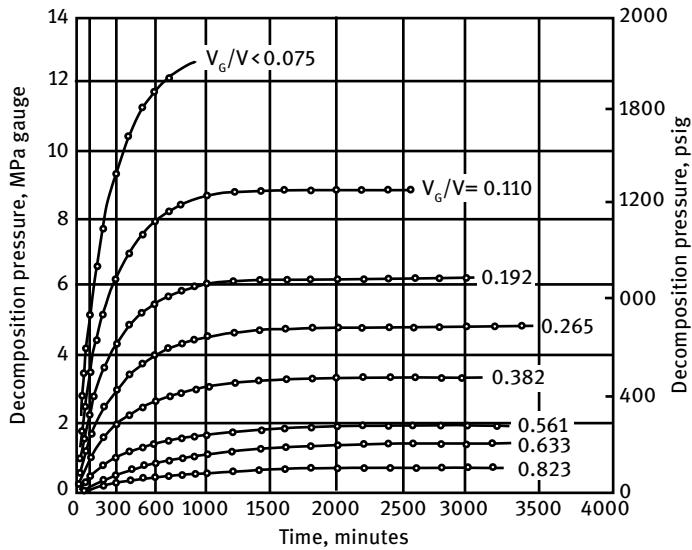


Figure 22: Decomposition pressure of pure nitric acid as a function of time and ullage at 349 K = 76 °C (reproduced and modified from [22] Contract AF33(038)10381)
 $\frac{V_g}{V}$ = Ratio of gas space : total container volume = “ullage”

Figure 23 shows the time required to reach equilibrium as a function of the temperature for 2 different ullage volume ratios, 20 and 80% ullage. It takes longer to reach equilibrium in a drum that is only 20% full (80% ullage).

The rate of decomposition can be decreased by addition of water, but that would adversely impact the rocket performance of this oxidizer. The effects of nitrogen dioxide and water on the rate of decomposition of nitric acid will be discussed in more detail in Section 4.4.1 on the decomposition of RFNA and the selection of RFNA compositions that no longer develop oxygen overpressure during long-term storage [153, 154].

Most studies of the kinetics of liquid HNO_3 decomposition used the rate of increase of pressure as a measure of the degree of conversion. The decomposition pressure is mostly caused by oxygen, which is only sparsely soluble in nitric acid, in contrast to NO_2 which is also formed but readily dissolves in HNO_3 [85]. The pressure measurements must be corrected for the amount of oxygen that is dissolved in the liquid and no longer contributes to the gas phase pressure. The solubility of oxygen in nitric acid was already discussed in the physical properties Section 3.11.

The thermal decomposition of highly concentrated nitric acid was observed at atmospheric pressure between 273 and 333 K (0 and 60 °C) for up to 273 days. The decomposition of highly concentrated nitric acid is a second order reaction in nitric acid. The

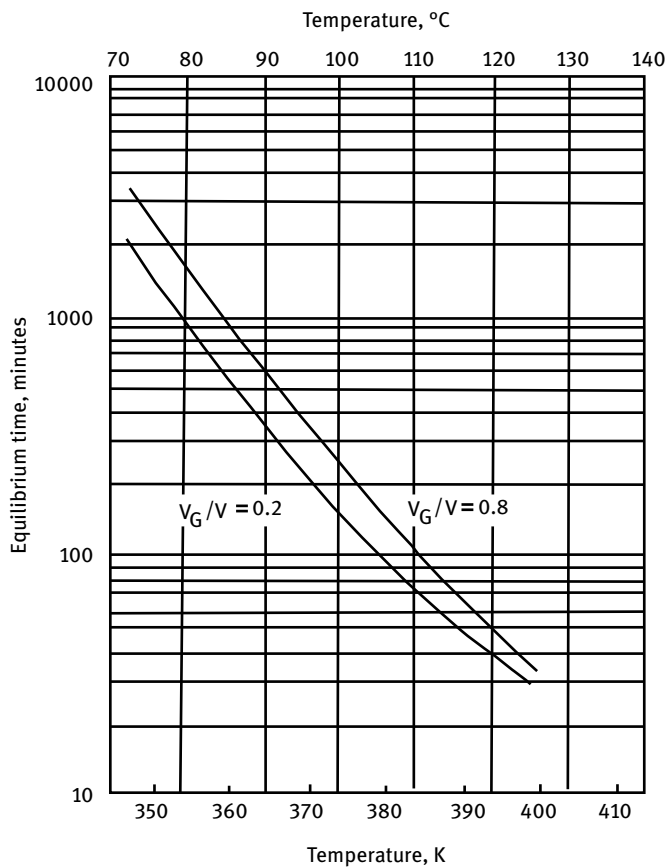
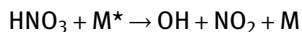


Figure 23: Time required to reach equilibrium as a function of the temperature for two different ullage volume ratios (reproduced and modified from Contract AF33(038)10381)

activation energy for decomposition of nitric acid was 134 kJ/mol [155]. See also [156, 157].

4.4.2 Rapid Decomposition of Nitric Acid Vapor

The rate coefficient for the reaction

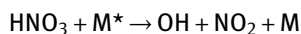


has been determined in mixtures of nitric acid and argon in incident shock wave experiments [158]. Quantitative OH time histories were obtained by CW narrow line width UV laser absorption of the $R_1(5)$ line at 32606.56 cm^{-1} (vacuum). The experiments were

conducted over the temperature range 990–1400 K and the pressure range 18–44 kPa (0.18–0.44 atm). The second-order rate coefficient was determined to be:

$$k_1 = 1.01 \times 10^{16} \exp(-17280/T) \quad [\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}]$$

See also [159–161]. At concentrations of 10^{-5} mol/cm^3 , the decomposition of nitric acid in shock waves is controlled by the unimolecular reaction:



the rate of which is [162]:

$$\log k = (15.2 \pm 1) - [(30.6 \pm 1.8)/2.303R] \times (1000/T) \text{ mol cm}^{-3} \text{s}^{-1}$$

4.5 Storage Stability of WFNA

Measurements of the pressure rise in sealed aluminum-61S-T6 containers, which had been filled at 294 K (21 °C) leaving only 10% ullage, as a function of the initial composition of the acid indicated that equilibrium pressure was achieved after 4 weeks of storage at 327 K (54 °C) [163]. The highest decomposition pressure (7.5 MPa = 75 atm) was observed if one started the test with pure nitric acid containing hardly any H_2O or N_2O_4 , see Figure 20 in *Encyclopedia of Oxidizers*, chapter “Red Fuming Nitric Acid”. A more detailed description of these experiments is contained in *Encyclopedia of Oxidizers*, chapter “Red Fuming Nitric Acid”.

Nitric acid tends to change in composition and to corrode containers and hardware when stored for long periods of time. The most significant changes which occur are an increase in water and soluble and non-soluble solids content. If the percentage of water appreciably exceeds 2%, the acid-fuel mixtures are no longer hypergolic. A high concentration of solids causes injector nozzle and filter clogging problems. Since both RFNA and WFNA are frequently stored for extended periods of time prior to use, a project to determine optimum storage conditions was initiated and led to the recommendation that the most stable storage conditions are a temperature of 333–348 K (60–75 °F), and a maximum drum pressure of 345 kPa (50 psi) [164]. See also [165].

4.5.1 Stabilizing Additives to Nitric Acid

It has been attempted to delay the decomposition of nitric acid by dissolving stabilizing additives. The additives tested include nitrates and perchlorates of aliphatic amines. Addition of 1% $[(\text{C}_2\text{H}_5)_3\text{NH}]\text{NO}_3$ was claimed to extend the time that nitric acid can be stored at high temperature without excessive pressure build-up. For storage at 366 K (93 °C) the duration to suffer a certain degree of decomposition was extended from 28 to 72 h. Another additive was even more active: Addition of 1% $[(\text{C}_2\text{H}_5)_3\text{NH}]\text{ClO}_4$ at 366 K (93 °C) extended the duration to suffer a certain degree of decomposition from 28 to 432 h [166].

A long list of alkyl-amine and aryl-amine nitrates and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or $\text{Na}_2\text{S}_2\text{O}_8$ have been patented as stabilizers for nitric acid [167].

4.5.2 Additives Capable of Shortening the Ignition Delays

In addition to additives capable of lowering the freezing point or slowing the rate of decomposition of nitric acid, other additives have been sought, which might be capable of shortening the ignition delay of nitric acid with organic amines and hydrazines, in particular at low temperatures.

Nitric acid is not hypergolic with kerosene JP-4, but a slightly exothermic reaction occurs that is not sufficiently exothermic to lead to ignition. The exothermic reaction of nitric acid with kerosene JP-4 is said to become more exothermic if 1% $[(\text{C}_2\text{H}_5)_3\text{NH}]\text{NO}_3$ or 1% $[(\text{C}_2\text{H}_5)_3\text{NH}]\text{ClO}_4$ is added to the acid beforehand [166].

4.6 Photolysis of Nitric Acid

Because NO_2 and nitric acid, in this case in the form of peroxyntic acid, play an important role in the production and decay of photochemical smog and stratospheric clouds, the photolysis of nitric acid has been thoroughly investigated. This is less likely to occur in rocket applications. Photolysis would not be an effective method of removing nitric acid from rinse waters of a rocket test stand installation. As long as nitric acid is stored in the dark, the rocket propellant chemist does not have to worry about photolysis of nitric acid.

4.7 Radiolysis of WFNA

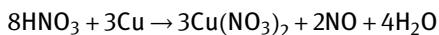
Radiolysis of WFNA may occur during long deep-space missions or in the vicinity of nuclear reactors, but this is not a likely scenario given the poor storability of WFNA and the lack of any plans to fly nuclear reactors again at any time soon. Radiolysis of nitrates occurs during the reprocessing of nuclear reactor fuel elements and isotope separation of the fission products.

5 Compatibility with and Corrosion Caused by WFNA

5.1 Corrosion Mechanisms in WFNA

As a strong acid, nitric acid can dissolve most metals. One is used to think that all metals will evolve hydrogen when attacked by acids. This is the case of metals dissolved by hydrochloric acid, but the reaction of nitric acid with metals goes a different route.

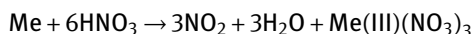
Instead of evolving hydrogen, the nitric acid becomes reduced to nitrous acid and nitric oxide. The reaction of nitric acid with copper shavings in the absence of oxygen is an easy method to produce nitric oxide (NO) in the laboratory:



If the apparatus is not purged of air prior to the experiment, the NO will contain varying amounts of NO₂. On the other hand, if the goal of the preparation is to obtain NO₂ instead of NO, one will allow plenty of air to pass through the apparatus to convert all NO to NO₂.

Strongly reducing metals, such as zinc or Devarda's alloy (45% Al, 50% Cu, 5% Zn), can reduce the nitrate ion all the way to ammonia. This is an antiquated method to determine nitrate in water, distilling the ammonia out of the water in a Kjeldahl apparatus and analyzing ammonia in the distillate by titration or nephelometric methods.

The corrosive action of nitric acid is extremely strong because nitric acid is both an acid and an oxidizer. Most metals, for instance iron, are converted to the nitrate salts of the metal in the highest state of oxidation of the corroded metal:



Both WFNA and RFNA are equally aggressive towards metals, RFNA being only little less aggressive than WFNA to some of the alloys. The metal nitrates formed as corrosion products either remain in solution in the acid or precipitate as a sludge or form a passivating crust on the surface of the metal. In many cases the layer formed on the metals consists not of nitrates, but their hydrolysis products, the metal oxides. A layer of insoluble metal oxide forms a protective layer and protects the underlying metal from further attack. Many metals owe their compatibility with nitric acids to this passivation phenomenon. Many metals are subjected to a special passivating pretreatment before the components are used for nitric acid service. Welded areas have to be repassivated because the passivation was lost in the heat-affected zone.

Most metals will dissolve in strong acids like nitric acid. The few metals that are compatible with concentrated nitric acid owe their resistance to the formation of an oxide passivation layer. This passivating layer will only form in concentrated acid and would dissolve in dilute acid. This often happens at tank closures where WFNA fumes mix with atmospheric moisture and become diluted and more corrosive.

The electrode potentials of aluminum and stainless steel immersed in WFNA were measured to determine their polarization characteristics under a number of conditions [168]. This included the variables of temperature, nitrogen dioxide content, water content, and acid content, as well as the effects of static versus agitated or stirred solutions. The phenomenon of anodic passivity of 2S aluminum in WFNA and the feasibility of cathodic protection of AISI Type 347 stainless steel were studied.

There is some overlap between material compatibility information discussed here for WFNA and additional information described later for RFNA. In order to obtain a complete overview, the reader should consult both sections.

5.2 Metals as Materials of Construction in WFNA

The most economic materials of construction for nitric acid systems are mostly steels and aluminum alloys. The selection of materials depends on the type of acid and will differ depending on the amount of corrosion inhibitor (hydrogen fluoride) added.

Particularly demanding requirements are imposed on components exposed to nitric acid [169]. Where metallic materials are concerned, attention must be paid not only to general corrosion, but also to intergranular and selective attack in many cases. A distinction is made between three conditions of exposure for which different materials are employed:

- Subazeotropic and azeotropic nitric acids not contaminated with oxidants,
- Subazeotropic and azeotropic nitric acids containing oxidants, such as chromates, and
- Superazeotropic, primarily highly concentrated nitric acids.

The nitric acid production industry has gained experience in the advantages and disadvantages of the materials used in the three sectors, namely austenitic chromium-nickel-(molybdenum) steels, high-silicon austenitic chromium-nickel steels, iron-silicon casting materials, glass-lined steel, glass, aluminum (alloys), titanium, zirconium, tantalum-niobium alloys, tantalum, and platinum [170]. See also [171].

Liquid droplet residues left behind after evaporation of dinitrogen tetroxide from tanks consist essentially of nitric acid. Therefore, a material compatibility study of N_2O_4 included material compatibility tests with 71% HNO_3 [172].

5.2.1 Corrosion of Steel as Material of Construction in WFNA

Steel and aluminum alloys are the main metals for use in nitric acid tanks, lines, and plumbing components. For valves and engines that must operate at higher temperatures one will prefer steels which have a better high temperature tensile strength than aluminum alloys.

Most other metals (except titanium alloys), copper, brass, bronze, silver, zinc, tin, magnesium, and their alloys are not suitable for nitric acid service. Most of these metals dissolve quickly in nitric acid under evolution of nitrous fumes (the nitric acid is reduced from the nitrogen oxidation state N^{+5} to lower oxides of nitrogen).

Stainless steel 18-8S has good corrosion resistance to nitric acid at all concentrations up to the boiling point at sea-level pressure [173].

A stainless-steel drum made from CRES 347 and used for storage and shipping of WFNA failed by leaking and was subjected to metallurgical examination [174].

The corrosion of carbon steel AISI-1020 in fuming nitric acid was less severe in the anhydrous acid [175].

Most of the investigations of steel corrosion in nitric acid solutions were done in support of designs of chemical process equipment, such as that used in the reprocessing of spent nuclear reactor fuel elements. Acid concentrations in those operations rarely go beyond 11.5 M (54%) HNO_3 [176, 177].

Iron alloys with high content of silicon ("Duriron", "Armco") can be used as storage tank materials, but they are very brittle and crack easily. They cannot be used if the nitric acid contains hydrogen fluoride as a corrosion inhibitor.

Sheet specimens of Armco iron, three types of carbon steel and stainless steel were tested to study chemical interaction of carbon and steels with dilute as well as fuming nitric acid having NO_2 contents ranging from 1 to 40% [178]. Various corrosion rate data were obtained and discussed in terms of sample weight losses and dissolution rates over periods of 120 h.

In the corrosion of stainless steels in nitric acid in heat exchangers, tests at various heat fluxes with steel surface temperature kept constant have shown that the cooler acid present at the surface under higher heat fluxes leads to slightly smaller corrosion rates than under isothermal conditions [179]. Crevice corrosion can develop under gaskets sealing the stainless-steel specimen to the test cell. This crevice corrosion can produce enhanced corrosion rates (by factors up to 100), not only on surfaces within the crevice, but also on those external to the crevice.

Three modifications of cast, low carbon stainless steels with about 15–20% Cr, 13% Ni, and 4.5–6.5% Si possess the mechanical and structural properties, castability, machinability, and weldability so that they can be used for pumps and valves in nitric acid plants [180]. Laboratory corrosion tests in boiling nitric acid between 50 and 98 mass-% HNO_3 proved the superior resistance of the Si-bearing alloys in the 90 and 98% acid compared to standard CrNi steels without Si. Comparative field tests with cast pump impellers and casings confirmed the very good corrosion resistance of the Si-bearing alloys in highly concentrated nitric acid under service conditions.

In highly concentrated HNO_3 , the presence of small amounts of HF will substantially reduce the corrosion of metallic materials. Mixtures consisting of HF and hypoaqueous nitric acid (<69.2 mass-% HNO_3) on the other hand will be strongly attacked: the metal loss will markedly increase with increasing HNO_3 and HF concentrations as well as with rising temperatures [181]. The investigation covered 12 stainless steel grades and nickel-base alloys. With constant HNO_3 content, corrosion rates rose linearly with increasing HF concentrations. With constant HF concentration (0.25 M), corrosion rates increased rapidly with increasing nitric acid concentration. (From 0.3 to 14.8 M). Alloys containing as much chromium as possible (up to 46 mass-%) will exhibit the best corrosion resistance. Alloy NiCr30FeMo (Hastelloy G-30) proved to be well suitable for service in WFNA.

The corrosion behavior of a high Si-alloyed austenitic stainless steel in RFNA was compared with CRES-316 by using linear and cyclic potentiodynamic polarization techniques, immersion corrosion test methods and scanning electron microscope (SEM) observations [182]. The inhibition effect of different concentrations of HF on the corrosion behavior of the alloys was studied. The results obtained from electrochemical measurements, immersion tests, and SEM observations were in good agreement and indicated that HF is a good inhibitor against uniform and intergranular corrosion. A high initial corrosion rate of 16.77 mpy was observed in absence of inhibitor, which was decreased to 0.24 mpy with addition of 0.6 mass-% HF. Moreover, pitting potential at the same condition increased from 1.57 to 2.31 V (vs. Ag/AgCl), indicating an improvement of the localized corrosion resistance with addition of HF inhibitor. Addition of the Si alloying element, on the one hand leads to increase the intergranular corrosion resistance but, on the other hand leads to a reduction of the general corrosion resistance. An initial corrosion rate of 1.18 mpy was obtained for CRES-316, lower than that of the Si-alloyed stainless steel.

5.2.2 Corrosion of Aluminum as Material of Construction in WFNA

Although aluminum is widely used in storage containers for WFNA, there is relatively little information on quantitative rates of corrosion and maximum operating temperatures. There is ample information on corrosion of aluminum and aluminum alloys in nitric acids with lower HNO₃ contents, but that does not apply to rocket-grade WFNA.

For maximum corrosion resistance, high purity metals are often used, such as chemically pure (CP) aluminum with higher than 99.99% aluminum content. In many cases it is not practical to produce a metal of high chemical purity because of cost considerations and because very pure metals have inadequate mechanical properties, being weak and soft. The advantage of increased corrosion resistance is thus offset by the greater thickness required and by the increased price of the superpure metal. Aluminum alloys have better strength than CP aluminum but may also be more susceptible to corrosion.

Aluminum is rapidly attacked by nitric acid at concentrations below 80%, but is better than stainless steel in hot, concentrated WFNA [173].

Corrosion characteristics of some aluminum alloys (1060, 1100, 3003, and 5052) in different concentrations of nitric acid were studied at different temperatures [183]. Alloy 3003 exhibited maximum corrosion in all the acid concentrations followed by 5052, 1100, and 1060 alloys. The corrosion rate of aluminum was found to increase in 20% and decrease with time in 70% HNO₃ solutions. In the concentration range of 20–50% of the acid, all the alloys exhibited slightly passivating tendency during the potentiostatic anodic polarization. The breakdown potential of the alloys varied inversely with temperature. The alloys exhibited negative steady-state corrosion potentials in a concentration range of 1–58% of the acid, but above this concentration

positive values of the potentials have been noted. The presence of different alloying elements may explain the different behavior of the four alloys.

A literature survey was made to examine the suitability of aluminum and aluminum alloys in contact with highly concentrated nitric acid, particularly with respect to the corrosion behavior of weld joints made using various welding processes [184]. The corrosion resistance of Al-99.5 in nitric acid was investigated as a function of temperature and acid concentrations. The linear corrosion rates were plotted in an Arrhenius diagram. Decreasing nitric acid concentrations were causing a parallel shift of the lines in the Arrhenius diagram towards higher corrosion rates. Starting with Al-99.5, the corrosion rates in nitric acid at and above 99.8% HNO_3 concentration decreased as the Al contents of the materials increased. Doping with copper should be avoided. After exposure of wrought as well as continuously cast Al and Al alloys to highly concentrated technical grade nitric acid at 303 K (30 °C) (1 year test period), the corrosion behavior of several alloys was comparable to that of pure aluminum grades.

After 10–15 years in use under harsh operating conditions, piping systems made of Al-99.5 in which highly concentrated nitric acid was flowing at a flow rate of 1 m/s exhibited flow-induced corrosion patterns [185]. In corrosion tests involving single phase flow, no relationship could be found between flow and corrosion of Al-99.5 in nitric acid of various concentrations. The following three testing methods were used: rotating disks of various configurations, rotating cylinders, and flow inside a tube. The influence of two-phase flow generated by a special mixing turbine resulted in weight losses of Al-99.5 with respect to nitric acids having concentrations of 90% to approximately 100%. In the Arrhenius diagram, the temperature dependence of corrosion data with anhydrous nitric acid was shown as a scatter band. Lower nitric acid concentrations were shifting the scatter band in the direction of higher corrosion rates. See also [186].

5.2.3 Corrosion of Titanium Alloys as Material of Construction in WFNA

Titanium and titanium alloys are resistant to corrosion by nitric acid, but can be ignited if a fresh, unpassivated metal surface (such as the shear plug in an explosive valve) is suddenly exposed to the oxidizing acid [187–189]. Titanium alloys resistant to boiling concentrated nitric acid may be alloyed with tantalum and niobium [190].

5.2.4 Compatibility Test Methods for Metals in Concentrated Nitric Acid

Candidate metals intended for use in concentrated nitric acid (WFNA or RFNA) can be tested in accordance with test method American Society for Testing and Materials (ASTM) method A279-44T3 and ASTM recommended practice A224-46 replaced by G 31 or like ASTM F359-82.

ASTM G 31-72 describes accepted procedures for laboratory immersion corrosion tests, particularly mass loss tests.

Other tests used at one time for testing steels in nitric acid are the Huey test [191] and the acidified copper sulfate test [192] recommended for the detection of intergranular attack in stainless steel, but they are somewhat removed from actual use conditions of nitric acid in a rocket, especially in the composition of the reagents used. The acidified copper sulfate reagent does not reveal knife-edge corrosion in steels stabilized with titanium or columbium. The attacking solution in the Huey test (65% HNO_3), it is not as aggressive against stainless steel as is nitric acid concentrated to 98.5%.

5.2.5 Corrosion Products in White Fuming Nitric Acid

Dilute nitric acid will corrode most metals faster than anhydrous nitric acid. Therefore, tanks that have contained fuming nitric acid should be rinsed quickly with a large excess of water and dried soon thereafter. If one allows puddles of half-diluted acid to linger anywhere in the system, dilute acid may penetrate and dissolve the passivating layer and cause severe corrosion.

Chemical, XRD, and spectrographic analyses of sludge samples collected from the sump of aluminum drums showed that most of the sludge was aluminum nitrate in the form of its hexahydrate $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. This salt was not very soluble in nitric acid and its saturation concentration in WFNA was only 0.1% [193] and its solubility in RFNA was 0.3% [194]. Some stainless steels contain columbium (niobium) as a phase-stabilizing additive. The sludge in drums made from columbium-containing steels consisted of columbium carbide, silicon carbide and anhydrous nickel(III) nitrate. The sludge in drums made from other steels contained only nickel nitrate and silicon dioxide.

The examination of corroded surfaces, for instance in a drum that was used for storing nitric acid but leaked, can give valuable information about the corrosion mechanism and the cause for failure [195].

5.2.6 Galvanic Corrosion in Fuming Nitric Acids

If different metals are immersed in nitric acid and in electrical contact with each other, chances are very high that they will form a galvanic element. The metal which is the more electronegative in the series of electronegativity will suffer accelerated galvanic corrosion. The electrochemistry of galvanic corrosion can be studied in a polarimeter. Some metals will passivate, and passivation will slow down the corrosion. The polarization and corrosion of a pair of aluminum and stainless-steel electrodes in nitric acid were measured with a potentiometer [156, 196–199]. The rate of corrosion was different in stagnant and in agitated fluids and was also dependent on the velocity of the fluid stream if the metal was exposed in a propellant feed system.

5.2.7 Corrosion of Welds in Fuming Nitric Acids

The heat-affected zone adjacent to welds is particularly susceptible to corrosion by nitric acid due to residual stress and carbon precipitation in stainless steels. In the case of Fe-18Cr-10Ni stainless steel, it appears that the only grade usable in the presence of concentrated nitric acid (98.5% HNO_3) is the low-carbon Fe-18Cr-10Ni steel, with less than 0.030 mass-% carbon. Alloys stabilized with titanium or columbium showed a form of attack along the weld line known as “knife-edge corrosion” which made them fall apart completely. According to the test plan, one batch of samples was removed after 7 days, the spent acid was replaced with fresh acid and some of the specimens were tested for another 7 days in the fresh acid. Partial (2/3) immersion of double-welded coupon samples in hot 98.5% WFNA kept in a constant temperature bath at 323 K (50 °C) with a reflux condenser showed that corrosion was more severe in the heat-affected zone and depended on the thickness of the coupons [200]. Corrosion of CRES-304 alloys with carbon content from 0.040 to 0.060% resulted in the formation of deep grooves and, eventually, in perforation of the sheet extending to several millimeters on both sides of the intersection of two weld lines. The metal had become sensitized by the welding as shown by the appearance of a groove on both sides of the weld line and extending to several millimeters away from it. Variation in thickness led to different results because in the course of welding, a thin sheet will be heated more quickly and cooled more rapidly than a thick sheet. It would therefore spend less time in the zone of carbide precipitation and as a result would be less susceptible to preferential attack. The decrease in thickness in the sensitized area was 10 times greater in the 1.5-mm thick sheet than in a 0.5-mm thick sheet. With equal carbon contents, the degree of sensitization depended on the thickness of the sheet. Therefore, one should impose more severe acceptance requirements on thicker sheets or where more than two welds are to be made on the same piece.

5.3 Non-metallic Materials of Construction for Nitric Acid Service

5.3.1 Gaskets

Many organic elastomers will be attacked and destroyed by nitric acids. There are only a few elastomers that are resistant to nitric acids. The suitability of commonly used gasket materials for nitric acid applications must be verified from case to case. Many manufacturers advertise their products as “acid resistant” but that does not guarantee that the material is resistant to the strong oxidizing action of nitric acid.

Flanged metal-to-metal connections that do not need to be opened very often can be sealed with crush gaskets made from soft aluminum.

Organic elastomers resistant to nitric acids are Teflon, Kel-F, Hostaflon-TF, and Hostaflon-C2. It is surprising that IRFNA containing HF as a corrosion inhibitor will attack Kel-F more strongly than uninhibited acid. The fluoropolymers by themselves tend to cold-flow under compression. Often asbestos or glass fibers impregnated with

fluoropolymers will be shaped into gaskets for valve seats, valve stem packings, and rotary seals and similar applications to reduce the cold-flow deformations.

Polyethylene may be used only as a temporary gasket material; it lacks long-term durability. A mixture of polyethylene and polyisobutylene showed a surprisingly good resistance against RFNA [201].

Most material compatibility reports list compatibility of candidate materials with specific propellants, one propellant at a time. The literature summary by Beach inverted those lists and primary indexed the information by plastic material, with the propellant type as a secondary sorting criterion [202].

5.3.2 Lubricants for WFNA

The only lubricants acceptable for nitric acid service are chemically inert perfluorinated hydrocarbons or chlorofluorocarbons. Examples for recommended lubricants are Fluorolube, Kel-F oil or Nordcoseal-147-S. Similar lubricants are used for N_2O_4 service. Conventional greases and oils must be avoided because they constitute an explosion hazard if mixed with nitric acid [203].

6 Components for Nitric Acid Service

Many mild steel components are commonly greased for storage and shipping to prevent them from rusting during shipment and storage. Components which are used with nitric acid for the first time should be disassembled and thoroughly degreased. In the past century components intended for fuming nitric acid service were often degreased with trichloroethylene as a vapor degreaser, but this practice has been discontinued. Other degreasing techniques must be found.

Once degreased, the rust and oxide layer can be removed by dipping the components into a chromic acid bath, rinsing, and then passivating with 60% nitric acid and drying before bringing them into contact with fuming nitric acids.

6.1 Hoses

Steel-braided Teflon hoses are the best choice for flexible connections in transferring nitric acids between containers and for fueling missiles and launch vehicles. Polyethylene hoses could be used for short times and then discarded. However, polyethylenes in contact with nitric acids are a fire hazard. After all, this combination has been used in hybrid rockets!

6.2 Pumps

Pumps for nitric acid service can be made from stainless steel. The supplier's lists must be scanned thoroughly before one can find a pump proven to be reliable for fuming nitric acid service in ground service equipment (GSE). Depending on the application, one may have to resort to have a pump custom-made from specially tested alloys.

6.3 Liquid Level Gauges

Sight glasses on nitric acid storage tanks are not recommended due to the breakage potential and leakage hazard. Floats have been used as liquid level indicators.

6.4 Nitric Acid Equipment

6.4.1 Feed Systems in Flight Vehicles

Short and intermediate range missiles and launch vehicles using nitric acids are usually pressure-fed. Pressurant gases for flight vehicles are nitrogen or helium. The high-pressure pressurant tanks are heavy and bulky.

Larger missiles may realize a weight and volume saving by using an on-board gas generator instead of stored gas to expel the oxidizer from the flight tank. Two such gas generators were developed at the US Naval Ordnance Test Station [204]. Operating principles and test results of two self-regulating variable-demand gas generators were described. Red fuming nitric acid was successfully expelled by direct pressurization from a propellant tank at variable flow rates while maintaining a constant tank pressure. The results showed that a variable-demand liquid-bipropellant gas generator is feasible for a pre-packaged storable propellants missile pressurization system. This unit was throttleable and its flow rate could be varied depending on the flight status of the missile.

It has also been attempted to pressurize and expel the oxidizer by direct tank injection of a hypergolic fuel [205]. The acid in the tank will be contaminated by absorbed combustion products (water), but that can usually be tolerated.

6.4.2 Storage Containers

Storage containers for WFNA or RFNA should be made from corrosion-resistant stainless steel with as few welding seams as possible. They should not have any bottom drain valves which might leak. Instead, storage tanks for nitric acids should have a dip tube extending into a sump where the last puddle of liquid will collect, and the tank can be emptied completely. Tanks should not be filled to more than 90%, leaving 10% ullage. Because WFNA decomposes slowly and can develop an oxygen overpressure

during storage, the tanks must have a pressure relief valve. In the vicinity of the relief valve moisture from the air will condense and create a more corrosive environment than in the rest of the system.

It would be best to channel the vented gases into a duct that can be continuously purged with dry air. From there they should be fed to a scrubber or a tall vent stack. Similar precautions are recommended for RFNA.

6.4.3 Nitric Acid Storage Facility Layout

Nitric acid tanks should not be exposed to direct sunlight but should be protected from sun and weather in a well-ventilated aluminum sheet-metal roofed storage shed. The building construction must avoid combustible materials such as wood, tar paper or rubber. Spilled nitric acid might autoignite in contact with combustible materials.

Each storage tank should be placed into a concrete-lined catch basin that can contain 110% of the capacity of the tank. It would be good practice to always keep one tank unit empty as a stand-by unit in case one of the other units starts leaking.

If WFNA nitric acid is shipped and stored in drums, the drums should be stored such that the bung is in the top position. When opening the bung plug, one must wear full body protection because the contents may have developed an overpressure during storage and the liquid may spray out when the drum is first opened.

6.4.4 Maintenance and Lay-up of Nitric Acid Facilities

Test facilities with nitric acids often suffer more corrosion during idle periods than during their actual use. Residual oxidizer in liners, valves, filters, and sumps may gradually be diluted by absorbed moisture and become more corrosive. It has been considered to neutralize surface acid films during lay-up of nitric acid facilities by passing ammonia gas through the system [206].

7 Toxicity of WFNA

The fumes emitted by WFNA (remember where the letter F in WFNA comes from!) are extremely irritating to mucous membranes of the nose and eyes and are immediately noticeable. Extended exposure to WFNA fumes will damage the respiratory tract and the lung tissues. As a result, the symptoms are cough, chronic cough, bronchitis, and bronchial dilation bronchiectasis.

All nitric acid compositions (WFNA, RFNA, or MA) cause severe chemical burns when spilled on the skin instantly within a fraction of a second. It is extremely important to flush spattered nitric acid off the skin with copious amounts of water as fast as possible. Otherwise the acid will eat into the flesh and cause deep and slowly healing wounds. Rinsing the exposed skin with water should be continued for at least 15 minutes, followed by treatment with dilute sodium bicarbonate solution to neutral-

ize residual acid. Skin that has been exposed to nitric acid turns persistently yellow. This color is caused by nitrated aromatic rings in proteins in the skin. Yellow xanthoproteic acid is formed when nitric acid contacts epithelial cells and is indicative of inadequate safety precautions when handling nitric acid. The color persists until the skin peels off.

Concentrated nitric acid as encountered during normal analytical laboratory use contains only 70 mass-% HNO_3 and is not as dangerous as WFNA. Nevertheless, nitric acid spilled on the skin or fingernails will cause a yellow stain due to the formation of xanthoprotein which persists for several weeks.

Nitric acid (like all acids) splattered in the eyes will permanently damage the cornea and can lead to blindness. If nitric acid is accidentally splattered into the eye, one must immediately rinse with lots of water for at least 15 min. and consult a physician soon thereafter. Eye wash fountains are a requirement anywhere where nitric acid is handled in large quantities.

7.1 Maximum Allowable Exposure Levels of WFNA

The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limits (REL) time-weighted average (TWA) for WFNA HNO_3 vapors is 2 ppm (5 mg/m^3) with a permissible short-term spike of 4 ppm (10 mg/m^3). The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) TWA is 2 ppm (5 mg/m^3).

The original NIOSH (Standards Completion Program, SCP) immediately dangerous to life and health (IDLH) for WFNA was 100 ppm. The chosen IDLH was based on older information that pulmonary edema may result from an exposure of 100–150 ppm for only 0.5–1 h. The revised IDLH is 25 ppm [207, 208]. This may be a conservative value due to the lack of relevant acute inhalation toxicity data for workers.

7.2 Protective Clothing for Safe Handling of WFNA

Commonly used clothing made from natural or synthetic fibers is quickly destroyed by nitric acid and in extreme cases spilled acid may even lead to ignition of the combustible fabric. Protective clothing for handling of nitric acids consists of a helmet with face splash shield, gas mask or supplied air, apron, arm-length gloves, and PVC-coated boots. Ordinary vulcanized rubber boots provide only insufficient protection against nitric acids. Protective clothing can be made from polymer fiber fabric coated with PVC or Teflon. The area where nitric acids are handled must have easily accessible safety showers and eye-wash fountains. A comprehensive summary of protective clothing for all types of corrosive chemicals, and the hazards of permeation of aggressive chemicals through the protective clothing during use, is provided in [209, 210].

8 Safe Handling of WFNA

8.1 Spill Containment and Neutralization

Nitric acid spills can be flushed with copious amounts of water before the diluted acid can be neutralized with lime suspensions or caustic soda solutions. The first responder personnel must wear full protection with gas masks or self-contained breathing apparatus because the spilled concentrated acid (in particular RFNA) will warm up and release copious amounts of nitrous fumes when first contacted with a water spray.

The diluted acid rinses can be neutralized with 5% sodium hydroxide or 5% sodium carbonate or sodium bicarbonate solution before the water is allowed to drain to a public sewer system. Some public sewer systems do not allow nitrates, even if it is neutral pH. The alkaline solutions should be kept away from aluminum components because they will attack aluminum, potentially worse than acids. Other neutralizing agents tested include calcium carbonate powder or potassium carbonate solutions [211].

At one time (a long time ago) it was recommended to reduce the NO_2 -formation during treatment of RFNA spills by adding 70% sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) to the spill [212]. The oxidizer was supposed to convert nitrous acid to nitric acid and reduce the NO_2 evolution. In view of the current restrictions in flushing hexavalent chromium down the drain this is not a good practice. Additional information on the handling of nitric acids can be obtained from the following references listed in Table 41.

Table 41: Literature summaries on safe handling of fuming nitric acids.

Authors	Year	References
Biondolillo	1955	[213]
Biondolillo	1955	[214]
Biondolillo	1955	[215]
Biondolillo	1955	[216]
Carter	1965	[217]
Henderson	1954	[218]
Henderson	1954	[219]
Sands	1944	[220]

8.2 Nitric Acid Transfer Operations

The GSE transfer of nitric acids can be performed by pumps or pressurized gas, depending on the scale of the operation. Larger facilities will use pumps, smaller facilities may use compressed gas transfer. Pressurizing gases include dry, oil-free com-

pressed air, nitrogen, argon or helium. The fumes vented from the tank being filled will need to be channeled into an exhaust duct leading to a scrubber or a tall vent stack.

At the time when the AGENA upper stages and the LANCE missile were still in use, the USAF had developed tank cars that would use pumps for transfer between the tank cars and stationary facilities [221].

9 Gelled Nitric Acids

Gelled propellants are non-Newtonian fluids and therefore exhibit a non-linear relationship between the stress and deformation rate. Depending on the gelling agent used, gelled propellants may also have a finite yield stress. Stresses applied to the fluid below the yield stress will not cause the fluid to flow but they deform like a solid. Numerous rheological models for non-Newtonian fluid mechanics exist and the choice of rheological model for a particular fluid depends on how well they match experimental data.

One of the potential benefits of gelled liquid fuels is that gelled liquid fuel propulsion systems in missiles can meet insensitive munitions (low vulnerability ammunition, IM-LOVA) safety criteria, while many of the solid propellant missiles currently in service cannot. Extensive safety testing, in particular cook-off behavior has been done with gelled propellant propulsion systems.

Like efforts with other rocket propellants, nitric acids have been gelled as a method to prevent or slow down leakage during storage or sloshing in a rapidly moving missile. Most of the gelling effort has been devoted to RFNA and IRFNA and only few investigators have attempted to produce WFNA gels. In either case, the selection of gelling agents for nitric acids is limited by the reactivity of most organic gelling agents with nitric acid. Organic gelling agents like those used for gelling fuels would rapidly be destroyed in fuming nitric acids. That leaves mostly the inorganic gelling agents, which have the necessary chemical resistance but will not improve the rocket performance properties of WFNA or RFNA. The inorganic gelling agents like fumed silica will add inert ballast to the propellant, will form troublesome residues in places where they interfere with the operation of the rocket engine, and may settle out during long-term storage. Despite half a century of research and development of gelled hypergolic bipropellants, substantial amounts of money invested in demonstration programs, these gelled propellants have not found any practical application and have not yet flown in a fielded, mass-produced missile.

9.1 Gelled White Fuming Nitric Acid

Rheological characterization of fuming nitric acid gel was performed in low-shear and high-shear rate ranges using Brookfield and capillary viscometers [222]. The gel behaved as a pseudoplastic thixotrope. There is also a section on gelled red fuming nitric acid in chapter “Red Fuming Nitric Acid”. The rheologic properties of these gelled nitric acids are very similar.

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List of Acronyms

1,1-DP	1,1-bis(difluoroamino)propane
1,2,2-TP	1,2,2-tris(difluoroamino)propane
1,2-DP	1,2-bis(difluoroamino)propane
1,3-DP	1,3-bis(difluoroamino)propane
1-DB	1-difluoroaminobutane
2,2-DP	2,2-bis(difluoroamino)propane
2,3-DB-1	2,3-bis(difluoroamino)butane
2-DB	2-difluoroaminobutane
2-EHN	2-ethylhexyl nitrate
2-NDPA	2-nitrodiphenylamine
ABL	airborne laser
ABL	Allegheny Ballistics Laboratory
ABMA	Army Ballistic Missile Agency (Huntsville, AL)
ABS	acrylonitrile butadiene styrene (a polymer)
ACS	attitude control system
ACGIH	American Conference of Governmental Industrial Hygienists
ADN	ammonium dinitramide
AFRL	Air Force Research Laboratory, Edwards AFB
AI	acceptability index
AIAA	American Institute of Aeronautics and Astronautics
AIT	autoignition temperature
AM1	Austin Model 1 = AM1
AN	ammonium nitrate
AP	ammonium perchlorate
ARC	accelerating rate calorimeter
ATO	assisted take-off (propulsion system)
ATR	attenuated total reflection (spectroscopy)
BAM	Bundesanstalt für Materialforschung und -prüfung (German Federal Institute for Material Research and Testing)
BAMAG	Berlin-Anhaltische Maschinenbau A.G.
BASF	Badische Anilin und Soda Fabrik
BDE	bond dissociation energy
BEI	biological exposure index (toxicity)
BET	Brunauer-Emmet-Teller (surface area)
BKW	Becker-Kistiakowsky-Wilson (equation of state)
BOL	beginning of life
BuNENA	<i>n</i> -butyl- <i>N</i> -(2-nitroxyethyl)nitramine
CARS	coherent anti-Stokes Raman spectroscopy
CAS RN	Chemical Abstracts Service Registry Number

ccCA	correlation consistent composite approach (a computational method)
CCSD	coupled cluster singles and doubles (method)
CEA	Chemical Equilibrium with Applications (a computer program)
CFD	compressible fluid dynamics
CGA	Compressed Gas Association
CGS	centimeter gram second system (system of units)
CISD	double excitation configuration interaction (method)
C-J	Chapman-Jouguet
CMDB	composite modified double base (propellant)
CNDO	Complete Neglect of Differential Overlap
CNT	carbon nanotube
COIL	chemical oxygen iodine laser
CPIA	Chemical Propulsion Information Agency
CPIAC	Chemical Propulsion Information Analysis Center
CRES	corrosion resistant eutectic steel
CRT	cathode ray tube
CSB	US Chemical Safety and Hazard Investigation Board
CW	continuous wave (laser)
DARPA	Defense Advanced Research Projects Agency
DATB	1,3-diamino-2,4,6-trinitrobenzene
DDP	2,2-bis(difluoroamino)propionitrile
DDT	deflagration-to-detonation transition
DEGDN	diethylene glycol dinitrate
DFAP	1,1,3,5,5-pentanitro-1,5-bis(difluoroamino)-3-azapentane
DFT	density functional theory
DIN	2-difluoroamino-2-methylpropionitrile
DINA	<i>N,N</i> -bis(β -nitroxyethyl)nitramine
DIPAM	dipicramid
DNA	deoxyribonucleic acid
DNA	dinitroamine
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DZP	double zeta plus polarization (basis set)
EDAX	energy dispersive X-ray analysis
EGDN	ethylene glycol dinitrate
EGMN	ethylene glycol mononitrate
EPA	Environmental Protection Agency
EPR	electron proton resonance (spectroscopy)
EPR	electron paramagnetic resonance (spectroscopy)
EOL	end of life
ERL	Explosives Research Laboratory of the National Defense Research Committee

ESA	European Space Agency
ESD	electron stimulated desorption
ESD	electrostatic discharge
ESR	electron spin resonance
ESR	electron spin resonance (spectroscopy)
FEP	fluorinated ethylene propylene (polymer)
FOI	Totalförsvarets forskningsinstitut (Swedish Defence Research Agency)
FTIR	Fourier transform infrared (spectroscopy)
GAP	glycidyl azide polymer
GC	gas chromatography
GC/MS	gas chromatography combined with mass spectrometry
GEO	geostationary Earth orbit
GTO	geostationary transfer orbit
GLC	gas liquid chromatography
GLYN	glycidyl nitrate
GSE	ground service equipment
GTN	glycerol trinitrate
HAN	hydroxylammonium nitrate
HAP	hydroxylammonium perchlorate
HBO	hyperbaric oxygen
HDA	high density acid
HEDM	high-energy density material
HETP	height equivalent to a theoretical plate
HF	Hartree–Fock (method)
HH	hydrazine hydrate
HH100	hydrazine hydrate 100% N ₂ H ₅ OH
HMX	1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane
HNDZ	1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane
HNF	hydrazinium nitroformate
HNFX	3,3,7,7-tetrakis(difluoroamino)octahydro-1,5-dinitro-1,5-diazocine
HNS	hexanitrostilbene
HOF	heat (enthalpy) of formation
HP1	hydrazinium(1+) perchlorate
HP2	hydrazinium(2+) perchlorate
HPE	1,2,3,5,6,7-hexakis(difluoroamino)-4-oxaheptane
HPLC	high-performance liquid chromatography
HREELS	high resolution electron energy loss spectroscopy
HTP	high text peroxide
HTPB	hydroxyl terminated polybutadiene
HVD	high velocity detonation
IBA	1,2-bis(difluoroamino)-2-methylpropane
ICP	inductively coupled plasma (source for emission spectroscopy)

ICT	Fraunhofer Institute of Chemical Technology
ID	inner diameter
ID	internal diameter
IDLH	immediately dangerous to life or health
IEDs	improvised explosive devices
<i>i.p.</i>	intraperitoneal (injection)
IPA	<i>iso</i> -propyl alcohol
IR	infrared
IRFNA	inhibited red fuming nitric acid
Isp	specific impulse
ISRU	In-Situ Resource Utilization
IUPAC	International Union of Pure and Applied Chemistry
<i>i.v.</i>	intravenous (injection)
JANAF	Joint Army Navy Air Force
JANNAF	Joint Army Navy NASA Air Force
JATO	jet-assisted take-off (propulsion system)
JCZ	Jacobs-Cowperthwaite-Zwisler (equation of state)
JWL	Jones-Wilkins-Lee (equation of state)
JSC	Johnson Space Center, Houston (NASA)
KHT	Kihara-Hikita (equation of state)
LAD	liquid acquisition device
LANL	Los Alamos National Laboratory
LCAO	Linear Combination of Atomic Orbitals
LCH	Low Cost Hydrazine (type of Aerojet catalyst)
LC50	lethal concentration 50%
LD50	dose that is acutely lethal to 50% of the animals exposed to it
LFL	lower flammability limit
LJD	Lennard-Jones Devonshire (equation of state)
LOVA	low vulnerability ammunition
LOX	liquid oxygen
LOZ	liquid ozone
LVD	low velocity detonation
m/e	mass-to-charge ratio (in mass spectrometry)
MA	mixed acid
MAO	monoamine oxidase
MATB	monoamino-2,4,6-trinitrobenzene
MEMS	M icro E lectro M echanical S ystems
MMH	methylhydrazine
MNDO	modified neglect of diatomic overlap
MO	molecular orbital
MON	mixed oxides of nitrogen
MP2	Møller-Plesset (perturbation theory)

MRMP2	Multi-Reference Second-Order Perturbation Theory
MS	mass spectrometry
MSFC	Marshall Space Flight Center (NASA)
MTA	mass spectral thermal analysis
NAAQS	National Ambient Air Quality Standard
NACA	National Advisory Committee for Aeronautics
NADPH	nicotinamide adenine dinucleotide phosphate
NASA	National Aeronautics and Space Administration
NBP	normal boiling point
NBS	National Bureau of Standards (now NIST)
NF	trinitromethane
NFPA	2,3-bis(difluoroamino)propyl acrylate
NG	glycerol trinitrate (misnamed nitroglycerin)
NIMMO	3-nitratomethyl-3-methyloxetane
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
NM	nitromethane
NMR	nuclear magnetic resonance (spectroscopy)
NOEC	no observed effect concentration (toxicity)
NOL	Naval Ordnance Laboratory
NONA	2,2',2'',4,4',4'',6,6',6''-nonanitro-1,1':3',1''-terphenyl
NPN	<i>n</i> -propyl nitrate
NPSH	net positive suction head
NTO	dinitrogen tetroxide
OB	oxygen balance
OD	outer diameter
OI	oxygen index
OMS	orbital maneuvering system
OPE	1,2,2,5,9,9,10-octakis(difluoroamino)-4,7-dioxadecane
OSHA	Occupational Safety and Health Administration
PAP	porous ammonium perchlorate
PBAN	polybutadiene acrylonitrile
PBX	plastic bonded explosive
PCDE	poly(1-cyano-2-difluoroamino)-2,3-epoxyethane
PCRL	Princeton Combustion Research Laboratory
PCTFE	polychlorinated tetrafluoroethylene
PCUK	Produits Chimiques Ugine Kuhlmann (absorbed into Arkema)
PEG	polyethylene glycol
PEL	permissible exposure limit
PES	photoelectron spectroscopy
PETN	pentaerythritol tetranitrate
PFA	perfluoroalkoxy alkane (polymer)

PFG	perfluoroguanidine
PGDN	propylene glycol dinitrate
PMD	propellant management device
PM3	parametric method 3 (quantum mechanics)
PMR	proton magnetic resonance (spectroscopy)
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
PVT	Pressure-Volume-Temperature
PYX	2,6-bis(picrylamino)-3,5-dinitropyridine (PYX)
RCS	reaction control system (also roll control system)
RDX	1,3,5-trinitro-1,3,5-triazacyclohexane
REL	recommended exposure limit
RFNA	red fuming nitric acid
RLPG	regenerative liquid propellant gun
RMS	root mean square (calculation method)
RNFX	5,5-bis(difluoroamino)hexahydro-1,3-dinitropyrimidine
RSD	relative standard deviation
SCF	self-consistent field (molecular orbital calculations)
SCP	Standard Completion Program
SEM	scanning electron microscope (microscopy)
SEOS	solid electrolyte oxygen separator
SPEGL	short-term public emergency guidance level
SRI	Stanford Research Institute
STEL	short-term exposure limit
STP	standard temperature and pressure (273 K and 101 kPa)
STS	Space Transportation System (Space Shuttle)
SYEP	5,5-bis(difluoroamino)-1,9-bisdinitro-1,9-difluoro-3,7-dioxanonane
SYFO	2,2-bis(difluoroamino)-bis(5-fluoro-5,5-dinitro)pentyl formal
TATB	1,3,5-triamino-2,4,6-trinitrobenzene
TBD	<i>tert</i> -butyldifluoroamine
TEA	triethanolamine
TEGDN	triethylene glycol dinitrate
TGA	thermogravimetric analysis
TLV	Threshold Limit Value
TMEA	2,3-bis(difluoroamino)-2-methyl-butane
TMETN	trimethylolethane trinitrate
TNB	trinitrobenzene
TNETB	2,2,2-trinitroethyl-4, 4,4-trinitrobutyrate
TNM	tetranitromethane
TNO	Nederlandse Organisatie voor Toegepast Natuurwetenschappelijk Onderzoek
TNT	2,4,6-trinitrotoluene

TOFLOX	trioxygen difluoride in liquid oxygen
TRL	technical readiness level
TSCA	Toxic Substances Control Act
TSI	thermal stability index
TVOPA	1,2,3-tris[1,2-bis(difluoroamino)]ethoxy propane
TWA	Time Weighted Average (toxicity)
TZP	triple-zeta plus polarization (basis set)
UDMH	unsymmetrical dimethylhydrazine
UFL	upper flammability limit
USBM	United States Bureau of Mines
UV	ultraviolet
VST	vacuum stability test
WFNA	white fuming nitric acid
WHO	World Health Organization
WSTF	White Sands Test Facility (JSC, NASA)
WW-II	World War II
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
Z-TACOT	1,3,7,9-tetranitro-6H-benzotriazole[2,1-a]benzotriazole-5-onium inner salt

Acknowledgments

The publication of this Encyclopedia has been made possible with the help from many individuals whose help is gratefully acknowledged. I want to thank Professor Dr. Thomas Klapötke of the Ludwig-Maximilians University of Munich, Germany, for writing the Foreword for the Encyclopedia and for reviewing several chapters of the book. I thank Dr. Karin Sora, Vice President Science, Technology, Engineering and Mathematics (STEM) of De Gruyter Publishers in Berlin, Germany, for the initiative to get this project started. The project was overseen by Dr. Bettina Noto, Senior Manager, of De Gruyter Publishers in Berlin, Germany. The tedious copyediting process was directed by Dipl.-Ing. Yvonne Schlatter at le-tex publishing services GmbH in Leipzig, Germany. Mr. Niklas Wingborg of FOI Sweden has reviewed and annotated the chapter on dinitramide oxidizers. My colleague Dr. Dieter Zube of Aerojet Rocketdyne in Redmond, WA, has reviewed sections of the introduction to the book. The In-Space Communications department of Aerojet Rocketdyne has provided a photo of the first 3-D printed Aerojet Rocketdyne RL-10 thrust chamber undergoing hot-fire testing with LOX/LH2 in West Palm Beach, Florida, which now decorates the covers of the first five volumes of Encyclopedia of Oxidizers. Numerous colleagues and organizations granted special request copyright permissions to reproduce images from their publications in my books. Many copyright permissions for reproduction of other images were obtained through Copyright Clearance Center with special privileges as an International Association of Scientific, Technical and Medical Publishers (STM) signatory member. My son Andreas Schmidt has drawn many of the illustrations and his skillful artwork is thankfully acknowledged. My wife Hildegard Schmidt has assisted in applying manuscript formatting changes using a computer word processor. Librarians at the Library of the University of Washington (UW), Seattle, WA, were of great help in granting use of the expansive collections of the UW library and in providing on-line access to data bases. Thanks go to the staff at U.S. Department of Defense, Defense Office of Prepublication and Security Review (DOPSR) in the Pentagon for reviewing and clearing the manuscript for public release.

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Bellevue, WA, USA
March 2022

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